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THE SURFACE TENSION OF PERFLUOROISOBUTANE AND MIXTURES WITH *n*-BUTANE FROM CLOSE TO ITS UPPER CRITICAL SOLUTION TEMPERATURE, 233.08 K, TO 260 K

*The orthobaric surface tensions of perfluoroisobutane and its mixtures have been measured at temperatures between 230 and 260 K. The upper critical solution temperature has been determined to be 233.08 K. The mixture shows negative azeotropy with no positive deviation in surface tension from linearity in mole fraction in conformity with the behaviour of normal alkane + perfluoro-alkane mixtures. The results resemble those for *n*-butane + perfluoro-*n*-butane and suggest that branching of the perfluorocarbon produces little effect in the surface tension of mixtures of low molar mass chain-molecule substances.*

1 — INTRODUCTION

Current molecular theory is not yet very successful at predicting the surface tension of mixtures of other than very simple molecules.

Nevertheless, it is possible on the basis of a very straightforward argument based on strong or weak unlike forces between pairs of unlike molecules in the mixture to account for the sign of the deviations of the surface tension from "ideal" behaviour. There is no simple statement of mixing ideality which has the standing in the surface thermodynamics of mixtures as that of Raoult's law in the bulk thermodynamics of mixtures. For that reason it is common practice, at least for mixtures of fairly small molecules, to take as a statement of ideality the linear dependence of the surface tension σ of a binary mixture, *i.e.* $\sigma = x_1 \sigma_1^* + x_2 \sigma_2^*$, where x_i is the mole fraction of component i and σ_i^* is its surface tension in the pure state at the same temperature. The rough argument then proceeds as follows. When the unlike forces are strong relative to those between pairs of like molecules the overall cohesion between the molecules is increased on mixing and therefore the surface tension deviations are positive — in the same way the vapour pressure of the mixture shows negative deviations from Raoult's law. Conversely, when the unlike forces are relatively weak the overall cohesion in the liquid is diminished on mixing and the surface tension is less than the mole fraction average — similarly the vapour pressure of the mixture shows positive deviations for Raoult's law.

Some backing for these arguments comes from GUGGENHEIM'S strictly regular solution theory of surface tension [1], which is essentially concerned with the effect on the surface tension of the mixture of the sign and magnitude of the interchange energy w . When w is zero the expression for the strictly regular solution ideal surface tension.

$$\exp\left(-\frac{\sigma a}{kT}\right) = x_1 \exp\left(-\frac{\sigma_1^* a}{kT}\right) + x_2 \exp\left(-\frac{\sigma_2^* a}{kT}\right),$$

where a is a mean molecular surface area, leads to values of σ not very different, if a is reasonably chosen, from those given by the linear expression. When w is positive the surface tension deviations are negative and vice-versa.

Either of these arguments accounts well for the general features of the surface tension of alkane + perfluoroalkane mixtures. This class of mixtures

is the simplest that has very large positive values of w which are reflected in large deviations from bulk ideality and, more often than not, liquid-liquid immiscibility with an upper critical solution temperature UCST at a fairly high temperature [2]. The surface tension deviations are thus, expectedly, strongly negative, leading in many instances to negative aneutropy or surface azeotropy.

Some alkane + perfluoroalkane mixtures, especially those containing relatively long chain-molecules, show, in addition, a tendency to positive deviations from ideality in mixtures dilute in perfluoroalkane — sometimes leading to positive aneutropy [3]. This behaviour, which is invariably associated with proximity to a UCST, can be partially explained either as some kind of critical phenomenon or as a competition between an energetic effect — which leads as outlined above to negative deviations — and an entropic effect related to differences in the chain flexibility of the components — which leads to positive deviations. A useful check on this latter explanation is afforded by measurements on mixtures of smaller molecules of inherently low chain flexibility. Such measurements have been carried out for the mixtures $n\text{-C}_5\text{H}_{12} + \text{C}_3\text{F}_8$, $n\text{-C}_4\text{H}_{10} + n\text{-C}_4\text{F}_{10}$, and $n\text{-C}_4\text{H}_{10} + \text{C}_3\text{F}_8$ [4]; no trace of positive deviations was found — only the characteristic large negative alkane + perfluoroalkanes deviation.

As a further study of the influence of differences of chain flexibility we decided to turn to the role of branching in either the alkane or the perfluoroalkane to check whether this has any effect on previous conclusions. Here we report the results of our measurements of the surface tensions close to the UCST of a alkane + perfluoroalkane mixture in which the perfluorocarbon component is branched: $n\text{-C}_4\text{H}_{10} + i\text{-C}_4\text{F}_{10}$.

2 — EXPERIMENTAL

2.1 — MATERIAL

Perfluoroisobutane was supplied by Fluorochem. Ltd. with a claimed purity of 97%; it was thoroughly degassed before use in view of the high solubility of air in perfluorocarbons. The n -butane was supplied by Matheson with a claimed purity of 99.5%; it was degassed before use.

2.2 — APPARATUS AND PROCEDURE

The surface tension was measured by the differential capillary rise technique using a Pyrex glass cell, shown in fig. 1, that consists of three Veridia precision bore capillaries A (nominal bore 1,0.5 and 0.3 mm) connected to a sample chamber B which accommodates a plunger C which can be moved by the grease-free screw D. The side arm E was used for making up the mixtures and found its greatest utility for mixtures in which phase separation occurred. The bore and constancy of bore each capillary were confirmed by weighing mercury threads of various accurately known lengths. The actual diameters were found to be 1.007, 0.5082 and 0.3004 mm. In the measurement of the surface tension of pure substances the bottom part of the cell was immersed in liquid nitrogen and approximately 2 cm³ of the substance was condensed into it through valve F from a storage bulb. The cell was then closed and almost entirely immersed in a low-temperature thermostat bath (Townson and Mercer "Minus Seventy" Model), with only the knob of the plunger actuating screw exposed. The constancy of the temperature of the bath was confirmed by a platinum resistance thermometer to be within ± 0.1 K during a measurement. After thermal equilibrium was reached the plunger C was lowered and the liquid was displaced from B and allowed to rise in the capillaries. After a further period of thermal stabilization, as evinced by constancy of the levels of liquid in each capillary over three successive periods of twenty minutes, the relative heights of the menisci were measured cathetometrically with a precision of ± 0.02 mm.

For measurements on mixtures, since there was a need to know the amount of each substance condensed into the cell and to ensure that the liquid in the capillaries was of the same composition as the liquid in B, the procedure was modified. The amount of substance was determined by gas volumetry in a calibrated burette on the vacuum line. Each substance was condensed separate in the cell and, as far as possible, complete mixing was carried out in side arm E by vigorous shaking for five or ten minutes once the cell was immersed in the bath. The mixture was transferred to B by tilting the cell and from this stage on, the procedure was identical to that for the pure substances.

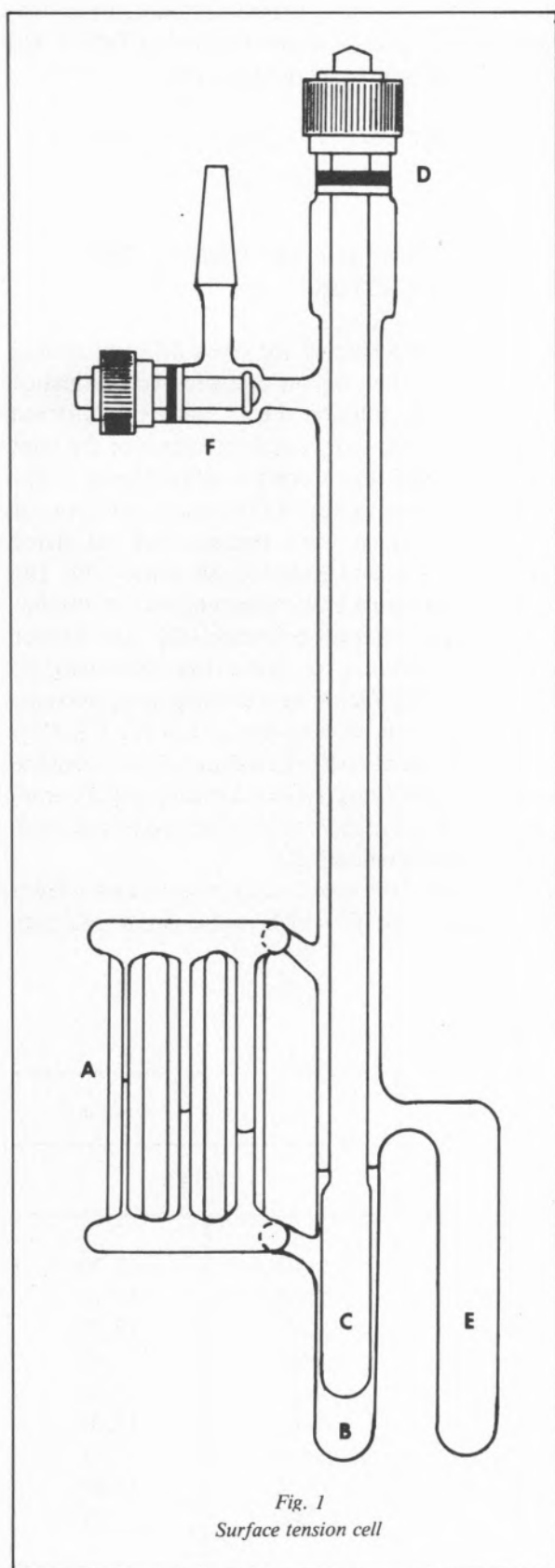


Fig. 1
Surface tension cell

All final heights were taken on receding menisci created by raising plunger D. In this way an essential zero contact angle was secured.

The UCST of the mixture was determined visually in the surface tension cell. We have measured the UCST at two different volume fractions close to 0.5 since it is known that the curve of reduced temperature $T/UCST$ against volume fraction ϕ is nearly flat around $\phi = 0.5$ [5].

3 — RESULTS

3.1 — CALCULATIONS

The surface tension σ was calculated from

$$\sigma = r_i r_j d g [3 \Delta h_{ij} - (r_i - r_j)] / 6 (r_i + r_j)$$

where Δh_{ij} is the measured difference in the height of the menisci in the capillaries of radius r_i and r_j , d is the density of the liquid phase (we neglected the density of coexisting gas phase) and g the acceleration due to gravity (9.81342 m s^{-2}) in the laboratory in Sheffield.

The surface tension for each composition was measured at various temperatures, but since the temperature was not easily reproduced the outcome of the series of measurements was a set of values of $\sigma(T, x)$. In order to obtain a set of isotherms $\sigma(x)$ we fitted $\sigma(T, x)$ for a particular overall composition to a linear equation in T , then interpolating to find σ at a given set of T . The corresponding values of x were also interpolated.

To compute the liquid composition the imperfection of the coexisting gas phase was taken into account.

3.2 — SURFACE TENSION OF PURE LIQUIDS

The surface tension of pure *n*-butane are reported elsewhere [6] and are represented by the equation

$$\sigma \text{ (238-273 K) / mN m}^{-1} = 47.242 - 0.1180(T/K) \\ SD_\sigma = 0.07 \text{ mN m}^{-1}$$

SD_σ being the standard deviations reported.

To obtain the surface tension of perfluoroisobutane the density of the liquid was needed. No values of the density have been published and due to shortage

Table 1
Surface tension of pure perfluoroisobutane
 $\sigma(\text{calc})/\text{mN m}^{-1} = 42.01 - 0.1160(T/\text{K})$

T/K	$\sigma/\text{mN m}^{-1}$	$\sigma(\text{calc})/\text{mN m}^{-1}$
229.2	15.48	15.42
233.9	14.84	14.88
238.9	14.33	14.29
242.1	13.83	13.92
249.8	13.02	13.03
264.2	11.39	11.36

of material at the time we were unable to measure it. We decided therefore to estimate the densities of perfluoroisobutane. The published values for the density of perfluoroisopentane, perfluoro-*n*-pentane, perfluoroisohexane and perfluoro-*n*-hexane show that the densities of the perfluoroisalkanes are higher than those of the corresponding perfluoro-*n*-alkanes by as much as 3 to 4% [7,8]. Thus we estimated the values for the density of perfluoroisobutane by adding 3.5% to the values of the density of perfluoro-*n*-butane. Since we believe that the error in our measurements is close to 1% we hope that the final results for the surface tension of perfluoroisobutane are not greatly affected by the procedure used to estimate the densities.

The results of our measurements of the surface tension of perfluoroisobutane are given in Table 1 and are well represented by the equation

$$\sigma(224\text{--}264\text{ K})/\text{mN m}^{-1} = 42.01 - 0.1160(T/\text{K})$$

$$SD_{\sigma} = 0.06\text{ mN m}^{-1}$$

3.3 — SURFACE TENSION OF THE MIXTURES

The system was studied for seven different overall compositions. The vapour pressures were estimated by the regular solution theory using the observed UCST, 233.08 K, the vapour pressures of the pure substances, and their second virial coefficients. Since no published values of the vapour pressures of perfluoroisobutane were available we calculated them using Lee and Kessler's correlation [9]. The critical temperature and pressure of perfluoroisobutane were taken from reference [10]. The vapour pressure of *n*-butane was taken from reference [11]. Pitzer's acentric factor was obtained using the same correlation at the boiling point, $T_b = 272.8\text{ K}$ [10]. The second virial coefficient of perfluoroisobutane was calculated using Pitzer's correlation [12], whereas that for *n*-butane was obtained from McGLASHAN and POTTER'S equation [13].

The density of the mixed liquid was estimated from a correlation for V^E which enables us to calculate

Table 2
Surface tension for *x* perfluoroisobutane + (1-*x*) *n*-butane

<i>x</i>	$\sigma/\text{mN m}^{-1}$	<i>x</i>	$\sigma/\text{mN m}^{-1}$	<i>x</i>	$\sigma/\text{mN m}^{-1}$
T = 235.1 K		T = 243.3 K		T = 250.4 K	
0.000	19.50	0.000	18.53	0.000	17.70
0.107	16.20	0.105	15.42	0.104	14.75
0.271	14.36	0.270	13.82	0.268	13.37
0.347	14.61	0.346	13.55	0.345	12.62
0.360	14.62	0.360	13.72	0.360	12.42
0.462	14.12	0.462	13.30	0.462	12.60
0.577	13.93	0.577	13.28	0.577	12.72
0.934	14.12	0.935	13.20	0.936	12.42
1.000	14.79	1.000	13.81	1.000	12.99

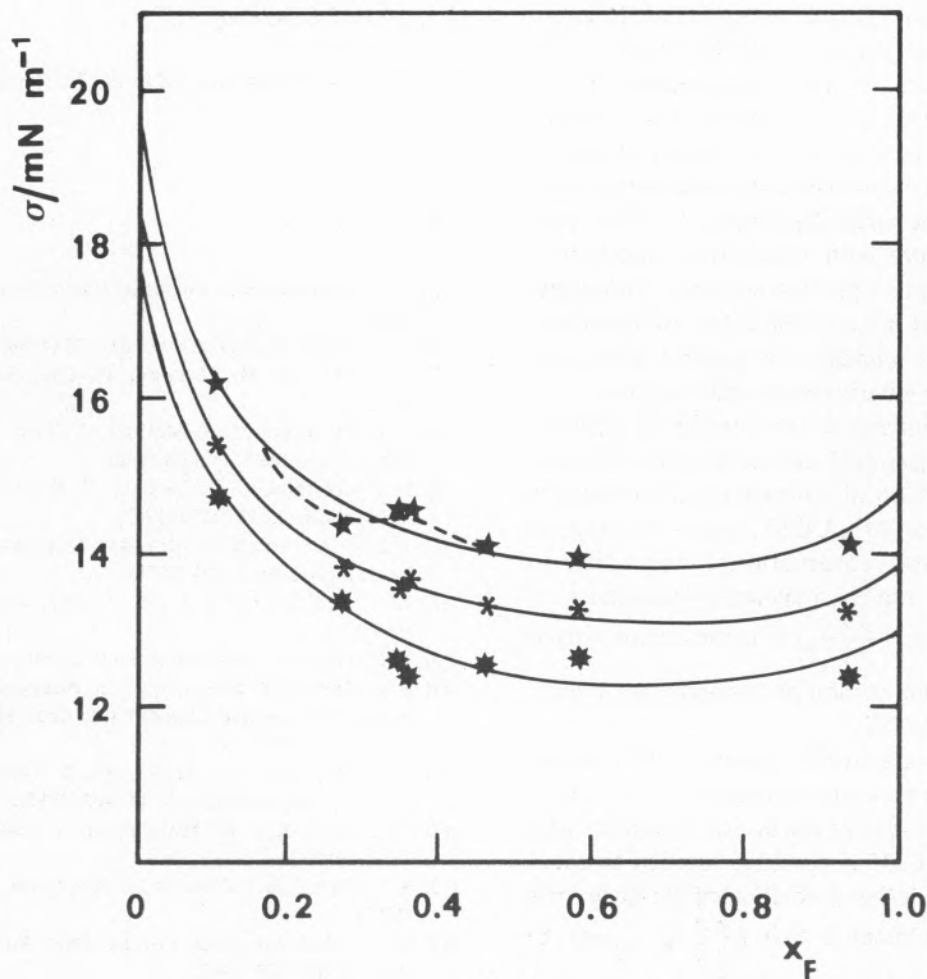


Fig. 2

Surface tension σ for x - i -C₄F₁₀ + $(1-x)$ - n -C₄H₁₀ at 235.1 K (★), 243.3 K (*) and 250.4 K (●).

the excess molar volumes as a function of $T/UCST$ for a mixture of volume fraction 0.5 [14]. Assuming that $V^E = A\phi_1\phi_2$, A can be computed at any temperature and V^E estimated for a particular composition. The density of n -butane was taken from reference [15].

A set of isotherms was derived using the procedure describe above. The results are presented in Table 2 and illustrated in fig 2.

4 — DISCUSSION

The results obtained for the surface tension of pure perfluoroisobutane show that, as for perfluoropentanes and perfluorohexanes, branching increases the surface tension by about 1% unlike the n -alkanes for which branching generally lowers the surface tension relative to that of the linear isomer.

The mixture studied in this work shows negative aneutropy and no positive deviation on the hydrocarbon rich side. This is the common behaviour for alkane + perfluoroalkane mixtures. The large drop in the surface tension of the alkane brought about by the addition of a small amount of perfluoroalkane is evidence of high positive adsorption of the perfluoroalkane at the interface. However, in this system the effect is somewhat less pronounced than that observed with linear perfluoroalkanes and this can be explained in part by the higher surface energy of the perfluoroisobutane.

A quantitative analysis of the results using the best available molecular theory is not possible due to the lack of experimental data for the pure perfluoroisobutane and its mixtures with n -butane. A qualitative interpretation of the composition dependence based on the quasi-crystalline or strictly regular solution

theory of GUGGENHEIM [1] can be advanced. Negative deviations from ideality are predicted by the theory for positive values for the exchange energy w , the deviations increasing as w increases. The observed behaviour for σ vs. x is therefore simply explained without the need to introduce any additional explanation due to the chain flexibility. This has been pointed out before with mixtures of short-chain linear hydrocarbons + perfluorocarbons. It appears likely that in this mixture the effect of branching does not greatly change the general behaviour found for alkane + perfluoroalkane mixtures.

It is a matter of interest to see whether the theoretical analysis of WIDOM [16], concerning the behaviour of interfacial tension of a binary liquid mixtures in the neighbourhood of a UCST, agrees or disagrees with experimental observations. According to theory σ should exhibit a sigmoid dependence on mole fraction with $(\frac{\partial \sigma}{\partial x})_T \approx 0$ for mixtures close

to the critical composition at temperatures slightly higher than the UCST.

Our data show signs of this feature at 235.1 K but are insufficiently accurate to permit us to state conclusively that it is really present. More precise work on this system at 235 K would be needed to check this suspicion. Another prediction of the early form as Widom's treatment is that $(\frac{\partial \sigma}{\partial T})_{x=x_c}$ can be positive in the vicinity of the UCST. No evidence in support of this prediction was found in our system but we did not make enough measurements close enough to the UCST to expect this feature to appear.

Finally, we want to stress the importance of studying the effect of branching of the components in order to understand the behaviour of alkane + perfluoroalkane systems. It seems that in systems where positive aneutropy is present the normal hydrocarbon should be replaced by a branched hydrocarbon so that the influence of chain flexibility can be identified reasonably unambiguously. Mixtures with even fewer carbon atoms also provide information of this kind and work on such systems is in progress.

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RESUMO

Mediram-se as tensões superficiais ortobáricas de perfluoroisobutano e suas misturas com n-butano a temperaturas entre 238 e 260 K. Determinou-se a temperatura crítica de imiscibilidade superior obtendo-se o valor UCST = 233,08 K. A mistura apresenta aneutropia negativa sem desvios positivos a linearidade na curva tensão superficial-fracção molar, em conformidade com o comportamento das misturas alceno + perfluoro-n-butano e sugere que a ramificação do perfluorocarboneto pouco efeito produz na tensão superficial de misturas de substâncias compostas por moléculas lineares de baixo peso molecular.