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# Mutual Diffusion Coefficients in Some Binary Liquid Mixtures

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**The mutual diffusion coefficient $D_{12}$ was measured in $CCl_4$ + $CS_2$, cyclohexane + $CS_2$, toluene + $CS_2$, and pyridine + water mixtures at 20 °C by using the quasi-elastic light scattering technique. The limiting diffusion coefficients at infinite dilution were evaluated. The concentration dependence of the mutual diffusion coefficients is discussed.**

The liquid-phase diffusion coefficients are of importance for the testing of models for the liquid state and for calculating the mass-transfer rates in various heat- and mass-transfer processes. They are also the fundamental parameters in the kinetics of certain reactions; e.g., the reactions of reactive species formed by irradiation are diffusion-controlled. Several attempts have been made to predict the liquid-phase diffusion coefficients at various compositions; however, the numbers obtained are generally much less satisfactory than those measured experimentally.

The use of quasi-elastic light scattering technique for measuring mutual diffusion coefficients has now been well established by the works of Gulari et al. (*1*), Czworniak et al. (*2*), and Krahn et al. (*3*). It is used in this study to measure the mutual diffusion coefficients of $CCl_4$ + $CS_2$, cyclohexane + $CS_2$, toluene + $CS_2$, and pyridine + water systems.

## Experimental Method

The diffusion coefficients in this work were measured by light scattering, as described elsewhere (*3*). For liquid mixtures, for which the thermal diffusion coefficients, $a$, is much greater than the mutual diffusion coefficient, $D_{12}$, the heat- and mass-transfer terms of the scattered electric field can be separated. The concentration fluctuations are the dominant source of scattering. The autocorrelation function, $K$, is described by the decay time, $t_c$, as

$$t_c = 1/(D_{12}K^2) \qquad (1)$$

The theory and the experimental set-up to obtain such an autocorrelation function is described in detail by Krahn et al. (*3*).

Spectroscopic grade (Uvasol, Merck) carbon disulfide, tetrachloromethane, cyclohexane, toluene, and pyridine were used. For the aqueous solutions triply distilled water was used. The mixtures were prepared by weight on a precision balance (Sartorius, Type 2842). The refractive indices were measured with the help of an Abbe refractometer (Zeiss, Type B). A cylindrical Hellmas optical cell, Model 165, with a path length of 5 cm, was used for the measurements. The temperature of the sample in the cell was maintained at 20 ± 0.02 °C with the help of a precision circulating constant temperature bath. The ambient temperature of the laboratory was also held constant at 20 ± 1 °C to avoid thermal convection.

## Results and Discussion

The experimental refractive indices ($n^D$) and diffusion coefficients ($D_{12}$) could be satisfactorily represented by the polynomials

$$n^D = \sum_{i=0}^{i=3} A_i x_1^{\,i} \qquad (2)$$

$$D_{12} \times 10^5/(\mathrm{cm^2\ s^{-1}}) = \sum_{i=0}^{i=3} B_i x_1^{\,i} \qquad (3)$$

**Table I. Constants and Standard Deviation for a Fit of Experimental Refractive Indices to Eq 2 at 20 °C**

| system | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $\sigma(n^D)$ |
|---|---|---|---|---|---|
| tetrachloromethane + carbon disulfide | 1.6270 | -0.3231 | 0.2385 | -0.0843 | 0.0019 |
| cyclohexane + carbon disulfide | 1.6276 | -0.3982 | 0.2872 | -0.0908 | 0.0005 |
| toluene + carbon disulfide | 1.6267 | -0.2851 | 0.2590 | -0.1070 | 0.0014 |
| pyridine + water | 1.3345 | 0.6048 | -0.7965 | 0.3671 | 0.0023 |

**Table II. Constants and Standard Deviation for a Fit of Experimental Mutual Diffusion Coefficients to Eq 3 at 20 °C**

| system | $B_0$ | $B_1$ | $B_2$ | $B_3$ | $\sigma(D_{12})$ |
|---|---|---|---|---|---|
| tetrachloromethane + carbon disulfide | 3.002 | -2.711 | 3.124 | -1.060 | 0.019 |
| cyclohexane + carbon disulfide | 2.850 | -0.742 | 0.079 | 0.392 | 0.010 |
| toluene + carbon disulfide | 2.456 | 1.331 | -5.808 | 4.575 | 0.058 |
| pyridine + water | 0.748 | -3.049 | 6.597 | -2.969 | 0.029 |

where $x_1$ is the mole fraction of the first-named component. Tables I and II list the $A_i$ and $B_i$ coefficients for the systems determined by the method of least squares along with the respective standard deviations. The diffusion data are also plotted in Figures 1-4. For these systems the measurements in the two dilute ranges ($x < 0.1$ and $x > 0.9$) could not be performed, as the amplitude of scattered light became too small. The amplitude of correlation function is a function of $\partial\epsilon/\partial c$ (partial differential of dielectric constant against concentration) and the quadratic mean value of the concentration fluctuations $\langle|\delta c|^2\rangle$. $\partial\epsilon/\partial c$ is dependent on the difference between the refractive indices of the two components. For equimolar solutions $\langle|\delta c|^2\rangle$ is maximum and its value decreases with dilution toward the two ends of the composition range. This limitation does not hold for all types of mixtures but is critical for the mixtures which show small variation of chemical potential with concentration.

The concentration dependence of the mutual diffusion coefficient follows from thermodynamics on the assumption that the driving force for the diffusion is the gradient of the chemical potential.

$$D_{12} = D_f f^{\mathrm{th}} \qquad (4)$$

where $D_f$ is the fundamental diffusion coefficient and $f^{\mathrm{th}}$ is the thermodynamic factor defined as

$$f^{\mathrm{th}} = \frac{\partial \ln a_i}{\partial \ln x_i} \qquad (5)$$

$a_i$ being the activity of component $i$ of the mixture at mole fraction $x_i$.

Generally the fundamental diffusion coefficient $D_f$ is calculated by assuming a linear mixing rule in mole fraction for the two limiting diffusion coefficients:

$$D_f = x_1 D_{21}^{\,0} + x_2 D_{12}^{\,0} \qquad (6)$$

Various authors use the thermodynamic factor $f^{\mathrm{th}}$ with an exponent $s \neq 1$, as well as different expansions for $D_f$ and have proposed a number of correlations for estimating $D_{12}$ from $D_{12}^{\,0}$ and $D_{21}^{\,0}$ (Carman and Stein (*4*), Rathbun and Babb (*5*),

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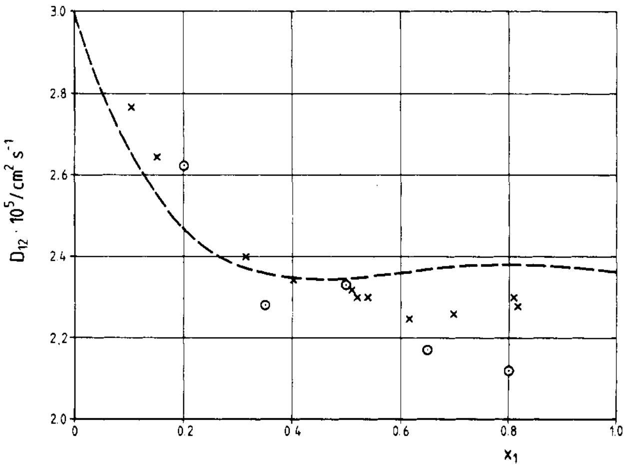

**Figure 1.** Mutual diffusion coefficient for the tetrachloromethane (1) + carbon disulfide (2) system at 20 °C: ×, our experimental results; ⊙, Czworniak et al. (*2*); ---, eq 4.

Vignes (*6*), Gainer (*7*), Leffler and Cullinan (*8*), Kosanovich and Cullinan (*9*), and Cussler (*10*)). They were all tested against the data of this work. The use of an exponent $s \neq 1$ (*5*, *9*, *10*) for the thermodynamic factor $f^{\mathrm{th}}$ gave rather unsystematic results, $s = 1$ being the best for the systems studied here on an average basis. Vignes' equation (*6*) was found to be slightly inferior to eq 4 using the mixing rule given by eq 6. We, therefore, did further analysis by using eq 4 and eq 6.

***Tetrachloromethane* (*1*) + *Carbon Disulfide* (*2*) *System*.** Smooth graphical extrapolation of the experimental data was performed to obtain the diffusivities at infinite dilution, i.e., the limiting diffusion coefficients at the two ends of the composition range $D_{12}{}^0$ and $D_{21}{}^0$. The values are 3.00 × $10^{-5}$ and 2.36 × $10^{-5}$ cm$^2$ s$^{-1}$, respectively. The values predicted by the recent correlation of Hayduk and Minhas (*11*) based on the radius of gyration are 2.49 × $10^{-5}$ and 1.96 × $10^{-5}$ cm$^2$ s$^{-1}$, respectively. The vapor-liquid equilibrium data of Hlavaty (*12*) have been used to calculate the thermodynamic factor, and the mutual diffusion coefficient at various compositions were then calculated according to eq 4–6. As seen from Figure 1 the concentration dependence of mutual diffusion coefficients, $D_{12}$, could be satisfactorily predicted.

Czworniak et al. (*2*) have reported $D_{12}$ for this system at five concentrations at 20 °C. Their values are also shown in Figure 1. The agreement between the two sets is not very good. However, our values of $D_{12}$ show the same trend of variation with composition as the thermodynamic factor.

***Cyclohexane* (*1*) + *Carbon Disulfide* (*2*) *System*.** This is also an apparently simple system with both nonpolar components. The mutual diffusion coefficient data has been extrapolated to obtain 2.85 × $10^{-5}$ and 2.58 × $10^{-5}$ cm$^2$ s$^{-1}$ as the two limiting diffusion coefficients $D_{12}{}^0$ and $D_{21}{}^0$, respectively. The values predicted by the Hayduk and Minhas correlation (*11*) are 2.55 × $10^{-5}$ and 1.95 × $10^{-5}$ cm$^2$ s$^{-1}$, respectively.

From the activity data of Bernatova and Boublik (*13*), the thermodynamic factors were evaluated at different compositions and then used to predict the composition-dependent diffusion coefficients which are shown in Figure 2. It can be seen that the prediction is rather unsatisfactory in this case.

***Toluene* (*1*) + *Carbon Disulfide* (*2*) *System*.** The extrapolated values for the two limiting diffusion coefficients $D_{12}{}^0$ and $D_{21}{}^0$ are 2.50 × $10^{-5}$ and 2.60 × $10^{-5}$ cm$^2$ s$^{-1}$, respectively, which are in reasonable agreement with the predictions of Hayduk and Minhas (*11*) being 2.49 × $10^{-5}$ and 2.95 × $10^{-5}$ cm$^2$ s$^{-1}$, respectively. The concentration dependence of $D_{12}$ for this system is particularly interesting, showing a sharp minimum at 0.77 mole fraction of toluene. However, this minimum coincides with that observed for the thermodynamic factor against concentration calculated by using the vapor–liquid equilibrium data of Schmidt (*14*). For this system again the concentration dependence of mutual diffusion coefficient could be predicted very well by using eq 4 as seen in Figure 3.

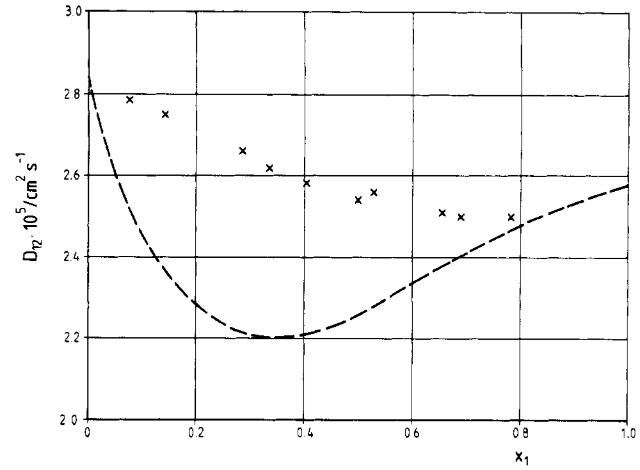

**Figure 2.** Mutual diffusion coefficient for the cyclohexane (1) + carbon disulfide (2) system at 20 °C: ×, our experimental results; ---, eq 4.

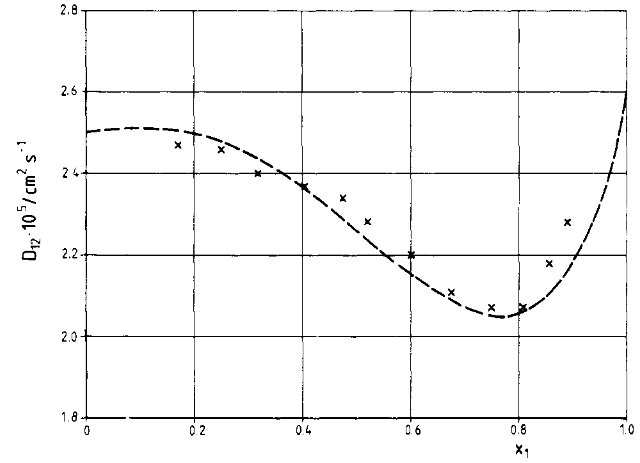

**Figure 3.** Mutual diffusion coefficient for the toluene (1) + carbon disulfide (2) system at 20 °C: ×, our experimental results; ---, eq 4.

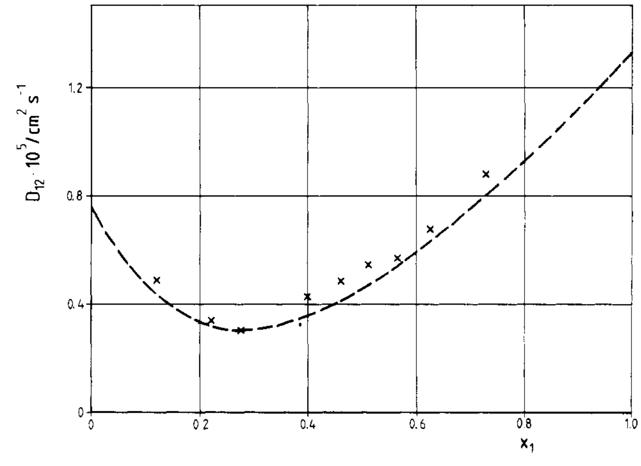

**Figure 4.** Mutual diffusion coefficient for the pyridine (1) + water (2) system at 20 °C: ×, our experimental results; ---, eq 4.

***Pyridine* (*1*) + *Water* (*2*) *System*.** This is a complex forming system. Brun and Salvinien (*15*) have measured the self (tracer)-diffusion coefficients for pyridine and water at 2, 13, 25, and 40 °C in this system. Our extrapolated values of 0.75 × $10^{-5}$ and 1.33 × $10^{-5}$ cm$^2$ s$^{-1}$ for the two limiting diffusion coefficients $D_{12}{}^0$ and $D_{21}{}^0$ at 20 °C agree very well with their values for tracer diffusion coefficient at infinite dilution for pyridine ($0.5 \times 10^{-5}$ cm$^2$ s$^{-1}$ at 13 °C and $0.875 \times 10^{-5}$ cm$^2$ s$^{-1}$ at 25 °C) and water ($1.175 \times 10^{-5}$ cm$^2$ s$^{-1}$ at 13 °C and $1.58 \times 10^{-5}$ cm$^2$ s$^{-1}$ at 25 °C), respectively.

The concentration-dependent $D_{12}$ calculated by using eq 4 and the activity data of Ewerth (*16*) are also shown in Figure 4 and seem to be in relatively good agreement with the experimental values.

## Glossary

| | |
|---|---|
| $a_i$ | activity for component *i* |
| $A_i$ | constants for eq 2 |
| $B_i$ | constants for eq 3 |
| $D_{12}$ | mutual diffusion coefficient, cm$^2$ s$^{-1}$ |
| $D_{12}^0$ | limiting diffusion coefficient for component 1 in component 2, cm$^2$ s$^{-1}$ |
| $D_{21}^0$ | limiting diffusion coefficient for component 2 in component 1, cm$^2$ s$^{-1}$ |
| $D_f$ | fundamental diffusion coefficient, cm$^2$ s$^{-1}$ |
| $f^{th}$ | thermodynamic factor |
| $K$ | autocorrelation function |
| $n^D$ | refractive index |
| $s$ | exponent to thermodynamic factor |
| $t_c$ | decay time |
| $x_i$ | mole fraction of component *i* |
| $\sigma(n^D)$ | standard deviation for refractive indices |
| $\sigma(D_{12})$ | standard deviation for mutual diffusion coefficients, cm$^2$ s$^{-1}$ |

**Registry No.** $CCl_4$, 56-23-5; $CS_2$, 75-15-0; cyclohexane, 110-82-7; toluene, 108-88-3; pyridine, 110-86-1; water, 7732-18-5.

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# Viscosities of Binary Liquid Mixtures

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**Measurements of viscosities for 21 binary mixtures at 25 °C are reported. The results are interpreted in terms of the nature of the interacting species in the mixture. Although viscosity data have been reported for a few systems in the literature, the 21 systems studied in this work were chosen because of the variety of interaction types.**

## Introduction

As part of a general research program (*1*, *2*) to accumulate experimental data on binary liquid mixtures, we now present viscosity data on 21 mixtures comprising of bromoform, carbon tetrachloride, dimethyl sulfoxide, cyclohexane, bromobenzene, dimethylformamide, methyl ethyl ketone, ethyl acetate, methanol, nitromethane, benzene, and *p*-xylene. Viscosities were measured over the entire composition scale at 25 °C, and the results are discussed in terms of the nature of interacting species in the mixture.

## Experimental Section

The solvents used in this study were of reagent grade. All of the solvents were purified by fractionating through a 5-ft. column. Gas chromatography of these solvents did not detect any impurities except cyclohexane wherein the mole percent impurity varied between 0.04 and 0.06. The boiling points and viscosities of the samples finally selected for investigation (shown in Table I) agreed well with the corresponding values quoted in the literature. Particular care was taken in handling the hygroscopic liquids as the slightest traces of water were found to affect the data of pure solvents quite markedly.

Table I. Data for Pure Components at 25 °C

| | boiling point, °C | | | viscosity, kg/m·s | | |
|---|---|---|---|---|---|---|
| solvent | found | lit. | ref | found | lit. | ref |
| benzene | 80.00 | 80.10 | (*4*) | 0.0601 | 0.0599 | (*4*) |
| carbon tetrachloride | 76.2 | 76.75 | (*4*) | 0.0892 | 0.0902 | (*4*) |
| cyclohexane | 80.10 | 80.74 | (*4*) | 0.0883 | 0.0886 | (*4*) |
| bromoform | 149.00 | 149.5 | (*7*) | 0.1873 | 0.1890 | (*7*) |
| methyl ethyl ketone | 79.00 | 79.6 | (*7*) | 0.0475 | 0.0480 | (*5*) |
| dimethyl sulfoxide | 190.00 | 189.85 | (*7*) | 0.2024 | 0.2021 | (*6*) |
| ethyl acetate | 77.10 | 77.26 | (*5*) | 0.0439 | 0.0424 | (*8*) |
| methanol | 64.20 | 65.15 | (*7*) | 0.0590 | 0.0547 | (*7*) |
| nitromethane | 100.2 | 100.8 | (*7*) | 0.0627 | 0.0620 | (*7*) |
| dimethylformamide | 152.80 | 153.00 | (*7*) | 0.0805 | 0.0800 | (*9*) |
| bromobenzene | 155.90 | 156.05 | (*5*) | 0.1081 | 0.1040 | (*9*) |
| *p*-xylene | 137.50 | 138.00 | (*9*) | 0.0615 | 0.0600 | (*9*) |

Solvent mixtures were prepared for several compositions. Mixtures were made by weighing an appropriate volume of each solvent. To minimize the preferential evaporation of one of the solvents in the mixture we used special airtight bottles. When once these mixtures were prepared, all the measurements were done on the same day. However, keeping the mixtures overnight and remeasuring them on the following day indicated an error of 0.5–1.5% in viscosity.

The viscosities were measured at 25 °C with an Ostwald viscometer by comparing the flow times of pure liquid or the

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