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Self-Diffusion Coefficients of Carbon Tetrachloride and Cyclohexane in the Carbon Tetrachloride-Cyclohexane System

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The carbon tetrachloride-cyclohexane system shows relatively small compositional dependence of density,[1] viscosity, and interdiffusion coefficient[2,3] compared with other organic binary systems. Equilibrium vapour pressures[1,4] determined indicate a high thermodynamical ideality of this binary system.[2] This suggests that the self-diffusion coefficients of both components also show small and simple compositional dependence. This was confirmed by determining the self-diffusion coefficients of both components for the whole composition range of the system by a capillary-cell technique.

Experimental

An apparatus with a cell of 8 cm diameter, a capillary of 0.8 mm I.D. and 40 mm length, and a stirrer similar to Wang's[5] was used. All determinations were made at 25± 0.02°C. The carbon tetrachloride and cyclohexane used were of spectrum analysis reagent grade. A sample solution having a certain composition in the cell was adjusted to a radioactivity of about 0.06 μCi/cc with the ^{14}C-labelled CCl_4 or C_6H_{12}. The capillary filled with an unlabelled solution of the same chemical composition was dipped in the cell solution to a depth of 5 mm. The velocity of the stirrer was 30 rpm. The diffusion time of 20—25 hr was so scheduled as to result in the diffusion of an amount corresponding to about one third of the final uptake. After the diffusion run the radioactivities of the solutions in the capillary and the cell were determined in toluene solutions of 2,5-diphenyloxazole and *p*-bis-[2-(5-phenyloxazolyl)]-benzene with a liquid scintillation counter. In scintillation counting, difference in the concentration of sample in scintillator solution generally causes a different degree of quenching effect on counting. A correction was made in calculating the concentration of tracer so as to give different sample solutions an equal counting efficiency. Equation (1) gives the ratio of amounts diffusing at time t and infinite time under the above boundary conditions.[6]

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \cdot \exp(-Dq_n^2 t/l^2) \qquad (1)$$

$$\tan q_n = -\alpha q_n \qquad (2)$$

where M_t and M_∞ are the amounts diffusing at time t and infinite time, α the ratio of volumes of solutions in the capillary and in the cell, l the length of the capillary, and D the diffusion coefficient which is to be determined. q_n in Eq. (1), not being zero, is the solution of Eq. (2).

Results and Discussion

Figure 1 shows both the self-diffusion coefficients of carbon tetrachloride, $D(CCl_4)$ and cyclohexane, $D(C_6H_{12})$ determined at 25°C, and the reported viscosity, η[2] as a function of mole fraction of CCl_4,

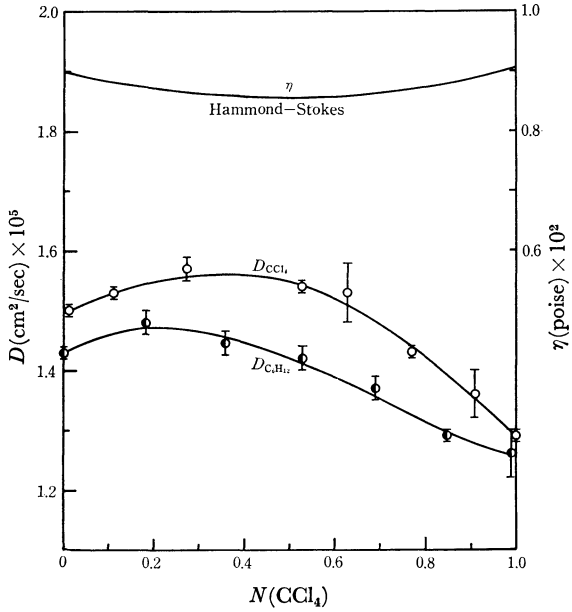

Fig. 1. Self-diffusion coefficients and viscosity as a function of composition for the CCl_4–C_6H_{12} system at 25°C.

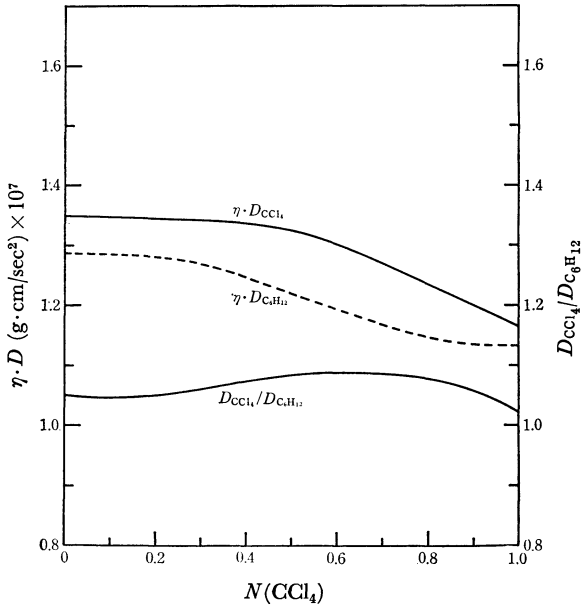

Fig. 2. The ratio of self-diffusion coefficients and the products of self-diffusion coefficients and viscosity as a function of composition for the CCl_4–C_6H_{12} system.

1) G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Amer. Chem. Soc.*, **61**, 3206 (1939).
2) B. R. Hammond and R. H. Stokes, *Trans. Faraday Soc.*, **52**, 781 (1956).
3) M. V. Kulkarni, G. F. Allen, and P. A. Lyons, *J. Phys. Chem.*, **69**, 2491 (1965).
4) I. Brown and A. H. Ewald, *Aust. J. Phys.*, **3**, 306 (1950).
5) J. H. Wang, *J. Amer. Chem. Soc.*, **73**, 510 (1951).
6) J. Crank, "The Mathematics of Diffusion," Clarendon Press, Oxford (1956), p. 53.

$N(CCl_4)$. All are the averaged values of more than four determinations. Both self-diffusion coefficients show similar, relatively small compositional dependence as predicted. The compositional dependence is in reverse trend to that for the viscosity as seen in Fig. 1. Figure 2 shows the ratio of $D(CCl_4)$ and $D(C_6H_{12})$ and the products of viscosity and respective self-diffusion coefficients as a function of composition. The compositional dependence of the ratio $D(CCl_4)/D(C_6H_{12})$ is small compared with many other organic binary systerms. The ratio is close to that of molar volumes for pure cyclohexane and pure carbon tetrachloride: $V(C_6H_{12})/V(CCl_4)=1.12$, which means that Bearman's relation[7] holds. Compositional dependence of $\eta \cdot D(CCl_4)$ and $\eta \cdot D(C_6H_{12})$ is also small compared with water-acetone[8] and many other organic binary systems. The results together with the small compositional dependence of density, viscosity, and equilibrium vapour pressure[1,4] indicate the thermodynamical ideality of the system. In consequence, molecular association will be negligible and the diffusing species for both components will be essentially single molecules in the carbon tetrachloride-cyclohexane system at 25°C.

7) R. J. Bearman, *J. Chem. Phys.*, **32**, 1308 (1960).
8) Y. Kamei and Y. Oishi, *Nippon Kagaku Zasshi*, **91**, 403 (1970).