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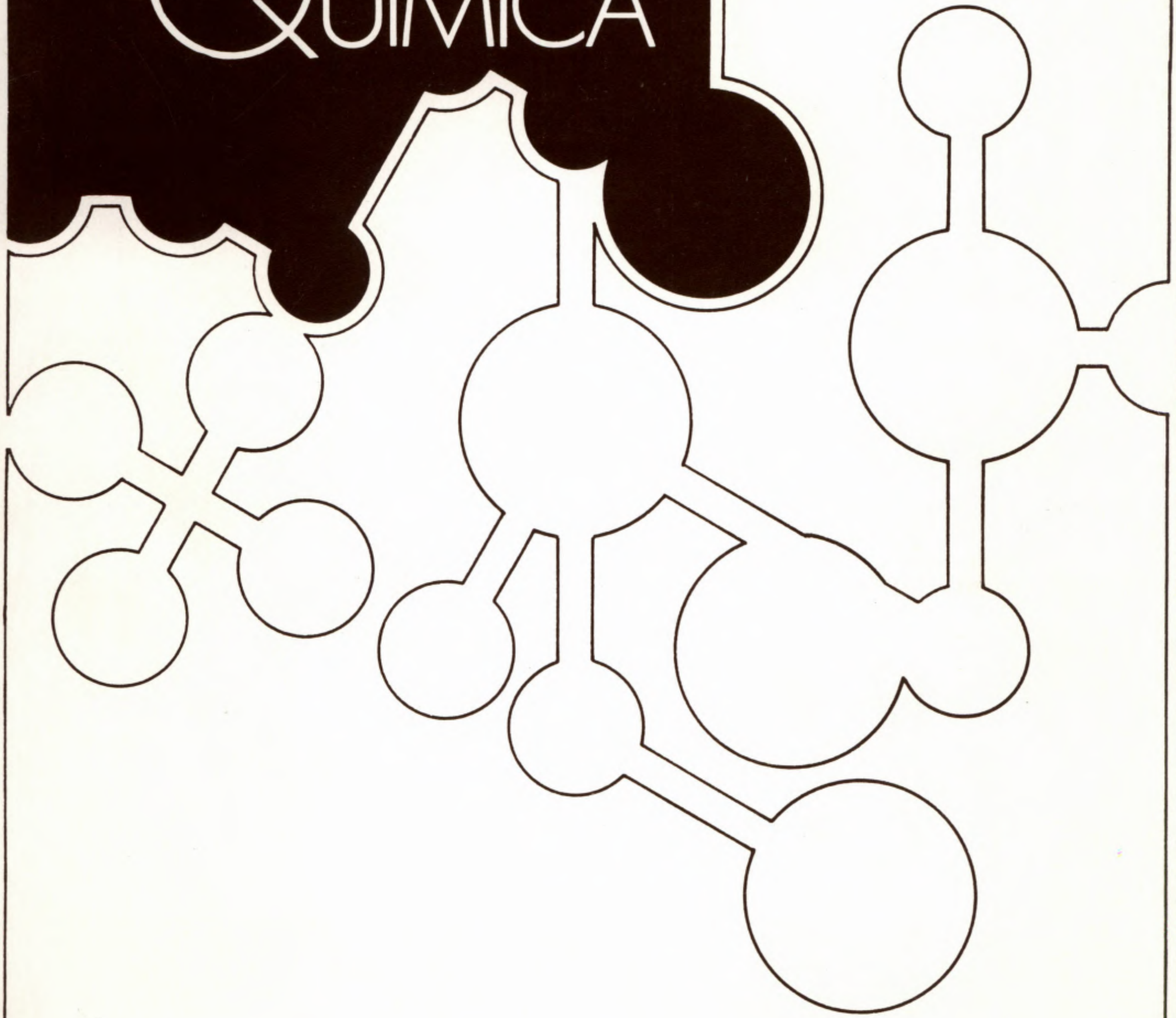

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REVISTA PORTUGUESA DE QUÍMICA

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Lisboa, 18 de Junho de 1984

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índice

M. Nunes da Ponte — 65 — PVT and Phase Equilibria of Simple and Not-so-simple Liquid Systems

L.A.K. Staveley — 74 — Recent Experimental and Theoretical Work on the Thermodynamic Properties of Molecularly Simple Liquid Mixtures

Jorge C.G. Calado
Paulette Clancy — 85 — The Development of a Flexible Iintermolecular Potential Energy Function for Ethylene

M.R. Tavares — 92 — Lista das Plantas de Origem Tropical com Actividade Farmacológica Estudadas Quimicamente em Portugal nas Últimas Décadas

M.R. Bermejo
F. Botana
M. Gayoso — 113 — Derivados Interhalogenados do Tl(III). IV — Complexos con TPPO

sundaresan Prabhakar — 119 — Some New Developments in the Chemisty of Aryl Hydroxylamines and Their Derivatives

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PVT AND PHASE EQUILIBRIA OF SIMPLE AND NOT-SO-SIMPLE LIQUID SYSTEMS

Although I am not supposed to be an impartial judge, let me begin by stating that I think this Conference has been very successful. We had two very good poster sessions, St. Peter answered quite positively to our prayers for good weather and, above all, there were four fine and authoritative plenary lectures, that covered most of the fields of interest of the participants.

The very success of this Conference, however, is my problem today. What am I going to say after all this? So I am afraid you will be soon to realize that my lecture is a typical case of last and... least.

Most of what I shall be reporting to you today are results obtained in the development of a project to obtain thermodynamic properties of relatively simple liquid mixtures, over extended ranges of temperature and pressure. When it started, several years ago, some important problems of liquid state physics were being solved. Noticeably, the repulsive part of the intermolecular potential had been identified as the essential cause of the structure of a non-hydrogen bonded liquid, the old van der Waals' ideas had been revived and sucessfully applied to liquid mixtures [1] and extensive computer simulations had fostered the development of perturbation theories.

This progress in our understanding of the liquid state called for suitable experimental results as, even in this age of computers, agreement with experiment must still be a measure of the success of a theory. Experimental data on liquid mixtures were, at the time, mostly measurements of excess thermodynamic properties of binary mixtures of condensed gases, as functions of composition, at one temperature (usually close to the triple point of the less volatile component of the mixture) and at the saturation vapour pressure (essentially zero pressure).

A theory of mixtures usually contains one or two adjustable parameters, supposedly characteristic of the potential between two unlike molecules in a mixture. These parameters can be obtained for instance, by fitting to the values of one or two excess functions for the equimolar mixture. As has already been pointed out in this Conference [2], this procedure does not leave much to be compared between theory and experimental results of the type described above. Moreover, as pointed

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Plenary Lecture, 2nd International Conference on Thermodynamics of Solutions of Non-Electrolytes, 25th March 1982, Lisbon.

out by SOARES *et al.* [3], agreement at one temperature does not warrant that the same will happen at other temperatures.

An example of what was thought to be a thorough understanding of simple liquid mixtures was the paper of LEE *et al.* [4] on the system Ar + Kr. When it was published, the available experimental data on this important system was limited to excess volumes V^E at 116 K and excess Gibbs energies G^E at 104 K and 116 K [5]. The perturbation theory calculations of LEE *et al.* agree very well with these results. They also calculated excess enthalpies H^E. Although there were no experimental results to compare with, they stated that their values should be very reliable, because the experimental G^E were accurately predicted at two different temperatures.

More recently, STAVELEY and coworkers [6] published the first available experimental excess enthalpies. Comparison with the Barker-Henderson theory calculations of LEE *et al.* is shown in fig. 1. There is a striking disagreement, especially in what concerns the symmetry about the x = 0.5 axis.

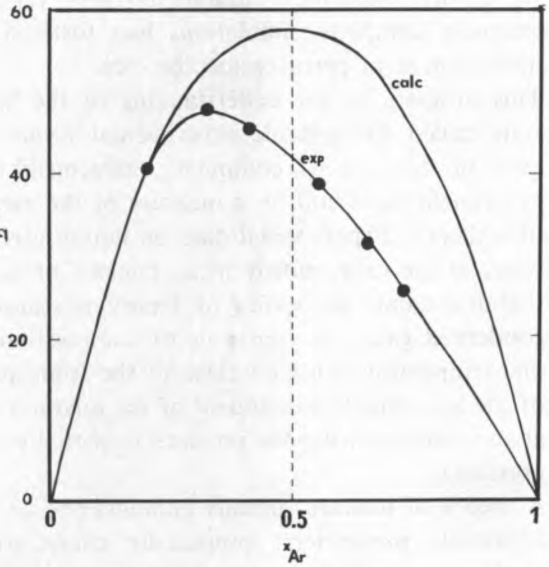

Fig. 1

Excess enthalpies H^E of argon + krypton liquid mixtures at 116 K: —●— experimental results reference [6]; —— calculated results, reference [4]

This proves how difficult it is to devise meaningful tests of a theory with limited experimental data. Results over a wide range of conditions (composition, temperature, pressure) would provide the best possible situation. For the important argon + krypton system, we have recently performed measurements of (p,V,T) properties [7] at several temperatures, up to the freezing pressure of krypton. Available results were therefore extended, so that most of the overlapping liquid ranges of argon and krypton have been covered. The dependence on pressure of the excess volumes V^E of an approximately equimolar mixture is shown in fig. 2. The main features of this dependence may be summarized as follows:

a) The first 20 MPa of applied pressure exert a remarkably strong effect on V^E.

b) At the highest pressures, V^E is essentially constant (independent of pressure and temperature) and approximately zero.

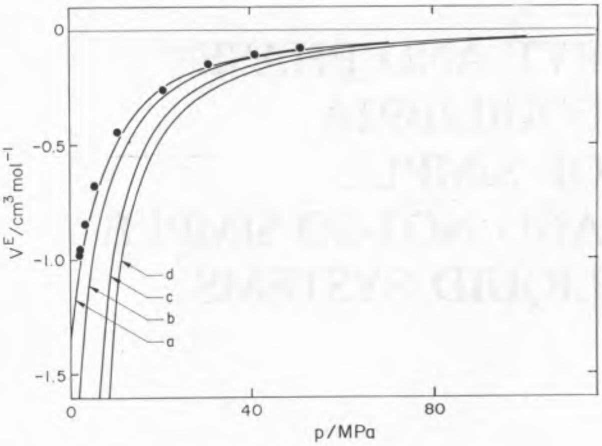

Fig. 2

Dependence on pressure of the excess volume V^E of an approximately equimolar mixture of liquid argon + krypton, at the following temperatures: (a) 129.32 K; (b) 134.32 K; (c) 142.68 K; (d) 147.08 K. ● data of reference [8], at 129.31 K

Fig. 3 showns the pressure effect on the composition dependence of V^E. At low pressures, the V^E *vs.* mole fraction x curves are quite obviously skewed to the side of the more volatile component, argon-rich mixtures yielding more negative V^E. This is a common feature for simple liquid mixtures. When pressure is raised, the curves become more symmetric up to about 20 MPa. When pressure is further increased, asymmetry is restored, but now in the opposite direction: argon — rich mixtures yield more positive V^E. As the

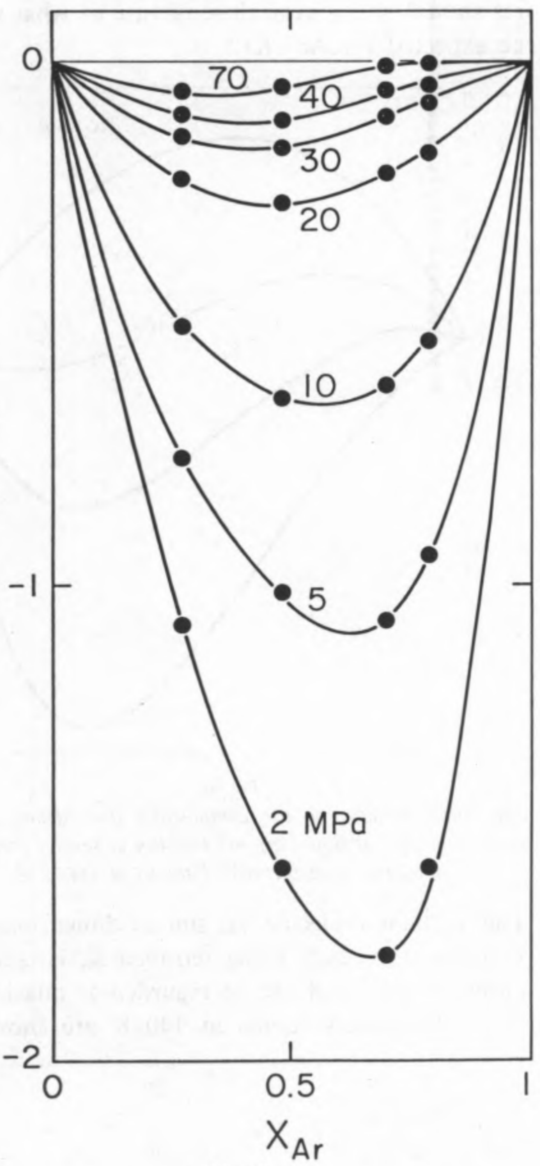

Fig. 3

Experimental excess volumes V^E for argon + krypton liquid mixtures, as function of composition, at several pressures and at 134.32 K

pressure approaches the freezing pressure of krypton, the V^E *vs.* x curves become almost S — shaped.

The temperature dependence of V^E, at several pressures, for $x = 0.5$, is shown in fig. 4. Steep curves indicate a strong effect of pressure on the excess enthalpy, given by:

$$\Delta H^E = H^E(p) - H^E(p_o) =$$

$$= \int_{p_o}^{p} [V^E - T(\frac{\partial V^E}{\partial T})_p] dp \qquad (1)$$

At low pressures, the entropy term $[-T(\partial V^E/\partial T)_p]$ is dominant and very strong effects are obtained. Fig. 5 compares ΔH^E with ΔG^E, the effect of pressure on the excess Gibbs energy

$$\Delta G^E = G^E(p) - G^E(p_o) = \int_{p_o}^{p} V^E dp$$

It shows, as has already been said in this Conference [2], that H^E is a very sensitive thermodynamic function; the very steep increase of H^E with pressure should be compared with the figure given in reference [6]:

$$H^E\ (x = 0.5,\ 116\ K,\ p = 0) = 42.7\ J\ mol^{-1}$$

On the other hand, V^E changes more rapidly with pressure for the argon-rich mixtures than for the krypton-rich ones. It is reasonable to expect that the same will also be true for the change of V^E with temperature, $(\partial V^E/\partial T)_p$, and from equation (3), ΔH^E at low pressures should therefore be larger for argon-rich mixtures. And so, although no measurements of H^E function of pressure have been performed yet for argon + + krypton mixtures, we may predict that the H^E *vs.* x curves should be very asymmetric at least for some ranges of pressure.

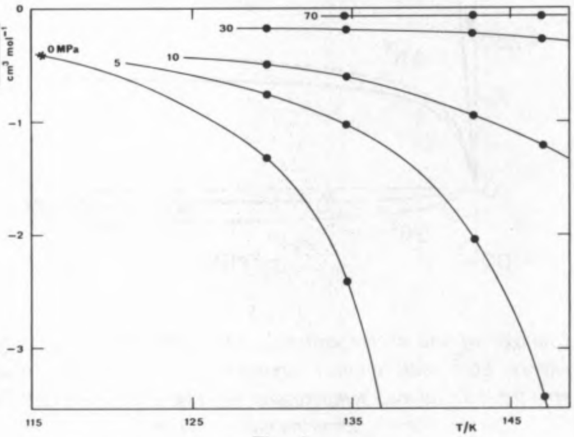

Fig. 4

Experimental excess volumes for an approximately equimolar mixture of liquid argon + krypton as a function of temperature, at several pressures: ✱ reference [5]; ● reference [7]

Some years ago, McDONALD [9], draw, from extensive computer simulations of simple liquid mixtures, the conclusion that "the G^E and the H^E dependence on composition is rather uninteresting". Although experiment proved him to be right about G^E, it does not certainly seem to be the case for H^E.

To examine how theory predicted excess enthalpies, we used the simple, but successful van der Waals-one fluid theory [1]. The excess enthalpies of argon + krypton mixtures were calculated using the equation of state of argon given by GOSMAN *et al.* [10], to characterize the reference fluid. The experimental pressure dependence of H^E, for an equivalent molar mixture, was very well reproduced by theory, as shown in fig. 5. This is a remarkable success for such a simple theory. As to the H^E *vs.* x curves, the theory gives very asymmetric curves at low pressures, symmetry about the x = 0.5 increasing with applied pressure, as shown in fig. 6. The larger pressure effect on argon-rich mixtures referred to above is correctly predicted.

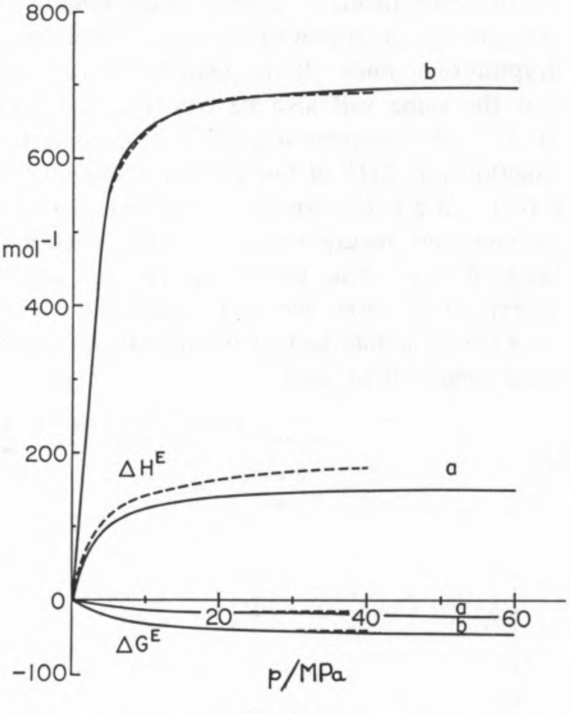

Fig. 5

Changes of the excess enthalpy ΔH^E and the excess Gibbs energy ΔG^E with applied pressure, for the mixture 0.485 Ar + 0.515Kr, at two temperature: (a) 134.32 K; (b) 142.68 K. (—— experiment; ---- theory)

WORMALD and collaborators made extensive measurements of enthalpies of mixing of simple liquids [11-13]. Although the system Ar + Kr was not included, the results obtained for Ar + CH_4 mixtures should give a very close picture of what would be expected for Ar + Kr.

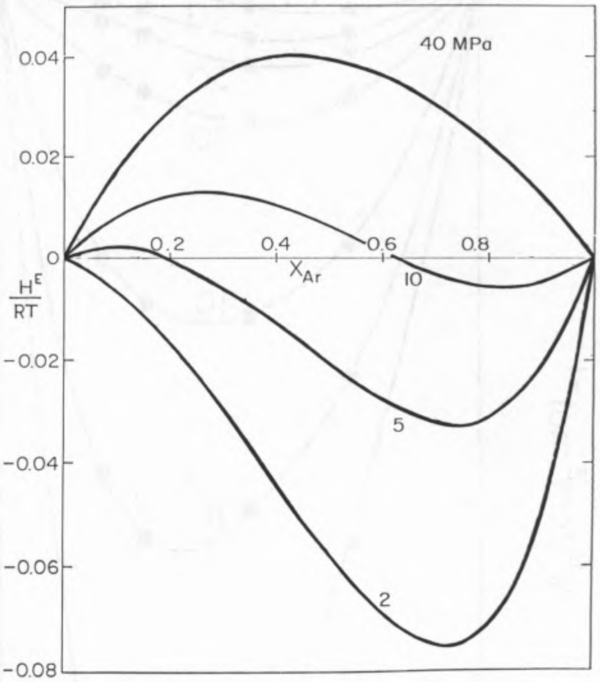

Fig. 6

Theoretical results for the composition dependence of the excess enthalpy of liquid argon + krypton at several pressures, calculated with the vdW-1 model at 134.32 K

The methane molecule has similar dimensions to a krypton atom and, being tetrahedral, is certainly quite compact and can be regarded as quasi-spherical. Wormald's results at 140 K are shown in

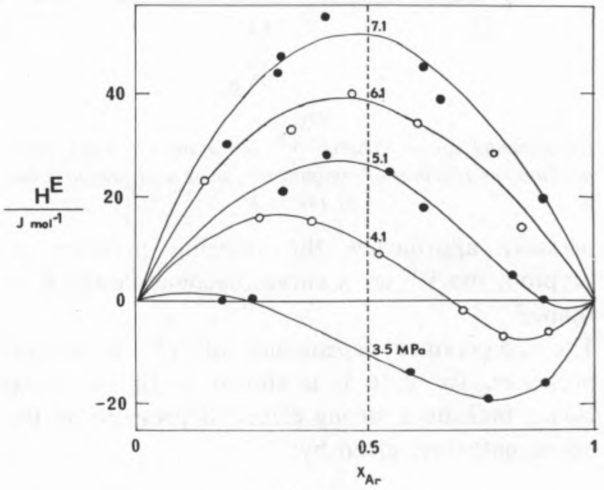

Fig. 7

Experimental excess enthalpies H^E for liquid argon + methane, as a function of composition at several pressures at 140.00 K, given in reference [13] fig. 7 and give a qualitatively very similar picture to the vdw-1 calculations of fig. 6.

Wormald's results are complemented by several sets of results on vapour-liquid equilibrium and (p,V,T) properties, which make argon + methane mixtures one of the best studied of the simple liquid systems.

Vapour-liquid equilibrium data were reviewed by KIDNAY *et al.* [14] (p,V,T) properties were measured by SOROKIN and BLAGOI [15], LIU and MILLER [16], SINGH and MILLER [17,18], and NUNES DA PONTE *et al.* [19,20]. Good agreement was obtained between the results of different authors, and the available data extend from the triple point of methane up to close to the critical point of argon.

Fig. 8 shows results of several authors for the pressure dependence of the excess volume V^E of an equimolar mixture of argon + methane. At high pressures, V^E reaches a limiting value, as for argon + krypton, but positive ($\sim +0.15$ cm^3 mol^{-1}), not zero.

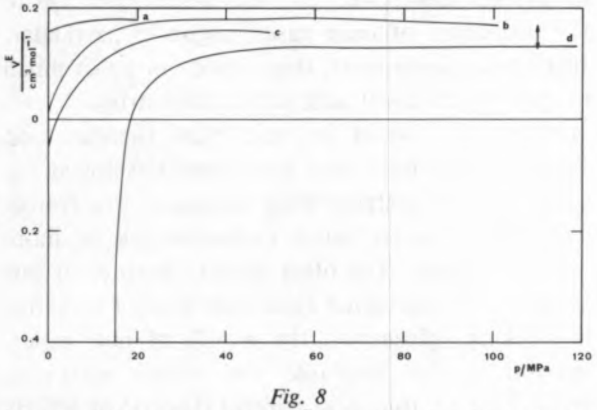

Fig. 8
Experimental excess volumes V^E for approximately equimolar mixtures of liquid argon + methane as a function of pressure, at the following temperatures: (a) 100.00 K, reference [17]; (b) 116.30 K, reference [19]; (c) 119.98 K, reference [15]; (c) 142.68 K, reference [20]

This effect may be interpreted in terms of the non-sphericity of the methane molecule. Fig. 9 shows a model for the interaction distance of two methane molecules. Collisional configurations where one hydrogen atom in one molecule fits the "hole" between three hydrogen atoms in the other one result in small carbon to carbon distances than in other configurations. An argon atom, however, has no protrusions that could give the same effect, and, therefore methane behaves on average as a bigger molecule in a methane-argon collision than in a methane-methane one.

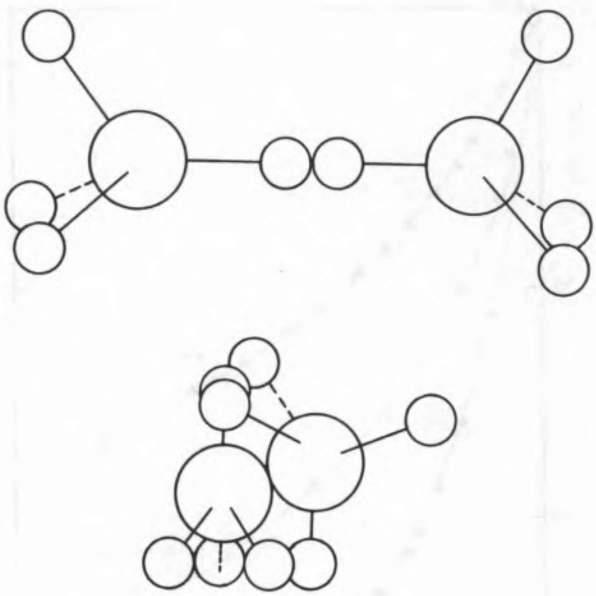

Fig. 9
Two possible relative orientations of two colliding methane molecules

In fig. 10 we compare (p,V) isotherms of methane, argon and an equimolar mixture of both substances, with calculations based on a perturbed hard-sphere equation method due to OELLRICH *et al.* [21]. Agreement with experiment is rather good, except for argon near the vapour pressure. Shortcomings of these perturbation methods near the critical point are well known, and as argon is only 8K from its critical temperature, those discrepancies were to be expected. However, at high pressures, the experimental molar volumes of the equimolar mixture are higher than the calculated values. This is because the equation of state of hard-sphere mixtures given by MANSOORI *et al.* [22] and used in these calculations admits the additivity of the hard-sphere diameters:

$$\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22}) \tag{3}$$

As methane behaves differently in 1-1 and 1-2 collisions, a deviation parameter j_{12} to the arithmetic rule can be introduced:

$$\sigma_{12} = \frac{1}{2}(1 + j_{12})\,(\sigma_{11} + \sigma_{22}) \tag{4}$$

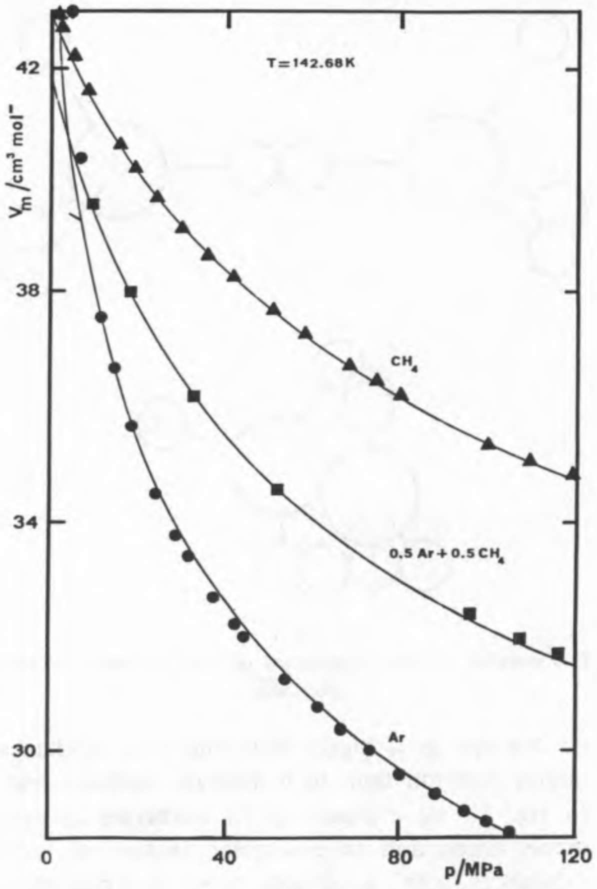

Fig. 10

(p, V) isptherms of liquid argon, methane and an equimolar mixture mixture. ● ▲ ■, *experimental;* —— *theory, reference [21], (T = 142.68 K)*

Calculation of j_{12} was performed for several methane containing mixtures, as well as for argon + + krypton. We fitted (p,V,T) results for argon + + krypton [7], argon + methane [19,20], nitrogen + methane [23], carbon monoxide + methane [24], and krypton + methane [25] by the equation of state of the [6,12] Lennard-Jones fluid given by NICOLAS *et al.* [26]. This gave us the distance and energy parameters σ and ϵ for each pure substance and equimolar mixture, and then, using the van der Waals-one fluid theory [1] mixing rules, we calculated j_{12} and also k_{12}, the deviation parameter for the geometric mean rule:

$$\epsilon_{12} = (1 - k_{12})\,(\epsilon_{11}\epsilon_{22})^{1/2} \tag{5}$$

Table 1 shows the results obtained with this procedure. Except for krypton + methane mixtures, the k_{12} values are all very similar. The trend in j_{12} is consistent with the high pressure values of the excess volumes, $V^E_{\text{lim.}}$, obtained for each equimolar mixture.

These values can be compared with the results of SINGH and MILLER [27], that used several van der Waals-like equations.

For krypton + methane, the geometric and arithmetic mean rules are essentially valid. Although there are obvious differences between a spherical krypton atom and a tethrahedral methane molecule, they are of about the same size, and intermolecular potentials are actually rather similar. This explains why these mixtures are very nearly ideal, as shown by measurements of their excess functions [8,25,28,29].

The work I have been describing is concerned with simple liquid mixtures. This kind of work is sometimes looked at with some contempt by application minded scientists and engineers, and referred to as "argonitis". This is supposed to be a disease that has struck theoretists and experimentalists alike, who pay too much attention to the properties of inert gases, argon in particular. Inert gases being inert, they could not be of much interest to chemical and related industries.

However it should be said that theories and prediction methods that have been developed for simple liquid systems have provided the framework for a much better understanding of more complex liquids. The other plenary lectures of this Conference have given good examples of how this is working. Moreover, the wealth of new experimental results available for simple mixtures, make it likely that new fruitful theoretical efforts could be undertaken in this field. On the other

Table 1

Deviation parameters to the arithmetic mean rule, j_{12} (equation 4), and to the geometric mean rule, k_{12} (equation 5), and high pressure limit of the excess volume, V^E_{lim}, for several equimolar mixtures

	j_{12}	k_{12}	$\frac{V^E_{lim}}{cm^3\ mol^{-1}}$
Ar + Kr	−0.0002	0.029	0.
Ar + CH_4	0.0056	0.025	0.15
N_2 + CH_4	0.0031	0.026	0.12
CO + CH_4	0.0015	0.026	0.02
Kr + CH_4	0.0000	−0.003	0.

hand, "argonitis" has proved to be a lot of fun for many people working in this field, including myself. As JORGE CALADO once said [30], argonitis would be a very applied science in planet Venus, where the atmosphere seems to be much richer in argon than on Earth. And Krypton, of course, is the planet of Superman. So, if you think of such a typical simple mixture as argon+-krypton as Venus+Superman, it is quite clear that "argonitis" can make your imagination wander.

Until now I have been talking about what may be considered simple liquid systems. Strictly speaking, only the condensed rare gases should be classified as such. However highly compact, small molecules, like nitrogen and methane, can be included in the list.

Many other liquids can be classified as "not-so--simple", this expression meaning, of course, that larger size and/or permanent multipole make the description of the intermolecular potential somewhat more complicated than in the case of spherically symmetric inert gases.

A significant share of the latest work on these liquids has been carried out in Oxford [31] and in Lisbon [32,33], and I will refer only to a small part I have been involved in.

We have recently concluded an experimental study of the equation of state of liquid carbon monoxide [34]. This is a small and compact molecule, with a small dipole and a large quadrupole: 0.112 Debye and -2.5×10^{-26} e.s.u. cm^2, following STOGRYN and STOGRYN [35]. Although it is of great theoretical and practical importance, experimental studies of its properties in the liquid phase are scarce, corresponding states methods being used in attempts to calculate them, with nitrogen as reference fluid [36].

Reduced second virial coefficients of nitrogen [37] and carbon monoxide [38,39] are plotted in fig. 11. At the higher temperatures the corresponding states principle is closely followed but at low temperatures there seems to be discrepancies, although definite conclusions can not be reached, because there is only one value for B (CO).

In the liquid phase, calculation based on a corresponding states correlation with nitrogen [36] depart somewhat from our experimental results. The influence of pressure on these deviations is shown in fig. 12. Although they increase with increasing pressure, they remain below one percent, indicating a reasonably successful application of the principle of corresponding states. At the freezing line, available results seemed to indicate until recently strong departures from corresponding states with nitrogen. FUKUSHIMA *et al.* [40] measured the melting pressure of carbon monoxide and their results departed considerably from those of MILLS and GRILLY [41] for nitrogen. However, our results [42] agree well with an extrapolation of the earlier ones of CLUSIUS *et al* [43] and VERSCHOYLE [44] and are much closer to the nitrogen melting line than those of FUKUSHIMA *el al.*

So, the available evidence is that despite its small dipole and large quadrupole, carbon monoxide

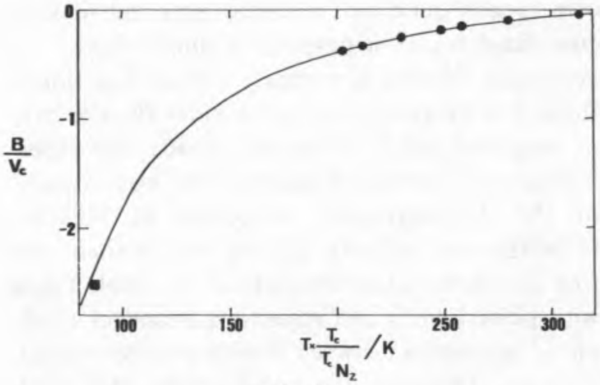

Fig. 11

Reduced second virial coefficients of nitrogen (——. reference [37]) and carbon monoxide (●, reference [39]; ■, reference [38])

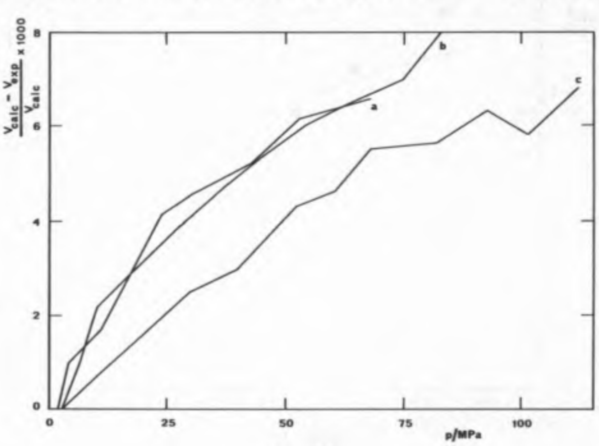

Fig. 12

Deviations between experimental [34] and calculated [36] molar volumes of carbon monoxide, as a function of pressure at: (a) 82 K; (b) 100 K; (c) 120 K corresponds quite well with nitrogen and may be considered for most purposes a simple fluid.

Hydrogen chloride is certainly a much less simple fluid. It is however as simple a polar fluid as may be imagined and therefore of considerable experimental and theoretical interest. The measurement of the thermodynamic properties of HCl-Xe, HCl-HBr and HBr-Xe [45,46] was perhaps the first systematic study of mixtures of simple liquid with polar liquids and remains a beautiful example of agreement between theory and experiment. POWLES, GUBBINS and collaborators [47] published results of a computer simulation on liquid HCl. They used a site-site [6-12] Lennard-Jones intermolecular potential, with parameters taken from previous results on Cl_2, N_2 and H_2, nitrogen being used for extrapolation to obtain the parameters for the H-H interaction. The potential thus obtained added to the dipolar and quadrupolar interactions, was proposed as a suitable approximation to the true potential for HCl molecules. However a much simpler potential was actually used in their computations, by taking only the site-site interactions but with parameters scaled by two factors f_ϵ and f_σ. These factors were chosen to give a best fit to the experimental liquid density and vapour pressure along the entire coexistence line. Then calculated values of the internal energy were compared with experimental data, as shown in fig. 13. At the time of publication there was only the value given by GIAUQUE [48] to compare with, in the liquid phase. More recent work [49], in good agreement with Giauque's, gave the other values of U plotted in the figure. They show that at low temperatures discrepancies between experimental and computation increase. POWLES *et al.* stated in their paper that it would be valuable to have values of U at several temperatures, which would allow for a fit of the factor f_ϵ independently of f_σ. We hope our values may lead in turn to a refining of their model.

I said most of what I intended to, but before I finish let me go back in time. Fig. 14 shows the excess functions, V^E, G^E, H^E and $T.S^E$ for carbon monoxide + methane liquid mixtures. It is taken from a paper by POOL and STAVELEY [46] that reported the first comprehensive thermodynamic study of a mixture of condensed gases. As I went through it, I realized that it had been received by the editor on the 26th of March 1957, that is, twenty five years tomorrow. It was a fortunate coincidence that this Conference was scheduled for this occasion, thus commemorating what may be described as the silver wedding of thermodynamics of simple liquid mixtures. And even more fortunately, we were able to start in this Conference the Lionel Staveley Lecture Series and had Lionel Staveley himself giving us the first. All this make it a great honour for me to have participated in this event and given this lecture today.

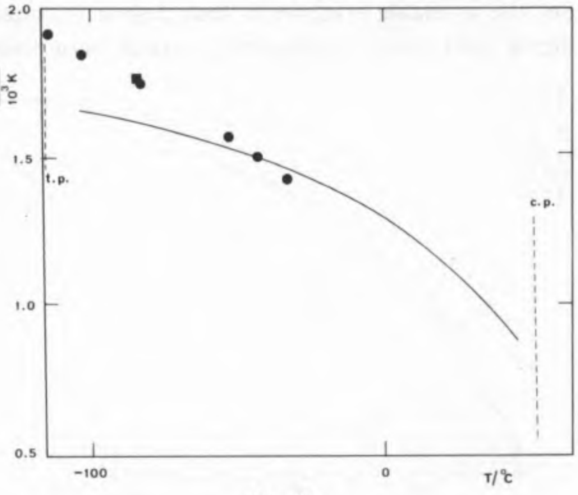

Fig. 13

Configurational internal energy of orthobaric liquid HCl, as a function of temperature: ——, computer simulation, reference [47]; ■, experimental, reference [48]; ●, experimental, reference [49]

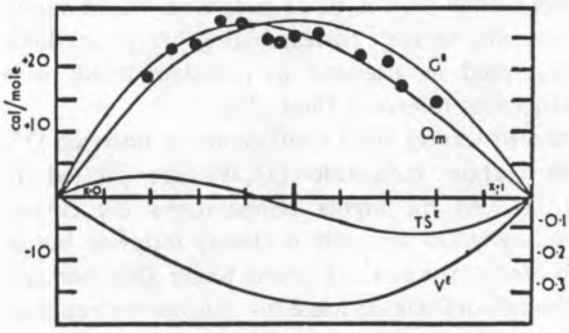

Fig. 14

Excess thermodynamic functions for the system $CO + CH_4$ at 90.67 K, against mole fraction of carbon monoxide. The points are the experimental values of H^E (Qm). The figure is taken from reference [46]

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RECENT EXPERIMENTAL AND THEORETICAL WORK ON THE THERMODYNAMIC PROPERTIES OF MOLECULARLY SIMPLE LIQUID MIXTURES

1 — INTRODUCTION

The thermodynamic properties of mixtures of liquids have interested chemists for many years. An enormous amount of experimental information has been amassed, and a great deal of effort has been devoted to developing theories which seek to account for the observed behaviour of such mixtures. These theories have more than academic interest and importance, for the better our understanding of liquid mixtures, the better are the chances of successfully predicting the properties of a particular mixture. Reliable predictions of this kind may have considerable technological value.

The thermodynamic properties of a liquid mixture are generally considered with reference to the corresponding properties of an ideal liquid mixture. The ideal solution, like the ideal gas, is a convenient fiction. In an ideal liquid mixture, the chemical potential μ_i of a component i at a temperature T must obey the equation

$$\mu_i = \mu_i^0 + RT\ln x_i, \tag{1}$$

where x_i is the mole fraction of component i. μ_i^0 is the chemical potential (or Gibbs energy per mole) of the pure liquid i at the temperature T. (Strictly speaking, μ_i^0 is a function of the pressure acting on the system, but most of the experimental work on liquid mixtures has been carried out at low pressures, of the order of one atmosphere, and moderate pressure changes in this region have almost no effect on μ_i^0). If the mixture of the vapours in equilibrium with the liquid mixture can be regarded as a mixture of ideal gases, it follows from eqn. (1) that the partial vapour pressure p_i of component i is given by the equation

$$p_i = p_i^0 x_i, \tag{2}$$

where p_i^0 is the vapour pressure of pure liquid i at the same temperature.

We are concerned in this lecture with real, and hence non-ideal, liquid mixtures, and we shall confine ourselves to mixtures of only two components. If x_1 moles of a liquid component 1 and $(1-x_1)$ moles of a liquid 2 are mixed to give one mole of a solution at a temperature T, then for

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any extensive thermodynamic function X, the change ΔX_m in this function is

$$\Delta X_m = X_m - x_1 X_1^0 - (1-x_1)X_2^0, \tag{3}$$

where X_m, X_1^0 and X_2^0 are respectively the values of X for a mole of the mixture, a mole of pure component 1 and a mole of pure component 2. ΔX_m can also be written as

$$\Delta X_m = X_m(\text{id}) + X^E, \tag{4}$$

where X^E is the excess function. For the Gibbs energy, it readily follows from eqn. (1) that

$$\Delta G(\text{id}) = RT[x_1 \ln x_1 + (1-x_1)\ln(1-x_1)]. \tag{5}$$

$\Delta S(\text{id})$ is given by $-R[x_1 \ln x_1 + (1-x_1)\ln(1-x_1)]$. From the above criteria of ideality, it follows that if two liquids mix to form an ideal solution, they do so with no enthalpy change (i.e. athermally), and with no volume change. So for a real mixture, we have $\Delta H_m = H^E$, the enthalpy of mixing, and $\Delta V_m = V^E$, the volume increase on mixing. S^E, of course, is given by $(H^E - G^E)/T$. In this review, values of the four excess functions G^E, H^E, V^E and S^E all refer to the formation of one mole of mixture.

G^E, H^E and V^E can all be determined by experiment. Of interest is not only their composition dependence, but also their temperature dependence (at constant pressure) and their pressure dependence (at a constant temperature). The aim of a theory is to calculate these excess functions for particular mixtures. We shall be concerned only with those theories which attempt to do this on the most fundamental basis possible, namely in terms of the intermolecular forces which operate between the molecules involved in a particular system. When such theories began to be advanced — essentially in the years following the Second World War — almost all the experimental data on the excess functions of binary liquid systems then available referred to mixtures of substances which are liquid at ordinary temperatures, involving therefore such compounds as benzene, cyclohexane, tetrachloromethane, *n*-hexane and so on. While the molecules of such substances may be simple to, say, an organic chemist, they are complex and difficult when it is a matter of finding a quantitative expression for the intermolecular energy of a pair of molecules as a function of their separation. So it at once became clear that these new statistical-mechanical theories of liquid mixtures could only be fairly and usefully tested on mixtures of the simplest and smallest molecules, or in other words on mixtures of liquefied gases. This was the primary consideration which prompted the initiation and development of the kind of experimental cryogenic work discussed in this lecture.

2 — EXPERIMENTAL METHODS

We shall not give a detailed account of the experimental methods for measuring G^E, V^E and H^E for liquid mixtures, but simply indicate the nature of these methods and draw attention to one or two salient points. G^E is determined by measuring the vapour pressure of mixtures of known composition. An equation connecting G^E with the mole fraction x of one component is assumed, such as the Redlich-Kister equation

$$G^E = ARTx(1-x)[1 + B(2x-1) + \\ + C(2x-1)^2 \ldots] \tag{6}$$

and the experimental results are then used to determine A,B,C... If the composition of the vapour in equilibrium with a liquid mixture is also measured, G^E can be evaluated without having to assume any specific form of equation connecting G^E and x. But in either event, it is essential to allow for the imperfection of the vapour phase. To deal adequately with this for pressures up to a few atmospheres it is not necessary to proceed beyond the second virial coefficient. There is, however, a serious shortage of experimental data on even the second virial coefficients of gas mixtures at low temperatures, and indeed even for some of the pure gases themselves, and work to remedy this deficiency would be valuable.

V^E is most commonly determined by the straightforward method of measuring the amount of each gas needed to fill a pyknometer at a known low temperature with a mixture of known composition. Recently, HAYNES and HIZA (1976, 1977), have described a magnetic method in which the quantity measured is the magnetic field required to balance the gravitational force on a barium ferrite cylinder immersed in the liquefied gas mixture. This method can be used to 50 atmospheres, and clearly has considerable potential. Another method, developed by SINGH and MILLER (1978), depends on measurements of the dielectric constant (permittivity) of the pure and mixed liquids, assuming the Mosotti-Clausius correlation between this property and the molar volume. All of these methods are capable of a precision of a few parts in 10^4.

The determination of H^E has proved to be more difficult. It can be deduced from measurements of G^E at more than one temperature, using the relation

$$(\partial G^E/\partial T)_p = -H^E/T^2, \qquad (7)$$

but a direct calorimetric method is to be preferred. My collaborators and I have constructed a series of calorimeters for measuring the enthalpy of mixing of two liquefied gases (see, e.g., LEWIS *et al.*, 1975). Known amounts of each pure component are liquefied into separate cavities. The two cavities are separated by a valve, and together form a closed system. Mixing is accomplished by opening the valve and shaking the whole cryostat. An indication of the sort of results obtained is shown for the system argon- methane in fig. 1.

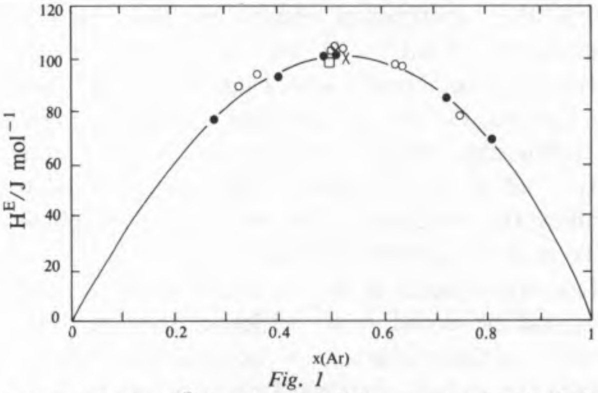

Fig. 1

Excess enthalpy H^E for the $Ar+CH_4$ system at 91.5K. Full circles, LEWIS, SAVILLE, STAVELEY (1975); open circles, LAMBERT and SIMON (1962); square, MATHOT (1958); cross, JEENER (1957)

The accuracy is ~ 1 to 2 per cent. A similar calorimeter has been more recently constructed by Professor W.B. Streett at Cornell University. This is more completely automated, and the mixing of the two liquids is effected by a rotating stirrer. This instrument is already giving results of higher precision. However, the vapour phase cannot be wholly eliminated from such calorimeters (unlike those operating at room temperature), and the corrections which have to be made on this account become increasingly more serious as the critical region is approached. Eventually it is necessary to change to a different type of calorimeter such as a flow calorimeter, even though these require considerably larger amounts of substance (see. e.g., MOSEDALE and WORMALD, 1977). The effort required to obtain reliable values of H^E has undoubtedly been worthwhile. In the first place, H^E (and likewise S^E) can be described as a more sensitive function than G^E. As just one example of what is meant by this, we may cite a result arising from studies of the equation of state of pure and mixed liquefied gases to which we shall refer later (Section 6(c)). From such studies on a system for which the excess functions are known for some low (effectively almost zero) pressure, it is possible to calculate how these excess functions will change with increasing applied pressure. A typical result is shown in fig. 2 for the nitrogen-methane system. It will be seen that the changes with pressure in H^E and TS^E are altogether larger than those in G^E. In theoretical predictions of these functions, if a theory gives an expression from which G^E can be calculated, to estimate H^E and S^E it is necessary to go further and evaluate $(\partial G^E/\partial T)_p$, which clearly makes a reasonably successful prediction of H^E and S^E a more exacting undertaking than the prediction of G^E. Another reason which makes H^E data

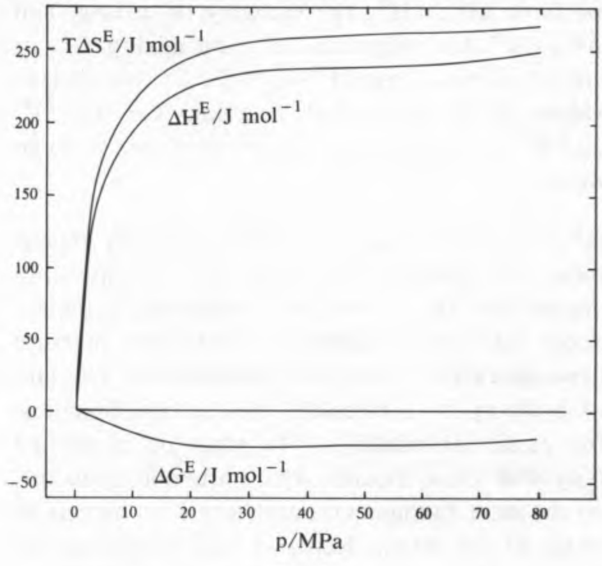

Fig. 2

The effect of pressure on the excess functions of an approximately equimolar mixture of N_2+CH_4 at 115K (NUNES DA PONTE et al., *1978)* highly desirable relates to the so-called combining rules. The intermolecular energy curve for a pair of molecules is often characterized by the parameters ϵ and σ, ϵ being the depth of the potential well and σ the separation at which the energy is zero. Since in a mixture of two components 1 and 2, the three pair interactions 1-1, 2-2 and 1-2 have to be considered, the problem arises of the relation between ϵ_{12} and σ_{12} for the unlike pair and the corresponding parameters for the two like pairs. It has been recognized for some time that the original Lorentz-Berthelot combining rules, namely

$$\sigma_{12} = 1/2(\sigma_{11} + \sigma_{22}) \text{ (Lorentz)} \tag{8}$$

and

$$\epsilon_{12} = (\epsilon_{11}\ \epsilon_{22})^{1/2} \text{ (Berthelot)} \tag{9}$$

are not adequate, and must be modified by introducing parameters j_{12} and k_{12}, such that

$$\sigma_{12} = 1/2(1 + j_{12})\,(\sigma_{11} + \sigma_{22}), \tag{10}$$

and

$$\epsilon_{12} = (1 - k_{12})\,(\epsilon_{11}\epsilon_{22})^{1/2} \tag{11}$$

It transpired that the calculated excess functions are sensitive to the values of j_{12} and k_{12} (especially the latter), small though these values may appear to be. In the absence of a general reliable method for estimating j_{12} and k_{12}, one is forced to sacrifice two pieces of experimental information to fix these parameters, for example one value of G^E (for a certain concentration and temperature), and similarly one value of V^E. If, therefore, the experimental data available for testing the theory are limited to G^E and V^E, there is little left to test, There remain only the concentration dependence of G^E and V^E (which is often almost symmetrical anyway, at least for G^E), and their values at other temperatures. If H^E is also known, however, the situation is much improved.

3 — SOME OBSERVATIONS ON CURRENT MOLECULAR THEORIES OF SOLUTIONS

It would need considerable space to do justice to all the theories relevant to our subject, and our comments here must necessarily be brief. There are two systems of absolutely fundamental importance on account of their extreme molecular simplicity, namely Ar + Kr and Kr + Xe. Considerable quantitative success has now been achieved in the theoretical treatment of these two systems, as was described by Professor Calado in his plenary lecture delivered at the conference held in 1979 at Santiago de Compostela (Calado, 1983). Two other very basic systems are $Ar + CH_4$ and $Kr + CH_4$, since the methane molecule, while not of course monatomic, is compact, highly symmetrical, and has no dipole or quadrupole moment. In recent years, my own experimental interest has been in studying systems the molecules in which, while remaining small, have dipoles, quadrupoles or octupoles. Such studies can be regarded as forming a planned programme through stages of increasing molecular complexity, which should eventually link up with the more complex molecules of substances liquid at ordinary temperatures. In the early stages of this experimental programme, Gubbins and Gray and their collaborators developed a perturbation theory of solutions designed to examine the effect on the excess functions of dipoles, quadrupoles and octupoles in the molecules of one or both components, and also of anisotropy in the dispersion and repulsive forces (Twu *et al* and Flytzani-Stephanopoulos *et al.*, 1975). Their theory has now been tested in a series of joint publications on several of the systems which we have investigated experimentally.

The types of system which have been studied experimentally, with examples of the actual systems chosen, are the following: — non-polar — dipole ($Xe + HCl$; $Xe + HBr$); dipole-dipole ($HCl + HBr$); non-polar-quadrupole ($Xe + N_2O$; $Ar + N_2$; $Ar + O_2$); non-polar-octupole ($Xe - CF_4$); dipole-quadrupole ($HCl + N_2O$); quadrupole-quadrupole ($N_2O + C_2H_4$); dipole-octupole ($HCl + CF_4$).

A perturbation theory, such as that developed by Gubbins and Gray, treats the real system by starting with a simpler system as a reference, and then converting this into the real system, as it were, by introducing a suitable kind of perturbation. Thus, the reference system might be a mixture of hard spheres, or of molecules such as argon and krypton for which the intermolecular pair potentials are functions only of the intermolecular separation (*i.e.* there are no orientational factors involved), and can be adequately represented by some relatively simple expression, such as a Lennard-Jones potential (12-6 potential). The perturbation then takes the form of the introduction into the molecules of one or both components of a dipole, a quadrupole or an octupole, and it also becomes necessary even for a simple diatomic molecule like nitrogen to allow for the angular dependence of the dispersion and repulsive (overlap) forces. Here it must be pointed out that a dipolar molecule like HCl also has a quadrupole moment, and it is found that the influence of this quadrupole moment is by no means negligible. It is of paramount importance to construct intermolecular potential functions for the molecules involved which are as good as possible, that is which give the best representation of, or the best consistency with, the bulk properties of the pure polar components. It might be thought that we are dealing with substances which are so simple and so well-known that all the necessary information on their bulk properties would be available. But this is by no means always the case. For HCl, for example, it would be invaluable to have p-V-T data on the liquid up to, say, 1000 bar, from which the configurational energy could be calculated as a function of volume. So here is a field in which the experimentalist can make a valuable contribution.

The first thermodynamic function to be calculated is the Helmholtz energy A, which is expanded in terms of the perturbing potential — not as a series, which generally converges too slowly, but as the Padé approximation

$$A = A_0 + A_2\left[\frac{1}{1-A_3/A_2}\right], \qquad (12)$$

where A_0 is the value of this function for the reference potential. (The term A_1 vanishes with a suitable choice of the reference potential). The required excess functions of the mixture are derived from A using standard thermodynamic relations.

4 — COMPARISON OF THEORY AND EXPERIMENT FOR SOME SELECTED SYSTEMS

As our first example, we take the system Xe+HCl (CALADO *et al.*, 1975, 1978). Generally, the comparison of theory and experiment is made by comparing the actual and calculated values of the excess functions, but in fig. 3 the predicted and measured behaviour of this very non-ideal system is shown on a different basis, namely as plots of the total vapour pressure against the composition of liquid and vapour phases at three different temperatures. The problem of the indeterminate parameter in the cross-interaction potential (in effect, the k_{12} of eqn. (11)) was resolved by assuming the experimental value of the vapour pressure for the equimolar mixture at the highest temperature. The agreement between the calculated and experimental curves in fig. 3 is impressive, and the same is true for V^E. When, however, the comparison is made for the function H^E (which earlier was described as being more "sensitive"), the outcome is rather different. Two calculated curves are shown in fig. 4, neither in close agreement with experiment (LOBO *et al*, 1980). As already pointed out, the HCl molecule has both a dipole moment (μ) and a quadrupole moment (Q). Curve (a) in fig. 4 was calculated by incorporating the four terms $\mu\mu$, μQ, $Q\mu$ and QQ in the intermo-

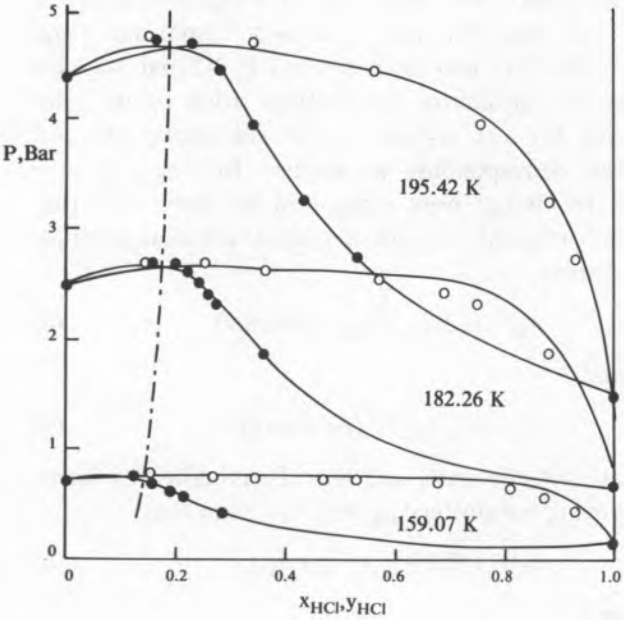

Fig. 3

Vapour — liquid equilibria for the system Xe+HCl from theory (lines) and experiment (points). The dash-dot line is the azeotropic locus. The open circles and x_{HCl} refer to the liquid phase, the full circles and y_{HCl} to the vapour phase. (CALADO et al., *1978)*

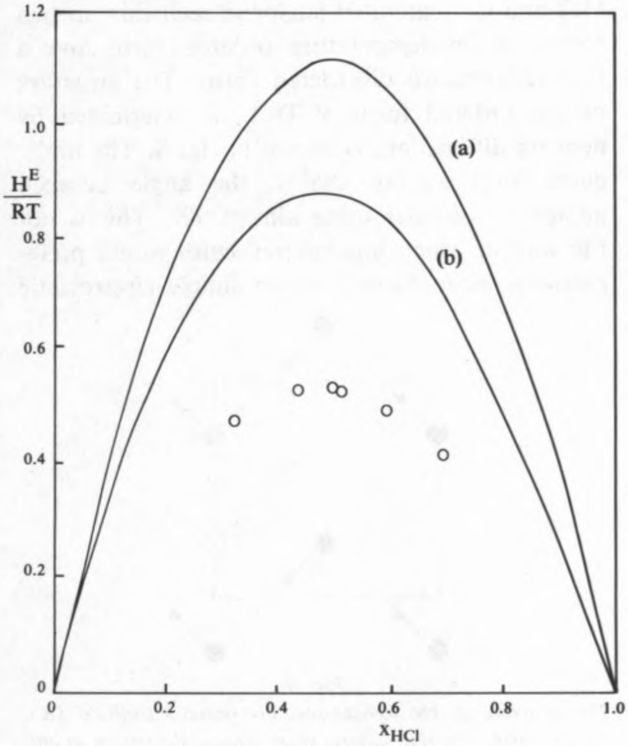

Fig. 4

*Comparison of experimental values of H^E for the system $Xe + HCl$ at 182.32K (open circles) with those calculated using two potential models (a) and (b) (*Lobo *et* al., *1980)*

lecular potential, but ignoring the anisotropy of the dispersion and overlap terms, whereas in the calculations leading to curve (b) this anisotropy was allowed for. This is an example of the sensitivity of a calculated H^E to the details of a theoretical treatment. The HCl molecule, in fact, has a deceptive simplicity, a point to which we will return later.

An example — and it is not the only one — where the theory of Gubbins and his collaborators achieves a notable success is with the non-polar-octupole system $Xe + CF_4$ (fig. 5, Lobo *et al.*, 1981). Here the agreement between the experimental and calculated H^E results is excellent. Once again, the value of G^E for the equimolar mixture has had to be sacrificed to deal with the indeterminate intermolecular energy parameter.

Systems of two quadrupolar molecules can be of two kinds, depending on whether the quadrupoles of species 1 and 2 have the same sign, or opposite signs. The way two quadrupolar molecules tend to associate is different, according to whether the signs of the two quadupoles are the same or not

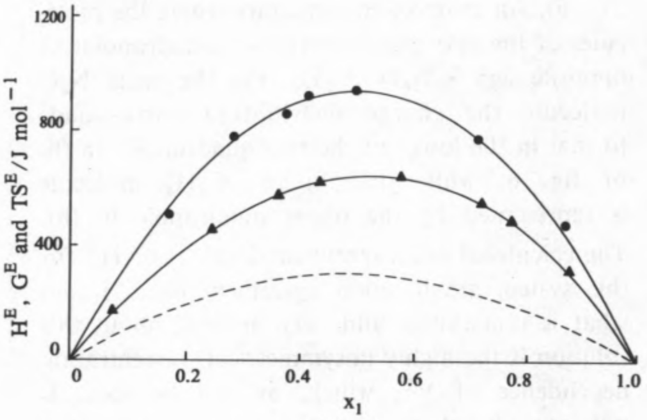

Fig. 5

*G^E at 159.01K (triangles) and H^E at 163.01K (circles) for $Xe + CF_4$ plotted against x_1, the mole fraction of xenon. Points are experimental results, the solid lines are calculated. The dashed line is TS^E. (*Lobo *et* al., *1981)*

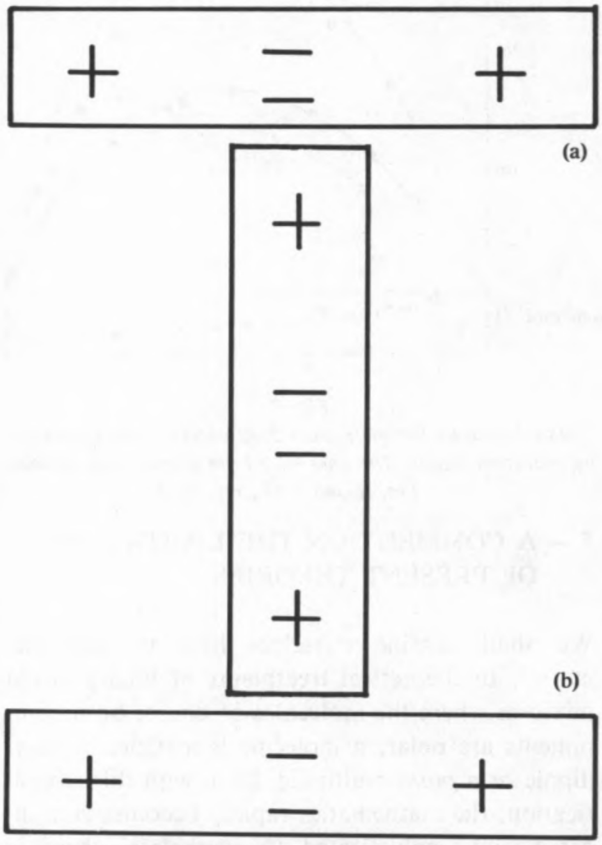

Fig. 6

Showing the preferred orientation for two quadrupoles of (a) the same sign, (b) of opposite sign (fig. 6). An example of a mixture where the molecules of the two components have quadrupoles of opposite sign is $N_2O-C_2H_4$. For the linear N_2O molecule the charge distribution corresponds to that in the lower of the two quadrupoles in (b) of fig. 6, while that in the C_2H_4 molecule is represented by the upper quadrupole in (b). The calculated and experimental values of H^E for this system are in good agreement (fig. 7), but what is remarkable and very unusual about this solution is the highly unsymmetrical concentration dependence of V^E, which, as will be seen, is not reproduced by the theoretical calculations (LOBO, STAVELEY, CLANCY and GUBBINS, unpublished work, reference [27]).

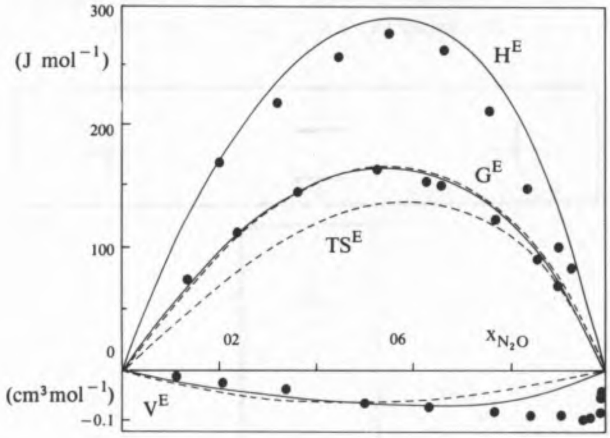

Fig. 7

Excess functions for the system $N_2O+C_2H_4$. The points are experimental results. The lines have been obtained by calculation. (LOBO et al., *ref. [27])*

5 — A COMMENT ON THE LIMITATIONS OF PRESENT THEORIES

We shall confine ourselves here to just one matter. In theoretical treatments of binary liquid mixtures where the molecules of one or both components are polar, a molecule is assigned a *point* dipole or a *point* multipole. Even with this simplification, the mathematics rapidly becomes complicated and sophisticated. Nevertheless, there is experimental evidence which suggests that it is desirable to try and improve on this approximation of *point* dipoles or multipoles. For example, the way in which two or more HCl molecules associate suggests hydrogen bonding rather than simple electrostatic attraction. In the solid state, HCl and its deuterated analogue each exist in two forms, a low-temperature ordered form and a high-temperature disordered form. The structure of the ordered form of DCl, as determined by neutron diffraction, is shown in fig. 8. The molecules form zig-zag chains, the angle between adjacent molecules being almost 90°. This is not the way in which dipolar molecules would preferentially group themselves on simple electrostatic grounds. The structure does, however, strongly suggest that the real ordering force is attraction between the proton or deuteron and the negative charge offered by a pair of unshared electrons in a p-orbital of the chlorine atom.

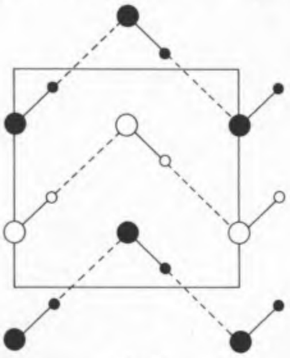

Fig. 8

The structure of the low-temperature ordered form of DCl. Large circles, chlorine atoms, small circles, deuterium atoms. The chains lie in the ab planes, the spacing between the planes for the open and full circles being c/2. (after SÁNDOR and FARROW, 1967)

In the low-temperature ordered form of HCl and DCl the orientational ordering is of course long-range. The high-temperature cubic form is orientationally disordered, and the liquid no doubt still more so, but neutron scattering studies have indicated that the same kind of ordering persists on a *local* scale even above the melting-point (BOUTIN and SAFFORD, 1964). It therefore seems that an intermolecular potential for HCl−HCl interaction which is to be used to treat the properties of liquid HCl and its mixtures should be based on a model which does not simply assign a point dipole to the molecule, but has charges so distributed within it as to simulate the tendency to form a hydrogen bond between a proton and a pair of p electrons. Perhaps the cause (or part of the cause) of the discrepancy between the experimental and calculated H^E values for the HCl−Xe system (fig. 4) is to be found here.

As a second example of the point under discussion we may cite the remarkable results obtained by CALADO and his coworkers for the system Xe-C_2H_6 — remarkable, in that all four excess functions G^E, H^E, S^E and V^E are negative. Thermodynamically, this is an indication of some special kind of attraction or association between a xenon atom and an ethane molecule. The ethane molecule has a quadrupole moment, and the xenon atom is the most polarisable of the rare gas atoms, so inevitably quadrupole — induced dipole attraction must be an important term in the Xe$-C_2H_6$ potential. But it is doubtful if any of the present theories could or would predict negative values for all four excess functions. The implication of the experimental results is that there is some especially favourable factor giving attraction between Xe and C_2H_6 molecules. Perhaps the spatial charge distribution in the ethane molecule happens to be particularly effective in relation to the size of the xenon atom, in which case once again a more detailed model will be required to do justice to the situation.

6 — POSSIBILITIES FOR FURTHER EXPERIMENTAL WORK

In this Section some suggestions are advanced for further work. The number of binary systems composed only of relatively simple molecules is of course limited by the number of suitable substances available. From what has been said in previous Sections it will be clear that for any one system, through the necessity of having to use some of the thermodymanic data to fix otherwise indeterminate parameters in theoretical expressions for the excess functions, it is desirable to make the experimental study as complete as possible. Some developments in the experimental field which might prove fruitful will be considered under four headings.

6.1 — *MORE DETAILED STUDIES OF SYSTEMS FOR WHICH NOT ALL THE PRIMARY EXCESS FUNCTIONS HAVE SO FAR BEEN DETERMINED*

The function for which information is most commonly lacking is H^E. It is still not available, for example, for the very important system Kr$-$Xe. Moreover, H^E can have a sensitive dependence on temperature (see (b.2) below), and therefore if possible it should be measured at more than one temperature.

An interesting system for which at present only G^E is available is Kr$-$NO. The importance of this mixture is that the NO molecule, having one unpaired electron, can associate with another molecule to form a dimer, but not any higher aggregate. It is therefore perhaps the simplest liquid mixture of two components one of which can associate to a dimer, and the best therefore on which to test a theoretical treatment of such association. CALADO and STAVELEY (1979) measured the vapour pressure of Kr$-$NO mixtures, which depart strongly from ideality, and in interpreting their results took into consideration both the dimerisation and what might be called the more general causes of non-ideality. They concluded that the latter were responsible for about 40 per cent of the observed non-ideality, and the dimerisation for the rest. Comparison of the calculated total vapour pressure with the experimental values is shown in fig. 9. It would be useful to have H^E and V^E data as well, since this could provide more information about the dimerisation, and a study of the similar system CH_4-NO would also be worthwhile.

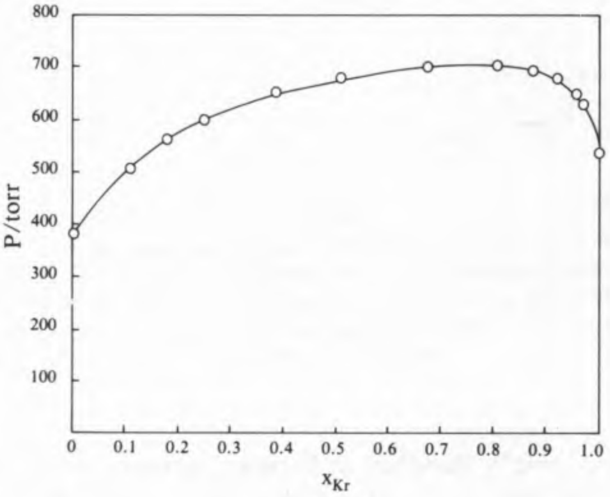

Fig. 9

Total vapour pressure of the system Kr+NO as a function of the krypton mole fraction x_{Kr}. The curve is calculated, and the points are the experimental results. (CALADO and STAVELEY, 1979)

6.2 — *EXTENSION OF THE TEMPERATURE RANGE*

In principle, a complete study of any one binary system would start at the lowest possible temperature (set by the melting-points of the components), and cover a sufficient range of temperature to pass through the critical region, so that finally the mixture would be one of two gases. Some of the systems considered in this review have been studied at two temperatures and a few at three, but for many the information on the excess functions still relates to just one temperature. Striking changes can take place as the critical region of one component is approached. Two illustrations may be given, one relating to H^E for the $Ar-CH_4$ system (fig. 10) and the other to V^E for the N_2-CH_4 system (fig. 11). Fig. 10 combines results obtained with a calorimeter of the type briefly described in Section 2 (LEWIS *et al.*, 1975) with results produced by flow calorimetry (MOSEDALE and WORMALD, 1977). It will be seen that before the critical temperature of argon (151K) is reached, H^E has changed sign and the mixing process has become exothermic. As for V^E for N_2-CH_4 mixtures, as the critical temperature of nitrogen (126K) is approached, the contraction on mixing the two components increases considerably. However, it must be pointed out that when the vapour pressure of the mixed liquids exceeds ~ 10 atmospheres, the determination of G^E becomes ever more difficult owing to the increasing importance of the non-ideality of the vapour phase and the difficulty in adequately allowing for this.

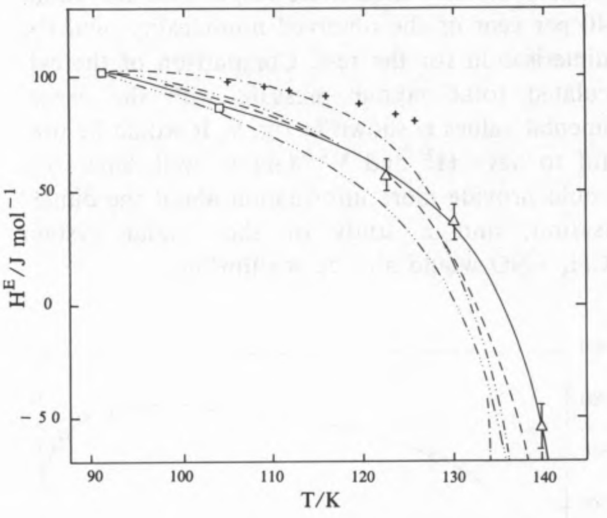

Fig. 10

Showing the effect of temperature on H^E for equimolar mixtures of $Ar+CH_4$. Squares, experimental results of LEWIS et al. *(1975); triangles, experimental results of* MOSEDALE *and* WORMALD *(1977). The crosses and the various curves have been obtained by calculation*

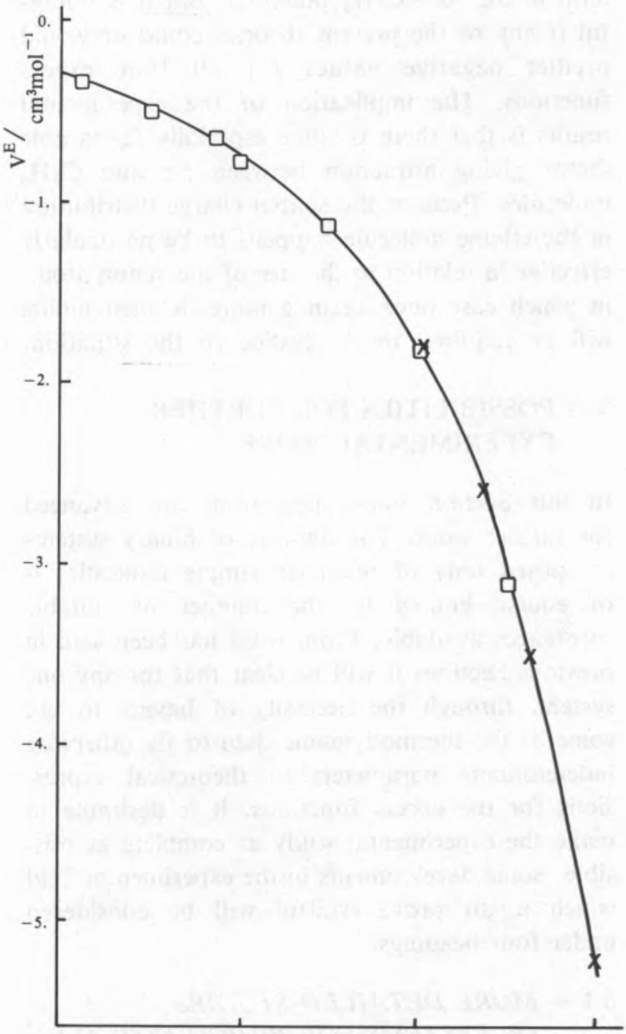

Fig. 11

Temperature dependence of V^E at the saturation vapour pressure for equimolar mixtures of N_2+CH_4. Squares, LIU *and* MILLER, *1972; crosses,* NUNES DA PONTE et al., 1978

6.3 — *STUDIES OF THE EFFECT OF PRESSURE ON THE EXCESS FUNCTIONS*

p-V-T studies have now been made on a few mixtures of liquefied gases up to pressures of the order of 10^3 atmospheres, and are being actively pursued both in Lisbon and at Cornell University. The first experiments of this kind were made in the USSR. The systems which have been studied so far include $Ar+Kr$ (BLAGOI and SOROKIN, 1969; BARREIROS *et al.*, 1982), and N_2+CH_4 (NUNES DA PONTE *et al.*, 1981). An example has already been given in fig. 2 of the sort of information which has emerged from this work. From the molecular point of view the consequence of applying pressure to a liquid mixture is to change the balance between the intermolecular forces of attraction and repulsion, the latter becoming increasingly important. The value of V^E at sufficiently high pressures tends to approach a fairly constant, small limiting positive value, which is rather a direct way of getting information about the parameter j_{12} modifying the Lorentz rule (eqn. (10)). In more general terms, the data resulting from these equation of state studies of pure and mixed liquefied gases really add another dimension to the material available for testing theories, and such studies are undoubtedly very valuable.

6.4 — *SOME POSSIBLE "NEW" SYSTEMS*

It has already been pointed out that the apparent simplicity of the HCl molecule as a small molecule with a dipole moment may be deceptive, in that the attraction between these molecules should be considered as a case of hydrogen bonding rather than as simply involving the electrostatic attraction of two dipoles. For a model system on which to test the consequences of the molecules of one component having a dipole moment, it would be better if this component is not a hydride. Its dipole moment must not, however, be too small, since the excess functions have a rather sensitive dependence on the moment μ, G^E, for example, increasing more rapidly than μ^2 (CHAMBERS and MCDONALD, 1975). The choice, therefore, of a "good" dipolar molecule is very limited. A possible candidate is ClF, which has a dipole moment of 0.88 Debye and a reasonably long liquid range, the melting-point being 117K and the normal boiling-point 173K. Systems which would appear to be worth investigating are Cl_2+ClF and $Xe+ClF$, and also $Xe+Cl_2$. (All three systems could be studied at the same temperature).

H_2S is a fairly simple polar molecule, but in the low-temperature form of the crystal the molecules are again arranged in a way implying hydrogen-bonding, so that the disadvantages associated with HCl probably apply to H_2S too. Nevertheless, systems like $Xe+H_2S$ and $HCl+H_2S$ would be worth studying.

Another respect in which the availability of suitable molecules proves to be rather frustrating is in attempts to make systematic studies of the effect of changing the relative sizes of the molecules of the two components. This is not surprising, of course, since compounds which are gaseous at ordinary temperatures do not have very large molecules. SF_6 is a possibility worth considering for providing a relatively large molecule, the molar volume of the liquid at its melting-point being about 75 per cent greater than that of xenon at its triple-point. A practical disadvantage of SF_6 is its comparatively high melting-point and triple-point pressure (222K and 2.2 atmospheres respectively). The SF_6 molecule is interesting in that it is of such high symmetry that it has no dipole, quadrupole or octupole, the first moment being a hexadecapole. Another relatively large molecule, somewhat similar to that of SF_6, is that of PF_5. This substance has a rather more accommodating range (melting-point 190K, normal boiling-point 198K).

Carbon dioxide, having a molecule with no dipole but with a large quadrupole, could be a useful component of a mixture, though again the high melting-point (with which is associated a high triple-point pressure) considerably reduces the useful liquid range — hence the preference for N_2O in our work as an example of a substance with quadrupolar molecules. The molecule COS is worth attention, as having a dipole as well as a quadrupole.

Systems involving the polar pyramidal molecules PH_3 and PF_3 might yield interesting results. The molecule NF_3, however, although pyramidal, has almost no dipole moment or basic (i.e.

electron donating) properties. NF_3, moreover, has a long liquid range (melting-point 66K, normal boiling-point 144K). It should therefore be possible to study binary systems of NF_3 and a variety of other substances, e.g. Ar, Kr, Xe, N_2, O_2, CO, CH_4, CF_4.

Finally, I should like to express my deep appreciation of the honour done to me by the organizers of the International Conference on the Thermodynamics of Mixtures of Non-Electrolytes in giving my name to one of the plenary lectures, and in asking me to deliver the first lecture bearing my name.

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THE DEVELOPMENT OF A FLEXIBLE INTERMOLECULAR POTENTIAL ENERGY FUNCTION FOR ETHYLENE

A recent experimental study of the equation of state of compressed liquid ethylene has allowed us to test several intermolecular potential models for this molecule. A suitable model function which includes contributions from multipolar (electrostatic), anisotropic dispersion, anisotropic charge overlap (shape) and induction forces, as well as the usual spherically-symmetric Lennard-Jones (n,6) potential has been developed. For this reference potential, the best value of n was found to be $n = 13$. The overall potential is a good, effective potential for liquid ethylene, but its ability to account for low-density properties, like the second virial coefficient or acoustic slope, deteriorates slowly as the temperature is lowered. The experimental values of the three major excess functions, G^E, H^E and V^E, for the liquid mixtures of ethane and ethylene, have also been used as a test of the potential model.

INTRODUCTION

There is considerable interest in making a close study of fluid ethylene due both to its industrial importance, as for example in its emergence as a powerful supercritical extracting solvent, and to theoretical interest where its complex electrostatic interactions yet relatively simple shape at the molecular level make it suitable for study by existing theoretical tools. Although numerous experimental data for ethylene existed in the literature there still remained a necessity for accurate and extensive experimental data at high pressures. To fill this need, a series of ~800 PVT measurements at temperatures from the triple point to the critical point (~110-280K) and from 0-130 MPa was conducted recently at Cornell University by CALADO, STREETT, and co-workers [1]. The data were then fitted to a Strobridge-type equation of state and a variety of derived thermodynamic properties were calculated.

In this paper we shall be concerned with the proposition of a theoretical intermolecular potential model for ethylene and its extensive testing in the quantitative prediction of thermodynamic properties over wide ranges of temperature and pressure. Theoretical predictions of these data were made using a perturbation theory approach for the microscopic description of the fluid, and Statistical Mechanics to link it to the macroscopically observed properties. The importance of including angle-dependent forces in the intermolecular potential energy function in affecting the accuracy of theoretical predictions of the experimental results is clearly demonstrated, and it appears that a good effective liquid potential for ethylene has been developed. However, it has long been the desire of theoreticians to propose intermolecular potential models which provide a quantitatively accurate description of the whole of phase space, including gas, liquid and solid phases. For ethylene, a fortuitous situation exists wherein high quality second virial coefficents and acoustic slope data (both low density properties), have been reported. The availability of this data provided the ideal opportunity to test whether the effective liquid potential was flexible enough to predict these gaseous properties as well. One further, and quite stringent test of the proposed potential

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model, was its ability to predict binary mixture excess properties which are known to be particularly sensitive to the intermolecular force models used. As one suitable example of this, the prediction of excess thermodynamic functions for the system ethylene/ethane, which has considerable industrial interest, are also given.

BACKGROUND THEORY

The essential premise of the theoretical approach used is that the macroscopic behaviour of fluid mixtures, illustrated in the thermodynamic properties, can be related to the microscopic interaction between particles (via the intermolecular potential function, u) using Statistical Mechanics. In perturbation theory the potential energy function of the real fluid, u_{real}, which is unknown can be represented as a sum of two contributions, each of which can be modelled accurately. These two contributions are a spherical reference potential and a perturbation term which must be much smaller than the contribution from the reference. In the theory proposed by GRAY, GUBBINS and co-workers [2-5] the reference is a spherical isotropic system where the potential energy depends only on the distance, r, separating any two molecules. The perturbation term, on the other hand, contains all the orientation-dependent information

i.e. $$u_{real}(r\omega_1\omega_2) = u_{ref}(r) + u_{pert}(r\omega_1\omega_2) \qquad (1)$$

where ω_i are the Euler angles ($\omega_i = \theta_i\phi_i\chi_i$)

Treatment of the reference system

In this theory a POPLE [6] reference potential was used, where u_{ref} is chosen to be an unweighted average over all orientations (this turns out to simplify later equations),

i.e. $$u_{ref}(r) = <u(r\omega_1\omega_2)>_{\omega_1\omega_2} \qquad (2)$$

where $$<(...)>_{\omega_1\omega_2} = \frac{\int\int d\omega_1\, d\omega_2\, (...)}{\int d\omega_1\, d\omega_2}$$

In practice, we use the well-known Lennard-Jones (n,6) potential to model u_{ref},

$$u_{ref} = u_{LJ} = f\epsilon\, [(\frac{\sigma}{r})^n - (\frac{\sigma}{r})^6\,]$$

where $$f = \frac{n}{n-6}\,(\frac{n}{6})^{6/(n-6)} \qquad (4)$$

(Note: f reduces to 4 for the LJ (12,6) potential, giving the more usual form for this equation).

n is the exponent of the (n,6) potential,
σ is the collision diameter, and
ϵ is the well depth

The thermodynamic properties of a Lennard-Jones (12,6) reference mixture are obtained using van der Waals one fluid theory (vdW1). This theory gives the pressure and Helmholtz free energy as,

$$P_{ref} = P_x \qquad (5)$$

and

$$A_{ref} = A_x + NkT \sum_\alpha x_\alpha \ln x_\alpha \qquad (6)$$

where T is the temperature, x_α the mole fraction of component α, and P_x and A_x are values for a pure fluid containing N molecules in volume V at temperature T, where the molecules interact with a L.-J. (12,6) potential having parameters σ_x and ϵ_x, where

$$\sigma_x^3 = \sum_{\alpha\beta} x_\alpha x_\beta \sigma_{\alpha\beta}^3 \qquad (7)$$

and

$$\epsilon_x \sigma_x^3 = \sum_{\alpha\beta} x_\alpha x_\beta \epsilon_{\alpha\beta} \sigma_{\alpha\beta}^3 \qquad (8)$$

α and β referring to the two binary mixture components. P_x and A_x are calculated from an existing equation of state arising from experimental data for a spherical molecule (such as argon) or a quasi-spherical one (such as methane).

However, we often require the properties for a L.-J. (n,6) mixture when n is *not* equal to 12. In this case we must first relate the properties of an (n,6) fluid to a (12,6) one before employing vdW1 theory. The free energy of an (n,6) fluid is obtained by expanding about the (12,6) value,

$$A^{(n,6)} = A^{(12,6)} + A_1{}^{(n,6)} \qquad (9)$$

The final expression for this equation is given in reference [2].

The anisotropic potential

Contributions from multipolar (electrostatic), anisotropic dispersion, anisotropic charge overlap (shape) and induction forces may be included. In practice not all of these are equally important and some terms may be omitted. But it is generally true that multipolar forces give the largest contribution to the anisotropic part of the potential.

These forces are approximated by the first few terms of a generalized spherical harmonic expansion. For example, for polar fluids a leading term in u_{pert} is that due to the dipole-dipole potential, $u(\mu\text{-}\mu)$. For linear molecules this is given by,

$$u_{\alpha\beta}(\mu\text{-}\mu) = -\frac{\mu_\alpha \mu_\beta}{r^3}(s_1 s_2 c_\phi - 2c_1 c_2) \qquad (10)$$

where μ_i is the dipole moment of component i and s_i, c_i are $\sin\theta_i$, $\cos\theta_i$ respectively, and $c_\phi = \cos(\phi_2 - \phi_1)$.

The Helmholtz free energy of the real system can be expanded in powers of the perturbing potential,

$$A_{real} = A_{ref} + A_1 + A_2 + A_3 + \ldots.. \qquad (11)$$

where A_i are the ith order terms. However, having chosen u_{ref} as the angle-averaged potential (as discussed earlier), $A_1 = 0$, giving a simplified expression

$$A = A_{ref} + A_2 + A_3 + \ldots.. \qquad (12)$$

Expressions for A_2 and A_3 (the second-order and third-order contributions) have been evaluated using Statistical Mechanics for a wide variety of intermolecular forces [4].

However the series for the free energy given in equation (12) is only slowly convergent. If the series is truncated at A_3 serious errors are incurred for the prediction of the free energy of strongly polar fluids. This has led to the use of a Padé approximant for the free energy, suggested by STELL *et al* [7] as a closure to the series. Thus,

$$A = A_0 + A_2(1 - A_3/A_2)^{-1} \qquad (13)$$

This has been shown by comparison to computer simulation results to offer a considerable improvement for highly polar fluids.

POTENTIAL MODELS FOR ETHYLENE AND PREDICTION OF PVT DATA

Various intermolecular models for ethylene were proposed in ref. [1], as shown below; each is assumed to be pairwise additive:

$$\text{Model A: } u = u_o^{(n,6)} \qquad (14)$$

$$\text{Model B: } u = u_o^{(n,6)} + u_{QQ}(224) \qquad (15)$$

$$\text{Model C: } u = u_o^{(n,6)} + u_{QQ}(224) + u_{dis}(202+022+224) \qquad (16)$$

$$\text{Model D: } u = u_o^{(n,6)} + u_{QQ}(224) + u_{dis}(202,022,224) + u_{ov}(202,022) \qquad (17)$$

All of these were implemented into the theory with an argon equation of state [8] reference and an experimental value [18] of the quadrupole moment, $Q = 4.09 \times 10^{-26}$ esu. One further model was tested, denoted as model M; this had the same potential model as D but used a methane equation of state [9] as reference in the theory and used the newer experimental value [20] of $Q = 3.54 \times 10^{-26}$ esu.

Potential parameters for each of these models, obtained by fitting to coexistence data (p_{liq}, ϱ_{liq}), are given in Table 1.

In predictions of the dense fluid properties of

Table 1
Potential Parameters for Pure Ethylene

Model	ε/k/K	σ, Å	n	Q × 10^{26} esu	Dispersion Coefficent, $\varkappa$	Overlap Parameter, δ_2
A	241.8^{19}	4.091^{19}	13.0^{19}	—	—	—
B	223.9^{5}	4.147^{5}	13.0^{5}	4.09^{20}	—	—
C	224.8^{1}	4.138^{1}	13.0^{1}	4.09^{20}	0.143^{21}	—
D	224.2^{1}	4.140^{1}	13.0^{1}	4.09^{20}	0.143^{21}	0.10^{1}
M	224.0^{1}	4.137^{1}	13.0^{1}	3.54^{22}	0.143^{21}	0.10^{1}

ethylene, with no further fitting or adjustment of parameters a clear distinction between the quality of each of these models was apparent, model A being overall the worst, and M the best, as shown in Table 2.

Table 2

Average Percentage Deviation Between Theory and Experiment (range 190-280 K, $p \sim -5$-1300 bar)

Model	$\vert \Delta\varrho \vert$ %	$\vert \Delta U^c \vert$ %	$\vert \Delta S^c \vert$ %
A	0.64	4.90	16.0
B	0.59	1.30	4.7
C	0.45	0.61	4.7
D	0.40	0.63	4.3
M	0.11	0.40	5.0

PREDICTION OF B(T) AND K(T)

Using these same potential models, the second virial coefficient and acoustic slopes may be predicted with no further fitting of parameters. The second pressure virial coefficient of gases, B(T), is simply related to the intermolecular potential energy function, $u(\mathbf{r}\omega_1\omega_2)$ which describes the interaction between molecules of a general shape. For linear molecules, this relationship is given by

$$B(T) = -\frac{N}{4}\int\int(e^{-\beta u}-1)\,d\mathbf{r}\,d\omega \tag{18}$$

where N is the number density, **r** the vector joining molecular centres and ω represents the Euler angles defining the molecular orientation.

An analogous quantity to the second pressure virial coefficient is the acoustic slope, K(T), otherwise known as the second acoustic virial coefficient. K(T) is defined by the equations

$$\frac{W^2M}{\gamma_0RT} = 1 + K\varrho + L\varrho^2 + \ldots.. \tag{19}$$

and

$$K = [2B + 2(\gamma_0-1)T\frac{dB}{dT} + \\ + \frac{(\gamma_0-1)^2}{\gamma_0}T^2\frac{d^2B}{dT^2}] \tag{20}$$

where equation (19) expresses the velocity of sound, W, as a virial series in density, with K the slope at zero pressure. Here γ_0 is the specific heat ratio at zero pressure, T the temperature and M the molecular weight. The results for B(T) from 423-223K, as given in fig. 1, show good agreement between the experimental results due to LEVELT SENGERS *et al.* [10] and DOUSLIN and HARRISON [11] and the theoretical curves at the higher temperatures. This agreement deteriorates slowly as the temperature is lowered. Quantitatively similar results are obtained for the acoustic slope data in comparison to the experimental results of GAMMON [12] and MEHL and MOLDOVER [13] (see fig. 2). This behaviour is characteristic of an effective liquid potential energy function and the discrepancies between theory and experiment should not be judged too harshly. The effective potential includes some indirect knowledge of the multibody forces in the liquid which enters through the use of an equation of state for a real fluid such as Ar and CH_4 (wich are certainly not strictly pairwise additive) used to produce the properties of the reference fluid. However, the second virial coefficient is determined solely by pair interactions and since the multibody potential is generally repulsive in nature the theoretical estimates of B are commonly too high in comparison to experiment. This effect will be increasingly important as the tempeature is lowered. There will also, of course, be inaccuracies in the potential model, but it is to be hoped that these will be less important than the effect of the inclusion of mul-

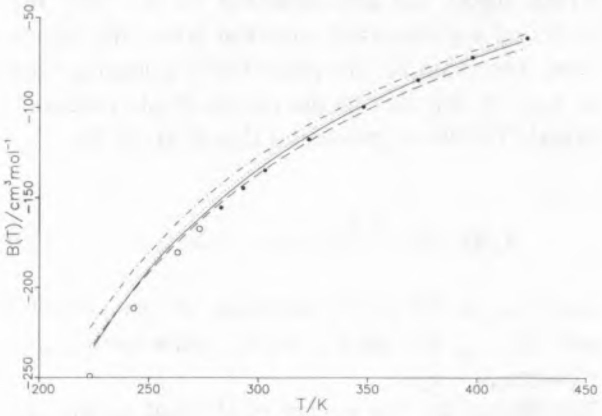

Fig. 1

The second virial coefficient of ethylene as a function of temperature

• Experiment (ref. 11); ○ Experiment (ref. 10); --- Model A; —— Model B; ··· Model D; —·— Model M

Note: Results for Model C are virtually identical to Model B tibody forces. Indeed, the theoretical prediction of B(T) shown in fig. 1 is unusually close to experiment for an effective liquid potential especially for such an anisotropic molecule. The inclusion of the non-pairwise additive forces within the model occurs in a convoluted way and it is not possible to calculate their contribution here in an accurate fashion.

Unfortunately though, unlike in the dense fluid region, the distinction between models does not follow a consistent pattern. The best description of B(T) and K(T) appears to be from models B and C which are the most attractive overall potentials. Model M on the other hand, with its smaller quadrupole moment, is less attractive overall than models B, C or D and gives a poorer prediction of these properties. The isotropic model A does not give the correct high temperature behaviour of either B(T) or K(T), a grave inadequacy, and shows the wrong temperature dependency in the slope of these functions although, fortuitously, for B(T) it is the closest model to experiment in the mid-range of the temperatures. The second virial coefficients B and K are obviously less discerning judges of the form of the potential model than dense fluid thermodynamic properties; this is borne out by the fact that fairly good estimates of B(T) may be achieved using a square-well potential which is a very unphysical model of the intermolecular interactions.

BINARY MIXTURE CALCULATIONS

Experimental measurements of the total vapour pressure, liquid density and the enthalpy of mixing of C_2H_6 and C_2H_4 were recently made by AZEVEDO and CALADO [14] around 161.4K, the triple point of xenon. These were used to determine the excess properties of G^E, V^E and H^E for various compositions.

For this system, the similar symmetry characteristics of the two fluids allow the same potential model for both molecules to be used. Here model D was used for both C_2H_4 and C_2H_6. This also implies that the mixture potential will have the same form as the models for the pure fluids. The appropriate parameters for pure ethane and for the mixture are given in Table 3. Modified Lorentz-Berthelot mixing rules were employed to obtain values for ϵ_{12} and σ_{12}, where the two adjustable mixture parameters involved are determined by fitting to the experimental values of $G^E_{1/2}$ and $V^E_{1/2}$. This means that the description of the excess free energy and the excess volume provides only a weak test of the theory, and indeed these properties are well represented by the theory as shown in fig. 3. The excess enthalpy, on the other hand, can be predicted without any fitting of parameters and will severely test the molecular models used. It can be seen that the theory predicts a value for H^E about 20% too high unless the strength of the overlap forces is artificially increased by about 25%, indicating the sensitivity of H^E to even subtle forces such as the description of molecular shape. Further evidence of the sensitivity of the excess enthalpy is demonstrated by the fact that if the value of the quadrupole moment of ethane proposed by AMOS [15] ($Q = -1.3 \times 10^{-26}$esu) is used instead of the BUCKINGHAM *et al.* [16] value ($Q = -0.8 \times 10^{-26}$esu) then the theoretical prediction of H^E is altered significantly bringing it to within 10% of the experimental value. Consideration of the fact that ethylene has a nonaxial quadrupole moment ($Q_{xx} \neq Q_{yy} \neq Q_{zz}$) improves the results by only about 3%. This results fits in with our expectations due to the weak quadrupole moment of ethane.

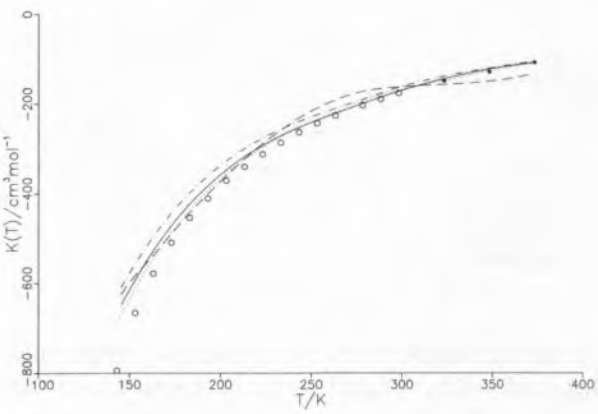

Fig. 2
The acoustic slope of ethylene as a function of temperature
• Experiment (ref. 13); ○ Experiment (ref. 12)
Key for theoretical models as for Fig. 1

CONCLUSIONS

A good effective liquid potential model for the interesting and complex molecule ethylene has been

Table 3
Potential Parameters for C_2H_6 and C_2H_4/C_2H_6

Pair	Ref. e.o.s.	ϵ/k/K	σ/ Å	n	$\mu/10^{-18}$ esu	$Q/10^{-26}$ esu	δ	γ	$\bar{\alpha}/10^{-24}$ cm^3
C_2H_6/C_2H_6	Methane	267.9	4.279	15	—	-0.80^{14}	0.10	0.753	4.44
C_2H_6/C_2H_4	a) Methane	252.8	4.183	14	—	—	0.10	—	—
(nonaxial treatment)	b) Methane	251.2	4.188	14	—	—	0.1125	—	—

developed which is able to predict the dense fluid behaviour over a wide range of temperature and pressure. The importance of incorporating anisotropic forces into the model was clearly demonstrated. The results of this study, and a similar one in progress for the molecule carbon tetrafluoride [17], suggest that the potential parameters for effective liquid models are best achieved by comparison to the dense fluid region rather than to the coexistence region where, for example, in this study it was difficult to distinguish between models B-D in terms of efficacy of fit. Models B-D were sufficiently flexible to predict the low density properties of the acoustic slopes and second virial coefficients with reasonable accuracy whereas the isotropic model A gave incorrect high temperature behaviour and had the wrong slope as a function of temperature. However, these properties are less sensitive to the exact nature of the intermolecular forces involved in the potential model.

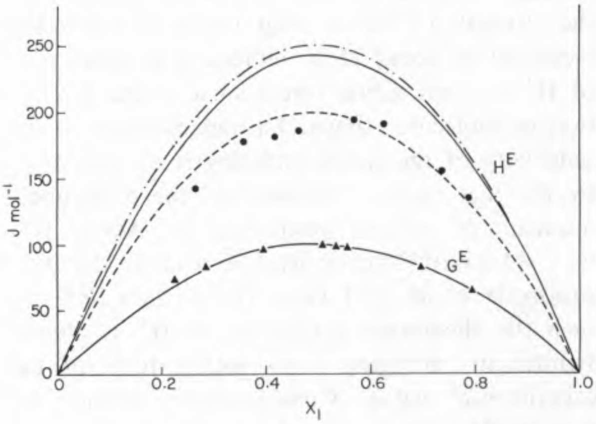

Fig. 3
Excess properties of a mixture of ethylene and ethane as a function of composition at 161.4K
▲: Experimental G^E values (CALADO and AZEVEDO [14]); •: Experimental H^E (CALADO and AZEVEDO [14]); ——: Theoretical prediction of G^E and H^E, non-axial treatment of the quadrupolar interaction, shape parameter $\delta_{\alpha\beta} = 0.10$; ---: Theoretical prediction of H^E, non-axial approximation, shape parameter $\delta_{\alpha\beta} = 0.1125$; —•—: Theoretical prediction of H^E, effective axial approximation, shape parameter $\delta_{\alpha\beta} = 0.10$

The prediction of excess functions for a binary mixture of ethylene and ethane showed that accurate mixture properties can be obtained using this potential model for ethylene. When ethylene is mixed with a fluid whose quadrupole moment is weak, such as ethane, there is little difference between taking the nonaxial nature of the quadrupolar interactions into account or not. However, for a binary mixture with N_2O, whose quadrupole moment is large, the difference between a correct nonaxial treatment and an effective axial approximation is quite striking, as shown in ref. [18]. The sensitivity of the excess enthalpy to even subtle intermolecular forces such as the molecular shape or the value of the quadrupole moment used was clearly demonstrated. In all these calculations the availability of accurate experimental data was of paramount importance in order that such investigations of the importance of anisotropic intermolecular forces in such fluids can be accomplished.

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RESUMO

Um estudo experimental recente da equação de estado do etileno líquido comprimido, numa grande gama de pressões e temperaturas, constitui um bom campo de ensaio de vários modelos de potencial intermolecular para aquela molécula. Com este objectivo, desenvolveu-se uma função potencial que inclui, além do usual termo Lennard-Jones (n,6) esfericamente simétrico, contribuiçĩes de forças multipolares (electrostáticas), de dispersão anisotrópica, de sobreposição de carga anisotrópica (efeito de forma) e de indução. O valor óptimo de n para o potencial de referência (n,6) é $n=13$*. O potencial global revelou-se um bom potencial efectivo para o etileno líquido, mas a sua utilidade em descrever as propriedades do fluido a densidades baixas (segundo coeficiente do virial, desvio acústico) diminui gradualmente com a descida de temperatura.*

Usou-se ainda um estudo termodinâmico das misturas líquidas de etileno+etano, englobando a medida das três propriedades de excesso fundamentais, G^E*,* H^E *e* V^E*, como teste do potencial proposto para o etileno.*

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LISTA DAS PLANTAS DE ORIGEM TROPICAL COM ACTIVIDADE FARMACOLÓGICA ESTUDADAS QUIMICAMENTE EM PORTUGAL NAS ÚLTIMAS DÉCADAS

A fitoquímica das plantas de origem tropical com actividade farmacológica estudadas em Portugal durante os últimos 25 anos é apresentada numa tabela conjuntamente com a bibliografia respectiva. Para cada uma das plantas refere-se o respectivo nome vernáculo, a sua origem e a parte da planta sobre o qual incidiu o estudo químico. Para além das suas propriedades medicinais e aplicações práticas mais correntes, referem-se também, os constituintes químicos detectados, as técnicas utilizadas no seu isolamento e identificação e ainda as determinações analíticas realizadas.

1 — INTRODUÇÃO

Nas últimas décadas intensificou-se de maneira extraordinária a pesquisa de princípios dotados de actividade farmacológica provenientes de plantas de origem tropical, capazes de explicar as acções terapêuticas que as populações autóctones lhes atribuem [1].

O objectivo do presente trabalho é a compilação da investigação realizada em Portugal nesta matéria nos últimos 25 anos, proveniente fundamentalmente de projectos de investigação no âmbito de interesses do Instituto de Investigação Científica Tropical [2]. *Não são*, neste trabalho, referidos estudos de plantas visando apenas a detecção e/ou caracterização de óleos essenciais, lípidos e/ou proteínas, uma vez que já se encontram publicadas revisões sobre estes temas [3,4].

2 — CONSIDERAÇÕES SOBRE A TABELA 1

A Tabela 1 sumariza, tão exaustivamente quanto nos foi possível, os estudos químicos, publicados por autores portugueses, no período indicado, encontrando-se as plantas classificadas por ordem alfabética dos seus nomes científicos. Para cada uma destas entradas, seguem-se as designações vernáculas mais correntes.

Ainda se regista a parte da planta (raízes, troncos, folhas, flores, sementes ou frutos) sobre a qual incidiu o estudo, bem como as propriedades medicinais e aplicações práticas a elas atribuídas pelos autóctones. São referidos também os constituintes químicos detectados, conjuntamente com as técnicas utilizadas. Não deixam, neste contexto, de ser assinalados os compostos químicos intencionalmente pesquisados e não detectados. Finalmente, regista-se a bibliografia referente a cada planta, sendo aquela apresentada, por ordem cronológica, na sequência da Tabela 1.

3 — CONSIDERAÇÕES SOBRE A TABELA 2

A Tabela 2 apresenta as plantas estudadas por zonas geográficas (cf. fig. 1).

Numa primeira análise pode concluir-se que o maior número de plantas e trabalhos publicados desde 1958 resulta de material proveniente de Angola.

Tabela 1

Planta	Designação Vernácula (a)	Origem	Parte da Planta Estudada	Propriedades Farmacológicas e Aplicações Práticas	Constituintes Químicos Presentes (b)	Técnicas Usadas no Isolamento e Identificação (c)	Compostos Ausentes (d)	Determinações Analíticas (e)	Ref. (f)
ALBIZZIA ADIANTHIFOLIA (SCHUMACK) W.F. WIGHT	mimosa goane	Moçambique	raíz	antidoto de mordeduras de serpentes	triterpeno do tipo I **	r. cromáticas, p.f.	—	humidade lipidos prótidos glúcidos cinzas	[27]
				ictiotóxico tónico	naringenina *	c.p., Rf(padrão), revelador			
				anti-diarreico	naringina *	c.p.,Rf(padrão), revelador			
				anti-tuberculoso	β-feniletilamina	c.p.,Rf, cloridrato(p.f.)		tensão superficial	
				lepra	arabinose *	c.p.,Rf, revelador			
				insecticida	ramnose *	c.p.,Rf, revelador			
				vermicida	ácido glucorónico *	c.p.,Rf, r. cromáticas			
ALBIZZIA TANGANYICENSIS, BAK. F	mupepe	Angola	casca	ictiotóxico	xilose	c.p.,Rf(padrão), revelador	taninos alcalóides essência ácidos urónicos	humidade glúcidos celulose azoto cinzas goma saponósidos	[15]
					ramnose	c.p.,Rf(padrão), revelador			
					glicose	c.p.,Rf(padrão), revelador			
					saponósido esterólico *	c.c., r. cromáticas			
ALCHORNEA CORDIFOLIA (SCHUMACK) MUELL. ARG.	bunce bengue bungi-bungi pó-d'arco	Guiné	raíz	estomáquico adstringente	ácido antranílico	c.p.p.,r.cromáticas, Rf(padrão), u.v.,p.f.	ácido xiquímico	alcalóides	[37]
				purgativo	ácido gentísico	c.p.p., r. cromáticas, Rf(padrão),u.v.	ácido ioimbico		
				anti-reumático	ioimbina **	r. cromáticas, c.p.p.,Rf(padrão), u.v.	α-epi-ioimbina		
				tratamento de úlceras afrodisiaco hipotensor	alcalóide indólico **	r. cromáticas, c.p.p.,Rf,u.v.			
ALOE VERA	babosa	Cabo Verde	folha	laxativo	barbaloina(II)	p.f.,p.f.m., iv.,u.v.			[29]
				anti-reumático tratamento de contusões					
ALSTONIA CONGENSIS ENGL.		Guiné	casca	febrífugo anti-reumático tratamento de filariose	equitamina(III)	c.p.,c.c.d.,u.v., p.f. prep. de derivados,i.v.(lit)			[48]
ALSTONIA CONGENSIS ENGL.		Guiné	casca (látex)	febrífugo	lupeol	c.c.,esterificação, p.f.(benzoato),i.v. (benzoato),$\lvert\alpha\rvert$			[55]
				anti-reumático tratamento de filariose	α-amirina	c.c.,p.f.,$\lvert\alpha\rvert$,acetilação,p.f.(derivado),i.v.			
					β-amirina(XVI)	c.c.,p.f.,i.v., esterificação			
					ácido-esteárico	c.p.,Rf(padrão)			
ANACARDIUM OCCIDENTALE LINN.	cajueiro caju	Índia	casca	anti-diabetogena	taninos catéquicos	r. cromáticas	taninos pirogálhicos saponinas alcalóides	taninos catéquicos lipidos glúcidos celulose prótidos cinzas humidade	[8]
				goma-resina	esteróides	r. cromáticas			

Planta	Designação Vernácula (a)	Origem	Parte da Planta Estudada	Propriedades Farmacológicas e Aplicações Práticas	Constituintes Químicos Presentes (b)	Técnicas Usadas no Isolamento e Identificação (c)	Compostos Ausentes (d)	Determinações Analíticas (e)	Ref. (f)
ANACARDIUM OCCIDENTALE LINN.	castanha de caju	Moçambique	pericarpo	alimentação	esteróides oses taninos	c.c., r. cromáticas r. cromáticas r. cromáticas	alcalóides heterósidos cianogenéticos	índice de iodo humidade cinzas glúcidos celulose lenhina prótidos oses holósidos bálsamo esteróides taninos gálhicos taninos catéquicos resinotanois	[31]
ANACARDIUM OCCIDENTALE LINN	castanha de caju	Moçambique	pericarpo		ácidos anacárdicos(IV) **	p.f.,i.v.		índice de refracção índice de iodo	[32]
ANACARDIUM OCCIDENTALE LINN.	caju	Moçambique	tegumento das sementes	sabões antisépticos corante	ácido anacárdico * esteróides fenóis	c.c.,i.v. r. cromáticas r. cromáticas		humidade lípidos taninos esteróides glúcidos prótidos celulose índice de acidez índice de saponificação índice de ésteres índice de iodo índice de refracção	[41]
ANACARDIUM OCCIDENTALE LINN	caju	Moçambique	óleo de amendoas		ácido palmitoleico ácido oleico ácido linoleico ácido esteárico ácido araquídico ácido palmítico	c.f.g.,metilação, hidrogenação c.f.g.,metilação, hidrogenação c.f.g.,metilação hidrogenação c.f.g.,metilação c.f.g.,metilação c.f.g.,metilação	ácido mirístico ácido linolénico	ácido palmítico ácido palmitoleico ácido esteárico ácido oleico ácido linoleico ácido araquídico	[42]
ANACARDIUM OCCIDENTALE LINN.	caju	Guiné	pedúnculo do fruto (maçã de caju)	medicina alimentação				pH acidez glúcidos taninos azoto lípidos substâncias minerais (cinzas) humidade	[52]
ANACARDIUM OCCIDENTALE LINN.	caju	Guiné	pedúnculo do fruto (maçã de caju)	medicina alimentação	ácido l-ascórbico (vitamina C)	r. cromáticas		teor de vitamina C	[53]

Planta	Designação Vernácula *(a)*	Origem	Parte da Planta Estudada	Propriedades Farmacológicas e Aplicações Práticas	Constituintes Quimicos Presentes *(b)*	Técnicas Usadas no Isolamento e Identificação *(c)*	Compostos Ausentes *(d)*	Determinações Analíticas *(e)*	Ref. *(f)*
ANACARDIUM OCCIDENTALE LINN.	caju	Cabo Verde	fruto (castanha de caju)	alimentação				humidade cinzas celulose azoto prótidos extracto	[54]
ANDROPOGON CITRATUS DC. ver CYMBOPOGON CITRATUS (DC) STAPF									
ARTOCARPUS INTEGRIFOLIA L.	Jaca Jacy Jackes	S. Tomé	lenho	adstringente afrodisiaco	cicloartenona ** (V ou VI)	c.c.,u.v.,r. cromáticas, p.f.		humidade glúcidos lipidos prótidos celulose cinzas	[3]
				anti-diarreico	2 flavonóides **	c.c.,c.p.,Rf, r. cromáticas, u.v., p.f.			
				corante têxtil	taninos pirocatéquicos	r. cromáticas			
BACCHARIS DIOSCORIDIS L. ver PLUCHEA DIOSCORIDIS (L.) DC									
BAUHINIA THONNINGII SCHUM. ou PILIOSTIGMA THONNINGII (SCHUMACH) MILNE REDH.	farrah fará barké mulolo musakanga muxacanga wsanga-saganafinda omututo omutuionfolo omongola mololo-a-makuku	Guiné	casca	adstringente	esteróide **	p.f.,p.f. do acetato, r. cromáticas	alcalóides quinonas hidroquinonas saponinas	glúcidos mucilagens	[34]
				anti-disentérico	carotenoide **	c.c.,u.v., r. cromáticas			
				feridas úlceras	sacarose	c.p.,Rf(padrão) r. cromáticas, α,i.v.,p.f.,p.f.m., derivados			
				corante téxtil sabão (cinzas dos frutos)	taninos pirocatéquicos	r. cromáticas			
					ácido dextrotartárico	c.p.,p.f.,p.f.m., r. cromáticas			
					ácido citrico	c.p., outras reacções			
					ramnetina(7-metil-quercetina)	r.cromáticas,p.f., u.v.,c.p., Rf(padrão)			
BURKEA AFRICANA HOOK	Kabelangu musese sakambua sagambua omukalati wild syringa wild lilac rhodesian ash	Angola	casca	tratamento de anginas indigestões intoxicações de gado bovino pelo otyikeké efeito hipertensor	tetraidroarmana (X) harmana diidroarmana	r.cromáticas, c.c., c.c.d, reveladores, p.f.,preparação derivados,p.f., p.f.m.,u.v.,i.v. (comparação com amostras autênticas).	flavonas quinonas		[68]
					harmalana N-óxido **	c.c.,c.p.p.,u.v., p.f.			
					β-sitosterol	c.c.,c.c.d.,Rf (padrão),p.f., preparação de derivados,p.f., p.f.m., i.v.(comparação com amostra autênticas).			

Planta	Designação Vernácula (a)	Origem	Parte da Planta Estudada	Propriedades Farmacológicas e Aplicações Práticas	Constituintes Químicos Presentes (b)	Técnicas Usadas no Isolamento e Identificação (c)	Compostos Ausentes (d)	Determinações Analíticas (e)	Ref. (f)
CASSIA ANGOLENSIS WELW. EX. HIERN.	mussambe	Angola	casca	purgativo	emodina(XIc)	c.c.p.,p.f.,u.v., i.v.(padrão),M			[77]
					1,8-dihidroxiantraquinona **	c.c.p.,p.f.,u.v., i.v.,M			
					1,8-dihidroxiantranquinona **	c.c.p.,p.f.,u.v., i.v.,M			
					fisciona (XIb)	c.c.p.,p.f.,u.v., i.v.(padrão),M			
					crisofanol	c.c.p., p.f.,u.v., i.v.(padrão)			
CASSIA OCCIDENTALIS L.	bentamare kasondi kalkashunda kasamarda nattamtakarai kasinda natiam-takara maioba pajoma-rioba mudianhoka kibulu-kunde omnipanyoka nhoka-nhoka	Angola S. Tomé Guiné	raiz folha semente	febrífugo diurético tóxico tónico purgativo	emodina(XIc)	r.cromáticas, p.f.,p.f.m.,c.p., Rf(padrão),u.v.	emodina (folhas) 4-hidroxi-2-metilantraquinona	antraquinonas	[9]
				tratamento de: enterites febres biliosas tuberculose	1,8-di-hidroxiantraquinona	r.cromáticas, p.f., p.f.m.,c.p.,Rf (padrão),u.v.	flavonas		
					ácido crisofânico (XIa)	r.cromáticas, p.f.,c.p.,Rf			
				cancro prostático antídoto de mordeduras de serpentes	reina ** (ácido 4,5-di-hidroxiantraquinona-2-carboxílico)	r.cromáticas, c.p., Rf,u.v.			
CASSIA SINGUEANA DEL.	senes	Angola	folha e raiz	purgativo diurético tratamento de: afecções de pele lepra oftalmias	hidroxi-antraquinonas (raíz)		alcalóides		[56]
					ácido crisofânico (1,8-di-hidroxi-, 3-metilantraquinona) (XIa)	c.c.,r.cromáticas, p.f.,u.v.,i.v. (padrão)			
				gonorreia	fisciona (1,8-di-hidroxi, 3-metil, (6-metoxiantraquinona) (XIb)	c.c.,r.cromáticas, p.f.,u.v.,i.v. (padrão)			
CASSIA SINGUEANA DEL.	senes	Angola	semente	purgativo diurético	ácido crisofânico (XIa)	c.c.,r.cromáticas, u.v.,i.v.,p.f. (padrão)			[57]
				tratamento de: afecções de pele	fisciona (XIb)	c.c.,r.cromáticas, u.v.,i.v.,p.f. (padrão)			
				gonorreia lepra oftalmias	2 hidroxiantraquinonas **	c.c.,r.cromáticas, u.v.,p.f.			
CASSIA SINGUEANA DEL.	senes	Angola	semente	purgativo diurético tratamento de: afecções de pele gonorreia lepra oftalmias	5 hidroxiantraquinonas **	c.c.,c.p.p.,p.f., r.cromáticas, u.v., i.v.,preparação de derivados			[63]
CATHARANTHUS ROSEUS G. DON ver VINCA ROSEA LINN.									

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CECROPIA PELTATA L.		S. Tomé	casca	adstringente	esteróides	c.c.,r.cromáticas	alcalóides	taninos	[16]
				emenagogo	flavanona	c.c.,r.cromáticas, u.v.			
				anti-asmático	glucose	c.p.,Rf(padrão), revelador			
				calmante (muscular)	taninos pirocatéquicos	c.c.,r.cromáticas			
				diurético	carotenos	c.c.,r.cromáticas			
				tanante	heterósido **	c.c.,r.cromáticas			
					aldeído **	c.c.,p.f.			
					ácido ursólico	—			
CINNAMONUM CASSIA (NEES) NEES EX BLUME	canela	S. Tomé	casca		aldeído cinâmico *	α,η		essência aldeído cinâmico	[6]
CISSAMPELOS MUCRONATA A. RICH.		Angola	raíz	afrodisiaco diurético tónico	4 alcalóides: d-isochondodendrina (XIIa)	c.c.d.,r.cromáticas,p.f.,u.v.,i.v. (padrão), preparação de derivados,r. de degradação			[47]
				tratamento de; doenças genito-urinárias blenorragia sifils gripe preventivo de aborto antídoto de mordeduras de serpentes	cicleanina ** (XIIb)				
COMMIPHORA ANGOLENSIS (ENGL.)	kalunsanje mungolo ombane njilema tilema mututu	Angola	casca	desinteria amibiana	taninos	r.cromáticas, c.c.,c.p.	comp.fenólicos	humidade	[21]
					petunidina--3-ramnósido	c.p.p.,c.p.,Rf, r.cromáticas, r. de hidrólise, r. de partilha	pigmntos flavónicos carotenos xantofila	cinzas glúcidos celulose azoto taninos	
CONOPHARYNGIA LONGIFLORA STAPF.		Guiné	raíz	medicina	alcalóides acetato de lupeol	r.cromáticas c.c.,c.c.d.,Rf, revelador,p.f., u.v.,i.v.,(padrão)			[61]
CYMBOPOGON AFF. GIGAN—TEUM (HOCHST.) CHIOV. ver **C. DENSIFLORUS (STEND) STAPF.**									
CYMBOPOGON CITRATUS (DC) STAPF. ou **ANDROPOGON CITRATUS D.C.**	chá do Gabão chá do Príncipe citronelle lemongrass, belgata matitiiti	S. Tomé	folha e rizoma	febrífugo	2 alcalóides indólicos	c.c.,c.p.,	azulenos quinonas flavonas taninos saponinas	citrol alcalóides essência	[17]
				anti-tússico estomáquico sudorífero anti-reumático lumbago entorses insectífugo anti-séptico essência		r.cromáticas, comparação com amostras autênticas de vários alcalóides			

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CYMBOPOGON CITRATUS (DC) STAPF.	belga-gata chá do Gabão chá do Principe matitiiti (citronelle lemon grass)	S. Tomé	rizoma	febrífugo anti-tússico diaforético estomáquico insectífugo entorses anti-reumático lumbago anti-séptico carminativo	alcalóide indólico **	c.p.,c.p.p.,Rf, u.v.,r.cromáticas	**gramina** **hordenina** **afraserpina**		[28]
CYMBOPOGON DENSIFLORUS (STEND) STAPF. e C. AFF. GIGANTEUM (HOCHST.) CHIOV.	saku-saku kaxinde hiangu musoso evalu onkotankota hotta-hotta	Angola	inflores-cência em parte frutifi-cada		hidrocarboneto saturado glicose ramnose lipidos: ácido araquidico ácido linolénico ácido oleico ácido beénico ácido lignocénico comp. flavó-nicos: quercetina campferol constituintes do óleo essencial	p.f. c.c.d.,c.p., Rf(padrão) reveladores » » » c.c.d.,Rf (padrão), revelador, p.f.,p.f.m. c.c.d.,Rf (padrão) » » » » » » r.cromáticas, p.f.,u.v. r.cromáticas, c.p.,Rf(padrão)		**humidade** **essência** **lipidos** **celulose** **azoto** **cinzas** **extractos** **comp. flavónicos** **indices analíticos das essências**	[49]
DIOSCOREA DUMETORUM PAX	inhames	S. Tomé	tubérculo	Vesicatoria dermatologia alimentação	3 alcalóides * di-hidrodios-corina	c.c.,c.p., r.cromáticas, u.v.			[19]
DIOSCOREA DUMETORUM PAX	inhames gamba ugamba	Angola	tubérculo	analépticas convulsivantes anestéticas alimentação	dioscorina * (VII) di-hidrodios-corina *	c.c.,c.p., r.cromáticas, u.v. c.c.,c.p., r.cromáticas, u.v.		**razão de % dos 2 alca-lóides (η e ϵ)**	[23]
DIOSCOREA DUMETORUM PAX		Guiné	tubérculo		dioscorina * (VII) di-hidrodios-corina * β-sitosterol caroteno **	c.c.p.,c.p., r.cromáticas,u.v. c.c.p.,c.p., r.cromáticas,u.v. c.c.,c.c.d.,c.c.p., r.cromáticas, p.f.,p.f.m. r.cromáticas, c.c.p.,u.v.			[43]
DIOSCOREA SANZIBAREN-SIS PAX	cuini coini	S. Tomé	tubérculo	venenoso convulsivante	3 alcalóides dioscorina * (VII)	r.cromáticas,c.p. c.p.,Rf(padrão), u.v.,r.cromáticas, preparação de derivados *			[7]

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DIOSPYROS BATOCANA HIERN		Angola	raiz	tratamento de lepra ictiotóxico	2-metilnaftazarina (XIXa)	c.c.p.,p.f..p.f.m., i.v.(padrão)			[79]
					7-metiljuglona (XIXb)	c.c.p.,p.f.,p.f.m., i.v.(padrão)			
					biramentaceona				
					rotundiquinona				
					mamegaquinona (XXV)				
					diospirina (XXX)	c.c.p.,(padrão)			
					diosquinona (XX)	c.c.p.,(padrão)			
					isodiospirina (XXI)	c.c.p.,(padrão)			
					batocanona (XXII)	c.c.p.,p.f.,i.v., u.v.,$[\alpha]$,c.d., r.m.n.,M			
					β-dihidrodiospirina *	c.c.p.,r.m.n., M			
					isodiospirina di-epóxido I	c.c.p.,M,u.v., r.m.n.,(síntese)			
					isodiospirina di-epóxido II	c.c.p.,M,u.v., r.m.n.(síntese)			
					isodiospirina-2,3-epóxido *	c.c.p.,M			
DIOSPYROS HETEROTRICHA (B. L. BURTT) F.WHITE		Angola	raiz	tratamento de icterícia	2-metilnaftazarina (XIXa)	c.c.,c.c.p.,p.f., u.v.,i.v.,(padrão), r.m.n.,M,an.el.			[64, 66a 67]
					7-metiljuglona (XIXb)	c.c.,c.c.p.,p.f., u.v.,i.v.(padrão)			
					8,8′-di-hidroxi-4,4′-dimetoxi-6,6′-dimetil-2-2′-bisnaftil-1,1′-quinona (XXIII)	c.c.,c.c.p.,p.f., u.v.,i.v.(padrão)			
					8′-hidroxi-isodiospirina (XXIV)	c.c.,c.c.p.,p.f., $[\alpha]$,u.v.,i.v. M,r.m.n.,c.d.			
DIOSPYROS KIRKII HIERN.		Angola	raiz		lupeol	c.c.,c.c.p.,p.f., p.f.m.,i.v.,c.f.g., c.c.d.,Rf(padrão) derivados(padrões),M	acetato de lupeol acetato de α-amirina acetato de ácido ursólico lactona de ácido ursólico		[78]
					β-sitosterol	c.c.,c.c.p.,p.f., i.v.,c.c.d.,c.f.g., p.f.m.(padrão)			
					betulina	c.c.d.,i.v.(padrão), derivados), p.f.			
					2 compostos não identificados	p.f.m.,M			
DIOSPYROS LYCIOIDES DESF. SUBSP. SERICEA (BERNH. EX KRAUSS) DE WINTER		Angola	raiz		isodiospirina (XXI)	c.c.,c.c.d.,M, u.v.,p.f.,r.m.n., i.v.(padrão)			[65, 66a 67]
					7-metiljuglona (XIXb)	c.c.,c.c.d.,p.f., u.v.,i.v.,(padrão)			
					8,8′-dihidroxi-4,4′-dimetoxi-6,6′-dimetil-2,2′-bisnaftil-1,1′-quinona (XXIII)	c.c., c.c.d.,p.f., u.v.,i.v.,(padrão)			
					2-metilnaftazarina (XIXa)	c.c.,c.c.p.,p.f., u.v.,i.v.,r.m.n., M,an.el.			
					8′-hidroxi-isodiospirina (XXIV)	c.c.,c.c.p.,p.f., $[\alpha]$,u.v.,M,i.v., r.m.n.,c.d.			
					mamegaquinona (XXV)	c.c.,c.c.p..p.f., u.v.,M,r.m.n.,i.v. (padrão),p.f.m.			
					8′-hidroxi-isodiospirina (racemato)	c.c.,c.c.p.,p.f., $[\alpha]$,u.v.,i.v.,M, r.m.n.,c.d.			

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ERYTHROXYLON DEKINDTII (ENGL.) O. E. SCHULZ	olokuto	Angola	folha	febrífugo	ecgonina	c.p.,Rf(padrão), revelador	cocaina benzoilecgonina arabinose glucose lactose levulose manita maltose sorbitol sorbose xilose	% de alcalóides	[50]
					metilecgonina	» » »			
					pseudotropina	» » »			
					tropacocaina	» » »			
					ramnose	» » »			
					galactose	» » »			
					sacarose	» » »			
EUCLEA DIVINORUM HIERN		Moçambique	raiz		diosindigo A	c.c.p.,p.f.,u.v.,i.v.(padrão),r.m.n.			[74]
					2-metilnaftazarina (XIXa)	» » »			
					7-metil-juglona (XIXb)	» » »			
					diospirina	» » »			
					lupeol	c.c.,p.f.,M, acetato,r.m.n.			
					betulina	c.c.,p.f.,M, diacetato, r.m.n.			
EUCLEA LANCEOLATA E. MEY EX D. C.	emboto mboto mumboto otinu omundine jimboto antinum otyime omokunia	Angola	raiz	purgativo anti-reumático tinturaria (peles)	8,8'-di-hidroxi-4,4'-dimetoxi-6,6'-dimetil-2,2'-binaftil-1,1'-quinona (XXIII)	c.c.,c.c.d.,p.f., u.v.,i.v.(padrão)			[58, 60, 69, 72]
					7-metiljuglona (XIXb)	c.c.,c.c.d.,p.f., u.v.,i.v.(padrão) M,r.m.n.			
					8'-hidroxidiospirina (XXVIII)	c.c.,c.c.p.,u.v., i.v.,r.m.n.,M, p.f.,p.f.m.			
					2-metilnaftazarina (XIXa)	c.c.,c.c.d.,p.f., u.v.,M,r.m.n. an.el.			
					diospirina (XXX)	c.c.,c.c.p.,p.f., u.v.,i.v.(padrão), M,r.m.n.			
					mamegaquinona (XXV)	c.c.,c.c.d.,p.f., u.v.,i.v.(padrão), M,r.m.n.			
					lupeol	c.c.,c.p.,Rf(padrão),i.v.(padrão), p.f.,derivados			
					betulina	c.c.,c.p.,Rf(padrão),i,v,,p.f., derivados			
					eucleolatina **	c.c.,c.c.p.,p.f., u.v.,M,i.v.			
EUCLEA NATALENSIS A. D C.	omutyilombo omunyine omunenne	Angola	raiz		7-metiljuglona (XIXb)	c.c.p.,c.c.,p.f., u.v.,i.v.(padrão)			[71, 75, 76]
					2-metilnaftazarina (XIXa)	c.c.p.,c.c..p.f., u.v.,i.v.(padrão)			
					biramentaceona	c.c.p.,c.c..p.f., u.v.,i.v.,M			
					mamegaquinona (XXV)	c.c.p.,c.c.,p.f., u.v.,i.v.,(padrão), r.m.n.			
					xilospirina	c.c.p.,c.c.d.,p.f., u.v.,i.v.(padrão)			
					diospirina (XXX)	c.c.p.,c.c.d.,p.f., u.v.,i.v.(padrão)			
(cont.)									

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(cont.)					isodiospirina (XXI)	c.c.p.,c.c.d.,p.f.,u.v.,i.v.(padrão)			
					natalenona (XXVI)	c.c.p.,p.f.,c.d.,u.v.,i.v.,r.m.n.,^{13}C r.m.n.,M, derivados, raios-X			
					galpinona (XXVII)	c.c.,p.f.,u.v.,i.v.,r.m.n.,M,			
					8′-hidroxidiospirina (XXVIII)	c.c.p.,p.f.,i.v.(padrão),u.v.			
					euclanona (XXIX)	c.c.p.,p.f.,u.v.,i.v.,r.m.n.,M.			
					derivado de 7-metiljuglona **	c.c.p.,p.f.,u.v.,i.v.,M.			
EUCLEA PSEUDEBENUS E. MEY. EX DC.	mumboto mundine musema amuzema	Angola	raiz		8,8′-dihidroxi-4,4′-dimetoxi-6,6′-dimetil-2,2′-binaftil-1,1′-quinona (XXIII)	c.c.,p.f.,u.v.,i.v.(padrão).			[70, 73]
					mamegaquinona (XXV)	c.c.,c.c.p.,u.v.,i.v.(padrão) r.m.n.,M.			
					eucleina = diospirina (XXX)	c.c.,c.c.p.,p.f.,u.v.,i.v.,r.m.n.,M, derivados			
					7-metiljuglona (XIXb)	c.c.,c.c.d.,u.v.,i.v.(padrão)			
					2-metilnaftazarina (XIXa)	c.c.d.,u.v.,i.v.,p.f.			
					isodiospirina (XXI)	c.c.,c.c.d.,p.f.,p.f.m.,u.v.,i.v.,M, (padrão)			
					8′-hidroxidiospirina (XXVIII)	c.c.,c.c.p.,p.f.,u.v.,i.v.,M(padrão)			
					8′-hidroxi-isodiospirina racémica	c.c.,c.c.p.,p.f.,α,i.v.,u.v.r.m.n.,M(padrão) c.d.			
					2 bisnaftoquinonas **	c.c.,c.c.p.,p.f.,u.v.,i.v.,M			
HYMENODICTYON FLORIBUNDUM (HOCHST E STEUD) B.L. ROBINSON	omuriatgimene	Angola	casca	febrífugo	berberina	r.cromáticas,c.p.,Rf(padrão), revelador	arabinose galactose lactose levulose manita sorbitol sorbose ramnose maltose	humidade cinzas celulose azoto glúcidos amido taninos	[51]
	omlyatymene ehilyalume elume-ilya emunkhwene			tratamento de eclampsia	xilose	c.p.,Rf(padrão)			
					glicose	» »			
					frutose	» »			
					sacarose	» »			
					escopoletina (XIVa)	c.p.,Rf(padrão) p.f.,p.f.m.,u.v.,an.el.			
					fabriatina (XIVb)	Rf(lit)c.p.			
					escopolina(XIVc)	» »			
					ácido **	p.f.			
JATRORRHIZA PALMATA (LAM.) MIERS	calumba	Moçambique	raiz	tónico eupéptico estomáquico	columbina (XV)	p.f.		alcalóides totais cinzas	[62]
JATRORRHIZA PALMATA (LAM.) MIERS	calumba	Moçambique	raiz	tónico geral antipirético	palmatina (XXXIa)	c.c.,c.c.d.,reveladores, u.v.,i.v.,p.f.,derivados		% de palmatina % de columbamina % de jatrorrizina	[59b]
				anti-helmintico	columbamina (XXXIb)	c.c.,c.c.d., reveladores,u.v.,i.v.,p.f.,derivados			
				tonicardiaco acção ritmizante	jatrorrizina (XXXIc)	c.c.,c.c.d.,reveladores,u.v.,i.v.,p.f.,derivados			

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JATRORRHIZA PALMATA (LAM.) MIERS	calumba	Moçambique	raiz	tónico geral antipirético anti-helmíntico tonicardíaco acção ritmizante	bisjatrorrizina (XXXII)	c.c.,c.c.d.,p.f., u.v.,i.v.,r.m.n., an.el.,derivados, síntese			[66b]
LIPPIA ASPERIFOLIA RICH.	umpepo omuanke efilampepe omupepe ondambi yolui	Angola	folha e ramo florido	rubefaciente vesicatório febrífugo	taninos catéquicos taninos pirogálhicos alcalóides	r.cromáticas » » » »		humidade cinzas glúcidos celulose azoto taninos essência	[13]
LOCHNERA ROSEA (LINN.) REICHB. ver VINCA ROSEA LINN.									
LONCHOCARPUS SERICEUS H.B. e K.	colma-doida mutala-menha	S. Tomé	casca	purgativo estomáquico anti-escorbútico ictiotóxico	vitamina C	r. com dicloro-fenol-indofenol	rotenonas saponinas quinonas alcalóides taninos pirocatéquicos	vitamina C	[20]
MAYTENUS SENEGALENSIS (LAM.) EXELL.		Angola e Moçambique	caule	anti-diarreico	β-amirina (XVI)	c.c.,r.cromáticas p.f.,$[\alpha]$,an.el.,i.v. (padrão),derivados		doseamento de β-amirina	[38]
MORINDA GEMINATA DC.		Guiné	raiz	febrífugo	damnacantal (XVIIa)	c.c.,r.cromáticas, p.f.,u.v.,i.v., derivados			[46]
				purgativo	nor-damnacantal (XVIIb)	c.c.,r.cromáticas, p.f.,u.v.,i.v., derivados			
				anti-helmíntico	rubiadina-l-metiléter (XVIIc)	c.c.,r.cromáticas, p.f.,u.v.,i.v., derivados			
				tratamento de dermatoses	morindona (XVIId)	c.c.,r.cromáticas, p.f.,u.v.,c.p., c.c.d.			
					rubiadina (XVIIe)	c.c.,p.f.,p.f.m., u.v.,i.v., derivados			
					1,2-dimetilantragalhol (XVIIf)	c.c.,r.cromáticas, p.f.,u.v.,i.v., derivados			
NEWBOULDIA LAEVIS SEEM	nandua de feiticeiro canhomburi becuape manjuaco	Guiné	raiz	abortivo vermífugo hemostático afrodisíaco anti-reumático febrífugo anti-disentérico tratamento de hemorragias uterinas	harmano * 3 alcalóides	c.p.,c.c.p.,Rf, revelador, u.v.		alcalóides	[39]

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NEWBOULDIA LAEVIS SEEM	nandua de feiticeiro canhom-buri becuape manjuaco	Guiné	raiz	abortivo	estaquiose (XVIII)	c.p.,Rf(padrão), reveladores, r.cromáticas,			[40]
				vermífugo hemostático afrodisiaco anti-reumático febrífugo anti-disentérico anti-malária tratamento de hemorragias uterinas		p.f.,p.f.m.,|α|, derivados,i.v.			
PENTACLETHRA MACROPHYLA BENTH.	moandi moandim muandi ubá	S. Tomé	casca	abortivo anti-helmíntico laxativo ocitóxico					[10]
PERSEA AMERICANA MILL. GARD. DICT. ou PERSEA GRATISSIMA GAERTN.	abacateiro	S. Tomé	folha	diurético	quercetol (3,3′,4′, 5,7-pentahidroxi-flavona)	c.c.,r.cromática, p.f.,p.f.m., derivados,u.v.	saponinas alcalóides quinonas	humidade índice de iodo quercetol cinzas:	[25]
					taninos pirocatéquicos glicerina ácidos gordos insaturados	r.cromáticas		nitratos potássio	
					esteróides β-sitosterol **	r.cromáticas » » p.f.			
PHYLLANTHUS RETICULATUS POIR.	tetenhe	Moçambique	folha	tratamento de queimaduras	flavonas	r.cromáticas	alcalóides	humidade cinzas azoto celulose glúcidos amidos taninos	[36]
				branqueamento de dentes	taninos	r.cromáticas			
					ácido elágico *	c.p.,Rf(padrão), revelador			
				excitante (casca)	ácido m-digálhico	c.p.,Rf(padrão), revelador			
					pirogalhol *	c.p.,Rf(padrão), revelador			
					ácido p-cumárico *	c.p.,Rf(padrão), revelador			
PILIOSTIGMA THONNINGII (SCHUMACH) MILNE REDH. ver BAUHINIA THONNINGII SCHUM.									
PLUCHEA DIOSCORIDIS (L.) DC. ou BACCHARIS DIOSCORIDIS L.	kitoko quitoco pequeno mambumbu kipangu-makutu ociyukula muhunza-hunza munze-hunze sibi	Angola	folha e ramo	abortivo dismenorreico	taninos: ácido protocatéquico *d*-catequina *l*-epicatequina	r.cromáticas c.p.,Rf(padrão), reveladores c.p.,Rf(padrão), reveladores c.p.,Rf(padrão), reveladores	ácido elágico ácido cafeico quercetina ácido-*p*-hidroxibenzóico ácido gálhico pirogalhol	humidade essência taninos glúcidos celulose azoto cinzas: sílica ferro alumínio cálcio magnésio manganésio potássio sódio	[24]

Planta	Designação Vernácula (a)	Origem	Parte da Planta Estudada	Propriedades Farmacológicas e Aplicações Práticas	Constituintes Químicos Presentes (b)	Técnicas Usadas no Isolamento e Identificação (c)	Compostos Ausentes (d)	Determinações Analíticas (e)	Ref. (f)
PLUMBAGO ZEYLANICA L.				tratamento da lepra	plumbagina (XIII)	p.f.,i.v.,r.m.n., comparação com amostra autêntica e análogos sintetizados			[59]
PSIDIUM GUAYAVA L.	goiaba guiava koy had djamboe	S. Tomé	folha	estomáquico	taninos catéquicos	r.cromáticas		humidade lipidos glúcidos prótidos celulose cinzas taninos	[5]
				febrífugo anti-diarreico	taninos pirogálhicos	gravimetria			
				tanante					
PYCNANTHUS ANGOLENSIS (WELW.) EXELL.	mutuge cassa cachão caixão	S. Tomé	casca	tratamento de estomatites	glicerol	tranf. em acroleína	taninos pirogálhicos	glúcidos cinzas humidade taninos pirocatéquicos	[14]
				cicatrizante	esteróides	r.cromáticas,c.c.	quinonas		
				desinfectante	flavonol	r.cromáticas,u.v.			
					naringina	r.cromáticas,u.v., p.f.,c.p.,Rf.			
					glucose	c.p.,revelador			
					ramnose	c.p.,revelador			
RAUWOLFIA NATALENSIS SOND.		Moçambique	raiz	antídoto de mordeduras de serpentes hipertensão sedativo tratamento de psicoses	reserpina	c.p.,Rf(padrão), mét. colorimétricos		água glúcidos lipidos prótidos celulose cinzas alcalóides totais alcalóides do tipo reserpina-rescinamina	[2]
RAUWOLFIA VOMITORIA AFZ.	cata-pequena	S. Tomé	raiz	tratamento de dores, abcessos e inflamações	reserpina	colorimetria		humidade glúcidos lipidos prótidos celulose cinzas alcalóides totais alcalóides do grupo reserpina-rescinamina	[4]
RAUWOLFIA VOMITORIA AFZ.		Angola	raiz		reserpina	c.p.,Rf(padrão), r.cromáticas, p.f.,$|\alpha|$,u.v.		humidade alcalóides totais reserpina	[12]
RAUWOLFIA VOMITORIA AFZ.		Angola	raiz		reserpina	c.c.,c.p.,p.f., p.f.m.,u.v.,$|\alpha|$		alcalóides totais reserpina	[35]
					ajmalina	c.c.,c.p.,p.f., p.f.m.,u.v.,$|\alpha|$			
					ajmalicina	c.c.,c.p.,p.f., u.v.,$|\alpha|$			
					vomalidina	c.c.,c.p.,p.f., u.v.,$|\alpha|$			

Planta	Designação Vernácula (a)	Origem	Parte da Planta Estudada	Propriedades Farmacológicas e Aplicações Práticas	Constituintes Químicos Presentes (b)	Técnicas Usadas no Isolamento e Identificação (c)	Compostos Ausentes (d)	Determinações Analíticas (e)	Ref. (f)
SARCOCEPHALUS ESCULENTUS AFZ.	quina do rio Nunez cinchona africana madronha quinino africano	Guiné	raíz	anti-palúdico tónico febrífugo anti-blenorrágico tóxico purgativo estomáquico emenagogo diurético hipotensor odontálgico corante anti-disentérico	alcalóide indólico ** antraquinona hidroxilada 7-hidroxicumarina *β*-sitosterol taninos pirocatéquicos	c.c.,c.p.,p.f. do picrato,u.v.,Rf, r.cromáticas r.cromáticas,u.v. c.p.,p.f.,Rf(padrão),reveladores r.cromáticas, p.f., p.f. do acetato			[33]
SECURIDACA LONGIPEDUNCULATA FRESEN.	utala omuipanyoka omusasa mututungu mbuaze mutata utata mudjaja omutimuneme buase boasi	Angola	raíz	emoliente purgativo resolutivo ictiotóxico bradicardia anti-reumático antídoto de mordeduras de serpentes sabão	taninos pirocatéquicos salicilato de metilo ácido laúrico esteróides * monotropitinósido	c.p.,reacções cromáticas aroma,reacções cromáticas destilação,p.f. reacções cromáticas p.f.,produto de hidrólise,Rf e reveladores, osazonas de xilose e glucose	alcalóides carotenoides quinonas flavonas	salicilato de metilo humidade glúcidos lípidos prótidos celulose cinzas	[1]
SOLANUM WRIGTII BENTH ou SOLANUM GRANDIFLORUM AUCT. PL. NON RUIZ ET PAVON		S. Tomé	folha	tóxico	solanidina (VIII) ramnose * arabinose * glucose *	r.cromáticas,c.p., p.f.,p.f.m.,u.v. c.p.,Rf c.p.,Rf,osazona c.p.,Rf,osazona			[26]
STERCULIA TRAGACANTHA LINDL.	quibondo-camanha popó nêspera de obó	S. Tomé	casca	tónico laxativo vermífugo tratamento de infecções tratamento de sifilis corante têxtil detergente cosmético (goma)	esteróides taninos pirocatéquicos flavonol do tipo da rutina **	c.c.,r.cromáticas c.c.,r.cromáticas c.c.,c.p.,r.cromáticas,u.v., solubilidade	alcalóides quinonas gomas	humidade cinzas alcalinas taninos pirocatéquicos	[11]
TEPHROSIA CANDIDA (ROXB.) DC.	bancá	S. Tomé	folha	ictiotóxico	1 alcalóide * flavonóide	c.c.,r.cromáticas c.p.,(Rf) r.cromáticas	rotenóides saponósidos		[18]
TERMINALIA MACROPTERA GUILL. E PERR.		Guiné	casca e folha	colagogo colerético laxativo diurético cicatrizante	quercimeritrina (IX) ácido clorogénico * taninos pirogálhicos taninos pirocatéquicos	r.cromáticas,c.c., p.f.,u.v.,c.p.,Rf (padrão) c.p.,Rf(padrão), r.cromáticas r.cromáticas r.cromáticas	quinonas alcalóides	glúcidos prótidos humidade	[30]
cont.)									

Planta	Designação Vernácula (a)	Origem	Parte da Planta Estudada	Propriedades Farmacológicas e Aplicações Práticas	Constituintes Químicos Presentes (b)	Técnicas Usadas no Isolamento e Identificação (c)	Compostos Ausentes (d)	Determinações Analíticas (e)	Ref. (f)
(cont.)				cardiotónico pele		—			
				estomatites	esteróide carboxilado **	c.c.,r.cromáticas, p.f.			
				corante têxtil	carotenóide **	r.cromáticas,c.c., u.v.			
TRECULIA AFRICANA DECNE	isa isaquente quicange disanha musanha mutali	S. Tomé	casca	anti-tússico	taninos-pirocatéquicos	r.cromáticas	saponinas		[22]
				laxativo	esteróides	r,cromáticas	alcalóides		
					lípidos	r.cromáticas			
				tratamento de lepra abortivo	flavanona **	c.c.,c.p.p.,r.cromáticas,u.v.			
				ictiotóxico	flavonol **	c.c.,c.p.p.,u.v., r.cromáticas			
					morina (pentahidroxiflavona)	c.c.,c.p.p.,p.f., r.cromáticas,u.v. (padrão)			
					pigmento antociânico	r.cromáticas,c.p., Rf			
					quinona **	r.cromáticas			
VINCA ROSEA LINN. ou CATHARANTHUS ROSEUS G. DON. ou LOCHNERA ROSEA (LINN.) REICHB.	maravilhas do cabo	Moçambique	raiz	anti-leucémico anti-diabético	alstonina	c.c.,c.c.d.,c.p., Rf(lit.) reveladores,p.f.,i.v.,u.v.	—		[44]
				hipotensor antibiótico anti-hemorrágico	ajmalicina	c.c.,c.c.d.,c.p., Rf(lit.),reveladores,p.f.,i.v.,u.v., raios X			
					catharantina	c.c.,c.c.d.,Rf(lit.), reveladores			
					lochnericina	» » »			
					lochnerina	» » »			
					lochneridina	» » »			
					sitsiriquina	» » »			
					tetra-hidroalstonina	» » »			
					vindolicina	» » »			
					vindolina	» » »			
					vindolinina	» » »			
					carosina	» » »			
					isoleurosina	» » »			
					neuleurosidina	» » »			
					neuleurocristina	» » »			
					pleurosina	» » »			
					vimblastina	» » »			
					vincamicina	» » »			
					vincarodina	» » »			
					vindolidina	» » »			
					catharosina	» » »			
					β-sitosterol	p.f.,c.c.d.,p.f.m. acetilação(p.f.)			
VINCA ROSEA LINN. ou CATHARANTHUS ROSEUS G. DON. ou LOCHNERA ROSEA (LINN.) REICHB.	maravilhas do cabo	Ilha da Madeira	caule folha	anti-leucémico	ajmalicina	c.c.d.,Rf(lit.),reveladores			[45]
				anti-diabético	carosina	» » »			
				hipotensor	catharantina	» » »			
				antibiótico	catharosina	» » »			
				anti-hemorrágico	isoleurosina	» » »			
					lochnericina	» » »			
					lochneridina	» » »			
					lochnerina	» » »			
					neuleurosidina	» » »			
					pleurosina	» » »			
					tetra-hidroalstonina	» » »			
					vimblastina	» » »			
					vincamicina	» » »			
					vindolidina	» » »			
					vindolina	» » »			

NOTAS À TABELA 1

(a) Designações vernáculas mais comuns.

(b) Não se introduziram alterações à nomenclatura utilizada nos respectivos trabalhos:

- * — composto isolado não completamente puro;
- ** — composto isolado puro, cuja estrutura não foi completamente esclarecida.

(c) Abreviaturas mais utilizadas:

- c.c. cromatografia em coluna
- c.p. cromatografia em papel
- c.c.d. cromatografia em camada delgada
- c.c.p. cromatografia em camada preparativa
- c.f.g. cromatografia em fase gasosa
- i.v. espectrometria de infravermelho
- u.v. espectrometria de ultravioleta
- M. espectrometria de massa
- r.m.n. espectrometria de ressonância magnética nuclear protónica
- ^{13}C r.m.n. espectrometria de ressonância magnética nuclear de carbono
- c.d. dicroísmo circular
- an. el. análise elementar
- p.f. ponto de fusão
- p.f.m. ponto de fusão misto
- $[\alpha]$ — poder rotatório específico.

(d) compostos intencionalmente pesquisados através de testes característicos.

(e) Referem-se a determinações de teores e índices específicos.

(f) Bibliografia referida por ordem cronológica.

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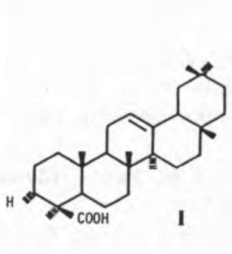

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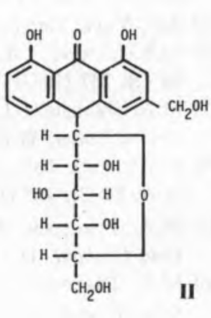

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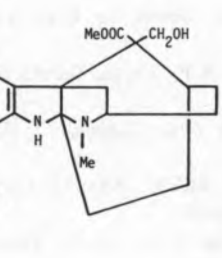
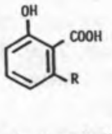
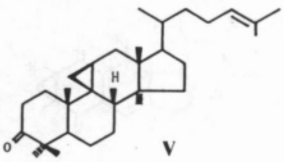


III

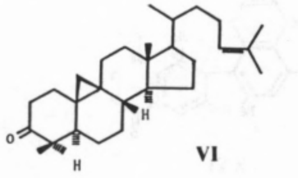


R = $C_{15}H_{27}$; $C_{15}H_{25}$; ...

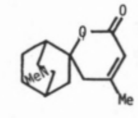
IV



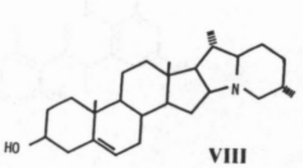
V



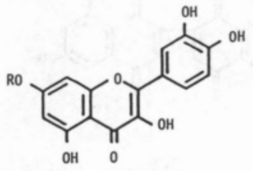
VI



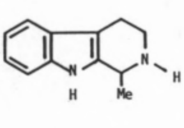
VII



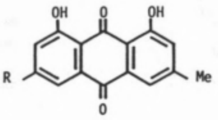
VIII



IX $R = C_6H_{11}O_5$



X

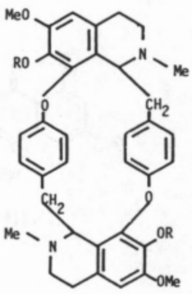


a. R=H

b. R=OMe

c. R=OH

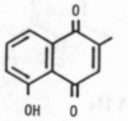
XI



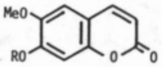
a. R=H

b. R=Me

XII



XIII

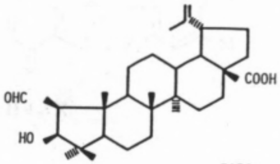


a. R=H

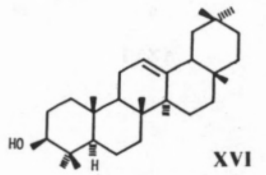
b. $R=C_5H_9O_4-C_6H_{10}O_4$

c. $R=C_6H_{11}O_5$

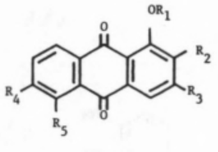
XIV



XV

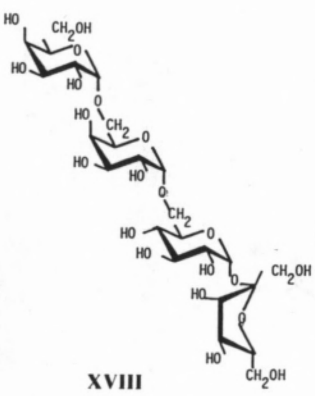


XVI

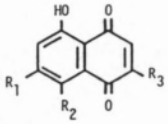


	R_1	R_2	R_3	R_4	R_5
a.	Me	CHO	OH	H	H
b.	H	CHO	OH	H	H
c.	Me	Me	OH	H	H
d.	H	Me	H	OH	OH
e.	H	Me	OH	H	H
f.	Me	OMe	OH	H	H

XVII



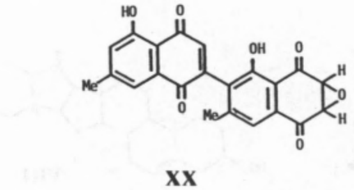
XVIII



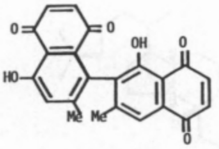
a. R_1= H; R_2=OH; R_3=Me

b. R_1=Me; R_2=R_3=H

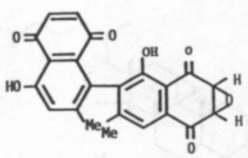
XIX



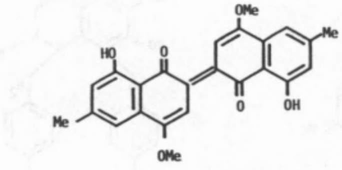
XX



XXI



XXII



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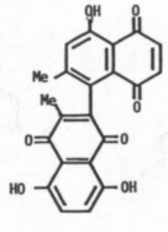
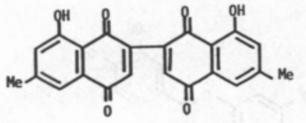
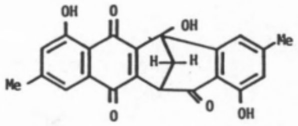


XXIV



XXV



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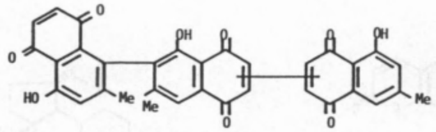

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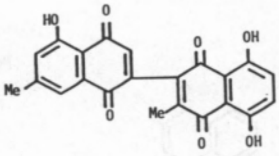
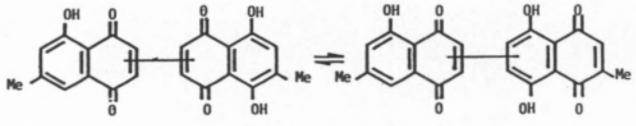
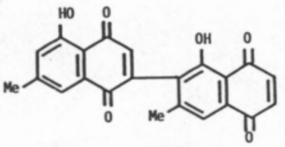


XXVIII



XXIX



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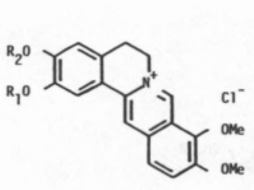
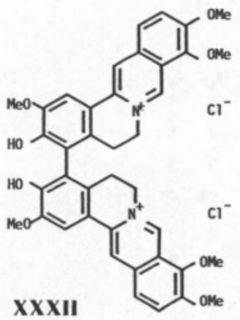


	R_1	R_2
a.	Me	Me
b.	H	Me
c.	Me	H

XXXI



XXXII

Tabela 2

ANGOLA	Ref.
Albizzia tanganyicensis	[15]
Baccharis dioscoridis (Pluchea dioscoridis)	[24]
Burkea africana	[68]
Cassia angolensis	[77]
Cassia occidentalis	[9]
Cassia singueana	[56,57,62]
Cissampelos mucronata	[47]
Commiphora angolensis	[21]
Cymbopogon densiflorus	[49]
Diospyros batocana	[79]
Diospyros heterotricha	[64,66a,67]
Diospyros kirkii	[78]
Diospyros lycioides	[65,66a,67]
Erithroxylon dekindtii	[50]
Euclea lanceolata	[58,60,69,72]
Euclea natalensis	[71,75,76]
Euclea pseudebenus	[70,73]
Hymenodyction floribundum	[51]
Lippia asperifolia	[13]
Maytenus senegalensis	[38]
Pluchea dioscoridis (Bacharis dioscoridis)	[24]
Rauwolfia vomitoria	[12,35]
Securidaca longipedunculata	[1]
CABO VERDE	
Aloe vera	[29]
Anacardium occidentale	[54]
GUINÉ	
Alchornea cordifolia	[37]
Alstónia congensis	[48,55]
Anacardium occidentale	[52,53]
Bauhinia thonningii (Piliostigma thonningii)	[34]
Cassia occidentalis	[9]
Conopharyngia longiflora	[61]
Dioscorea dumetorum	[43]
Morinda geminata	[46]
Newbouldia laevis	[39,40]
Piliostigma thonningii (Bauhinia thonningii)	[34]
Sarcocephalus esculentus	[33]
Terminalia macroptera	[30]

ÍNDIA	
Anacardium occidentale	[8]
MADEIRA	
Vinca rosea (Catharanthus roseus)	[45]
MOÇAMBIQUE	
Albizzia adianthifolia	[27]
Anacardium occidentale	[31,32,41,42]
Cathararanthus roseus (Vinca rosea)	[44]
Euclea divinorum	[74]
Jatrorrhiza palmata	[59b,62,66b)
Lochnera rosea (Vinca rosea)	[44]
Maytenus senegalensis	[38]
Phyllantus reticulatus	[36]
Rauwolfia natalensis	[2]
Vinca rosea (Catharanthus roseus)	[44]
S. TOMÉ E PRÍNCIPE	
Andropogon citratus (Cymbopogon citratus)	[17]
Artocarpus integrifolia	[3]
Cassia occidentalis	[9]
Cecropia peltata	[16]
Cinnamonum cassia	[6]
Cymbopogon citratus (Andropogon citratus)	[17,28]
Dioscorea dumetorum	[19]
Dioscorea sanzibarensis	[7]
Lonchocarpus sericeus	[20]
Pentaclethra macrophylla	[10]
Persea americana (Persea gratissima)	[25]
Psidium guayava	[5]
Pycnanthus angolensis	[14]
Rauwolfia vomitoria	[4]
Solanum wrigtii (Solanum grandiflorum)	[26]
Sterculia tragacantha	[11]
Thephrosia candida	[18]
Treculia africana	[22]

O maior número de publicações existente refere-se às do género *Diospyros* e *Euclea* da família das *Ebenaceae*, seguidas de *Anacardium occidentale*. O género *Diospyros* muito difundido geograficamente e englobando um grande número de espécies reveste-se de grande interesse económico pelas madeiras que fornece, entre as quais se destacam os reputados ébanos [5]. É de assinalar ainda, que várias espécies de *Diospyros* produzem frutos comestíveis ou são utilizados na medicina africana nomeadamente no tratamento da lepra, enquanto outras possuem propriedades ictiotóxicas, pelo que são usadas em certas regiões na captura de peixes [5].

O género *Euclea* atraiu desde muito cedo o interesse dos químicos, dadas as inúmeras referências a propriedades farmacológicas que se estendem a uma larga gama de aplicações: purgativas, anti-

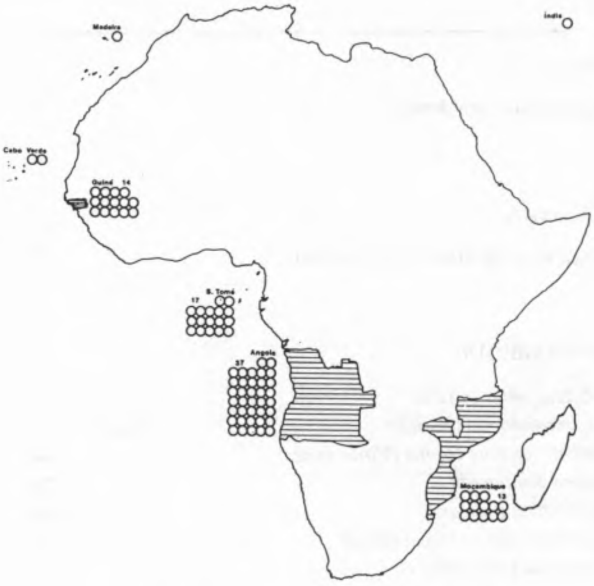


Fig. 1
Distribuição Geográfica das Publicações

-diabéticas e anti-reumáticas [1]. O interesse indicado pelos inúmeros estudos sobre o *Anacardium occidentale* (nome vulgar: cajueiro ou caju) é possivelmente o reflexo da enorme importância económica desta espécie, já que Moçambique era, na década de 60, o maior produtor mundial e contribuía com cerca de 50% da produção mundial de castanha de caju [6]. Uma referência de 1983 [7] cita ainda que as cascas moídas da castanha do caju são utilizadas em Moçambique para o controle de caracóis, tratando-se portanto de uma espécie com actividade moluscicida notável.

Recebido 10.2.84.

AGRADECIMENTO

Aos Prof. J.A.C. Silva, Presidente do Instituto de Investigação Científica Tropical, Prof. J. Silva, Vice-Presidente do I.I.C.T., Prof. J.E.M. Ferrão, Director da Missão de Estudos Agronómicos do Ultramar, agradeço o interesse demonstrado pelo presente trabalho.

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Agradeço à Fundação Calouste Gulbenkian e à Junta Nacional de Investigação Científica e Tecnológica o apoio financeiro concedido.

Agradeço especialmente à Prof. A. Lobo e ao Prof. S. Prabhakar todo o apoio prestado nas suas observações e sugestões.

REFERÊNCIAS E NOTAS

[1] J.M. Watt, M.G. Breyer-Brandwijk, «Medicinal and Poisonous Plants of Southern and Eastern Africa», E.S. Livingstone Ltd., Edimburgh and London, 2nd ed., 1962.

[2] cf. a bibliografia que se segue à Tabela 1. Para uma listagem de plantas anterior à década de 40, consulte-se a obra: *Conde de Ficalho*, «Plantas Úteis da África Portuguesa», Agência Geral das Colónias, Lisboa, 2.ª ed., 1947.

[3] A.F. Costa, «Elementos da Flora Aromática. O Laboratório de Farmacognosia no Estudo de Óleos Essenciais de Portugal e Angola», Junta Nacional de Investigação Científica do Ultramar, Lisboa, 1975 e referências aí citadas.

[4] J.E.M. Ferrão, «Flora de S. Tomé e Príncipe, Ácidos Gordos e Proteínas de Algumas Sementes», Junta de Investigação Científica do Ultramar, Lisboa, 1979, e referências aí citadas.

[5] A.C. Alves, M.A.C. Costa, *Rev. Port. Farm.*, **31**, 24 (1981).

[6] A. Pereira Jor., J.B. Graça, J. Pereira, M.M.A. Pereira, *Garcia de Orta (Lisboa)*, **14**(4), 483 (1966); A.B. Esteves, Garcia de Orta (Lisboa), **14**(4), 537 (1966).

[7] G. Webbe, J.D.H. Lambert, *Nature*, **302**, 754 (1983).

ABSTRACT

List of medicinal plants of tropical origin chemically studied in Portugal during the last few decades

The phytochemistry of the tropical plants studied in Portugal during the past 25 years is presented in a table form and relevant literature referenced are cited. Each plant is referred to its vernacular name, its origin and the part of the plant on which the study was undertaken. Besides their medicinal properties and current practical applications, their chemical constituents, the techniques used to isolate them and the analytical methods employed to arrive at their structures are referred to.

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DERIVADOS INTERHALOGENADOS DO Tl(III). IV — COMPLEXOS CON TPPO*

Teñense preparado e caracterizado por análise elemental os complexos: $TlCl_3.(TPPO)_2$; $TlBr_2Cl.(TPPO)_2$; $TlI_2Cl.(TPPO)_2$; $TlBr_3.(TPPO)_2$; $TlIBr_2.(TPPO)_2$; $TlI_2Br.(TPPO)_2$; $TlI_3.(TPPO)_2$; $TlIBrCl.(TPPO)_2$. *Todolos sólidos aillados compórtanse como non electrolitos en disolución en acetonitrilo. Se discuten os seus espectros vibracionais, de xeito especial as tensións Tl-X, e se propoñen estruturas pra os complexos.*

INTRODUCION

O coñecemento da química do talio(III) ten avantado moito [1] dende que, hai vinte anos, COTTON [2] conqueríu estabilizar por vez primeira compostos de fórmula xeral $TlX_3.nD$. Nembargantes non é moita a información estrutural que se ten distes compostos e tampouco e moito o que se sabe sobor da estabilización de compostos de fórmula xeral $TlXX'_2.nD$.

En anteriores traballos iniciamos o estudio da estabilización de complexos tipo $TlXX'_2.nD$, conquerindo a sua estabilización cando o ligando posúe un átomo dador duro, dacordo ca terminoloxía de PEARSON [3]. Ligandos como o óxido de piridina — PyO — e os seus derivados [4]; a hexametilfosforotriamida — HMTP — [5] os óxidos de picolina — 2,3,4-PicO — [6]; a piridina e as picolinas [7], son capaces de estabilizar aos derivados interhalogenados preferentemente na relación molar dador-aceptor 2:1.

Na presente investigación seleccionamos como ligando estabilizador ao óxido de trifenilfosfina — TPPO —. Dita base é xa coñecida nosa, por canto que foi empregada no estudio da estabilización dos TlX_3 ($X=Cl,Br,I$) frente a bases de diferente dureza [8], demostrando a súa outa capacidade estabilizadora. Se intenta non soio estudiar a estabilización dos interhaloderivados de talio(III) sinon, ao tempo, tentar de obter cristais axeitados pra realizar estudios difractométricos con eles.

EXPERIMENTAL

REACTIVOS

TlCl, TlBr, TlI, bromo e óxido de trifenilfosfina (produtos Merck para sínteses) e IBr (produto Schuchart para síntese) usáronse sin purificación previa. O cloro preparóuse *in situ* por un procedimiento habitual. Iodo (produto Analema) foi sublimado varias veces antes da sua utilización. Os disolventes precisos purificáronse seguindo métodos ben coñecidos.

PREPARACIÓN DOS COMPLEXOS

O procedimiento seguido na obtención dos complexos foi unha variante do método proposto por COTTON [2], tal e como xa temos discutido con

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* Comunicación presentada ao «6.º Encontro Anual da Sociedade Portuguesa de Química», Aveiro (1983).

** Autor a quen debe dirixirse a correspondencia.

anterioridade [5]. Os compostos $TlCl_3.2TPPO$ e $TlBr_3.2TPPO$, xa preparados por nos [8], obtense neste traballo polo novo procedimiento debendo resaltar que: a) o rendimiento con que se obteñen agora é mais alto (rendimiento cáseque cuantitativo); b) este procedimiento é mais rápido e doado de realizar.

Tódolos complexos preparados neste traballo son con relación molar aceptor-dador 1:2 e o disolvente a utilizar foi sempre acetonitrilo. Ainda que os compostos preparados resultaron ser moi estábeis as operacións de manipulación foron realizadas, ate onde foi posíbel, no interior dunha caixa seca.

$TlCl_3(TPPO)_2$

A $2,5.10^{-3}$ moles de TlCl e $6,2.10^{-3}$ moles de TPPO no disolvente se fai pasar unha corriente de cloro ate que se obtén unha disolución transparente de coor amarelo claro. Cando esta disolución se concentra na línea escomenza a caer un sólido blanco, que se recristaliza en acetonitrilo obténdose finalmente un sólido de aspecto cristalino.

$TlBr_2Cl(TPPO)_2$

A $0,8.10^{-3}$ moles de TlCl e 2.10^{-3} moles de TPPO engádeselle $0,9.10^{-3}$ moles de bromo. Obtense un sólido blanco de aspecto cristalino con rendimiento do 75%.

$TlI_2Cl(TPPO)_2$

A $4,2.10^{-3}$ moles de TlCl e 10^{-2} moles de TPPO engádese $4,7.10^{-3}$ moles de iodo. Obtense un sólido amarelo de aspecto cristalino con rendimiento do 90%.

$TlBr_3(TPPO)_2$

A $1,8.10^{-3}$ moles de TlBr e $4,5.10^{-3}$ moles de TPPO engádese 2.10^{-3} moles de bromo obtense un sólido blanco con rendimiento superior ao 90%, recristalizado en acetonitrilo permite obter cristais optimos pra facer estudios difractométricos.

$TlIBr_2(TPPO)_2$

A $2,1.10^{-3}$ moles de TlBr e $5,2.10^{-3}$ moles de TPPO engádese $2,3.10^{-3}$ moles de IBr. Obtense un sólido amarelo con rendimiento do 81%, dito sólido recristalízase en acetonitrilo e permite obter optimos cristais.

$TlI_2Br(TPPO)_2$

A $1,8.10^{-3}$ moles de TlBr e $4,4.10^{-3}$ moles de TPPO engádese 2.10^{-3} moles de iodo. Se obtén un precipitado amarelo con rendimiento do 88% que se pode recristalizar en acetonitrilo dando unhos bóns criatais amarelos.

$TlI_3(TPPO)_2$

A $3,3.10^{-3}$ moles de TlI e 8.10^{-3} moles de TPPO engádese $3,7.10^{-3}$ moles de iodo. Se forma un precipitado laranxa con rendimiento do 92%. Este sólido pódese recristalizar en acetonitrilo dando un sólido de aspecto cristalino.

$TlClBrI(TPPO)_2$

A $2,5.10^{-3}$ moles de TlCl e 7.10^{-3} moles de TPPO engádese $2,8.10^{-3}$ moles de IBr. Obtense un precipitado amarelo con rendimiento do 88% e que recristalizado en acetonitrilo da un sólido de aspecto cristalino.

ANÁLISE QUÍMICO

C, N e H foron analizados cun analizador Perkin-Elmer 240-B. O talio se determinóu complexométricamente con AEDT [9] usando laranxa de xilenol como indicador. Os resultados analíticos, xunto con algunhas das propriedades físicas dos compostos recóllense na Táboa 1.

MEDIDAS FÍSICAS

Os dados de conductividade medíronse nun conductivimetro WTW modelo LF-3 provisto de célula especial. Os espectros IR se rexistraron, pra o ligando e os complexos, num aparato Perkin-Elmer 180 provisto de accesorios pra o IR lonxano, as mostras se prepararon como suspensión en nujol colocada entre ventás de NaCl ou de polietileno. Os espectros Raman se rexistraron nun espectrofotómetro Jarrel-Ash 25-300 utilizando un láser de He-Ne de 125 mW, a zona rexistrada foi a mesma que no IR.

Táboa 1
Composición e algunhas propriedades dos complexos

Composto	Coor	% C	% H	% Tl	P_F (°C)	Λ_M**
$TlCl_3.(TPPO)_2$	Blanco	48,8 (49,8)*	3,5 (3,5)	23,4 (23,6)	136	27,2
$TlBr_2Cl.(TPPO)_2$	Blanco	45,1 (45,2)	3,1 (3,2)	21,0 (21,4)	184	12,7
$TlI_2Cl.(TPPO)_2$	Amarelo	41,2 (41,2)	2,8 2,9	19,1 (19,5)	144	60,5
$TlBr_3.(TPPO)_2$	Blanco	43,3 (43,2)	2,9 (3,0)	20,2 (20,4)	184	12,0
$TlIBr_2.(TPPO)_2$	Amarelo claro	39,9 (41,3)	2,8 (2,9)	19,8 (19,5)	156	39,8
$TlI_2Br.(TPPO)_2$	Amarelo	39,6 (39,5)	2,7 (2,8)	18,6 (18,7)	146	64,3
$TlI_3.(TPPO)_2$	Laranxa	37,9 (37,9)	2,5 (2,7)	18,1 (17,9)	125	60,8
$TlIBrCl.(TPPO)_2$	Amarelo claro	44,1 (43,1)	3,1 (3,0)	20,8 (20,4)	158	40,3

* As porcentaxes teóricas danse entre as parenteses
** ohm^{-1} cm^2 mol^{-1} disolucións 10^{-3}M en CH_3CN

DISCUSION DOS RESULTADOS

Cáseque tódolos complexos se prepararon como uns sólidos poorentos que, doadamente, se poden recristalizar en acetonitrilo permitindo obter cristais válidos pra realizaren estudios difractométricos. Son sólidos mais ou menos cooreados, pro a cooración intensifícase en función da presencia do iodo nos interhaloderivados. Os puntos de fusión son relativamente baixos (125-180), pra o que lles correspondería a sustancias con masa molecular superior a mil, o que parece indicar a presencia de sustancias moleculares con moi débiles interacións no sólido.

Estos compostos son moi estábeis tanto á luz como ao aer e se hidrolizan con lentitude incluso na presença de ácidos diluidos, tan soio os ácidos concentrados ou os oxidantes os atacan con facilidade. Se trata de sólidos pouco solúbeis en disolventes con baixa constante dieléctrica; pero que incrementan a solubilidade nos disolventes con constante dieléctrica elevada.

Estudiouse a variación da conductividade molar frente a $C^{1/2}$, en acetonitrilo, pra os desemellantes complexos e as formas das curvas son as características dos electrolitos débiles; tan soio o complexo $TlI_3.2TPPO$ presenta un comportamiento anómalo xa denunciado en algúns outros iodocomplexos de talio [2,5]. A conductividade das disolucións non sofre variación notabel co paso do tempo o que nos leva a decir que non existen graves problemas de solvolise, neste disolvente. Os valores da conductividade molar, en acetonitrilo, a concentración 10^{-3} M (ver Táboa 1) son moi baixos en comparanza cós valores que a bibliografía [10-12] dá pra electrolitos 1:1 — 120-160 ohm^{-1} cm^2 mol^{-1} — e se atopan en concordancia con valores encontrados pra sistemas análogos [2,13-15].. Rematar siñalando que os valores dos iododerivados, un pouco elevados, están dentro do orde que corresponde a complexos desta naturaeza e por tanto se pode decir que os complexos preparados se comportan, en disolución, como sólidos moleculares con naturaeza pouco ionógena.

Táboa 2
Bandas mais significativas dos ligandos e dos complexos (1200-400) cm^{-1})

Compostos	ν(P-O)	aβ(C-H)	cβ(C-H)	q(X-sens)	q ′(X-sens)	dβ(C-H)	t(X-sens)
TPPO	1187mf	1180mf	1160h	1120m	1090m	1070m	455m
$TlCl_3.(TPPO)_2$	1145mf	1180mf	1168h	1123m	1087m	1072m	462m,447m
$TlBr_2Cl.(TPPO)_2$	1152mf	1180f	1165h	1118f	1086m	1069m	452m
$TlI_2Cl.(TPPO)_2$	1154mf	1178f	----	1118f	1086m	1068m	454m
$TlBr_3.(TPPO)_2$	1150mf	1180m	1165h	1117f	1084m	1067m	468m,452m
$TlIBr_2.(TPPO)_2$	1152mf	1180hf	1165h	1118f	1086f	1068m	452m
$TlI_2Br.(TPPO)_2$	1152mf	1180hf	1165h	1118f	1084m	1068m	454m
$TlI_3.(TPPO)_2$	1153mf	1178hf	----	1117f	1086m	1068d	452m
$TlIBrCl.(TPPO)_2$	1150mf	1175hf	1165h	1117f	1083m	1068d	455m

A asignación do espectro vibracional do TPPO atópase ben documentado na bibliografía [15,16]. Na Táboa 2 recóllense as frecuencias de vibración mais características do ligando e dos complexos preparados; a nomenclatura empregada na asignación das bandas e a proposta por WIFFEN [17]. Na Táboa 2 pódese observar como a maioria das bandas do ligando non sofren modificación por efecto da complexación e os espectros se poden interpretar axeitadamente en términos de modos do ligando lixeiramente alterados pola formación do enlace dador-aceptor. O unico modo que sofre ostensibel variación é o modo ν(P-O) que se desplaza, nos complexos, hacia números de onda menores con valores de $\Delta\nu$ entre 33-42 cm^{-1}; este desplazamiento confirma que a coordinación se realiza por medio do oxígeno do grupo P-O. Estos desplazamientos son concordantes con valores observados para complexos de Hg(II), Sb(III) e Sn(IV) con TPPO [15,16,18].

As bandas correspondientes aos modos de vibración ν(Tl-X) e ν(Tl-O) que se poden utilizar como diagnose estrutural, atópanse por baixo dos 500 cm^{-1}. Na Táboa 3 se recollen as bandas do ligando e dos complexos nesta zona e se señala a correspondiente asignación. Dita asignación se realizóu por comparanza dos espectros IR e Raman dos nosos complexos e tendo diante outros espectros por nos preparados con estes aceptores e outros ligandos relacionados [4-6]. Na asignación das bandas ν(Tl-O) débese facer constar o seu caracter de provisionalidade, non soio por mor da discrepancia existente na bibliografía sobor da sua ubicación [19]; senón tamén porque a zona por nos selecionada como ν(Tl-O) ($\simeq$300 cm^{-1}) corresponde a unha zona na que, ademais, se pode presentar os modos ν(Tl-Cl) e, por riba, é unha zona onde o ligando presenta bandas (ver fig. 1).

O reducido número de bandas, característico dos nosos espectros vibracionais, ansí como a posición na que presentan, nos leva a prescindir da existencia de formas iónicas e covalentes dímeras ou polímeras, seguindo argumentacións xa dadas [5] e coincidindo co xa indicado acontece en disolución. Doutra parte a coordinación 5, no entorno do talio, se pode postular debido a: 1° As bandas ν(Tl-X) aparecen en posicións idénticas as de sistemas xa investigados por raios X [20]; 2° As asignacións presentan relacións ν(Tl-Br) / ν(Tl-Cl) $\simeq$0,7 e ν(Tl-I) / ν(Tl-Cl) $\simeq$0,6, en boa concordancia cás observadas por CARTY [21] en sistemas $InCl_3.2L$. De todolo anterior dedúcese que os complexos deste traballo deben ser monómeros e presentarán estrutura bipiramidal trigonal mais ou menos distorsionada.

Táboa 3
Bandas mais características na zona baixa do espectro (400-80 cm^{-1})

Compostos		ν(Tl-Cl)	ν(Tl-Br)	ν(Tl-I)	Outras bandas
TPPO		---	---	---	302mf,291f,262m
$TlCl_3.(TPPO)_2$	IR	307f,a	---	---	296f*,260m,130$^+$ f
	R	314d,291f	---	---	295m,260d,220*m
$TlBr_2Cl.(TPPO)_2$	IR	305f,a	218mf,200f	---	295*hf,258m,130$^+$ m,110m
	R	312mf,a	212mf,202f	---	267m
$TlI_2Cl.(TPPO)_2$	IR	295f,a	---	190f,178f	285*hf,256m,130$^+$ m,105m
$TlBr_3.(TPPO)_2$	IR	---	216mf	---	302m,296*m,262d,87$^+$ m
	R	---	217mf,200mf	---	300d,296m,214*m
$TlIBr_2.(TPPO)_2$	IR	---	213mf,200mf	178f	311m,295*f,258m,110$^+$ m
$TlI_2Br.(TPPO)_2$	IR	---	200mf	192hf,176mf	310f,292*mf,256m,110$^+$ f
$TlI_3.(TPPO)_2$	IR	---	---	173mf	308f,291*f,258m.101$^+$ f
$TlBrCl.(TPPO)_2$	IR	295*mf,a	210f,a	181f	305hf,256m,105$^+$ f

* Bandas asignadas provisoriamente como ν(Tl-O)
+ Bandas asignadas provisoriamente como δ(Tl-X)

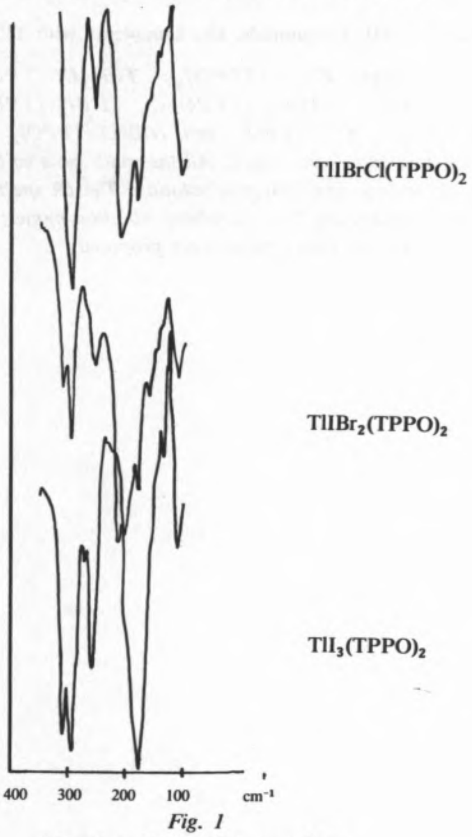

Fig. 1
Espectros IR dalgúns complexos

Os datos de difracción de raios X pra o complexo $TlBr_3(TPPO)_2$ mostran [22] que se trata dun cristal monoclínico que pertenece ao grupo espacial $P_{2_1/c}$ (Nr.14) con disposición bipiramidal trigonal distorsionada no entorno do talio. As moléculas de dador ocupan as posicións "trans" e o ángulo de enlace O-Tl-O é de 175,4. A simetría no entorno do átomo central é, aproximadamente, D_{3h} e débese esperar a presencia de 4 vibracións de tensión: 2 activas soio no Raman, ν_sTl-O (A_1') e ν_sTl-X (A_1'); 1 activa soio no IR, ν_{as}Tl-O (A_2''); 1 activa no IR e no Raman, ν_{as}Tl-X (E'). Os espectros IR, e Raman que se poideron rexistrar, pra os complexos $TlX_3.(L)_2$ confirman a presencia desa simetría distorsionada no entorno do talio.

Dispoñemos dos primeiros datos difractométricos [23] pra os complexos $TlI_2Br.(TPPO)_2$ e $TlIBr_2.(TPPO)_2$ e indican estereoquímica bipiramidal trigonal cós ligandos ocupando as posicións apicais. Nestes complexos a simetría local do talio debería ser C_{2v} e, como consecuencia, presentar 5 vibracións de tensión, todas activas no IR e no Raman: 1 modo ν(Tl-X) (A_1), 2 modos ν(Tl-X') (A_1+B) e 2 modos ν(Tl-O) (A_1+B_2). Os datos vibracionais, recollidos na Táboa 3, confirman que os complexos $TlXX'_2(TPPO)_2$ deben ser bipiramides trigonais cós ligands en posición apical e os halóxenos no plano ecuatorial.

O composto $TlIBrCl(TPPO)_2$ ainda non foi posíbel estudialo por raios X; pero do análise espectral, e tendo in mente os resultados obtidos nos outros complexos deste traballo, se pode suxerir unha estrutura análoga cos átomos de halóxeno ocupando o plano ecuatorial dunha bipiramide trigonal.

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SUMMARY

Interhalide Tl(III) compounds. IV. Complexes with TPPO

The complexes $TlCl_3.(TPPO)_2$; $TlBr_2Cl.(TPPO)_2$; $TlI_2Cl.(TPPO)_2$; $TlBr_3.(TPPO)_2$; $TlIBr_2.(TPPO)_2$; $TlI_2Br.(TPPO)_2$; $TlI_3.(TPPO)_2$ *and* $TlIBrCl.(TPPO)_2$ *have been prepared and characterized. All the solids isolated behave as non electrolytes in acetonitrile solution. The IR spectra are discussed, specially the Tl-X stretching vibration modes; molecular structures for the complexes are proposed.*

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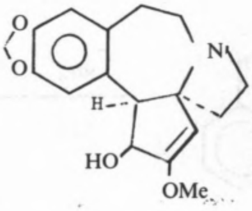
SOME NEW DEVELOPMENTS IN THE CHEMISTRY OF ARYL HYDROXYLAMINES AND THEIR DERIVATIVES

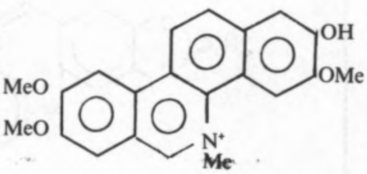
This review is not a detailed account of all the new developments in the chemistry of arylhydroxylamines and their derivatives. Instead it is confined essentially to those new reactions discovered in our laboratory during the past five years.

One of the persisting problems in organic synthesis is to develop new and better methods for effecting a *C-C* bond connection. Simple as it may seem, it remains, even today, a challenge in terms of regiospecificity, enantioselection and chemical yield when applied to synthesis of complex organic molecules.

The content of the review is a "spin-off", as it were of our efforts to synthesize the anti-leukaemic alkaloids, cephalotaxine **(I)** and fagaronine **(II)**.

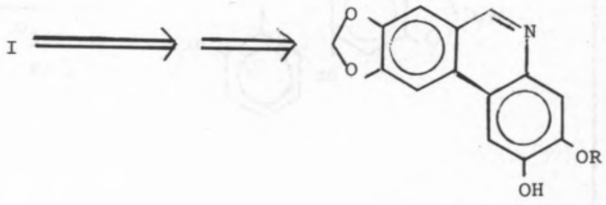


I



II

By retrosynthesis **(I)** could be reduced to a simple synthon **(III)** — a phenanthridine derivative.



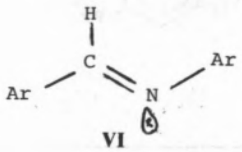
III

By one of many disconnection processes available **(II)** could be reduced to two simple units **(IV)** and **(V)**.

The literature describes various methods to obtain the phenanthridine skeleton and to give only a few examples, the yields are usually low (Table 1). The basic problem in the photocyclisation processes resides essentially in two factors.

a) entropic b) electronic

Schiffs'bases, normally tend not only to adopt the *trans*-geometry **(VI)** [3b] (unfavourable situation for C-C bond formation) but also suffers n-π^*



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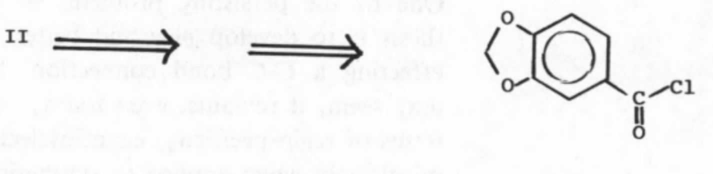
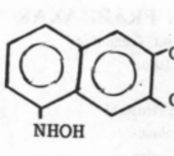


IV



V

Table 1

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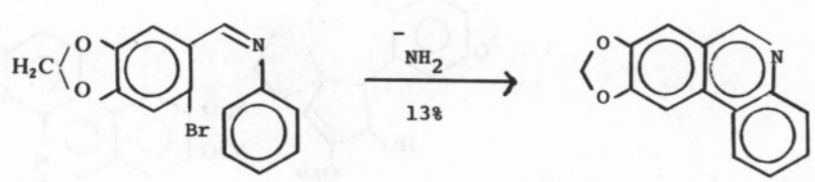
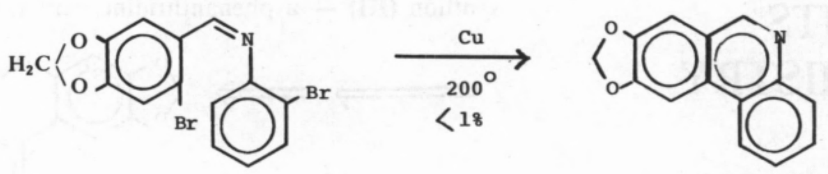
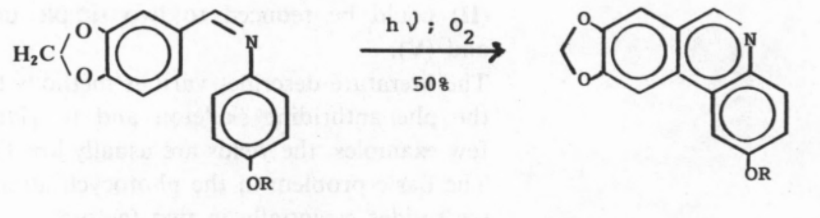
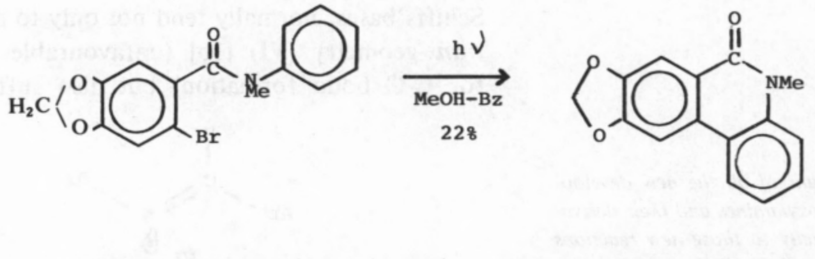
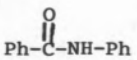
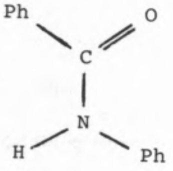
	1
	2
	3a 3b
	4

excitation on absorption of light which is non-productive in terms of intramolecular cyclisation [3b].

Secondary amides, such as benzanilide, exist predominantly in the *trans*-configuration **(VII)** and the principal reason for low yield in photocyclisation is due to entropic reasons [3c].



$$\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}Ph}$$



VII

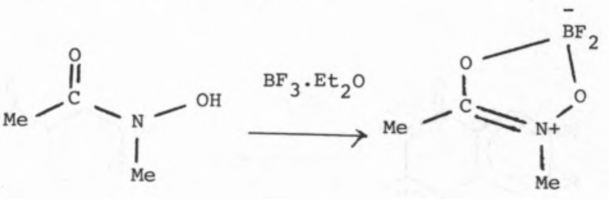
Question

How to overcome these adverse effects-entropic and electronic?

Solution:

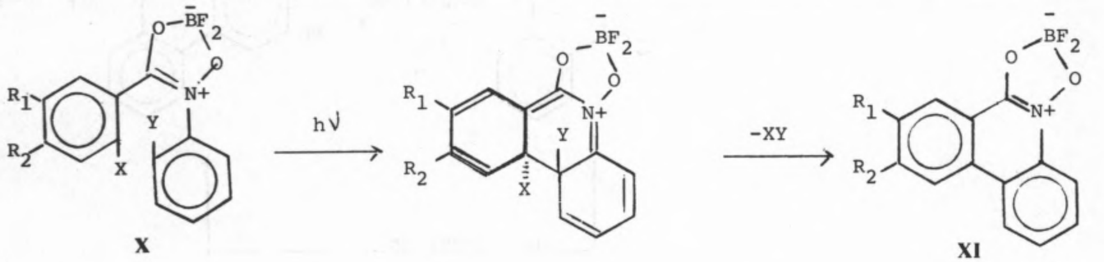
Force the molecule to adopt thes *cis*-configuration and make n → π* transition energetically prohibitive.

The hydroxamic acid **(VIII)**, the acetylderivative of $\mathrm{H}\overset{\mathrm{OH}}{\overset{|}{\mathrm{N}}}\mathrm{Me}$ is known to form the thermally stable derivative **(IX)** of boron [5].



VIII **IX**

It was considered that *C, N*-diarylhydroxamic acids would also form compounds of this type and if properly substituted undergo rapid cyclisation in high yield. Given the fact that the bond strength between **B-O** and **B-F** is relatively high it was anticipated that these complexes would not only be photostable but also possess ideal condi-



X **XI**

i) $R_1 = R_2 = OMe$; $X = Y = H$	i) $R_1 = R_2 = OMe$
ii) $R_1 = R_2 = OMe$; $X = Br$; $Y = H$	ii) $R_1 = R_2 = OMe$
iii) $R_1 = R_2 = OCH_2O$; $X = Br$; $Y = H$	iii) $R_1 = R_2 = OCH_2O$
iv) $R_1 = R_2 = OMe$. $X = H$; $Y = Cl$	iv) $R_1 = R_2 = OMe$
v) $R_1 = R_2 = OMe$; $X = H$; $Y = OTs$	
vi) $R_1 = R_2 = OMe$; $X = H$; $Y = BR$	vi) $R_1 = R_2 = OMe$

Compound **X**	Mp/°C	Product **XI**	M.p/°C	% yield	Irradiation time/h
i	199-200	i	318-320	96*	33
ii	158-159	i	318-320	92	4
iii	176-176.5	iii	325-328	93	6
iv	189-191	i	318-320	91	13
v	168-170	—	—	0	18
vi	167-169	i	318-320	92	9

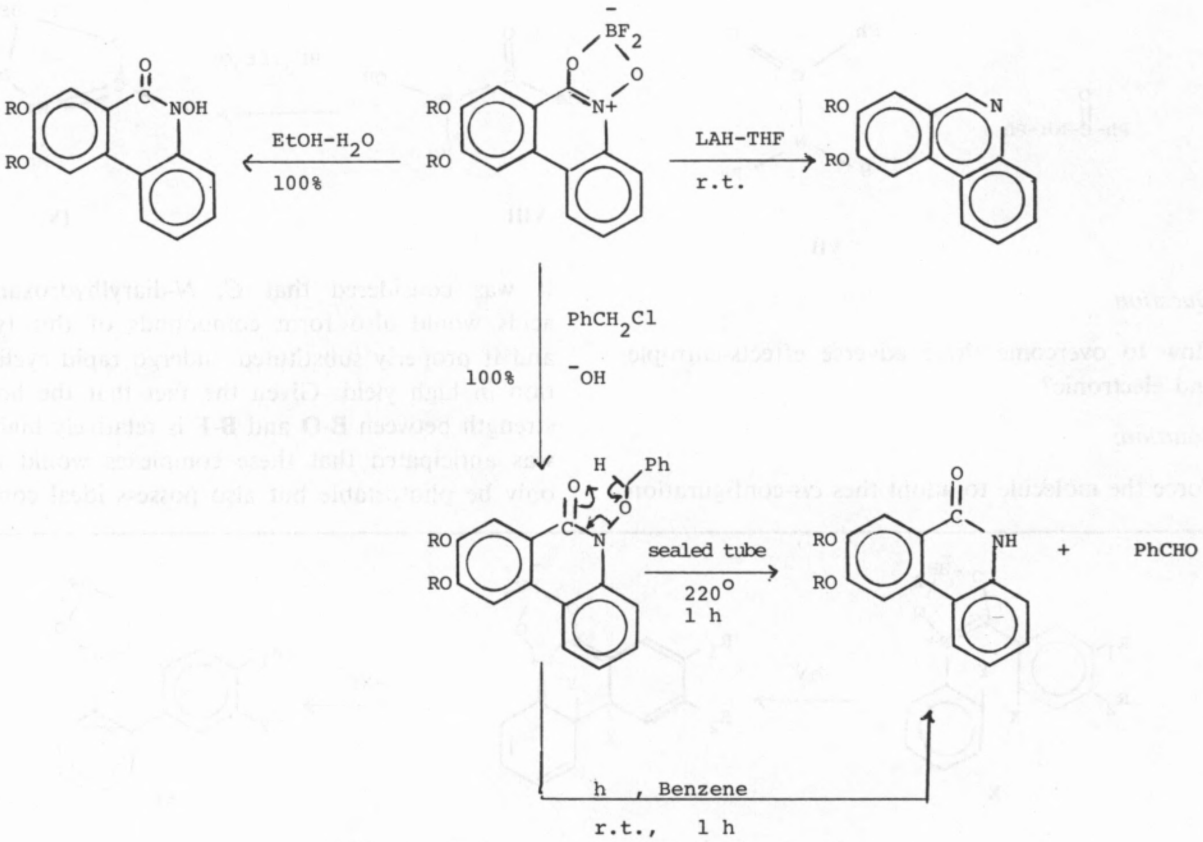
---

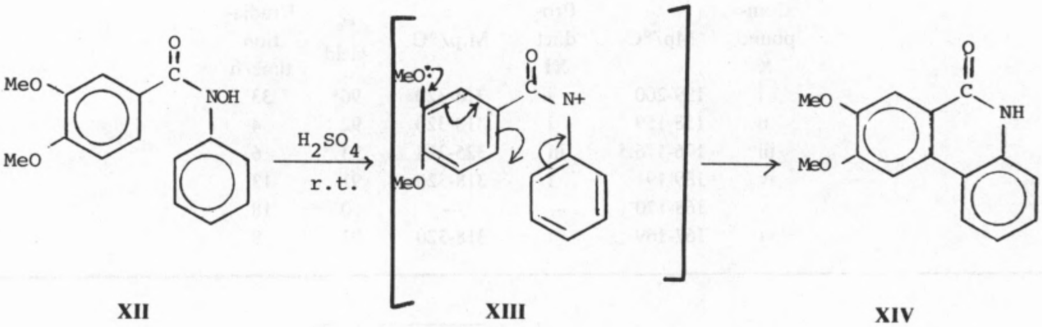
* In the presence of 1 equiv. of iodine.

tions to undergo in high yield a conrotary photocyclisation. This expectation was fully realised in practise and our results [6] are presented below.

These cyclised compounds (**XI**) undergo the following reactions:

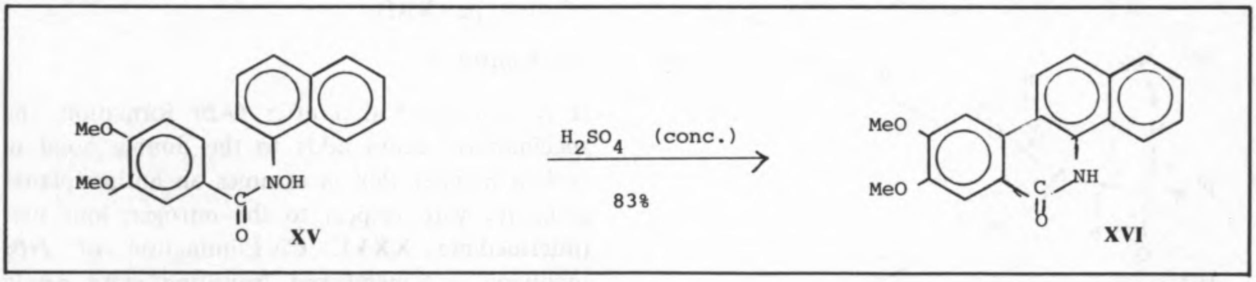
It was subsequently found [7] that properly substituted benzohydroxamic acids, such as (**XII**) cyclise rapidly on treatment with conc. H_2SO_4, to give the corresponding phenanthridone **XIV** in high yield.
The intermediate is presumed to be the reactive



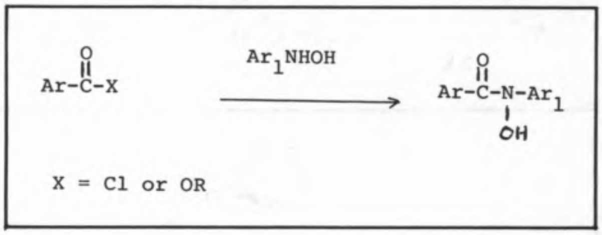


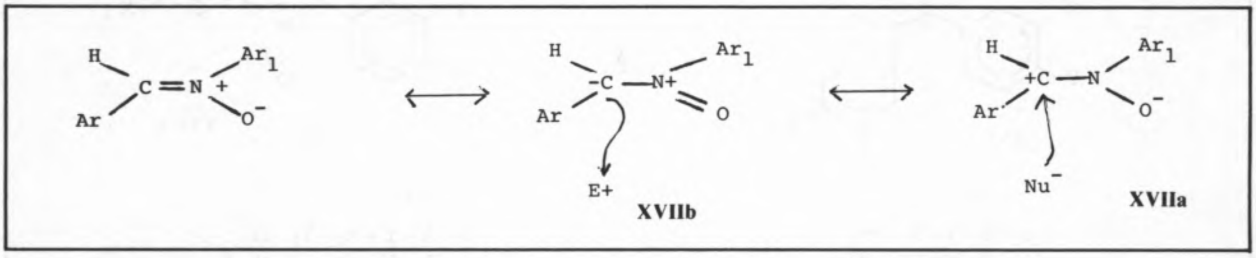
XII **XIII** **XIV**

acylnitrenium ion **(XIII)**. Similarly **(XV)** yielded **(XVI)**.



Since hydroxamic acids have thus been shown to be useful substrates for constructing condensed heterocycles, a new method for the preparation of the former was sought. Generally, aromatic hydroxamic acids are synthesized by condensing acid chlorides or esters with aromatic hydroxylamines.

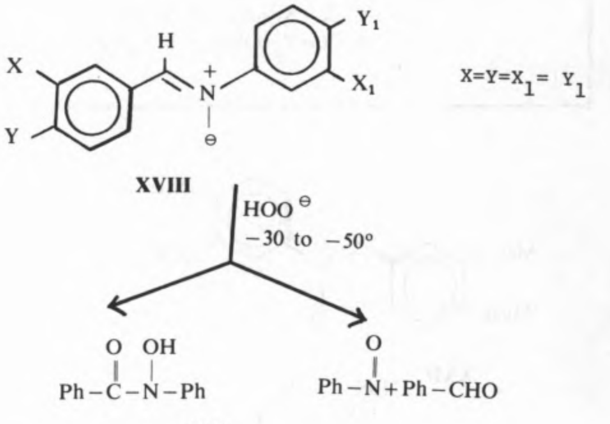




However, arylhydroxylamines are obtained by controlled reduction of the corresponding nitro compounds and the reaction is often capricious and the yield is at best modest.

C, N-diarylnitrones could in principle be converted into hydroxamic acid by either nucleophilic or electrophilic substitution at the α-carbon atom of the nitrone group. The canonical forms **XVIIa** or **XVIIb** explain the chemical reactivity in a simple way without recourse to a more sophisticated treatment.

On treatment with alkaline hydrogen peroxide *C, N*-diphenylnitrone **(XVIII)** yielded rapidly the hydroxamic acid **(XIX)**, the major products being nitrosobenzene and benzaldehyde:

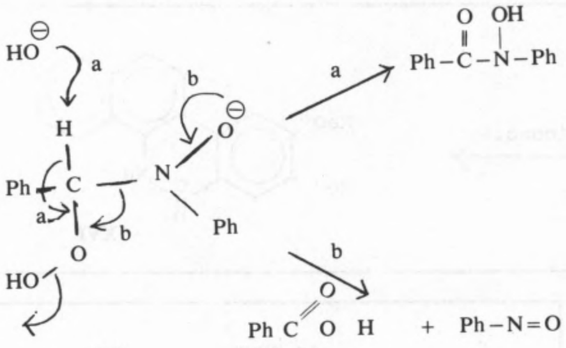


The formation of the products could be explained on the basis of two concurrent reactions (path a and b) involving the common intermediate **(XX)**: When NBS is treated with the nitrone **(XVIIIa)** in the presence of DABCO a relatively slow reaction occurred and the product, after aqueous work-up, was found to be exclusively the thermodynamically less stable *cis*-nitrone **(XXI)**.

The tetramethoxynitrone **(XXII)**, similarly, yielded initially the *cis*-nitrone **(XXIII)** wich on heating isomerised to the *trans*-compound **(XXIV)** the structure of which was confirmed by X-ray analysis.

The various α-succinimidyl nitrones prepared by the above method, as well as their physical properties are collected (Table 2).

All attempts to hydrolyse these compounds to give the corresponding hydroxamic acids proved to be infructuous.

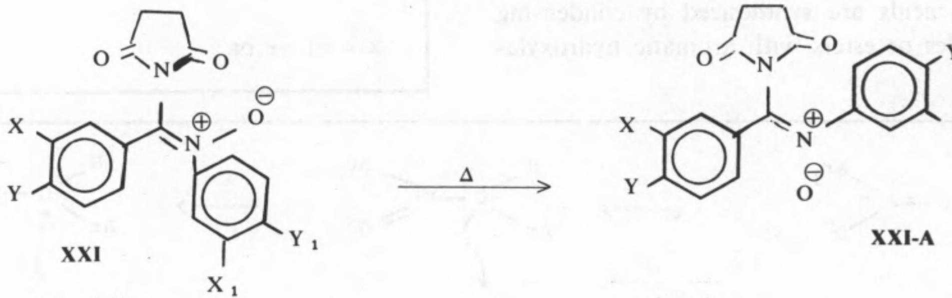


XX

There are two possible mechanisms that could explain the formation of the unstable *cis*-nitrone of the type **(XXI)**:

Mechanism A

It is proposed * that after *O-Br* formation, the succinimidyl anion adds to the double bond in such a manner that is assumes an antiperiplanar geometry with respect to the nitrogen lone pair (intermediate **XXV**). *Cis*-Elimination of *HBr* involving a 5-membered transition state would lead to the observed product.

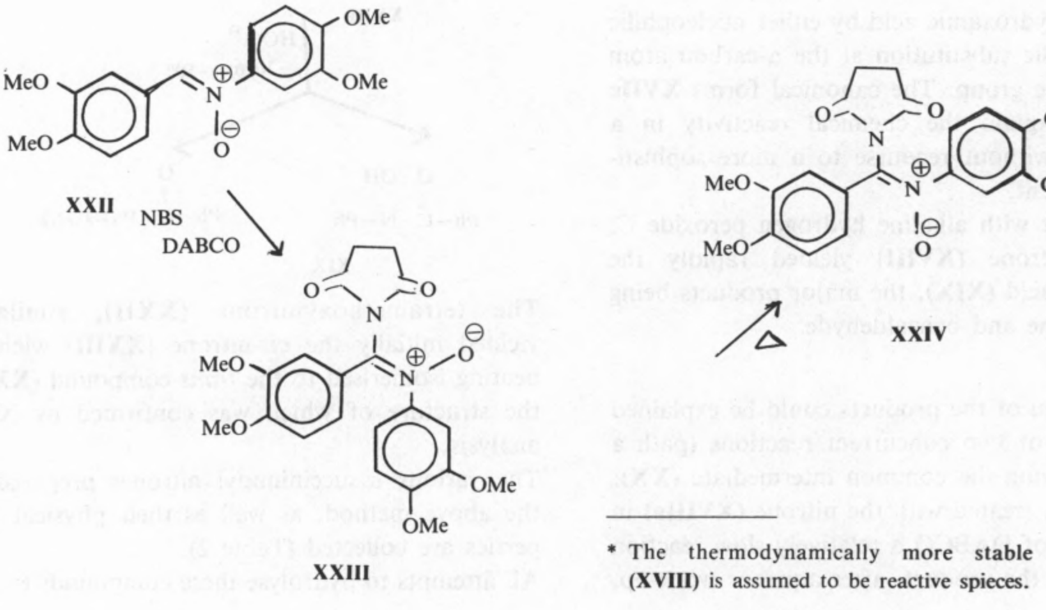


XXI (*cis*)

a $X=Y=X_1=Y_1=H$
b $X=X_1=Y_1=H;\ Y=Br$
c $X=X_1=Y_1=H;\ Y=NO_2$
d $X=Y=OMe;\ X_1=Y_1=H$

XXI-A (*trans*)

a $X=Y=X_1=Y_1=H$
b $X=X_1=Y_1=H;\ Y=Br$
c $X=X_1=Y_1=H;\ Y=NO_2$
d $X=Y=OMe;\ X_1=Y_1=H$



XXII

XXIII

XXIV

*** The thermodynamically more stable *trans* nitrone (XVIII) is assumed to be reactive spieces.**

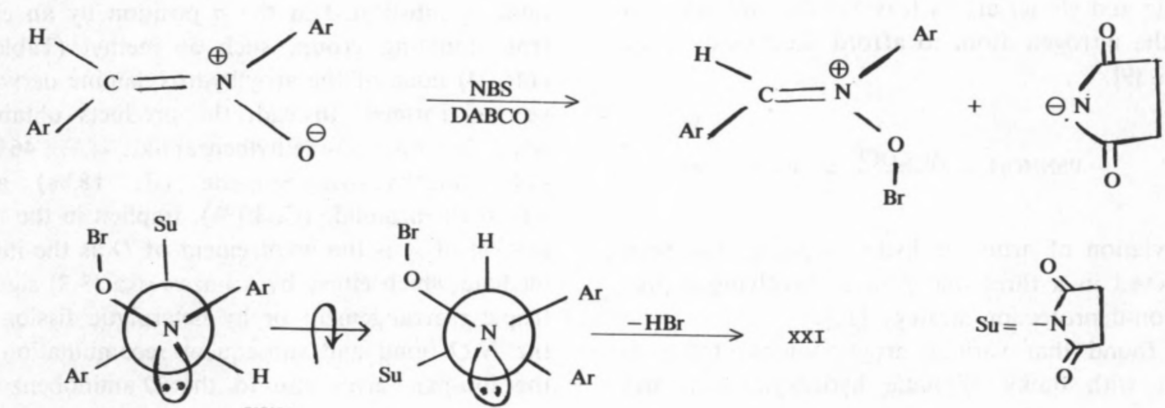
Table 2
Physical Properties of the C-Succinimidyl Nitrones XXI and XXI-A

Compound X	Y	X_1	X_1		Yield (**XXI** + + **XXI-A**)[(c)] (%)	m.p. (°C)	I.R. (KBr) (cm^{-1})	^1H NMR ($CDCl_3$) δ (ppm)	m/e[(d)] (M^+)	(M^+-O)	(M^+-$C_4H_4NO_2$)	(M^+-$C_4H_4NO_2$-O)
H	H	H	H	**XXI** a	56	≃130[(a)]	1785, 1725	7.36-7.17 (10H, m, ArH) 3.17-2.81 (4H, m, $-CH_2-CH_2-$)	294	278	196	180
				XXI-A a		170-172	1785, 1725	8.46-7.88 (2H, m, ArH) 7.50-7.41 (8H, m, ArH) 2.98-2.18 (4H, m, $-CH_2-CH_2-$)	»	»	»	»
H	Br	H	H	**XXI** b	60	92-102[(a)]	1785, 1720	7.36-6,95 (9H, m, ArH) 3.11-2.78 (4H, m, $-CH_2-CH_2-$)	373	357	275	259
				XXI-A b		102-104	1792, 1723	7.43-7.29 (8H, m, ArH) 7.00 (1H, d, J 3Hz, ArH) 3.09-2.86 (4H, m, $-CH_2-CH_2-$)	»	»	»	»
H	NO_2	H	H	**XXI** c	83	(a)	1788, 1723	8.07 (2H, d, J 8Hz, ArH) 7.42-7.36 (7H, m, ArH) 3.19-2.86 (4H, m, $-CH_2-CH_2-$)	339	323	241	225
				XXI-A c		187 (dec.)	1790, 1726	8.34 (4H, d, J 2.4Hz, ArH) 7.44 (5H, s, ArH) 2.91-2.29 (4H, m, $-CH_2-CH_2-$)	»	»	»	»
OMe	OMe	H	H	**XXI** d	40	(b)						
				XXI-A d		186 (dec.)	1785, 1730	8.78 (1H, d, J_m2.1Hz, 2-H) 7.43 (5H, s, ArH) 7.12 (1H, dd, J_o8.7Hz, J_m2.1Hz, 6-H) 6.89 (1H, d, J_o8.7Hz, 5-H) 3.98 (3H, s, CH_3O) 3.94 (3H, s, CH_3O) 2.94-2.19 (4H, m, $-CH_2-CH_2-$)	354	338	256	240
OMe	OMe	OMe	OMe	**XXIII**	64	(b)						
				XXIV		185-190 (dec.)	1785, 1730	8.77 (1H, d, J_m2.2Hz, 2-H) 7.14-6.75 (5H, m, ArH) 3.96-3.93-3.90-3.86 (4×3H, 4s,4×CH_3O) 2.95-2.29 (4H, m, $-CH_2-CH_2-$)	414	398	316	300

(a) On heating compounds (**XXI**) isomerise slowly to (**XXI-A**).

(b) Detected only on t.l.c. of the reaction mixture, but on attempted crystallisation isomerised to **XXI-A**.

(c) Crude yield.



XXV

Mechanism B

Presupposes a significant barrier to nitrogen inversion in the intermediate **(XXV)** (preliminary MNDO calculations seem to support this hypothesis) and that it reacts with Br^+ to give **(XXVI)**. *Trans*-elimination of HBr followed by loss of Br^+ could explain the production of **(XXI)**.

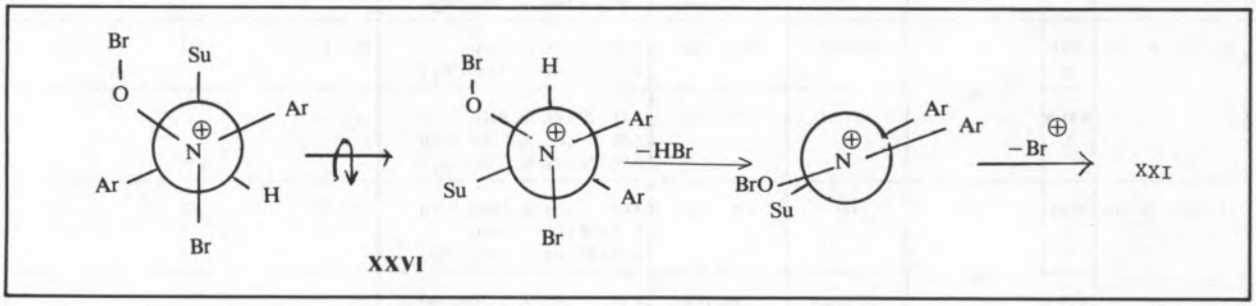
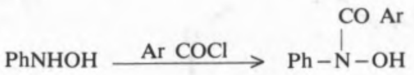


Table 3

	I	II		III		IV		
	R	R_1	R_2	Yield (%)	I.R. cm^{-1})	R_3	M.p. (°C)	I.R. (cm^{-1})
1	C_6H_5	CH_3O	CH_3O	90	1730	CH_3	132-134	1760, 1690
2	C_6H_5	H	H	88	1735	4-NO_2-C_6H_4	136-138	1770, 1690
3	C_6H_5	H	CH_3	83	1735	4-NO_2-C_6H_4	123.5-125.5	1770, 1695
4	C_6H_5	O-CH_2-O		86	1725	CH_3	97-99	1760, 1695
5	4-Br-C_6H_4	CH_3O	CH_3O	87	1730	—	—	—
6	4-Br-C_6H_4	H	H	83	1730	4-NO_2-C_6H_4	142-144	1770, 1680
7	4-CH_3-C_6H_4	H	H	0	—	—	—	—
8	$C(CH_3)_3$	CH_3O	CH_3O	91	1710	C_6H_5	oil	1760, 1670
9	$CH(CH_3)_2$	CH_3O	CH_3O	87	1710	C_6H_5	oil	1770, 1670
10	CH_3	CH_3O	CH_3O	0+	—	—	—	—
11	H	CH_3O	CH_3O	0+	—	—	—	—

(+) Corresponding hydroxamic acid was obtained (>80%).

Generally in the absence of special factors (electronic and steric) arylhydroxylamines are acylated on the nitrogen atom to afford the hydroxyamic acids [9].

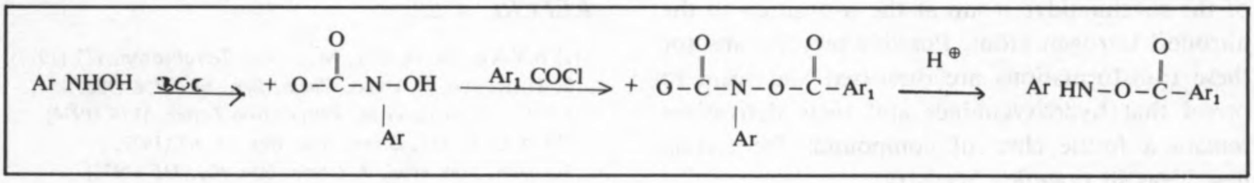


$$\mathrm{PhNHOH} \xrightarrow{\mathrm{Ar\ COCl}} \mathrm{Ph-}\overset{\mathrm{CO\ Ar}}{\mathrm{N}}\mathrm{-OH}$$

0-acylation of aromatic hydroxylamines has been achieved in a three-step process involving a protection-deprotection strategy [10].

We found that various aroylcyanides (Table 3) react with bulky aliphatic hydroxylamines and aromatic hydroxylamines exclusively on the oxygen atom [11] to afford directly the *O*-aroylated products.

Whereas *N*-t-butyl and *N*-isopropylhydroxylamines reacted with veratroyl chloride to give the corresponding hydroxamic acids in 40% and 100% yield respectively, both these hydroxylamines afforded almost exclusively the *O*-aroyl products with veratroylcyanide. When the phenylhydroxylamine is substituted in the *p* position by an electron donating group, such as methyl (Table 3 entry 4) none of the aroylhydroxylamine derivative was formed. Instead, the products obtained were 2-hydroxy-4-methylbenzanilide (A, 46%), 4,4′-dimethylazoxybenzene (B, 18%) and 4-methylbenzanilide (C, 10%). Implicit in the formation of *A* is the invòlvement of *D* as the intermediate which either by a l-aza-l-oxa [3,3] sigmatropic rearrangement or by heterolytic fission of the *N-O* bond and subsequent recombination of the ion-pair gives rise to the *O*-aminobenzoate

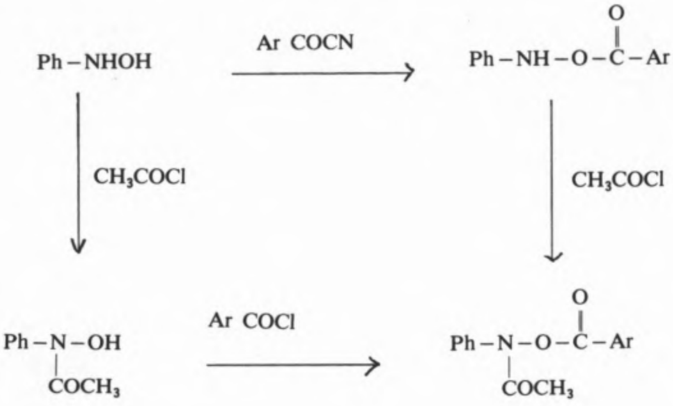


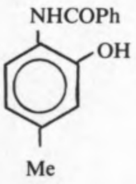
$$\mathrm{Ar\,NHOH} \xrightarrow{\mathrm{BOC}} +\ \mathrm{O{-}\overset{\overset{\displaystyle O}{|}}{C}{-}\underset{\underset{\displaystyle Ar}{|}}{N}{-}OH} \xrightarrow{\mathrm{Ar_1\,COCl}} +\ \mathrm{O{-}\overset{\overset{\displaystyle O}{|}}{C}{-}\underset{\underset{\displaystyle Ar}{|}}{N}{-}O{-}\overset{\overset{\displaystyle O}{|}}{C}{-}Ar_1} \xrightarrow{H^{\oplus}} \mathrm{Ar\,HN{-}O{-}\overset{\overset{\displaystyle O}{|}}{C}{-}Ar_1}$$

(*E*).*O* to *N* transfer of benzoylgroup generates *A*. However, hydroxylamine and its *N*-methylderivative yielded with the above acyl transfer reagent only the corresponding hydroxamic acids. The formation of these acids appears not to involve initial *O*-acylation followed by a rapid *O* to *N* rearrangement. Thus when *N*-methylhydroxylamine is allowed to react with benzoylcyanide in $CDCl_3$ at-40° and the reaction monitored by n.m.r. only the N-methyl signal (δ.3.41 s) of the corresponding hydroxamic acid is observed. Further studies are underway to explain the profound difference in reactivity between aroylcyanides and aroylchlorides towards hydroxylamines and the differing ambident properties of the latter.

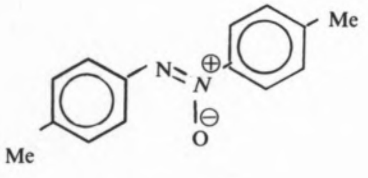
Concluding remarks

Although hydroxylamines and hydroxamic acids have been studied for over a century, there is still scope for discovering new and interesting reactions that they might undergo. Thus the ability of the latter to form stable boron complexes could be exploited for the construction of heterocyclic systems present in pharmacologically active compounds. The general assumption that hydroxylamines lead to hydroxamic acids on acylation is shown to be erroneous. Instead it is found that the nature of the product formed (*O versus N*) acylation) is subject profoundly to the type of acylating agent used. Whereas arylhydroxylamines form the corresponding arylhydroxamic acids with aroylchloride, the use of aroylcyanide, as a transacylating agent, leads, almost always, to the thermodynamically *less stable O*-acylated compound. *C, N*-Diarylnitrones were tested as potential starting materials for *C, N*-diarylhydroxamic acids. Treatment of the former with NBS-DABCO was found to yield, not the acids, but to substitution





A



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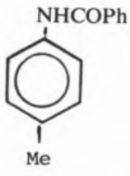

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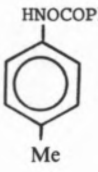

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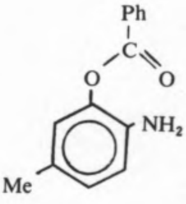

E

of the succinimidyl group at the α-position to the nitrones' nitrogen atom. Possible mechanisms for these transformations are discussed and seem to reveal that hydroxylamines and their derivatives remain a fertile class of compounds for testing new ideas in organic chemistry.

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REVISTA PORTUGUESA DE QUĪMICA

Reunida a 20 de Março de 1983 decidiu a Direcção Nacional da Sociedade Portuguesa de Quīmica exarar os seguintes louvores, que devem ser publicados na Revista Portuguesa de Quīmica e no Boletim da Sociedade.

- Ao abandonar, a seu pedido, o cargo de Editor da Revista Portuguesa de Quīmica, que desempenhou durante vinte e um anos, ē o Engº Carlos Moura Pulido merecedor do conhecimento pūblico da gratidão da Sociedade Portuguesa de Quīmica e da comunidade quīmica portuguesa em geral pelos valiosos serviços prestados naquele cargo ā causa da promoção da Quīmica em Portugal, com dedicação e durante um tão longo perīodo de tempo.

- Ao abandonar, a seu pedido, o cargo de Editor-Adjunto da Revista Portuguesa de Quīmica, que desempenhou durante cerca de seis anos, ē o Doutor Engº. Luīs FIlipe Vilās-Boas merecedor do conhecimento pūblico da gratidão da Sociedade Portuguesa de Quīmica e da comunidade quīmica portuguesa em geral pelos valiosos serviços prestados naquele cargo ā causa da promoção da Quīmica em Portugal. Sō devido ao seu esforço incansāvel e ā sua abnegação foi possīvel pōr a Revista Portuguesa de Quīmica em dia apesar de todas as dificuldades encontradas.

Numa ēpoca em que a crītica ē mais frequente, porque mais fācil, do que a colaboração construtiva, mais imperiosa se torna esta pūblica homenagem ao Engº Carlos Moura Pulido e ao Doutor Engº Luīs Filipe Vilas-Boas.

A DIRECÇÃO DA SPQ