663. *Thermal Diffusion Factors in the Benzene–Methanol System*

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New measurements of the thermal diffusion factor α for this system are described. These confirm that α changes in sign as the composition changes. Reasons for this change are discussed.

THERMAL diffusion in binary mixtures of a non-associated and an associated liquid were first studied systematically [1] by a thermogravitational method. It was shown that, in many cases, the sign of the thermal-diffusion separation in these systems could be changed by changing the composition; the results [1] for the benzene–methanol system are shown in Figure 1. This system has also been studied with a diaphragm cell,[2] and by examination of the pure Soret effect.[3,4] The results obtained by these different workers for the thermal diffusion factor α differ considerably, though all show that α changes in sign at some value of the composition.

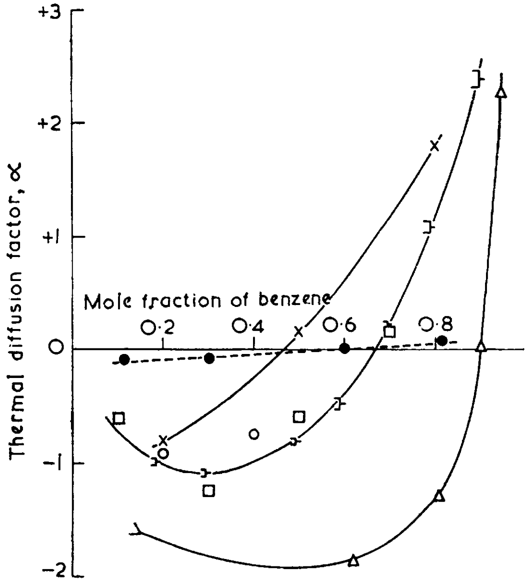

FIGURE 1. Thermal-diffusion factors in benzene–methanol solutions

△ Thermogravitational, $T_m = 50°$ (ref. 1);
× Diaphragm cell, $T_m = 40°$ (ref. 2);
● Pure Soret effect, $T_m = 29°$ (ref. 3);
○ Pure Soret effect, $T_m = 45°$ (ref. 4);
□,]-This work. $T_m = 25°$. Values shown as □ from ref. 7.

We have re-examined this system by the beam-displacement method,[5,6] at mean

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[1] I. Prigogine, L. de Brouckère, and R. Amand, *Physica*, 1950, **16**, 577, 851.
[2] L. J. Tichachek, W. S. Kmak, and H. G. Drickamer, *J. Phys. Chem.*, 1956, **60**, 660.
[3] G. Thomaes, *Physica*, 1951, **17**, 885.
[4] S. Whitaker and R. L. Pigford, *Ind. Eng. Chem.*, 1958, **50**, 1026.
[5] H. J. V. Tyrrell, J. G. Firth, and M. Kennedy, *J.*, 1961, 3432.
[6] H. J. V. Tyrrell and M. Zaman, *J.*, 1964, 6216.

temperatures of 25 and 30°. The cell was of the modified Tanner type with a plate displacement of about 2·2 mm., and a temperature gradient of approximately 5° cm.$^{-1}$ was used throughout. The variation of refractive index with concentration and with temperature, necessary for the calculation of α from experimental data, was obtained from refractive-index measurements with a Pulfrich refractometer on known mixtures.[7] Solutions were made up by weight from AnalaR benzene dried over sodium, and from AnalaR methanol dried over Hidrite and redistilled. The beam-displacement below the optic axis was measured at five-minute intervals, after the application of the temperature field, for at least one hour, or approximately 10θ (θ = characteristic time, defined as a^2/π^2D, where a is the plate separation and D the diffusion coefficient for the system). Since the characteristic time was so short, it was not practicable to analyse the rate of approach to the steady state to obtain the thermal-diffusion factor, but any large abnormalities in the displacement–time curves could easily be detected by inspection. In methanol-rich solutions, benzene, the denser and more highly refracting component, migrated to the cold wall, and the displacement–time curves were reproducible and of the expected shape (Figure 2, curve A). The initial large deflection due to the temperature field increased further as the benzene migrated down the temperature gradient and finally reached a reproducible limiting value. In benzene-rich solutions, the observed deflection decreased initially from that due to temperature alone (benzene moving to hot wall), reached a minimum, and then began to increase again; these curves were not particularly reproducible (Figure 2, curves B and C). This suggests that some unwanted re-mixing process tends to oppose the migration of benzene to the hot wall and no recognisable steady state was attained. The positive thermal diffusion factors listed in the Table, derived from experiments in this concentration region, were calculated from the observed displacements at the minimum of curves of the form shown in Figure 2 B and C, and are presumably underestimates of the true values. From the Table it can be seen that a change in mean temperature (T_{m}) of 5° had little effect on the values of α except to increase the experimental uncertainty. Hence, the fact that different workers used different values of T_{m} is unlikely to account for the observed discrepancies.

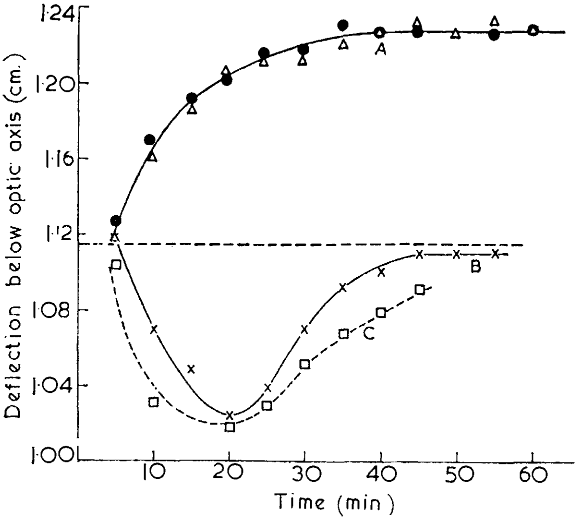

FIGURE 2. Beam-deflection–time curves for separations in 2·2-mm. cell

Curve A: 0·5 mole fraction benzene in methanol. Points are from independent experiments under similar conditions.

Curves B and C: 0·8 mole fraction benzene in methanol. Both curves from independent experiments under similar conditions.

The horizontal broken line indicates the approximate deflection due to temperature gradient alone.

Thermal-diffusion factors at 25°, taken from the Table, are displayed in Figure 1, for comparison with the earlier results. Our values agree quite well with other, incomplete data,[4] and the concentration at which inversion of the sign takes place appears from

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[7] J. G. Firth, Ph.D. Thesis, Sheffield, 1961.

Thermal-diffusion factors at 25 and 35° for the benzene–methanol system. A positive sign indicates that benzene concentrates at the hot wall

$T_{\mathrm{m}} = 25°$		$T_{\mathrm{m}} = 30°$	
Mole fraction of benzene	α	Mole fraction of benzene	α
0·897	+2·38 (±0·08)	0·950	+8·5
0·790	+1·07 (±0·04)	0·892	+2·7 (±0·2)
0·70 (ref. 7)	+0·16	0·757	+0·9 (±0·2)
0·699	+0·21 (±0·02)	0·700	+0·6 (±0·15)
0·588	−0·48	0·499	−0·7 (±0·04)
0·50 (ref. 7)	−0·60	0·385	−0·7 (±0·08)
0·494	−0·81 (±0·01)	0·234	−1·1 (±0·08)
0·30 (ref. 7)	−1·25	0·170	−0·75 (±0·02)
0·295	−1·09 (±0·02)		
0·183	−0·99 (±0·02)		
0·10 (ref. 7)	−0·62		

Where limits of error are quoted, these, when added to or subtracted from the mean value listed, give the experimental values from which the mean was derived.

these two sets of results to lie between 0·6 and 0·7 mole fraction of benzene. The small discrepancy between the two sets may be due to differences in the values used for the refractive-index parameters, and it should be noted that the Soret cells used in both cases, though of different design, had plate separations of only a few millimetres. Thomaes, using a 10-mm. spacing, obtained values which are too small, though his inversion concentration lies in the same region. We also studied this system in cells with plate spacings of 7 and 10 mm. and invariably found that the separation curves were abnormal in shape, and showed that the degree of de-mixing was far smaller than in the 2·2-mm. cell. Parasitic re-mixing processes which interfere with the normal development of the Soret equilibrium are much more easily induced in non-aqueous than in aqueous solutions, and the presence of such processes probably accounts for the low α values reported by Thomaes (cf. also ref. 4). The present values lie between those obtained with a diaphragm cell, and those with a thermogravitational cell, but all show that when the benzene is in excess it migrates to the hot wall, and the positive thermal-diffusion factor, which represents the magnitude of this tendency, increases rapidly as the methanol concentration falls.

Methanol is an associated solvent, and, for dilute solutions of methanol in benzene, the excess heat of mixing rises sharply with methanol concentration.[8] This corresponds to the endothermic breaking of hydrogen bonds as the associated solute molecules are broken down on solution in the benzene. It has been shown [9] that, for solutions in a normal solvent of a solute which associates into dimers, the magnitude of the thermal-diffusion factor is greatly affected by the enthalpy of association. If heat is absorbed in the breakdown of the dimers to monomers, the solute migrates to the cold wall when the solution is dilute. In very concentrated solutions, where dimerisation is almost complete, the main factor affecting the magnitude of α is the heat of transfer of the dimeric solute. If this heat of transfer has a sign which opposes the enthalpy of association effect, then α will change in sign as the concentration changes. A similar argument applies to the methanol–benzene system. Heat is absorbed in the breakdown of the associated methanol molecules as they pass into an environment of benzene molecules, and the monomeric methanol molecules should, and do, migrate towards the cold wall. In dilute solutions of benzene in methanol, benzene migrates to the cold wall. Hence, the heat of transfer $Q_{\mathrm{benz.}}{}^{*}$ which is related to the thermal-diffusion factor used in the Table by the equation,

$$\alpha = -Q_{\mathrm{benz.}}{}^{*}/\boldsymbol{R}T(1 + \partial \ln \gamma_{\mathrm{benz.}}/\partial \ln m)$$

must be positive ($\gamma_{\mathrm{benz.}}$ is the activity coefficient of the benzene on the molality scale in an m-molal solution). A positive heat of transfer is characteristic, for example, of non-polar

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[8] G. Scatchard, L. B. Ticknor, J. R. Coates, and E. R. MacCartney, *J. Amer. Chem. Soc.*, 1952, **74**, 3721; G. Scatchard and L. B. Ticknor, *ibid.*, p. 3724.

[9] I. Prigogine and R. Buess, *Bull. Classe Sci.*, *Acad. roy. Belg.*, 1952, **38**, 851.

solutes in water,[6] and would not be unexpected for benzene in solution in methanol. A further point of interest is that [2] the methanol–carbon tetrachloride system in the composition range 0·2—0·8 mole fraction does not show a change in sign for α, the carbon tetrachloride always migrating to the cold wall. The excess heat of mixing [8] for dilute solutions of methanol in carbon tetrachloride rises much less steeply than in the benzene–methanol case, *i.e.*, fewer hydrogen bonds are broken on solution.[10] Because of this, the excess entropy in the carbon tetrachloride–methanol system does not change sign with changing concentration, whereas for benzene–methanol at 35° it becomes slightly positive for dilute solutions of methanol in benzene. Clearly, the extent to which the associated solute is broken down on solution is much less in carbon tetrachloride than in benzene; an adequate explanation for this has been given.[10] This behaviour supports the view that the difference in the thermal-diffusion properties of the two systems can be associated with the endothermic breakdown of associated solute molecules on solution in the one case, this breakdown not occurring, or occurring to a smaller extent, in the other. On this basis, the " natural " direction of diffusion for the non-polar component in both cases should be towards the cold wall. When the associated methanol molecules dissolve as monomers, the enthalpy change in this process becomes dominant in determining the direction of thermal migration. Possibly, a reversal in sign of this may also occur for very dilute solutions of methanol in carbon tetrachloride; no study of this kind has yet been carried out.

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[10] Cf. J. S. Rowlinson, " Liquids and Liquid Mixtures," Butterworths, London, 1959.