Thermal Diffusion in Mixtures of Alcohols and Aromatic Hydrocarbons *

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The thermal diffusion factors observed for these systems vary considerably with concentration, and frequently show a change in sign at some concentration. New data on ethanol-toluene mixtures show that the sign and magnitude of the separation of the components in a thermal gradient are also strongly dependent on the mean temperature of the system. These observations, together with earlier ones on similar systems, can be given a semi-quantitative interpretation in terms of a shift in the average degree of association of the alcohol along the temperature gradient.

The de-mixing of a binary solution in a temperature gradient in the absence of convective re-mixing is expressed either in terms of the Soret coefficient σ, or of the thermal diffusion factor α. These are defined by Eq. (1).

$$\alpha = \sigma T = \frac{1}{N_2} \frac{\operatorname{grad} \ln N_1}{\operatorname{grad} \ln T} . \qquad (1)$$

N_1 and N_2 are the molar fractions of the two components. In this paper, component 2 refers to the alcohol. The experimental quantity is the ratio $\operatorname{grad} N_1 / \operatorname{grad} T$ which, for a given value of α, is a maximum at $N_1 = N_2 = 0.5$. α is comparatively small, usually between 0.3 and 3.0, and, even in favourable circumstances, is not easy to measure precisely. The comparatively small concentration changes due to thermal diffusion are easily masked by convective re-mixing especially in non-aqueous solutions[1]. The experimental difficulties are particularly acute when either N_1 or N_2 is large. In this work we have used an optical technique[1-3] for measuring refractive index gradients in a horizontal liquid film less than 1 mm thick. The film is enclosed between metal blocks (Fig. 1). For technical reasons, a double cell is used, one side containing solvent and the other the solution. The narrow gap between the upper and lower bounding surfaces minimises convection, and gives a large temperature gradient (and hence high sensitivity) with a small temperature interval ($<1°$). We have found this to be an essential requirement if meaningful results are to be obtained from experiments on mixtures of alcohols with aromatic hydrocarbons.

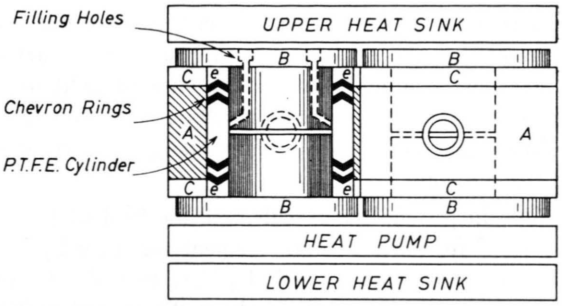

Fig. 1. Improved double-cell for the measurement of thermal diffusion in horizontal liquid films.

Thermal diffusion factors calculated from early data on benzene-methanol mixtures[4] did not agree well except in respect of the conclusion that α changed sign at a molar fraction of benzene of about $0.6-0.7$.

At low concentrations of benzene in methanol, the benzene (component 1) migrated to the cold wall, i. e., α as defined by Eq. (1) was negative in these solutions, becoming positive when $N_1 > 0.7$. More accurate work[2, 5, 6] has since confirmed this, the best estimate of the composition at which $\alpha = 0$ being $N_1 = 0.67$ when the mean temperature $T_m = 25°$. Discrepancies in the earlier results were probably due to problems with convection and to the use of rather large temperature intervals. A similar reversal in the sign of α, occurring at lower

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[1] L. GUCZI and H. J. V. TYRRELL, J. Chem. Soc. **1965**, **6576**.

[2] G. FARSANG and H. J. V. TYRRELL, J. Chem. Soc. (A) **1969**, 1839.

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[4] H. J. V. TYRRELL, Diffusion and Heat Flow in Liquids, Butterworth, London 1961, p. 256.

[5] H. J. V. TYRRELL, J. G. FIRTH, and M. ZAMAN, J. Chem. Soc. **1965**, 3613.

[6] M. J. STORY and J. C. R. TURNER, Trans. Faraday Soc. **65**, 1523 [1969].

benzene concentrations ($\alpha = 0$ when $N_1 \sim 0.32$) has been observed[2] for benzene-ethanol mixtures ($T_m = 25^\circ$), and Fig. 2 shows the experimental values of α for this system and the benzene-methanol one at this mean temperature.

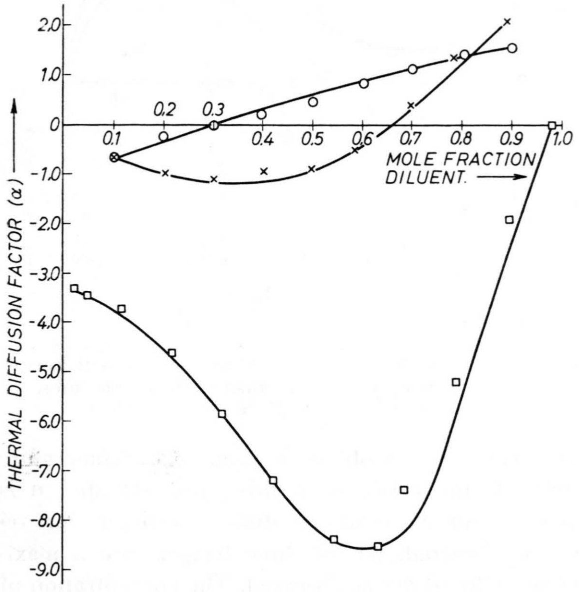

Fig. 2. The variation of thermal diffusion factors with mole fraction of diluent for alcohol-diluent systems.
○ Methanol—Benzene (Ref. [2]),
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□ Methanol—Carbon Tetrachloride (Ref. [6]).

The shape of the curve is partly dependent upon the thermodynamic behaviour of the solutions, since a steady state thermodynamic treatment shows that the heat of transport (Q_2^*) of component 2 is related to the thermal diffusion factor α by Eq. (2).

$$\alpha = \frac{Q_2^*}{R\,T\,N_1(1+\partial \ln f_i/\partial \ln N_i)_{T,P}}\,. \tag{2}$$

The activity coefficient of component i on the mole fraction scale is denoted by f_i, and Eq. (3) applies.

$$N_1\,Q_1^* + N_2\,Q_2^* = 0\,. \tag{3}$$

When a binary system approaches a consolute point at which separation into two phases takes place $(1+\partial \ln f_i/\partial \ln N_i)_{T,P}$ approaches zero, and if Q_2^*/N_1 remains finite, α tends to infinity. This is the reason for the very steep increase in α found near $N_1 = 0.8$ for benzene-methanol mixtures, a phenomenon not seen for the benzene-ethanol system. The plots of Q_2^*/N_1 against composition for these two systems (Fig. 3) are however rather similar, apart from the difference in composition at which $\alpha = 0$. The system carbon tetrachloride-methanol was studied by **Turner** and **Story**[6], their results being also shown in Figs. 2 and 3. The inert diluent (carbon tetrachloride) migrated to the cold wall in all cases though the separation decreased markedly and became almost negligible for dilute solutions of methanol in carbon tetrachloride. The algebraic minimum in α at a carbon tetrachloride molar fraction of ~ 0.65 was again due to the influence of the thermodynamic term, and is not apparent in the plot of Q_2^*/N_1 shown for this system in Figure 3.

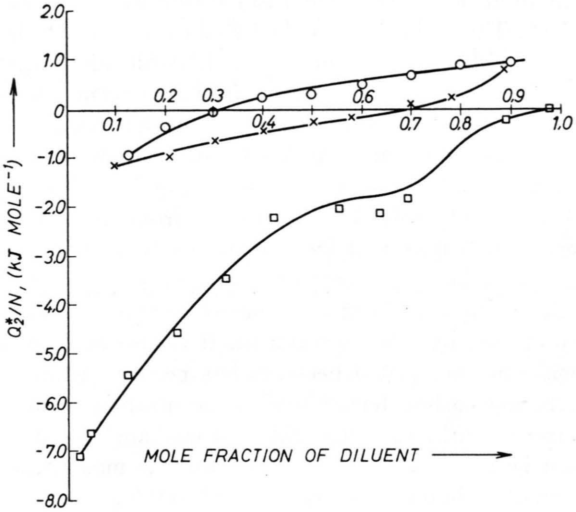

Fig. 3. The variation of Q_2^*/N_1 with mole fraction of diluent for alcohol-diluent systems.
○ Methanol—Benzene (Ref. [2]),
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These differences can be predicted qualitatively from the observed differences in the excess thermodynamic functions[7]. In dilute solutions of ethanol and methanol in benzene the excess entropy (s^E) is initially positive, rises to a maximum, falls to zero and then becomes negative as the alcohol concenration increases.

$T\,s^E$ becomes zero at lower benzene concentrations for benzene-ethanol mixtures (at 45 °C) than for benzene-methanol mixtures (at 35°). At all accessible concentrations, $T\,s^E$ is negative for the carbon tetrachloride-methanol system (at 35°). The positive values found for $T\,s^E$ in the mixtures of

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[7] J. S. Rowlinson, Liquids and Liquid Mixtures, 2nd ed., Butterworth, London 1969, p. 163.

alcohols with benzene can be attributed to the breakdown of the associated alcohol species when placed in a large excess of benzene. This breakdown occurs more readily in ethanol than in methanol, and benzene is more effective at causing this breakdown when added to methanol than is carbon tetrachloride. It would be expected that $T\,s^{\mathrm{E}}$ should become positive for carbon tetrachloride-methanol mixtures when the methanol is sufficiently dilute, but this must correspond to a concentration region where successful experiments have not been carried out. When alcohol is in excess, all three systems reviewed above show similar behaviour in a thermal gradient, the diluent species moving to the cold wall (α negative). This behaviour could be taken as characteristic of either benzene or carbon tetrachloride diffusing in an associated solvent. At high concentrations of benzene, the benzene goes to the hot wall, and this was interpreted [2] as behaviour characteristic of monomeric alcohol molecules moving in a diluent. This model enabled us to predict from the known excess entropies that the sign reversal for α should occur at lower benzene concentrations in benzene-ethanol than in benzene-methanol mixtures, a view confirmed by later experiment. It is also consistent with the fact that α becomes less negative with increasing carbon tetrachloride concentration in mixtures of carbon tetrachloride and methanol but does not become positive, if at all, until the molar fraction of carbon tetrachloride exceeds 0.986.

This explanation is not entirely correct as has now been shown by the experiments on toluene-ethanol systems reported below. The excess thermodynamic functions for this system have been studied in detail [8] and are known to be extremely temperature-dependent. For dilute solutions of ethanol in toluene $T\,s^{\mathrm{E}}$ is positive, but the position of the maximum, and the point at which $T\,s^{\mathrm{E}}$ falls through zero to negative values, are very sensitive to temperature. It would therefore be expected that the thermal diffusion factor α should also vary rapidly with temperature, and this has now been shown to be true. Figure 4 shows data, which are not yet fully confirmed, at mean temperatures of 20°, 25° and 35°. The variation of α with temperature in this system is so large that it is clear that meaningful values of α can only be obtained when small temperature intervals are used, as in this work. At 20°, α is positive for all solutions studied, and no sign reversal occurred. At all three temperature a maximum value of α was observed. The concentration of toluene at which the maximum occurred decreased with temperature. At 35°, α was negative at low concentrations of toluene, became positive, reached a maximum and, in sufficiently high concentrations of toluene, again became negative. This type of behaviour would be expected theoretically for a system in which a chemical reaction takes place [9, 10].

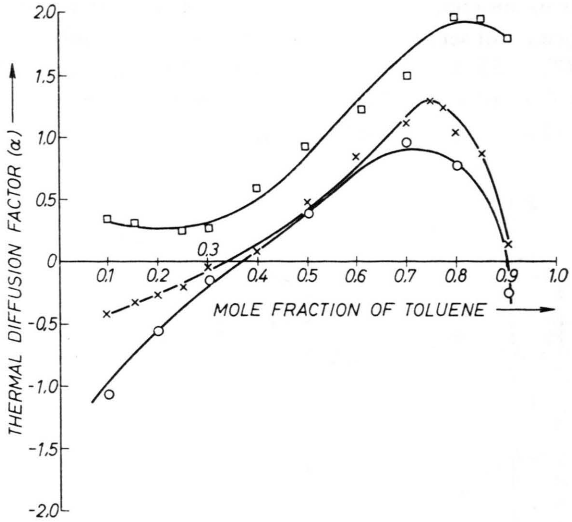

Fig. 4. The variation of thermal diffusion factor with composition and temperature for ethanol-toluene mixtures. □ At 20 °C; × At 25 °C; ⊙ At 35 °C.

Suppose that component 2 can exist as monomer (A) and a polymer (A_ν) according to the equilibrium

$$\nu A \rightleftarrows A_\nu \tag{4}$$

and that the enthalpy change in this process is ΔH. Such a system will not behave as a thermodynamically ideal system, and it can be assumed that the observed deviations from ideality arises *solely* from the equilibrium (4). This is probably not a correct assumption, but it simplifies the theoretical treatment. Because of this association equilibrium, it can be shown [10] that the thermal diffusion factor can be split into two parts, namely.

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[8] S. C. P. Hwa and W. T. Ziegler, J. Phys. Chem. **70**, 2672 [1966].

[9] I. Prigogine and R. Buess, Acad. Roy. Belg. Bull. Cl. Sci. (5), **38**, 851 [1952].

[10] B. Baranowski, A. E. de Vries, A. Haring, and R. Paul, Adv. Chem. Phys. **16**, 101 [1969].

(i) a "physical" part, $\alpha_{\text{phys.}}$, which is a complex function of composition, diffusion coefficients and thermal diffusion coefficients, and

(ii) a "chemical" part, $\alpha_{\text{chem.}}$. This involves the enthalpy change ΔH in reaction (4). If x_2 is the true molar fraction of monomeric A, $x_{2\nu}$ that of the polymeric form, and x_1 that of the inert component 1, then it can be shown that

$$\alpha_{\text{chem.}} = - \frac{\chi_{\text{d}}(1-\chi_{\text{d}})}{\nu} \frac{\Delta H}{R\,T} \left\{ \frac{(\nu-b) - R_0(b-1)}{b-(b-1)\,\chi_{\text{d}}} \right\} \tag{5}$$

where

$$\begin{aligned} \chi_{\text{d}} &\equiv x_2/(x_2+\nu\, x_{2\nu}), \\ R_0 &\equiv (x_2+\nu\, x_{2\nu})/x_1 = N_2/N_1, \\ b &= (a_0\, b_0 + R_0)/(a_0+R_0), \\ b_0 &= \nu\, D_{\nu 1}/D_{21}, \\ a_0 &= D_{2\nu}/D_{\nu 1}. \end{aligned}$$

$D_{\nu 1}$ is the binary diffusion coefficient of A_ν in component 1 (the "inert" diluent), D_{21} that of monomer A in 1, and $D_{2\nu}$ that of monomeric A in the polymer.

$D_{\nu 1}/D_{21}$ must be roughly proportional to ν^{-n} where n probably lies between 0.3 and 0.5 [11]. The ratio $a_0 = D_{2\nu}/D_{\nu 1}$ must be close to one since $D_{2\nu}$ and $D_{\nu 1}$ both refer to the diffusion of the polymeric form A_ν in a medium of small, non-associated molecules. If $a_0 = 1$, the term in braces in Eq. (5) reduces to

$$\frac{(\nu-b_0)\,(1+R_0)}{b_0(1-\chi_{\text{d}})+\chi_{\text{d}}+R_0}\,. \tag{6}$$

When R_0 is large, $\chi_{\text{d}} \rightarrow 0$, and when R_0 is small $\chi_{\text{d}} \rightarrow 1$. Hence, Eq. (6) reduces to $(\nu - b_0)$, a positive quantity, both in excess diluent and excess A. Since b_0 is normally greater than 1, at intermediate concentration, $(b_0(1-\chi_{\text{d}})+\chi_{\text{d}})$ is also greater than 1. Hence,

$$0 < \frac{(\nu-b_0)\,(1+R_0)}{b_0(1-\chi_{\text{d}})+\chi_{\text{d}}+R_0} \leqq (\nu - b_0)\,. \tag{7}$$

The formation of the polymeric species A_ν from monomer must be exothermic (ΔH negative). Hence, from Eqs. (5) and (7), the chemical contribution to α is positive, and reaches a maximum when $\chi_{\text{d}} = (1-\chi_{\text{d}}) = 0.5$. A reasonable value for $-\Delta H/\nu$ in the alcohol case could be 3 kcal mole^{-1} (1 hydrogen bond) and in such a case,

$$\alpha_{\text{chem.}} = 2.5\,\beta(\nu - b_0) \tag{8}$$

where β is a numerical factor between 0 and 1.

Assume that $\nu = 3$, and that $b_0 = \nu^{1/2} = 1.7$. Then,

$$\alpha_{\text{chem.}} \sim 3\,\beta\,. \tag{9}$$

Our results for toluene-ethanol systems where the maximum positive contribution of $\alpha_{\text{chem.}}$ to α, predicted by Eq. (6), is observed, show that the peak lies about 1.5 units above the values found at either end of the concentration scale, where $\alpha_{\text{phys.}}$ is the main contributor to α. In the circumstances this is reasonable agreement with the result in Eq. (9), and confirms the view that the variaiton of α with concentration in these systems is due largely to a chemical contribution. For benzene-ethanol and for benzene-methanol, the expected maximum in α was not observed presumably because χ_{d}, the average degree of dissociation of the polymeric species, never reached the value 0.5 at the lowest alcohol concentrations examined. In the latter case, the fact that the system approached a critical solution temperature at $N_1 \sim 0.8$ meant that the resulting sharp fall in $(1 + \partial \ln f_i / \partial \ln N_i)$ caused an increase in α which could mask the purely chemical effect.

The reason why the maximum is apparently seen in toluene-ethanol at 25° and not in benzene-ethanol at this temperature is probably associated with the greater π-electron density in the toluene molecule. This makes toluene more efficient than benzene in breaking down the associated ethanol clusters. A better general criterion than the concentration at which $\alpha = 0$, of the ease with which hydrogen bonded clusters can be broken down by a diluent, would be the concentration at which α reaches a maximum. It will be seen that, in the ethanol-toluene system, this point falls at the highest toluene mole fraction for the lowest temperature studied. The hydrogen-bonded clusters are therefore more stable at low than at high temperature as would be expected, and as is confirmed by the change in the excess entropy curves with temperature. Such maxima in α should therefore fall in experimentally accessible concentration ranges for systems like ethanol-benzene and methanol-benzene at sufficiently high temperatures.

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[11] Ref. [4], pp. 173–180.