

Thermal Diffusion in the n-Heptane–Benzene System at 25 °C

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Thermal diffusion factors and heats of transfer have been determined for liquid mixtures of n-heptane and benzene over a wide range of concentrations at 25 °C. A pure Soret effect cell, with a liquid layer less than 1 mm thick, was used. The results agree well with some recently published data obtained by Korsching using a different method.

This system was first studied by Bierlein, Finch, and Bowers¹ over a wide range of mean temperatures ($T_m = 20\text{--}60$ °C) using an optical beam displacement method and an all-metal cell. In the lower temperature range (20–40 °C), the thermal diffusion factor † α , defined as in equation (1), where the mole fraction (N)

$$\alpha = \frac{T}{N_1 N_2} \left(\frac{\partial N_1}{\partial T} \right)_{\text{stat.}} \quad (1)$$

gradient is that measured in the steady state, was found to be almost independent of temperature. The n-heptane concentrated at the hot wall, that is, suffix 1 in equation (1) refers to this component, and α increased steadily as the concentration of benzene increased. Measurements made some years ago ($T_m = 25$ °C) by one of us (J. D-P) on equimolar mixtures, and on mixtures rich in benzene, using the method described by Guzzi and Tyrrell,² suggested that the earlier values were low. A value similar to our own for the equimolar mixture ($T_m = 35.5$ °C) was obtained by Korsching³ using the 'Spalt-Apparat.'⁴ A more detailed study by use of an improved form of the Guzzi–Tyrrell cell⁵ was then undertaken to extend and confirm the earlier results at $T_m = 25$ °C. During this work, a more complete examination of this system ($T_m = 35.5$ °C) was published by Korsching.⁶ As will be seen, the two sets of results agree quite well in spite of the difference in the mean temperature at which they were obtained. This confirms the conclusion reached by Bierlein, Finch, and Bowers that temperature changes have little effect on the thermal diffusion factor, at least at temperatures below 40 °C. However, all the later results are substantially higher than theirs.

† The thermal diffusion factor is the product of the Soret coefficient $\sigma (N_1 N_2)^{-1} (\partial N_1 / \partial T)_{\text{stat.}}$ and the mean temperature of the experiment. The chief advantage of its use is that it is a dimensionless quantity, usually with a convenient magnitude.

¹ J. Bierlein, C. R. Finch, and H. E. Bowers, *J. Chim. phys.*, 1957, **54**, 872.

² L. Guzzi and H. J. V. Tyrrell, *J. Chem. Soc.*, 1965, 6576.

³ H. Korsching, personal communication.

EXPERIMENTAL

The optical apparatus was identical with that described earlier,³ and the experimental technique used was essentially the same. The improved cell described by Farsang and Tyrrell⁵ was used in most of the experiments. The refractive index increments with concentration, $(\partial \mu / \partial N)_T$, and with temperature, $(\partial \mu / \partial T)_N$, have been reported for this system.⁷

AnalaR benzene and spectroscopically pure n-heptane (Fluka) were used. These were dried by prolonged storage over 3A grade molecular sieve and then distilled through a 50 cm column packed with multicoil helices. The middle fraction (70%) of the distillate was collected over molecular sieve, and then redistilled in the same manner. The purified products were stored under dry conditions. The special precautions required to avoid evaporation losses during solution preparation, handling, and storage, based on those devised by Horne and Bearman,⁸ have been described.^{2,5}

RESULTS

In any given experiment a small temperature interval was applied to the double cell (*ca.* 0.25 °C over a distance of less than 1 mm), and the steady-state refractive index gradients measured in the reference and solution sections several times during *ca.* 30 min. The temperature interval was then increased in a step-wise manner until the maximum interval (*ca.* 0.75 °C) was attained, the steady-state refractive index gradients being measured several times after each increase. Hence a number of independent thermal diffusion factors could be calculated from observations made during a single experiment. The detailed results on three solutions are shown in Table 1. The results for each run are clearly internally consistent, and show that there is little, if any, effect of temperature

⁴ H. Korsching, *Z. Naturforsch.*, 1955, **10a**, 242; 1965, **20a**, 968.

⁵ G. Farsang and H. J. V. Tyrrell, *J. Chem. Soc. (A)*, 1969, 1839.

⁶ H. Korsching, *Z. Naturforsch.*, 1969, **24a**, 444.

⁷ J. Demichowicz-Pigoniowa and H. J. V. Tyrrell, *Roczniki Chem.*, 1969, **43**, 433.

⁸ F. H. Horne and R. J. Bearman, *J. Chem. Phys.*, 1962, **37**, 2857.

TABLE 1

Effect of temperature interval upon the measured thermal diffusion factor α (N_2 = molar fraction of benzene, ΔT is the temperature across the cell) in $^{\circ}\text{C}$

$N_2 = 0.1993$		$N_2 = 0.5002$		$N_2 = 0.8009$	
ΔT	α	ΔT	α	ΔT	α
0.274	0.807	0.257	1.52	0.250	2.14
0.275	0.803	0.259	1.48	0.250	2.12
0.277	0.866	0.258	1.49	0.249	2.12
0.276	0.846	0.258	1.49	0.249	2.14
0.436	0.825	0.386	1.49	0.379	2.10
0.438	0.831	0.386	1.47	0.380	2.06
0.438	0.846	0.386	1.46	0.379	2.11
0.436	0.874	0.386	1.48	0.379	2.10
0.594	0.854	0.509	1.50	0.504	2.10
0.593	0.865	0.511	1.47	0.506	2.09
0.592	0.892	0.509	1.47	0.507	2.07
0.593	0.906	0.509	1.49	0.505	2.07
0.733	0.868	0.637	1.45	0.629	2.11
0.733	0.846	0.636	1.45	0.631	2.08
0.734	0.870	0.636	1.46	0.630	2.08
0.731	0.859	0.636	1.45	0.630	2.10
		0.764	1.47	0.756	2.08
		0.764	1.47	0.756	2.08
		0.764	1.46	0.755	2.07
		0.764	1.47	0.754	2.08

interval upon the calculated thermal diffusion factor. Such consistency is good evidence for the soundness of the experimental techniques used.

TABLE 2

Thermal diffusion factors for the n-heptane-benzene system at 25°C

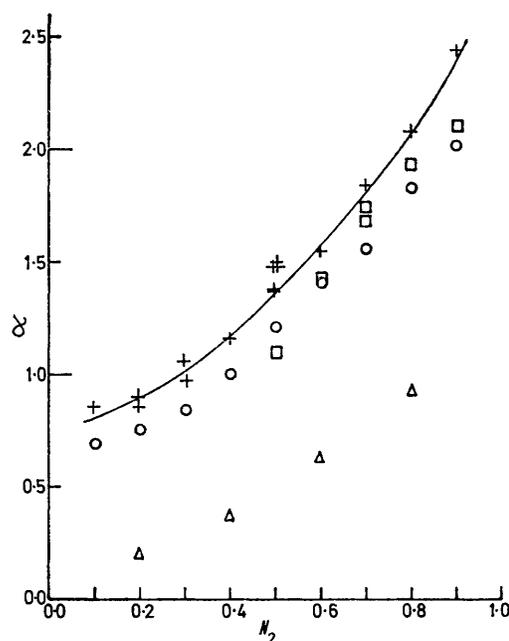
Molar fraction of benzene, N_2	Reference liquid	Mean thermal diffusion factor	Standard deviation
0.1005	n-Heptane	0.855	0.075
0.1993	n-Heptane	0.855	0.063
0.1993	n-Heptane	0.898	0.027
0.3102	n-Heptane	0.971	0.045
0.2980	n-Heptane	1.06	0.045
0.4004	n-Heptane	1.16	0.018
0.4989	Benzene	1.48	0.030
0.5002	Benzene	1.48	0.015
0.5004	n-Heptane	1.50	0.021
0.5004	n-Heptane	1.37	0.018
0.5010	n-Heptane	1.38	0.018
0.5010	n-Heptane	1.51	0.036
0.5992	Benzene	1.55	0.021
0.6990	Benzene	1.84	0.021
0.8009	Benzene	2.08	0.015
0.9023	Benzene	2.44	0.060

Table 2 shows mean thermal diffusion factors calculated by averaging all the experimental values found in each independent experiment. The fourth column shows the standard deviation of this mean. The reference solvent was always the same as the major component in the solution. For equimolar solutions, both benzene and n-heptane were used as reference solvents in independent experiments.

With benzene as the reference liquid, two independent runs on almost equimolar solutions gave identical values of α ($\alpha = 1.48$). These agreed closely with two measurements with n-heptane as the reference, but were ca. 7% higher than the thermal diffusion factors obtained in two other runs, with this reference fluid. The last, ($\alpha = 1.37, 1.38$), in fact, fit better with values found for α at higher and lower benzene concentrations, as can be seen from the

Figure. Deviations of this order between the results of independent experiments on the same solution have been observed before with this technique,³ and may arise from small errors in the calculation of the large contribution of the temperature gradient to the measurement total refractive index gradient. The standard deviations shown in column 4 of Table 2 refer only to thermal diffusion factors calculated from data on a single experiment, and the deviations between results on independent experiments are, almost certainly, larger than these.

These results are compared with values from other sources in the Figure. They are consistently slightly higher than those recently published by Korsching, but the two curves of thermal diffusion factor against solution



Thermal diffusion factors for benzene-n-heptane mixtures (n-heptane concentrates at hot wall)

+ This work, modified cell design ($T_m = 25^{\circ}\text{C}$); \square Preliminary work, original cell design ($T_m = 25^{\circ}\text{C}$); \circ Korsching (ref. 6, $T_m = 35.5^{\circ}\text{C}$); \triangle Bierlein *et al.* (ref. 1, $T_m = 25^{\circ}\text{C}$)

composition run almost parallel. Some measurements obtained by one of us (J. D-P) using a cell of the original Gucci-Tyrrell design for solutions with benzene mole fraction between 0.5 and 0.9 show a slightly different concentration-dependence, but are in moderately good agreement both with Korsching's results and with those in Table 2. The original values of Bierlein, Finch, and Bowers are clearly too low, though they show a rather similar concentration-dependence.

The thermal diffusion factor α , defined by equation (1), is related to the heat of transfer Q_2^* of the benzene in the solution by equations (2) and (3),

$$\alpha = \frac{Q_2^*}{RT \cdot N_1 B_2^N} \quad (2)$$

$$\text{where } B_2^N = \left(1 + \frac{\partial \ln f_2}{\partial \ln N_2} \right) T, P \quad (3)$$

Brown and Ewald⁹ have studied the liquid-vapour equilibria for this system at 60 and 80 °C and have calculated activity coefficients for each component over the whole concentration range at each temperature. Corrections for non-ideality of the gas phase were included. From their values for $\log f_2$ at rounded concentrations the quantity B_2^N was calculated by use of a simple finite difference technique. The values obtained are shown in Table 3.

TABLE 3
Values of the thermodynamic factor B_2^N derived from vapour pressure data⁹

$T = 60\text{ }^\circ\text{C}$		$T = 80\text{ }^\circ\text{C}$	
N_2	B_2^N	N_2	B_2^N
0.0317	0.967	0.0324	1.0003
0.1403	0.958	0.0448	0.931
0.2406	0.940	0.0693	0.994
0.3403	0.882	0.1540	0.962
0.4375	0.858	0.2389	0.929
0.5331	0.794	0.3396	0.927
0.5793	0.795	0.4430	0.869
0.6319	0.798	0.5385	0.816
0.7374	0.786	0.6503	0.837
0.8435	0.842	0.7385	0.813
0.9191	0.893	0.8377	0.914
0.9608	0.920	0.9128	0.906
		0.9609	0.953

There is a small temperature effect, and, in principle, it would be preferable to correct the values at 60 to 25 °C by use of heat of mixing data. In view of the relative crudity of the calculation of B_2^N , this refinement was omitted, and interpolated values of B_2^N derived from the 60 °C data were used to calculate Q_2^*/N_1 from the experimental thermal diffusion coefficients in Table 2. The mean values of Q_2^*/N_1 thus obtained are shown in Table 4.

In this mixture, as in other mixtures of benzene with aliphatic hydrocarbons, the benzene concentrates at the cold wall over the whole concentration range. Qualitatively, this is in agreement with the simple idea that the component with the highest solubility parameter should go to the cold wall, since the solubility parameter¹⁰ for benzene is 9.15 and that for n-heptane is 7.45. In the same way, at any given concentration, the separations observed by Korsching⁶ for the benzene-n-hexane, benzene-n-heptane, and benzene-n-octane mixtures are highest for the first-

named, and lowest for the last-named, mixture, the solubility parameters for n-hexane and n-octane being 7.30 and 7.55 respectively.

The strong variation of both α and Q_2^*/N_1 with concentration for this system contrasts with the results for the

TABLE 4
Values of Q_2^*/N_1 for n-heptane-benzene mixtures (N_2 and Q_2^* are respectively the mole fraction and heat of transfer of benzene)

N_2	Thermal diffusion factor α	B_2^N	$(Q_2^*/N_1)/\text{kJ mol}^{-1}$
0.1005	0.855	0.960	2.03
0.1993	0.876	0.925	2.01
0.3050	1.03	0.870	2.18
0.4004	1.16	0.851	2.37
0.5000	1.45	0.821	2.95
0.5992	1.55	0.803	3.08
0.6990	1.84	0.803	3.64
0.8009	2.08	0.824	4.25
0.9023	2.44	0.870	5.29

benzene-carbon tetrachloride system where benzene enriches at the hot wall, the thermal diffusion factor being almost independent of concentration^{2,11} and having a sign opposite to that expected from the solubility parameter rule. This dependence of α upon concentration appears to be the rule for mixtures of benzene with the saturated hydrocarbons n-hexane,⁶ n-heptane,⁶ n-octane,⁶ n-tetradecane,⁶ and cyclohexane.¹¹ The thermal diffusion factor for all these mixtures (taken as positive when benzene concentrates at the cold wall) increases as the concentration of benzene increases. This is true even for mixtures with cyclohexane where cyclohexane enriches at the cold wall (in disagreement with the solubility parameter rule) except when it is in dilute solution in benzene.¹¹ Story and Turner¹¹ have shown the inadequacies of the available theories of thermal diffusion in connection with their results on the cyclohexane-benzene mixture, and a more detailed discussion of the present results is not possible at the moment.

We thank the S.R.C. for support.

[0/1179 Received, July 10th, 1970]

⁹ I. Brown and A. H. Ewald, *Austral. J. Sci.*, 1958, A, 4, 198.

¹⁰ J. H. Hildebrand and R. L. Scott, 'The Solubility of Non-Electrolytes,' Dover Publications, New York, 1964, Appendix I.

¹¹ M. J. Story and J. C. R. Turner, *Trans. Faraday Soc.*, 1969, 65, 349.