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## REFRACTIVES INDEXES AND EXCESS MOLAR VOLUMES OF THE SYSTEM BENZENE + TOLUENE AT 303 K

*An accurate method for measuring the composition of liquid mixtures using differential refractometry is presented. The refractometer used can easily detect changes in refractive index of the order of 1 part in  $10^7$ , and so can be applied to the determination of small changes in composition. The refractive indexes of binary mixtures of benzene + toluene have been measured at 303.15 K and compared with absolute measurements made with a Pulfrich refractometer. The results show that it is possible to detect changes in refractive index with an uncertainty amounting to no more than a few parts per million. For the system studied here, this corresponds to a change in mole fraction of the order of 0.001.*

*Excess molar volumes as a function of composition were evaluated for this system using the Lorenz-Lorentz equation. From these, the molar excess volume for an equimolar mixture was found to be  $+0.080 \text{ cm}^3 \text{ mol}^{-1}$ . Comparison with available literature data suggests that the present values are accurate to within  $\pm 0.001 \text{ cm}^3 \text{ mol}^{-1}$ .*

## INTRODUCTION

Differential refractometry of the type used in high pressure liquid chromatography is often sufficiently sensitive to detect changes in refractive index of the order of one part in  $10^7$ ; the technique can provide a very accurate means of measuring very small changes in composition. In our laboratory in Lisboa we have developed a method, using a commercial differential refractometer (Waters Model R401), which allows us to measure the relative adsorption on activated charcoal and silica of liquid compounds which are chemically very similar. The first such system to be studied was the adsorption by silica from benzene + toluene mixtures.

Benzene and toluene have very similar values of refractive index [1]; the difference in refractive index for the pure components is only 0.00352 at 303.15K. This suggests that a change in mole fraction of 0.001 will produce a change in refractive index of the order of only  $3 \times 10^{-6}$ . Such small change in refractive index can be measured reliably only with a differential device.

In this work we present the experimental values of refractive index obtained in mixtures of benzene + toluene at 303K and also the excess molar volumes calculated using the Lorenz-Lorentz equation. A comparison with literature results is shown in the last part of this note.

## PROCEDURE

The differential device operates by comparing the refractive index of a test sample with that of a reference fluid; the output signal is related to the difference in refractive index,  $\Delta n$ , between sample and reference; this relation is linear providing  $\Delta n$  does not exceed 0.001. Consequently, in order to obtain a full curve of refractive index vs. mole fraction ( $0 < x < 1$ ) a series of intermediate reference fluids must be used. Toluene (Fluka, > 99.5% GLC) was taken as the first refe-

rence fluid and  $\Delta n$  was measured for several toluene-rich mixtures up to a composition  $x'_1$  is benzene such that the refractive index at this composition differed by no more than 0.001 from that of pure toluene. This mixture ( $x'_1$ ) was then taken as the second reference and  $\Delta n$  was measured for a further set of compositions from  $x'_1$  to  $x'_2$ , once again within 0.001 of the refractive index of  $x'_1$ . This procedure was followed up to a mole fraction of benzene  $x_1$  of about 0.5, and then repeated in the reverse direction starting with pure benzene (Fluka, > 99.5% GLC) as the first reference, until a mole fraction of toluene  $x_2 = 0.5$  had been reached. Measurements were carried out at the wavelength of the sodium D-line.

The experimental value for a particular composition  $x_j$  was obtained using the expression

$$n_j = n_{b,i} + \sum_{j=1}^N \Delta n_j \quad (1)$$

where  $n_{b,i}$  refers either to benzene or to toluene (depending on which was the first reference fluid chosen) and the summation is taken over all  $N$  intermediate reference mixtures. Such a method is clearly very prone to the accumulation of intermediate reference errors which would show up as a mis-match at  $x = 0.5$  between the two sides of the refractive index vs. mole fraction curve. The absence of any such mis-match gives us confidence in the reliability of our experimental procedures.

For binary mixtures, the molar refraction,  $R_m$ , in terms of the molar volume,  $V_m$ , is given by:

$$R_{m,12} = \left[ \frac{n_{12}^2 - 1}{n_{12}^2 + 2} \right] V_{m,12} = x_1 R_{m,1} + x_2 R_{m,2} \quad (2)$$

where

$$R_{m,i} = \left[ \frac{n_i^2 - 1}{n_i^2 + 2} \right] V_{m,i} \quad (3)$$

Using (2) and (3) one gets for the molar excess volume  $V^E$ :

$$\begin{aligned} V^E &= V_{m,12} - x_1 V_{m,1} - x_2 V_{m,2} \\ &= \left[ \left( \frac{n_{12}^2 + 2}{n_{12}^2 - 1} \right) \left( \frac{n_1^2 + 2}{n_1^2 - 1} \right) - 1 \right] V_{m,1} x_1 + \\ &\quad + \left[ \left( \frac{n_{12}^2 + 2}{n_{12}^2 - 1} \right) \left( \frac{n_2^2 + 2}{n_2^2 - 1} \right) - 1 \right] V_{m,2} x_2 \end{aligned} \quad (4)$$

## RESULTS

The experimentally measured refractive indexes and the derived molar volumes are shown as a function of composition in Table I. In Figure 1, the excess refractive index (defined for a binary solution as  $n^E = n_{12} - (n_1 x_1 + n_2 x_2)$ ) is plotted against

Table I

Refractive index and molar volume at 303K for  $C_6H_6 + C_6H_5CH_3$

$x_1$	$n$	$V_m/\text{cm}^3 \text{mol}^{-1}$
0.0	1.49126 <sup>a</sup>	107.444
0.0186	1.491290	107.123
0.0371	1.491322	106.804
0.0737	1.491380	106.174
0.1457	1.491499	104.934
0.2847	1.491790	102.532
0.3738	1.492014	100.986
0.4432	1.492214	99.779
0.4942	1.492377	98.890
0.5442	1.492550	98.016
0.5934	1.492733	97.154
0.6417	1.492927	96.307
0.6892	1.493131	95.472
0.7359	1.493346	94.649
0.7818	1.493565	93.840
0.8269	1.493798	93.043
0.8712	1.494035	92.259
0.9149	1.494276	91.485
0.9578	1.494524	90.724
0.9737	1.494619	90.442
0.9869	1.494699	90.207
1.0	1.49478 <sup>a</sup>	89.974

<sup>a</sup> — values obtained from reference [1]

the benzene mole fraction  $x_1$ , together with the results at 301K of Trew and Spencer [2] and some recent unpublished measurements at 303K by Maczek and Humphreys [3]. Although the excess function  $n^E$  has no particular theoretical significance, this method of

mended by Myers and Scott [4]. The optimum degree of the fit  $k$  was found using the criteria of minimum variance. The series in equation (5) converges rapidly and a value of  $k=2$  is adequate to describe the experimental points. As the excess refractive index curve is only

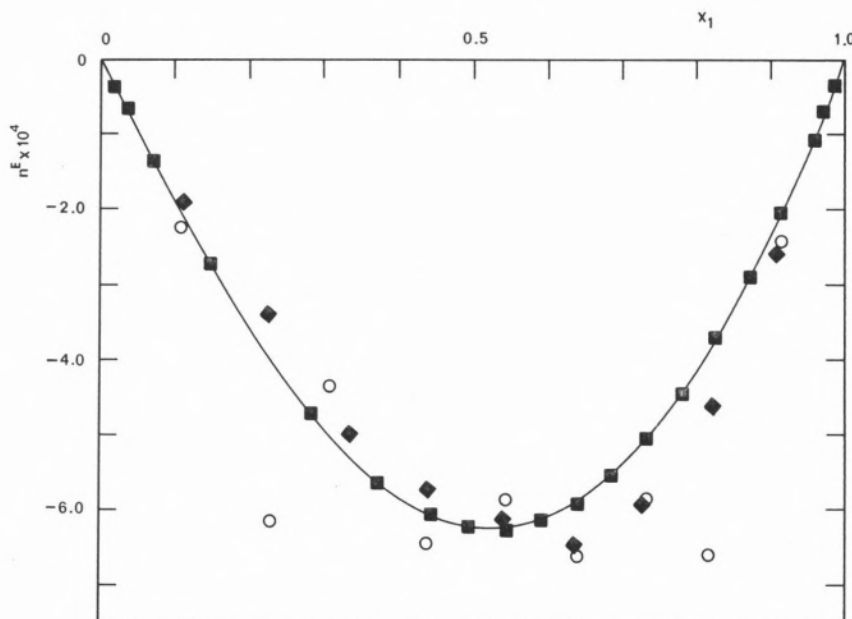


Figure 1

The excess refractive index  $n^E$  for the system benzene+toluene at 303K as a function of mole fraction of benzene

- ◆ — Maczek and Humphreys [3]
- — Trew and Spender [2], at 301K
- — present work

presentation reveals very clearly any experimental uncertainty in the raw data, and provides an immediate visual test of their internal consistency.

The fitted curve in Figure 1 has been obtained using an equation of the Redlich-Kister type

$$n^E = x_1 x_2 \sum_{j=0}^k a_j (1 - 2x_1)^j \quad (5)$$

with the coefficients  $a_j$  found by a least-squares method using a fitting program recom-

slightly skewed, there is no need for an additional skewing parameter, as described by Myers and Scott [4], in order to fit the data. The optimised parameters for this fit are:

$$\begin{aligned} a_0 &= (-24.96 \pm 0.03) \times 10^{-4} \\ a_1 &= (3.186 \pm 0.063) \times 10^{-4} \\ a_2 &= (2.073 \pm 0.130) \times 10^{-4} \end{aligned}$$

with a root mean square deviation for the fit of  $1.56 \times 10^{-6}$  units of refraction index.

The absolute data of Maczek and Humphreys [3] lie close to our data but are slightly more skewed; the results of Trew and Spencer [2] show considerable scatter around the least-squares curve.

The results show that our method can detect changes in refractive index with an uncer-

$V_{m,2}$  for the pure components were taken from reference 1. In Figure 2 we show the calculated values and a curve fitted to equation with the same form than equation (5) by the method of Myers and Scott [4] as used earlier.

Once again the series converges rapidly and an order of fit  $k=2$  is adequate to describe the

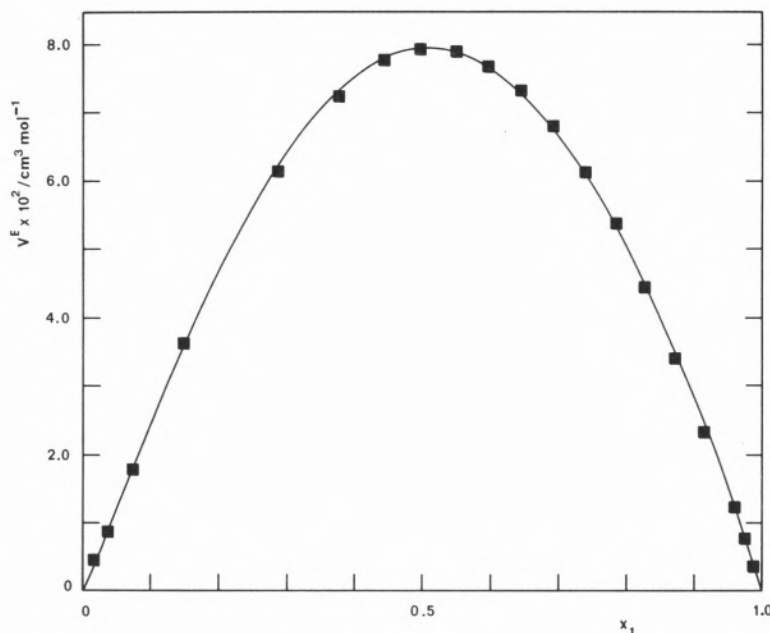


Figura 2

The excess volume  $V^E$  for the system benzene+toluene at 303K as a function of mole fraction of benzene

tanty that amounts to no more than a few parts per million. For the system benzen + toluene this corresponds to an uncertainty in mole fraction of about  $\pm 0.001$ . This system, in which the difference in the refractive index of the pure components is so small, is a very stringent test of the method we propose for measuring small changes in composition, and illustrates how useful differential refractrometry can be in the pursuit of this experimental objective.

The excess molar volumes were calculated from equation (4); the molar volumes  $V_{m,1}$  and

derived data. The optimised parameters for this fit are:

$$a_0 = (+31.81 \pm 0.07) \times 10^{-2} \text{ cm}^3 \text{ mol}^{-1}$$

$$a_1 = (-1.782 \pm 0.147) \times 10^2 \text{ cm}^3 \text{ mol}^{-1}$$

$$a_2 = (-4.121 \pm 0.302) \times 10^2 \text{ cm}^3 \text{ mol}^{-1}$$

with a root mean square deviation of  $0.0004 \text{ cm}^3 \text{ mol}^{-1}$ .

Figure 3 shows a deviation plot between the experimental points and the value evaluated with the fit. It can be seen that no experimen-

tal point deviates from the fit by more than  $0.001 \text{ cm}^3 \text{ mol}^{-1}$ . Table II contains some literature values [5,8] for the molar excess volume at equimolar composition together with the results obtained by us. A graphical comparison is made in Figure 4.

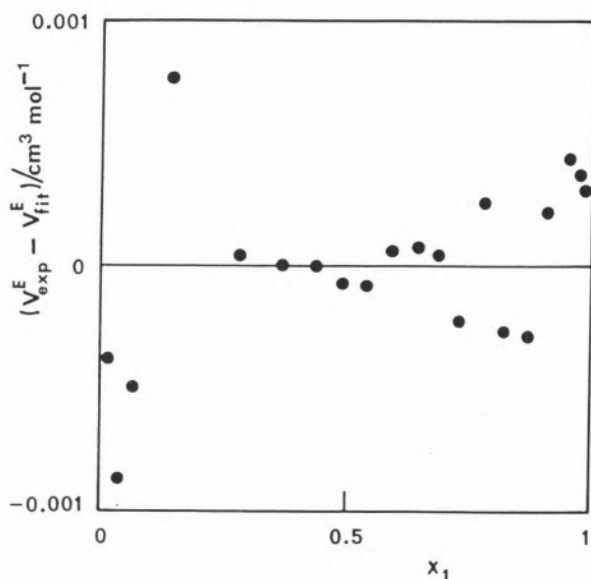


Figure 3

The deviations between the measured excess volumes and the values given by the numerical fit

Over so small a temperature range it is reasonable to assume a linear variation of  $V^E$  with temperature. on this basis, as Figure 4 shows, our result lend support to those of Ocon *et al.* [5] and Murakami *et al.* [7], but lies outside the mutual uncertainties of the results of Iguchi [8] and of Diaz-Pena and Delgado [6]. The excess molar volume is very small (of the order of  $0.1 \text{ cm}^3 \text{ mol}^{-1}$ ) and we believe that

our method provides a relatively straightforward means of measuring such small quantities.

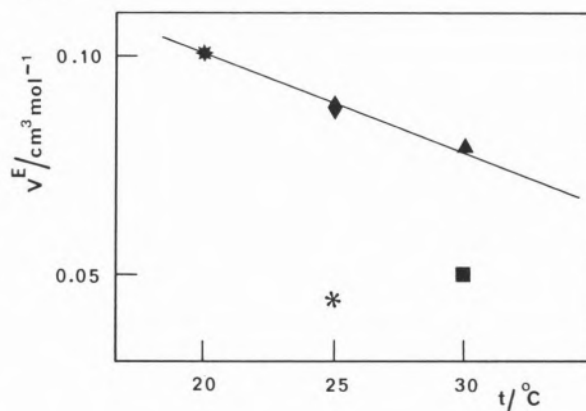


Figure 4

The equimolar excess volume  $V^E$  for the system benzene+toluene as a function of temperature

- \* — Ocon *et al.* [5]
- \* — Diaz Peña *et al.* [6]
- ◆ — Murakami *et al.* [7]
- — Iguchi *et al.* [8]
- ▲ — present work

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Table II

Equimolar excess volume data for  $C_6H_6 + C_6H_5CH_3$

T / K	$10^6 V^E / \text{m}^3 \text{mol}^{-1}$	Reference
273	$0.108 \pm 0.002$	5
298	$0.044 \pm 0.003$	6
298	$0.088 \pm 0.002$	7
303	$0.050 \pm 0.005$	8
303	$0.080 \pm 0.001$	Present work

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## RESUMO

### Índice de refração e volume molar de excesso do sistema benzeno + tolueno a 303 K

Apresenta-se um método de grande exactidão para determinação da composição de misturas líquidas binárias através da refracto-

metria diferencial. O refractómetro usado detecta facilmente variações de índice de refração da ordem de  $1 \text{ em } 10^7$  pelo que pode ser utilizado na determinação de pequenas variações de composição. Mediram-se os índices de refração de misturas binárias de benzeno + tolueno a 303.15 K e compararam-se com as medidas absolutas feitas com um refractómetro Pulfrich. Os resultados mostram que é possível medir variações de índice de refração com uma incerteza não superior a algumas partes por milhão. Para o sistema estudado isto corresponde a uma variação de fracção molar da ordem de 0.001.

Os volumes molares de excesso em função da composição foram determinados através da equação de Lorenz-Lorentz. O volume molar de excesso encontrado para a mistura equimolar foi  $0,080 \text{ cm}^3 \text{ mol}^{-1}$ . A comparação deste valor com os valores experimentais encontrados na literatura sugere que os resultados presentes têm uma exactidão de  $\pm 0,001 \text{ cm}^3 \text{ mol}^{-1}$ .