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Self-Diffusion Coefficients and Interdiffusion Coefficient in Acetone-Benzene System

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Self-diffusion coefficients of acetone and benzene have been determined in the whole composition range of the binary system at 25°C by a capillary-cell method using the ^{14}C-marked tracer. The results were in a good agreement with those determined by the NMR spin-echo method by McCall and Douglass. The products of the respective self-diffusion coefficients and the viscosity of this system showed a relatively constant compositional dependence. Bearman's relation was shown to hold between the self-diffusion coefficients and the partial molar volumes for the system. The validity of Darken's equation was confirmed for the self-diffusion coefficients and the interdiffusion coefficient of the system.

The relationship between the self-diffusion coefficients of the components and the interdiffusion coefficient for a binary system has been described by Darken[1] and by Hartley and Crank[2] as Eq. (1):

$$D_{12} = (N_1D_2^* + N_2D_1^*)\ (\mathrm{d}\ln a_1/\mathrm{d}\ln N_1) \qquad (1)$$

where D_{12} is the interdiffusion coefficient, D^* the self-diffusion coefficient, N the mole fraction, a the activity, and the subscript i refers to component i. In the present work, the self-diffusion coefficients of both components were determined for the whole composition range of the acetone–benzene system to test the validity of Eq. (1) for this system by comparing the interdiffusion coefficient experimentally determined and that theoretically calculated with Eq. (1).

Experimental

The capillary-cell method was used for determining self-diffudion coefficients. The employed apparatus and technique have been described elsewhere.[3] All the determinations were made at 25±0.02°C. The acetone and benzene used were of spectrum analysis reagent grade. The radioactivity of the tracer in the sample solution in the capillary was adjusted so as to be about 0.06 μCi/cc with ^{14}C-labelled $(CH_3)_2CO$ or C_6H_6. The radioactivity of the tracer was determined in a toluene solution of 2,5-diphenyloxazole with a liquid scintillation counter.

Results

Figure 1 shows the self-diffusion coefficients of acetone, $D^*((CH_3)_2CO)$ and benzene, $D^*(C_6H_6)$ determined at 25°C as a function of mole fraction of acetone.

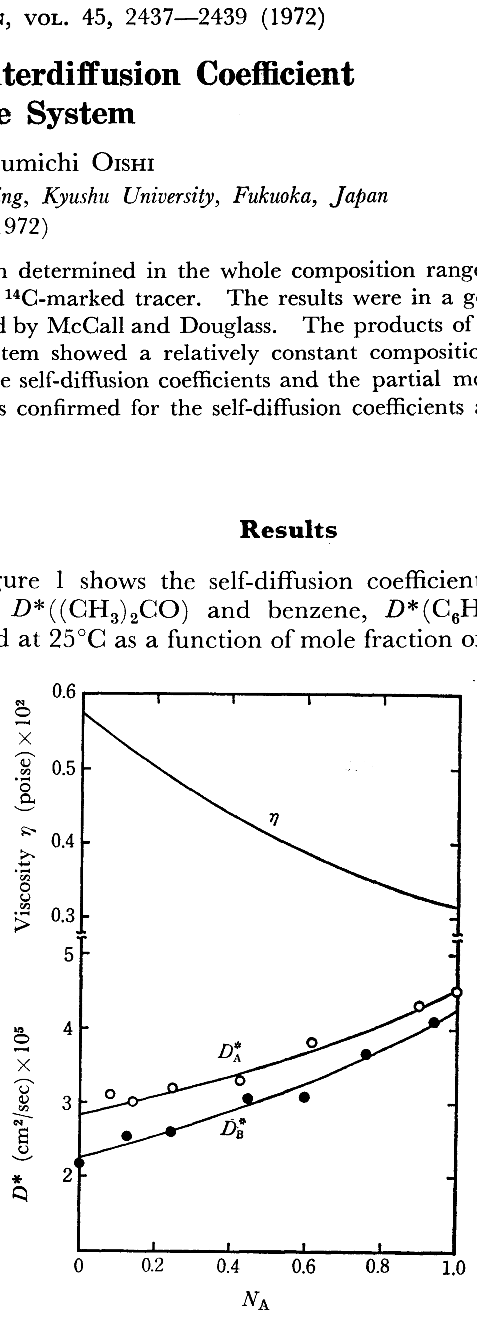

Fig. 1. Self-diffusion coefficients and viscosity for acetone-benzene system as a function of mole fraction of acetone at 25°C. D_A^* and D_B^* are self-diffusion coefficients of acetone and benzene. η is viscosity.

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[1] L. S. Darken, *Trans. Amer. Isnt. Min. Met. Ent.*, **175**, 184 (1948).

[2] G. S. Hartley and J. Crank, *Trans. Faraday Soc.*, **45**, 801 (1949).

[3] A. Nishi, Y. Kamei, and Y. Oishi, This Bulletin, **44**, 2855 (1971).

All are the averaged values of more than three determinations. The self-diffusion coefficients of pure acetone[4] and benzene[5-9] were taken from the literatures. Both self-diffusion coefficients show similar and relatively linear compositional dependence.

Discussion

(1) *Comparison of the Results with Those by NMR Spin-Echo Method.* Self-diffudion coefficients of both components for the acetone–benzene system have been determined by McCall and Douglass using the NMR spin-echo method.[10] They confirmed the accuracy of their method by comparing their results with Mills data determined by a diaphragm-cell method for the benzene–cyclohexane system.[11] For the acetone–chloroform system, the results by McCall *et al.* and those by Hardt *et al.* by a capillary-cell method[12] are in a good agreement only for the self-diffusion coefficients of acetone, but show a large discrepancy of about 18% for chloroform. For the acetone–benzene system, however, our results by the capillary-cell method are in good agreement with McCall and Douglass's results by the NMR spin-echo method for both components.

(2) *Products of Self-Diffusion Coefficient and Viscosity.* The compositional dependence of both self-diffusion coefficients and that of the viscosity, η[13] are in reverse trends as seen in Fig. 1. Figure 2 shows the products of the viscosity and the respective self-diffusion coefficients as a function of composition where $\eta\cdot D^*((CH_3)_2CO)$ and $\eta\cdot D^*(C_6H_6)$ remain constant for the whole composition range of the system. The similar results have been showed previously for the carbon tetrachloride–cyclohexane[3] and acetone–water[4] systems.

(3) *Bearman's Relation.* The relationship between the self-diffusion coefficients and the partial molar volumes for a binary regular solution has been described by Bearman[14] as Eq. (2):

$$D_1^*/D_2^* = \overline{V}_2/\overline{V}_1 \qquad (2)$$

where $\overline{V}_1$ and $\overline{V}_2$ are the partial molar volumes of components 1 and 2, respectively. $D^*((CH_3)_2CO)/D^*(C_6H_6)$ is shown as a function of compositon in Fig. 2. $\overline{V}(C_6H_6)/\overline{V}((CH_3)_2CO)$ ranges within 1.19 to 1.24 for the whole composition range of the system and in a good agreement with $D^*((CH_3)_2CO)/D^*(C_6H_6)$ shown in Fig.2. This means that Bearman's relation holds for this system.

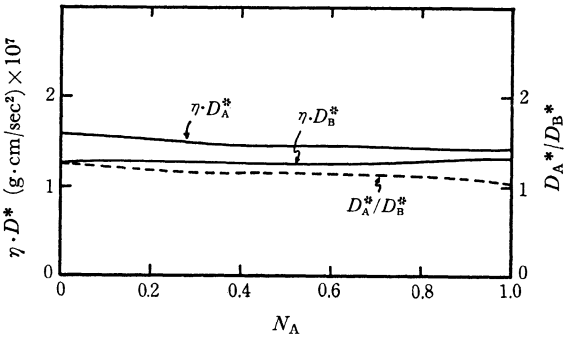

Fig. 2. Compositional dependence of $\eta\cdot D_A^*$, $\eta\cdot D_B^*$, and D_A^*/D_B^*.

(4) *Darken's Equation.* The theoretical interdiffusion coefficient calculated by Eq. (1) is compared with those determined experimentally by Anderson, Hall, and Babb[15] and by Cullinan and Toor[16] in Fig.3 as a function of mole fraction of acetone. The ther-

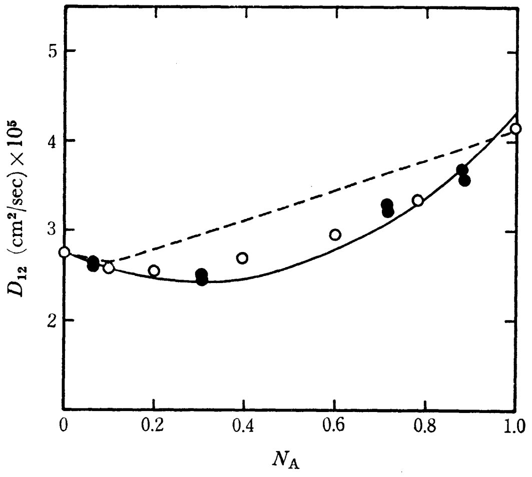

Fig. 3. Comparison of theoretical and experimental interdiffusion coefficients for acetone-benzene system at 25°C.

—— theoretical, present work
- - - theoretical, McCall and Douglass (Ref. 10)
○ experimental, Anderson et al (Ref. 15)
● experimental, Cullinan and Toor (Ref. 16)

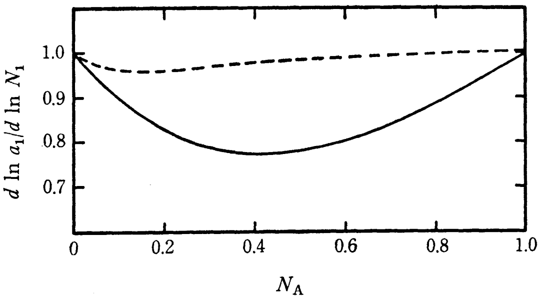

Fig. 4. Thermodynamic factor for acetone-benzene system as a function of acetone mole fraction.

—— present work
- - - McCall and Douglass (Ref. 10)

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15) D. K. Anderson, J. R. Hall, and A. L. Babb, *J. Phys. Chem.*, **62**, 404 (1958).

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modynamic factor for the system necessary for the calculation was estimated from the excess free energy calculated from equilibrium vapour pressure at 45°C determined by Brown and Smith[17] and shown in Fig.4. The theoretical and experimental interdiffusion coefficients are in a good agreement within ±6%. This confirms the validity of Darken's equation for the acetone–benzene system. A similar comparison of the theoretical and experimental interdiffusion coefficients has been made by McCall and Douglass.[10] Their results, however, showed a fairly large discrepancy between the experimental and theoretical values as shown together in Fig.3. As described already, the self-diffusion coefficients of the respective components determined by them are close to our determinations. The cause of their discrepancy is in their thermodynamic factors, shown in Fig.4, which they estimated from the vapour-liquid equilibrium at boiling points for varied compositions.[18]

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