Fluid Phase Equilibria, 36 (1987) 195–205
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

MUTUAL DIFFUSIVITY IN n-HEPTANE + n-HEXANE ISOMERS

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ABSTRACT

A preliminary study of the effect of branching in the binary diffusion of hexane isomer + n-heptane systems is presented. Measurements have been performed with an instrument modeled for the Taylor dispersion technique, at several compositions, at 297 K, for the n-hexane + n-heptane and 2,2-dimethylbutane + n-heptane binary mixtures. The accuracy is estimated to be 1%. The influence of branching is discussed. It was found that the rough hard sphere model for binary diffusion can reproduce the experimental data within 6%. This model was used to predict the binary diffusion coefficients in the 2-methylpentane + n-heptane and 3-methylpentane + n-heptane mixtures, with an estimated accuracy of 5%.

I. INTRODUCTION

In the study of transport properties of binary liquid mixtures considerable effort has been devoted to the coefficient of mutual diffusion, or mutual diffusivity. Either theoretically, experimentally, or for correlation purposes, the subject has been dealt with by several authors in the past, and continues to be a standard research effort. Diffusion coefficients provide fundamental information in a number of engineering applications, and from a fundamental point of view, they are probably the easiest transport coefficients of liquids to derive theoretically.

The transport of mass in binary systems is both influenced by mass effects and by the different molecular energies involved in the process of the motion of a molecule in a potential field caused by both similar and different molecules. In the case of mutual diffusion in mixtures of isomers the mass effects are in principle negligible, if not totally absent.

Some earlier studies of the diffusion of hexane isomers in argon in the gas phase, (Grushka and Schnipelsky, 1976), seem to show that the diffusion coefficients increase with increasing branching, a result also found for the diffusion of octane and heptane isomers (Grushka et al., 1973, 1974), and for pentane and isopentane (Elliot and Watts, 1972). However, for butane and

0378-3812/87/$03.50

isobutane a reverse trend was found (Elliot and Watts, 1972; Wakeham and Slater, 1974).

Because the diffusion process in the liquid state is more complicated than in the gaseous state when considering intermolecular forces, a research program to investigate the effect of branching in the diffusion in binary mixtures of liquid alkanes has been initiated in our laboratory. This effort involves the experimental measurement of these coefficients in several selected binary mixtures and the use of the rough hard sphere model in order to test its validity.

The Taylor dispersion technique (Taylor, 1953; Aris, 1956; Alizadeh et al., 1980; Wakeham, 1981) has now been established as an absolute technique for the measurement of the binary diffusion coefficients in liquid mixtures, and it is capable of producing data with an accuracy on the order of 1%, if the instrument is carefully designed (Nieto de Castro, 1987). This technique has been previously applied in this laboratory to the measurement of mutual diffusivities in mixtures of n-alkanes, and it has been shown to produce data with an accuracy of 1% (Matos Lopes and Nieto de Castro, 1985, 1986).

The rough hard sphere model (Dymond, 1974, 1976; Chandler, 1974) has been applied with success to the description of mass transport in the pure liquids. It was extended to mixtures (Czworniak et al., 1975; Bertucci and Flygare, 1975) with remarkable satisfactory results. The model was applied previously to the mutual diffusion in mixtures of n-alkanes (Matos Lopes and Nieto de Castro, 1985) and to the system water + heavy water (Matos Lopes and Nieto de Castro, 1986), where it was shown that it was capable of reproducing the isotope binary diffusion within 3%. However, for the n-alkane mixtures studied it predicts a weaker composition dependence than found in the experiment.

This paper reports experimental measurements on the diffusion of n-hexane and 2,2-dimethylbutane in n-heptane, as a function of composition and the prediction of the mutual diffusion coefficients for these systems and for 2-methylpentane and 3-methylpentane in n-heptane.

II. TAYLOR DISPERSION TECHNIQUE

The Taylor dispersion technique is based on the dispersion of a pulse of injected material in a laminar flowing stream of different composition, by the joint action of convection and molecular diffusion. The ideal model of the equipment to measure diffusivities using this method consists of an infinitely long straight tube of uniform, circular cross section, radius a_0, through which flows a binary mixture of a fluid with physical properties independent of composition, at a velocity $\bar{u}_0$. A mixture of the same components, but with a slightly different composition, is injected into the tube as a δ-function, at a distance L from the detection point. Under suitable conditions that are fully described elsewhere (Alizadeh et al. 1980), it is possible to calculate the mutual diffusivity D_{12} of the binary mixture from the two first temporal moments of the concentration Gaussian distribution:

$$D_{12} = \frac{a_0^2}{24\bar{t}_{id}} \frac{(1 + 4\Gamma_{id}^2/\bar{t}_{id}^2)^{1/2} + 3}{(1 + 4\Gamma_{id}^2/\bar{t}_{id}^2)^{1/2} + 2\Gamma_{id}^2/\bar{t}_{id}^2 - 1} \left[\frac{1}{2} + \frac{1}{2}(1 - \delta_a)^{1/2}\right] \quad . \qquad (1)$$

In equation (1), $\bar{t}_{id}$ denotes the first raw moment of the distribution, Γ_{id}^2 denotes its second central moment, and

$$\delta_a = 12.7997\ \xi_0 \qquad (2)$$

with

$$\xi_0 = \bar{u}_0\ a_0^2/48\ L\ D_{12} \qquad (3)$$

There are some restrictions to the use of equations (1) to (3) which affect the equipment design (Alizadeh et al., 1980). These constraints have been applied in the design of the instrument used in this work (Matos Lopes and Nieto de Castro, 1985, 1986). Some of the effects arise from the fact that a real instrument nearly always departs from its ideal model. Several of these effects cannot be rendered negligible by a suitable design and must, therefore, be accounted for. Thus, the experimentally measured moments of the concentration distribution must be corrected in order to obtain the ideal moments, to be used in equation (1). The corresponding corrections can be applied in the form:

$$\bar{t}_{id} = \bar{t}_{exp} + \sum \delta t_i \qquad (4)$$

$$\Gamma_{id}^2 = \Gamma_{exp}^2 + \sum \delta\ \Gamma_i^2 \qquad (5)$$

Finally a correction must be added to the flowing composition in order to obtain the reference state of the measurement. If the injected solution is at the same temperature as the flowing mixture and if there is no pressure variation in the injection, then the diffusivity measured must be referred to the equilibrium temperature, the pressure of the flow, and to a composition x_r given by (Alizadeh et al., 1980):

$$x_r = x_f + \delta x \qquad (6)$$

III. EXPERIMENTAL

The mixtures of n-heptane + n-hexane or 2,2-dimetylbutane were prepared gravimetrically from the pure liquids (supplied by Fluka AG). The liquids were distilled under reduced pressure and degassed. Gas chromatography analysis showed that their purity was better than 99.4%. The error in the molar fraction of the mixtures prepared is less than 0.0001. The measurements were made at 297 K.

As was already shown in a previous publication (Matos Lopes and Nieto de Castro, 1985), the time of duration of an experiment is chosen to avoid secondary effects from coiling of the diffusion tube, that enhance molecular diffusion. Times of the order of 4 ks were used in the measurements herein reported. The characteristics of the diffusion tube employed were the same as those used in a previous publication (Matos Lopes and Nieto de Castro, 1986). The analog data obtained with the differential refractometer were amplified and digitized, in order to obtain better precision in the evaluation of the moments. A nonlinear least squares analysis showed that it was possible to fit a Gaussian curve to the digitized data, with a precision of 0.08% in the root mean square deviation, Γ^2, and a precision of 0.002% in the first moment of the distribution, $\bar{t}$. This is a logical consequence of the theory of the method which predicts that the eluted concentration distribution should depart negligibly from a Gaussian distribution. This procedure has been applied previously by other authors (Alizadeh and Wakeham, 1982; Anderson and Berglin, 1981). Figure 1 shows a run for the injection of a mixture with a molar fraction of n-heptane, $x_1 = 0.098$. It can be seen that the Gaussian fit improves the signal significantly, and that the digital signal is much more irregular than a signal normally recorded on a x(t) analog recorder, due to the inevitable integration time required by the recorder. It is estimated that the accuracy of the measurements is better than 1%, a figure already found for the system $H_2O + D_2O$ (Matos Lopes and Nieto de Castro, 1986).

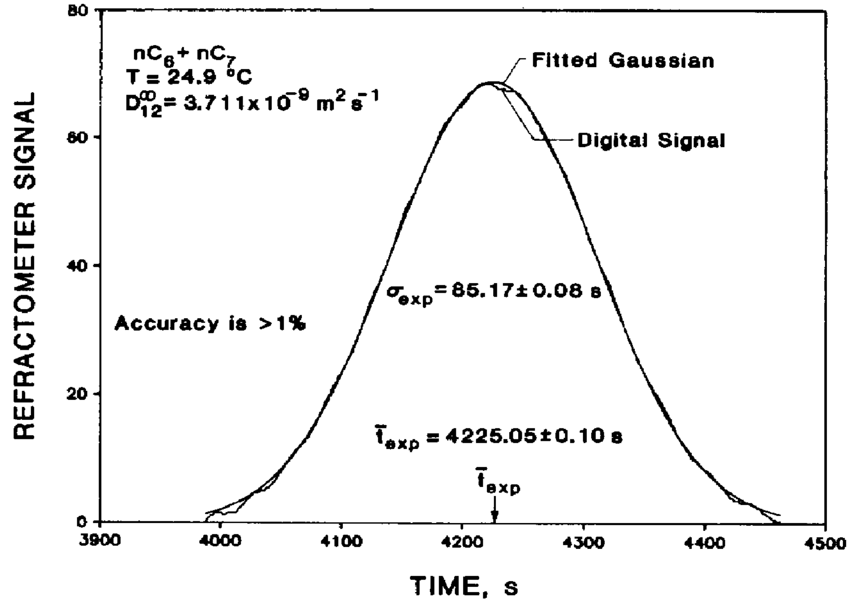

Figure 1. The eluted concentration profile for an infinite dilution test of n-heptane in n-hexane. The digital signal compared with the fitted Gaussian. Estimates of the errors in the measured variables are also shown.

IV. DISCUSSION

Table I displays the results obtained for the infinite dilution of n-heptane in n-hexane at 297.00 K. This result can be compared with results

TABLE I. Infinite dilution data for the diffusion of n-heptane in n-hexane at 297 K.

10^9 D_{12}/m^2s^{-1}	Method	Reference	Accuracy
3.61 ± 0.04	TDM	Alizadeh & Wakeham (1982)	1%
3.72 ± 0.04	MZD	Bidlack et al. (1969)	1%
3.69 ± 0.07	DCT*	Lo (1974)	2%
3.66 ± 0.04	TDM	This work	1%

TDM - Taylor dispersion method; MZD - Mach Zender diffusiometer; DCT* - Diaphragm cell technique, data correlated. All data were corrected to 297 K using $\partial D_{12}/\partial T$ = 4.85×10^{-11} $m^2s^{-1}K^{-1}$ quoted by Alizadeh and Wakeham, 1982.

previously obtained by different investigators (Alizadeh and Wakeham, 1982; Bidlack et al., 1969) and with a correlation developed for n-alkane binary mixtures (Lo, 1974). The data used for comparison were corrected to 297.00 K using the law proposed by Alizadeh and Wakeham (1982) for the temperature dependence of the diffusivity for this system. An agreement of 1.4% is found with Alizadeh and Wakeham's data (1982) and 0.8% with the correlation of Lo (1974). A departure of about 1.6% is found from the data presented by Bidlack et al., 1969, obtained with a Mach-Zender diffusiometer. All sets of data deviate by amounts within the claimed mutual uncertainty. Table II shows the results obtained for the system 2,2-dimethylpentane + n-heptane at 297.00 K, for which no data was found in the literature. The experimental data was obtained for several compositions and the previous discussions seem to support an accuracy of 1%.

TABLE II. Mutual diffusivity in the system 2,2-dimethylbutane + n-heptane at 297 K and atmospheric pressure.

x_r	$10^9\ D_{12}/m^2s^{-1}$
0.0027	3.08 ± 0.03
0.2543	3.15 ± 0.03
0.5018	3.08 ± 0.03
0.7526	2.93 ± 0.03
0.9972	2.75 ± 0.03

A first conclusion to be gained from the data obtained for the diffusion in the system 2,2-dimethylbutane + n-heptane in the liquid state is that the diffusivity is about 15% smaller than the corresponding value for the diffusivity in the system n-hexane + n-heptane, at 297.00 K. This result is totally opposite to the one found for the gas phase diffusion of alkane isomers in argon (Grushka et al., 1973, 1974, 1976; Elliot and Watts, 1972), although a similar trend was found for the diffusion of butane isomers. An analysis of the possible structure of an n-hexane + n-heptane mixture in comparison with the structure of the 2,2-dimethylbutane + n-heptane, based on the values of density, viscosity and molecular arrangement seems to indicate that the diffusion of the branched isomer must be slower and, therefore, its diffusivity smaller. However, further investigation with this system at other temperatures and with other branched isomers of n-hexane is required before any definitive conclusion can be drawn.

The rough hard sphere model, usually designated the van der Waals model, was applied to the mixtures obtained experimentally and to the binaries 2-methylpentane + n-heptane and 3-methylpentane + n-heptane. For all four systems it was possible to obtain the necessary density and viscosity data (Eicher and Zwolinsky, 1972; Vargaftik, 1975). The rough hard sphere model considers the real fluid as being composed of rough hard spheres, with a specific diameter σ (Dymond, 1974, 1975), thus permitting translational-rotational coupling during molecular collisions (Chandler, 1974). Application of this theory to pure fluids yields values of hard core volumes $V_0 = N_0 \sigma^3/\sqrt{2}$, where N_0 is Avogadro's number, as well as the translational-rotational coupling constant for viscosity, B. The procedure followed has been explained previously (Matos Lopes and Nieto de Castro, 1985) and Table III shows the values obtained for σ, V_0 and B for the pure components, together with the corresponding statistical errors, at a 95% level of confidence. The values for the diffusional translational-rotational coupling constant A were obtained previously for n-hexane and n-heptane. No self-diffusion data for the branched hexane isomers was found and, therefore the constant A for these compounds was assumed to be equal to the corresponding linear hexane. It can be seen from Table III that the values for the hard

TABLE III. Rough hard sphere theory volumes and translational-rotational coupling constants for the pure fluids.

Fluid	$10^6 V_0/m^3 mol^{-1}$	$10^8\ \sigma/m$	B	number of points	data from
n-hexane	82.13 ± 0.08	5.78 ± 0.01	1.10 ± 0.02	7	a
	82.11 ± 0.13	5.78 ± 0.01	1.09 ± 0.03	8	b
2-methyl-pentane	82.27 ± 0.15	5.78 ± 0.01	1.08 ± 0.04	7	a
3-methyl-pentane	81.60 ± 0.14	5.77 ± 0.01	1.06 ± 0.03	8	a
2,2-dime-thylbutane	85.25 ± 0.03	5.85 ± 0.00	1.08 ± 0.01	5	a
n-heptane	94.71 ± 0.18	6.06 ± 0.01	1.14 ± 0.04	11	b

a - Eicher and Zwolinsky, 1972
b - Vargaftik, 1975

core volumes for all the hexane isomers are very similar, being about the same, except for 2,2-dimethylbutane. This is probably due to the structure of the molecule, where the existence of a tertiary carbon atom makes the molecule bulkier, increasing therefore the value of the hard core volume and, consequently, the effective hard sphere diameter. This fact would imply an increased difficulty of movement for this molecule and, consequently, explain its lower diffusivity.

The values of the coupling constant B are the same for all n-hexane isomers (average value $B = 1.08 \pm 0.02$), a result that can be considered interesting as the branching could, in principle, influence the translational-rotational interaction in a molecular collision. These results seem to show that the collisional processes that determine viscosity in the liquid hexanes are the same.

The rough hard sphere theory was extended to binary mixtures with the assumption that the kinetic diffusion coefficient, D_{12}^{kin}, of a two-component fluid is equal to that of a two-component mixture of rough hard spheres of masses equal to those of corresponding molecules, with the same temperature, number density and mole fraction of the real fluid (Bertucci and Flygare, 1975; Czworniak et al., 1975). Details of the application of the theory can be found in these last two papers and in the previous work by the authors (Matos Lopes and Nieto de Castro, 1985, 1986).

The experimental diffusion coefficient is related to the kinetic diffusion coefficient D_{12}^{kin} by the relation:

$$D_{12} = D_{12}^{kin} \left(1 + \frac{\partial \ell n\, \gamma_1}{\partial \ell n x_1}\right) \qquad (7)$$

where γ_1 is the activity coefficient of component one. This thermodynamic factor was calculated from an expression developed by van Geet, 1961, for n-alkane mixtures. The value for the mixture n-hexane + n-heptane was found to be less than 1.0005, a direct consequence of the ideality of such a mixture. For the mixtures of the branched hexanes with n-heptane it was assumed that the thermodynamic factor was unity within the accuracy of the theoretical calculations. The densities of the mixtures were calculated assuming the solutions to be ideal.

The values for the translational-rotational coupling constant for diffusion, A, were found previously to be 0.99 and 0.96 for pure n-hexane and pure n-heptane, respectively (Matos Lopes and Nieto de Castro, 1985). Some data obtained at this laboratory for n-hexane + n-heptane mixtures in the intermediate range of composition and the Alizadeh and Wakeham data (1982) suggests that the value of A for this mixture should be A = 0.97, totally in agreement with what we would expect from the values of the pure components. With this value it was possible to reproduce the experimental data for this system within 4%.

For the mixture 2,2-dimethylbutane + n-heptane, the value obtained for A, using the same procedure that was reported previously by the authors (Matos Lopes and Nieto de Castro, 1985, 1986), was found to be A = 0.92. This value reflects the fact that the molecule of 2,2-dimethylbenzene is rougher than the corresponding linear isomer. The comparison between theory and experiment is shown in figure 2 and it can be seen that the theory does not predict the correct composition dependence of D_{12}, at a fixed temperature. The maximum departure is 10.4%, with a root mean square deviation of 5.4%.

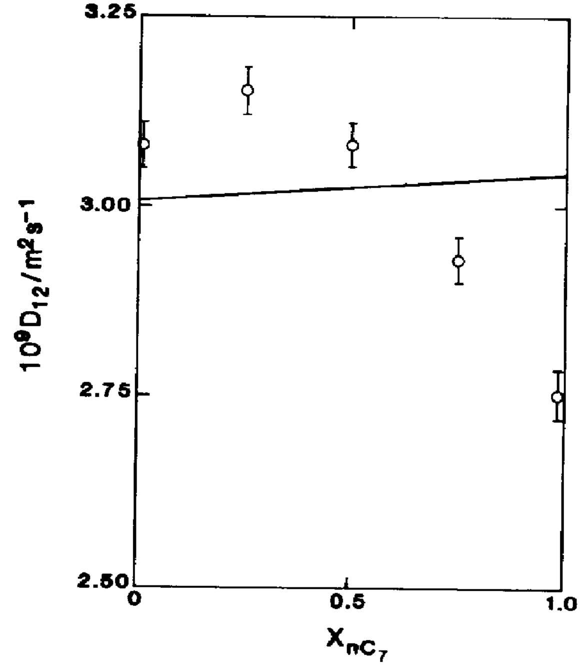

Figure 2. The diffusion coefficient for the 2,2-dimethylbutane + n-heptane system as a function of composition at 297 K.
Φ - experimental points; — rough hard sphere model

In order to predict the binary diffusivity in the systems 2-methylpentane + n-heptane and 3-methylpentane + n-heptane, and in the absence of any experimental information, we have assumed that the value of A for these mixtures is identical to the one found for the n-hexane + n-heptane mixture. This was based on the fact that the viscosity coupling constant was found to be the same for these isomers and n-hexane. Table IV reports the predicted values of the diffusivity in these binary systems, for T = 297 K, as a function of composition. It can be seen that the diffusivity decreases almost linearly with composition and that the infinite dilution diffusion coefficients of 2-methyl and 3-methylpentane in n-heptane are the same. The predicted values have an estimated uncertainty of 5%. A recent study on the predictive capability of existing empirical methods (Matthews et al., 1986) has shown that, even for infinite dilution coefficients, the errors are of that order of magnitude or larger.

TABLE IV. Predicted values of the binary diffusion coefficients for the 2-methylpentane + n-heptane and 3-methylpentane + n-heptane mixtures at 297 K and atmospheric pressure.

	$10^9\ D_{12}/m^2s^{-1}$	
x_{C_7}	2MP + n-C_7	3MP + n-C_7
0.0	3.99	3.61
0.2	3.81	3.52
0.4	3.65	3.45
0.6	3.50	3.38
0.8	3.37	3.32
1.0	3.26	3.27

2MP - 2-methylpentane; 3MP - 3-methylpentane; nC_7 - n-heptane

We hope to report in the near future additional experimental data on these systems, at different temperatures.

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