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The Diffusion of Gases at High Pressures. IV. The Diffusion of CTH_3 in the CH_4-CO_2 System

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The diffusion coefficients of radioactive methane (CTH_3) in normal methane, in carbon dioxide, and in a mixture of normal methane with carbon dioxide (0.522 mol fraction of methane) were measured at the temperatures of 25, 50, and 75°C in the 15—250 atm pressure range. The measurements were made through a plug of porous bronze in the diffusion cell, using the radioactive tracer technique. The diffusion coefficient-density products, $D\rho$, for the CTH_3–normal methane system and the CTH_3– the binary mixture system increased slightly with an increase in the density in the lower-density region at 25 and 50°C, but they were nearly constant at 75°C. The $D\rho$ for the CTH_3–carbon dioxide system decreased with an increase in the density at each temperature. The $D\rho$-values at 1 atm, obtained by extrapolation, agreed fairly well with those reported in the literature. The density dependence of the $D\rho$ values at high densities could not be predicted by Enskog-Thorne's theory.

Although the diffusion coefficients of gases at high pressures have been reported by several investigators since 1950,[1] the relative scarcity of high-pressure diffusion data suggests a need for additional measurements in order to evaluate the various theoretical relations[2] and the generalized chart[3] available for the prediction of the transport properties of dense gases. In the present investigation, the diffusion coefficients of radioactive methane (CTH_3) in methane, in carbon dioxide, and in a mixture of normal methane with carbon dioxide (0.522 mole fraction of methane) were measured at the temperatures of 25, 50, and 75°C in the 15—250 atm pressure range, and the depencence on the pressure, the temperature, and the composition was studied.

Experimental

The apparatus and the experimental procedure were the same as those described previously.[4] The diffusion path in the cell was a porous bronze plug with a grain size of 60—70 μ. Radioactive methane, obtained from New England Nuclear Corp., was diluted with non-radioactive methane to a specific activity of about 20 μCi per m*l* at NTP. The purities of the carbon dioxide and non-radioactive methane used in this investigation were 99.9 and 99.6% respectively. The mixture of carbon dioxide with non-radioactive methane was prepared in a storage cylinder. The exact composition (0.522 mol fraction of methane) was determined by absorbing carbon dioxide from the sample into a potassium hydroxide solution. Under the conditions studied, the mixture is not in a liquid state.[5]

The proportionality betweeen the concentration of radioactive methane and the ionization current, essential for a quantitative treatment of the diffusion data, was confirmed experimentally for pure methane, carbon dioxide, and the mixture at a constant temperature and pressure. As examples, the results at 50°C are shown in Fig. 1.

Results and Discussion

The experimental results are given in Table 1. *D* is

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1) Z. Balenovic, M. N. Myers, and J. C. Giddings, *J. Chem. Phys.*, **52**, 915 (1970).

2) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley & Sons, Inc., New York (1954), Chap. 9.

3) J. C. Slattery and R. B. Bird, *A. I. Ch. E. Journal*, **4**, 137 (1958), A. N. Berezhnoi and A. G. Usmanov, *Teor. Osn. Khim. Tekhnol.*, **2**, 820 (1968).

4) S. Takahashi and H. Iwasaki, This Bulletin, **39**, 2105 (1966), S. Takahashi, *ibid.*, **41**, 1573 (1968).

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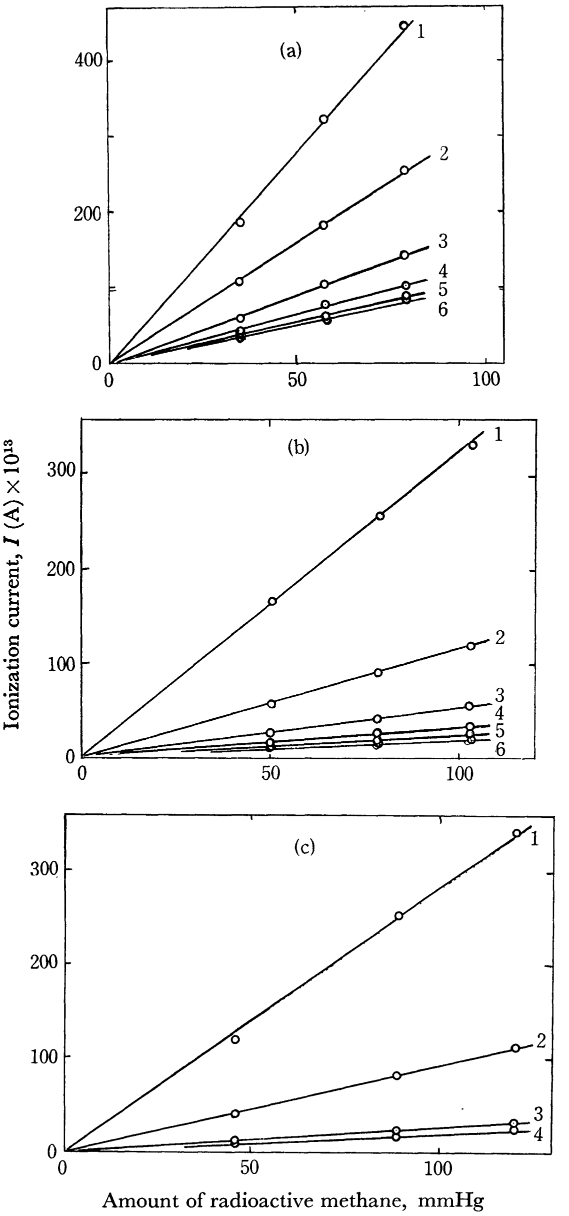

Fig. 1. Relations between the amount of radioactive methane and the ionization current at 50°C.
Composition, (a): $x_3=1.000$, (b): $x_3=0.522$, (c): $x_3=0.000$. Pressure, 1: 14.55 atm, 2: 49.4 atm, 3: 97.8 atm, 4: 146.2 atm, 5: 194.6 atm, 6: 243.0 atm

the diffusion coefficient of radioactive methane in the CH_4–CO_2 system. The densities of the gases, ρ (mol/*l*), were calculated from the compressibility data given by Kvalnes and Gaddy for methane,⁶⁾ by Michels and Michels for carbon dioxide,⁷⁾ and by Reamer *et al.* for the mixture.⁸⁾

The diffusion coefficient-density products, $D\rho$, are plotted against the density in Fig. 2. The open circles refer to the values obtained in the present experiment. Curves have been drawn through the experimental points for the three systems where the mole fractions of methane, x_3, are 1.000, 0.522, and 0.000. The D at $x_3=1.000$ is the diffusion coefficient of radioactive methane with normal methane, D_{13}, where the 1 and 3 subscripts denote radioactive methane and normal methane respectively. The $D_{13}\rho$ increases slightly with an increase in the density in the lower-density regions to 5 mol/*l*, and decreases slightly in the higher-density regions. Extrapolations of $D_{13}\rho$ *vs.* ρ curves to 1 atm provide a basis for comparison with published low-pressure experimental results. Applying the mass correction⁹⁾ to the self-diffusion coefficient of normal methane, D_{33}, reported by Winn,¹⁰⁾ the diffusion coefficient of radioactive methane with mormal methane, D_{13}, was obtained; the values of $D_{13}\rho$ thus calculated are denoted by darkened triangles in Fig. 2. As can be seen from Fig. 2, the values reported by Winn yield values which are in agreement with those extrapolated in this investigation. The D at $x_3=0.000$ is the diffusion coefficient of radioactive methane with carbon dioxide, D_{12}, where the 2 subscript denotes carbon dioxide. The $D_{12}\rho$ decreases with an increase in the density at each temperature. Applying the mass correction to the diffusion coefficient of normal methane with carbon dioxide, D_{23}, calculated by the empirical formula,¹¹⁾ the diffusion coefficient of radioactive methane with carbon dioxide, D_{12}, at 1 atm was obtained; the values of $D_{12}\rho$ at 1 atm are denoted by darkened circles in Fig. 2. The empirical formula yields values which agree with those extrapolated. The $D\rho$ at $x_3=0.522$ increases slightly with an increase in the density in the lower-density regions to 5 mol/*l*, decreases in the higher-density regions at 25 and 50°C, and is nearly constant at 75°C. The diffusion coefficient of the trace of radioactive methane in the mixture, D, at 1 atm may be calculated using the following equation:

$$1/D=x_2/D_{12}+x_3/D_{13} \qquad (1)$$

where x_2 and x_3 are the mole fractions of carbon dioxide and non-radioactive methane respectively, and where $x_2+x_3=1$. The calculated values of $D\rho$ at 1 atm are shown by darkened squares in Fig. 2. As Fig. 2 shows, Eq. (1) yields values which are about 7% lower than those extrapolated at 25 and 50°C, and 4% lower at 75°C.

The D_{23}(CH_4 trace) and the D_{23}(CO_2 trace) were obtained by applying the mass correction to the diffusion coefficient of the trace of radioactive methane with normal carbon dioxide measured in the present investigation, and to the diffusion coefficient of the trace of radioactive carbon dioxide with normal methane reported in the previous paper, respectively. They are shown by open circles and open triangles in Fig. 3. The extrapolation of the $D_{23}\rho$(CH_4 trace) *vs.* ρ curves to 1 atm yields values which agree with those obtained by the extrapolation of the D_{23}(CO_2 trace) *vs.* ρ curves to 1 atm. This means that the values of D_{23} in such

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6) H. M. Kvalnes and V. L. Gaddy, *J. Amer. Chem. Soc.*, **53**, 394 (1931).

7) A. Michels and C. Michels, *Proc. Roy. Soc.* (London), **153A**, 201, 214 (1935).

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9) F. Hutchinson, *J. Chem. Phys.*, **17**, 1081 (1949).

10) E. B. Winn, *Phys. Rev.*, **80**, 1024 (1950).

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12) C. R. Wilke, *Chem. Eng. Progress*, **46**, 95 (1950).

Table 1. Experimental results

P atm	ρ mol/l	$D\times10^3$ cm^2/sec	$D\rho\times10^3$ cm$^2\cdot$mol/sec$\cdot l$
	25°C		
	$x_3=1.000$		
14.41	0.6035	16.5	9.96
24.7	1.0528	9.41	9.91
50.2	2.2330	4.58	10.23
66.0	2.9633	3.46	10.25
103.2	4.9583	2.03	10.07
151.5	7.5404	1.39	10.48
175.9	8.7597	1.12	9.81
211.7	10.3564	0.970	10.01
	$x_3=0.522$		
14.41	0.6095	14.7	8.96
14.41	0.6095	14.2	8.65
14.41	0.6095	14.4	8.78
45.5	2.1477	4.32	9.28
49.9	2.3921	3.77	9.02
99.0	5.7532	1.56	8.97
101.1	5.9300	1.58	9.37
149.3	10.065	0.833	8.38
149.3	10.065	0.843	8.48
149.3	10.065	0.878	8.83
153.1	10.355	0.814	8.42
	$x_3=0.000$		
14.41	0.6342	11.3	7.17
36.5	1.8957	3.69	6.99
36.6	1.9031	3.61	6.87
46.7	2.7235	2.41	6.56
49.3	2.9824	2.26	6.74
	50°C		
	$x_3=1.000$		
14.38	0.5513	18.2	10.04
14.44	0.5635	18.8	10.41
51.1	2.0485	4.95	10.14
51.3	2.0571	5.05	10.39
103.3	4.4615	2.40	10.71
151.2	6.5020	1.66	10.79
201.5	8.6069	1.26	10.84
252.3	10.4255	1.01	10.53
	$x_3=0.522$		
14.41	0.5619	16.5	9.27
49.0	2.0743	4.45	9.23
81.2	3.7225	2.44	9.08
104.1	5.0581	1.85	9.36
124.2	6.2859	1.42	8.93
161.2	8.5234	1.03	8.78
199.4	10.6192	0.813	8.63
	$x_3=0.000$		
14.33	0.5698	12.5	7.12
14.41	0.5731	12.4	7.11
50.0	2.4112	3.06	7.38
50.3	2.4332	2.99	7.28
60.0	3.1127	2.25	7.00
76.2	4.6343	1.50	6.95
82.5	5.4483	1.26	6.86
92.9	7.2333	0.935	6.76
102.2	9.6988	0.620	6.50
	75°C		
	$x_3=1.000$		
14.41	0.5101	21.3	10.87
50.1	1.8285	5.97	10.92
103.0	3.8844	2.85	11.07
105.0	3.9636	2.73	10.82
153.1	5.8456	1.93	11.28
202.3	7.6886	1.44	11.07
243.5	9.0358	1.21	10.93
250.0	9.2394	1.17	10.81
	$x_3=0.522$		
15.30	0.5499	17.0	9.35
15.38	0.5528	17.1	9.45
50.4	1.9241	5.09	9.79
50.5	1.9283	5.04	9.72
69.2	2.7299	3.53	9.64
100.9	4.1901	2.23	9.34
133.8	5.7908	1.65	9.55
173.9	7.7407	1.24	9.60
233.8	10.3740	0.892	9.25
	$x_3=0.000$		
14.41	0.5249	14.9	7.82
14.41	0.5249	14.6	7.66
50.0	2.0675	3.65	7.55
51.0	2.1279	3.63	7.72
72.3	3.3323	2.22	7.40
72.5	3.3460	2.19	7.33
104.8	5.8402	1.28	7.48
123.3	7.7370	0.910	7.04
129.2	8.4064	0.837	7.04
155.3	11.1898	0.633	7.08

limiting cases as when $x_2\to0$ and $x_3\to0$ are identical at 1 atm. Similar results were reported by Walker and Westenberg.[13] for the CO_2—N_2 system. Although the $D_{23}\rho$(CH_4 trace) decreases with an increase in the density at each temperature, the $D_{23}\rho$(CO_2 trace) is nearly constant, and the difference between them become larger with an increase in the density. This means that the D_{23} is dependent on the composition at high densities.

According to Enskog-Thorne's theory, which is the only theoretical treatment offering any practical application, the binary diffusion coefficient is given by the following equation:

$$D_{ij}\rho=(D_{ij})^0\rho/\chi_{ij} \tag{2}$$

where $(D_{ij})^0$ is the binary diffusion coefficient calculated on the basis of the low-density kinetic theory as follows:

$$(D_{ij})^0=\frac{3}{16n\sigma_{ij}^2\,\Omega_{ij}^{(1,1)*}}\left(\frac{2kT}{\pi\mu}\right)^{\frac{1}{2}} \tag{3}$$

where n is the number density of the molecules (cm^{-3}); σ_{ij}, the collision diameter (cm); $\Omega_{ij}^{(1,1)}$,* the reduced

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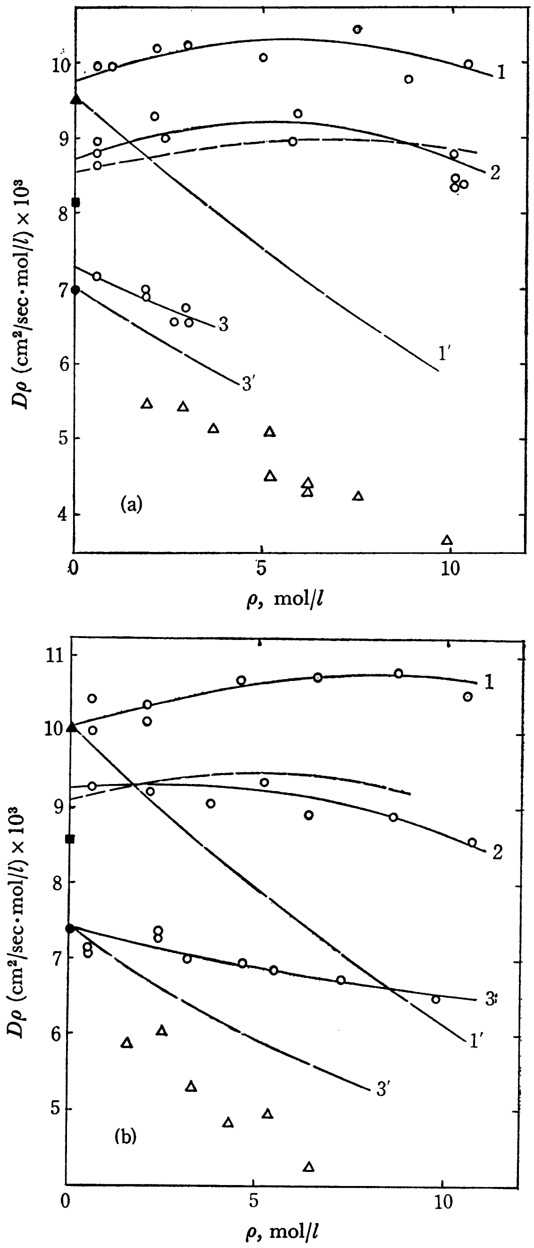
[13] R. E. Walker and A. A. Westenberg, *J. Chem. Phys.*, **29**, 1139 (1958).

collision integral; k, the Boltzmann constant; T, the absolute temperature (°K), and μ, the reduced mass. χ_{ij} is a correction factor which is given for a two-component gas by the following series:

$$\chi_{ij}=1+0.2618n_i\sigma_i^3(8-3\sigma_i/\sigma_{ij}) \\ +0.2618n_j\sigma_j^3(8-3\sigma_j/\sigma_{ij})+\cdots \qquad (4)$$

where n_i and n_j are the number densities of the i and j species (cm^{-3}); σ_i and σ_j, the collision diameters of the i and j species between like molecules (cm), and σ_{ij} is that between unlike molecules, which may be obtained from the empirical combining law: $\sigma_{ij}=(\sigma_i+\sigma_j)/2$, and hence $\sigma_1=(\sigma_1+\sigma_j)/2\fallingdotseq(\sigma_3+\sigma_j)/2$, $(j=2,3)$. The collision diameters, $\sigma_2=3.996$ Å and $\sigma_3=3.882$ Å, were taken from Ref. 2. They are those determined from the viscosity measurement for the Lennard-Jones model. Since the 1 species is present only as a trace in this investigation, the second term on the right hand of Eq. (4) may be neglected. As the $(D_{1j})^0\rho$ quantity is constant at a constant temperature and is independent of the density, the extrapolated values of the $D_{1j}\rho$ to 1 atm were used in place of the $(D_{1j})^0\ \rho$. As is shown in Fig. 2, the theoretical values of both the $D_{12}\rho$ and the $D_{13}\rho$ decrease with an imcrease in the density and are about 20—26% lower than those obtained in the present work at $\rho=5$ mol/l.

The diffusion coefficient of a trace amount of CTH_3 in methane, D_{13}, measured at high pressures using a



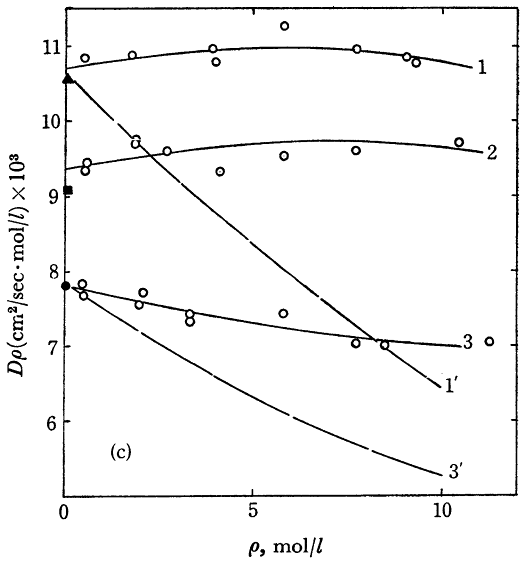


Fig. 2. Variation of $D\rho$ with density.
Temperature, a: 25°C, b: 50°C, c: 75°C
○: Present work, ▲: $D_{13}\rho$ obtained from D_{33} reported by Winn, ●: $D_{12}\rho$ obtained from D_{23} calculated by the empirical formula, ■: $D\rho$ calculated by Eq. (1) for the mixture, △: $D_{13}\ \rho$ reported by Jeffries and Drickamer. Solid lines are the smoothed curves for the experimental values obtained in the present work, 1: $x_3=1.000$, 2: $x_3=0.522$, 3: $x_3=0.000$. Long-dashed lines are the theroretical curves, 1′: $D_{13}\rho$, 3′: $D_{12}\ \rho$. Dashed lines are the smoothed curves for $D_{13}\rho$ obtained from $D_{33}\rho$ reported by Dawson *et al.*

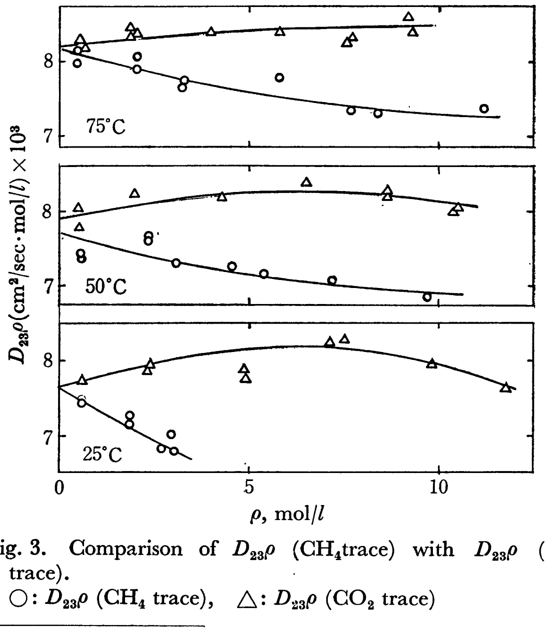


Fig. 3. Comparison of $D_{23}\rho$ (CH_4trace) with $D_{23}\rho$ (CO_2 trace).
○: $D_{23}\rho$ (CH_4 trace), △: $D_{23}\rho$ (CO_2 trace)

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[14] S. Chapman and T. G. Cowling, "The Mathematical Theory of Non-uniform Gases," Cambridge Univ. Press, London (1960), p. 292.

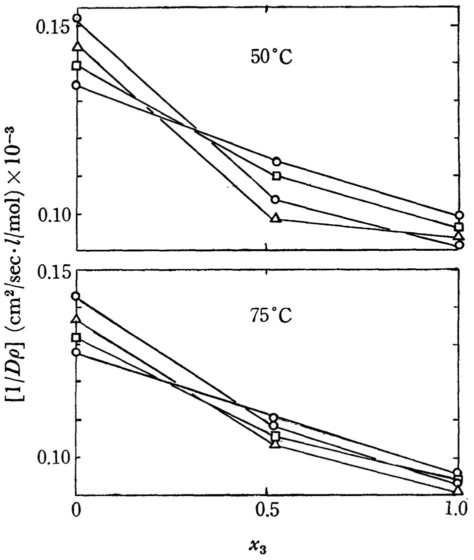

Fig. 4. Variation of $1/D\rho$ with composition.
○: 1 atm, □, △, and ●: 2,5, and 10 mol/l

modified Loschmidt-type diffusion cell was reported by Jeffries and Drickamer.[15] As is shown in Fig. 2, their values of the $D_{13}\rho$ decrease monotonously with an increase in the density and much lower than those obtained in the present work.

The self-diffusion coefficient of CH_4, as measured by the use of a pulsed NMR spectrometer, were reported by Trappeniers and Oosting[16] and Dawson *et al.*[17] The values of the $D_{13}\rho$ obtained by applying the mass correction to the results of Dawson *et al.* are shown by dashed lines in Fig. 2. These are 10% lower than those obtained in this investigation, but the shapes of the $D\rho$ *vs.* ρ curves are similar. It may be noted that the values obtained by the extrapolation of their curves to 1 atm agree well with those calculated by Eq. (3). The experimental values obtained by Trappeniers and Oosting agree very well with those calculated by Eq. (3); hence, the $D\rho$ is independent of the density.

The data may be cross-plotted to show the composition dependence of the diffusion coefficient at a constant density. If Eq. (5) derived from Eq. (1) is valid, the $1/D\rho$ *vs.* x_3 plots should be linear:

$$1/D\rho = x_2/D_{12}\rho + x_3/D_{13}\rho \qquad (5)$$

Fig. 4 shows that such cross-plots made at 2, 5, and 10 mol/l are concave lines and that Eq. (5) is not valid in this system.

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[15] Q. R. Jeffries and H. G. Drickamer, *J. Chem. Phys.*, **21**, 1358 (1953).

[16] N. J. Trappeniers and P. H. Oosting, *Phys. Lett.*, **23**, 445 (1966).

[17] R. Dawson, F. Khoury, and R. Kobayashi, *A. I. Ch. E. Journal*, **16**, 725 (1970).