ison. Experimental results which were obtained with the newly designed apparatus are italicized. The significantly larger uncertainty of the results for Freon-116 is a consequence of its extremely small solubility, which is close to the limit of the apparatus.

No significant difference was observed in the precision or accuracy of the results obtained by the two methods. However, the new version has several advantages over the Douglas version. The main advantage is that degassed water is transferred directly to the side arm of the microgasometric apparatus without the use of an intermediate transfer vessel or syringe. The risk of contamination by air is thereby practically excluded. The new method also allows continuous monitoring of the degassing process. Finally, the high-vacuum Rotaflow valve seals off the degassed water in the side arm from atmospheric contamination better than the Teflon plug used in the Douglas system.

Literature Cited

(1) Scholander, P. F. *J. Biol. Chem.* **1947**, *167*, 235.
(2) Parmelee, H. M. *Refrig. Eng.* **1953**, *61*, 1341.
(3) Ashton, J. T.; Dawe, R. A.; Miller, K. W.; Smith, E. B.; Stickings, B. J. *J. Chem. Soc. A* **1968**, 1793.
(4) Wen, W.-Y.; Muccitelli, J. A. *J. Solution Chem.* **1979**, *8*, 225.
(5) Wilhelm, E.; Battino, R.; Wilcock, R. J. *Chem. Rev.* **1977**, *77*, 219.
(6) Steen, H. *Limnol. Oceanogr.* **1958**, *3*, 423.
(7) Douglas, E. *J. Phys. Chem.* **1964**, *68*, 169.
(8) Weiss, R. F. *J. Chem. Eng. Data* **1971**, *16*, 235.
(9) Battino, R.; Bogan, M.; Banzhof, M.; Wilhelm, E. *Anal. Chem.* **1971**, *43*, 806.

Received for review September 30, 1981. Accepted March 8, 1982. We acknowledge the partial support of this work via NIH grant GMS 14710-12.

Viscosities and Densities at 298.15 K for Mixtures of Methanol, Acetone, and Water

Katsuji Noda,* Mitsuhisa Ohashi, and Kiyoharu Ishida

Department of Chemical Engineering, Shizuoka University, Hamamatsu 432, Japan

Viscosities and densities at 298.15 K are presented for the ternary methanol–acetone–water system and the binary mixtures composed of its constituents. The obtained data are correlated by using the McAllister equation of the four-body interactions.

Introduction

The viscosities of liquid mixtures are required for many practical problems concerning heat transport, mass transport, and fluid flow. Many viscosity–composition curves are not always simple functions of the compositions. The deviation from ideality is especially large for the systems including hydrogen bonds.

In this study, the viscosities and the densities at 298.15 K are determined for the binary methanol–acetone, acetone–water, and water–methanol systems and for the ternary methanol–acetone–water system. The viscosities of the binary systems are correlated by using the McAllister equation of the four-body interactions (*1*). This equation is expanded to the ternary system and used to correlate the data.

Experimental Section

Viscosities and densities were measured with an Ostwald-type viscometer and a 10-mL pycnometer, respectively. These are calibrated by using deionized distilled water. This equipment was immersed in a water bath at 298.15 ± 0.05 K. The estimated uncertainties in these measurements are ±0.002 $\mu m^2\ s^{-1}$ in viscosities and ±0.2 $kg\ m^{-3}$ in densities. Methanol and acetone used in this experiment were chromato-grade reagents purchased from Wako-Pure Chemicals, Japan. As the physical properties for the pure liquids listed in Table I are consistent with values in the literature within the experimental error, these chemicals were used without further purifications.

Results and Discussion

Experimental viscosities and densities for the binary and ternary liquid mixtures are presented in Tables II and III.

Table I. Physical Constants of Pure Compounds at 298.15 K

	methanol	acetone
viscosity, mPa s	0.542 (this work)	0.301 (this work)
	0.541 (*3*)	0.302 (*2*)
	0.5445 (*4*)	0.304 (*4*)
density, kg m^{-3}	786.7 (this work)	784.7 (this work)
	786.9 (*3*)	784.3 (*2*)
	786.64 (*4*)	784.4 (*4*)
	786.53 (*5*)	785.01 (*5*)

Table II. Viscosity and Density Data for the Binary Systems at 298.15 K

x_1	viscosity, $\mu m^2\ s^{-1}$	density, kg m^{-3}	x_1	viscosity, $\mu m^2\ s^{-1}$	density, kg m^{-3}
		Methanol (1) + Acetone			
0.0	0.384	784.7	0.3551	0.431	788.6
0.1219	0.415	786.3	0.4628	0.440	789.7
0.2100	0.413	787.2	0.6406	0.477	790.5
0.2292	0.418	787.5	0.7026	0.499	790.5
0.2781	0.419	788.0	0.7901	0.535	790.1
0.2939	0.421	788.0	0.8780	0.589	789.4
0.2977	0.418	787.9	1.0	0.689	786.7
0.3077	0.420	788.4			
		Methanol (1) + Water			
0.0	0.893	997.1	0.4856	1.505	884.5
0.0507	1.126	983.4	0.5542	1.396	869.9
0.1125	1.385	966.9	0.7133	1.149	837.7
0.1411	1.480	960.2	0.8040	0.992	821.0
0.2276	1.657	941.1	0.8345	0.952	816.0
0.2927	1.683	925.7	0.9140	0.825	800.1
0.4198	1.593	898.4			
		Acetone (1) + Water			
0.0583	1.239	974.2	0.5266	0.764	848.1
0.1460	1.454	943.9	0.6181	0.613	832.1
0.2056	1.393	925.0	0.7699	0.489	810.1
0.3020	1.211	897.8	0.8195	0.474	804.0
0.4597	0.869	861.4			

Several empirical and semiempirical relations have been used to represent the dependence of the viscosities on the compo-

0021-9568/82/1727-0326$01.25/0

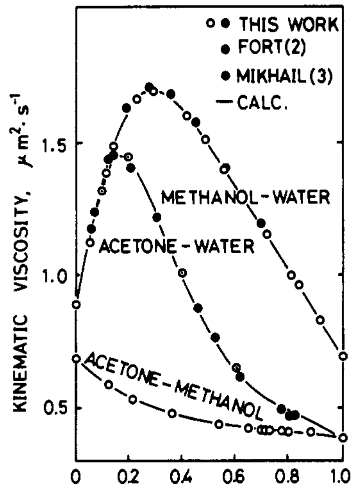

Figure 1. Kinematic viscosities of binary liquid mixtures.

Table III. Viscosity and Density Data for the Methanol (1)-Acetone (2)-Water (3) System at 298.15 K

x_1	x_2	viscosity, $\mu m^2\ s^{-1}$	density, $kg\ m^{-3}$
0.2111	0.1463	1.388	900.6
0.0729	0.4940	0.752	844.2
0.0761	0.2801	1.179	889.8
0.0903	0.2433	1.259	897.0
0.1282	0.0734	1.541	939.8
0.1549	0.2501	1.174	883.6
0.1579	0.4331	0.780	843.7
0.1643	0.2443	1.174	883.3
0.1687	0.0978	1.526	923.5
0.1712	0.2998	1.034	869.1
0.1916	0.2695	1.086	872.5
0.2965	0.3541	0.791	838.5
0.2830	0.0574	1.560	911.3
0.3321	0.4161	0.660	822.4
0.3385	0.2880	0.882	844.5
0.3587	0.1837	1.108	863.4
0.3527	0.4500	0.599	814.4
0.4118	0.0939	1.302	874.9
0.4839	0.3069	0.696	819.0
0.4477	0.2443	0.852	836.4
0.4966	0.3255	0.653	814.3
0.5560	0.1062	1.056	845.3
0.5934	0.1061	1.003	838.4
0.6478	0.2200	0.669	808.8
0.6743	0.1829	0.707	811.0
0.0981	0.2709	1.179	888.7
0.1722	0.3448	0.930	859.1
0.1616	0.1701	1.366	903.6

sitions in binary mixtures. When hydrogen bondings are included in the systems, the viscosity–composition behavior of these systems is complex. The McAllister equation of the four-body interactions may be used more favorably for these systems. This equation is given as follows:

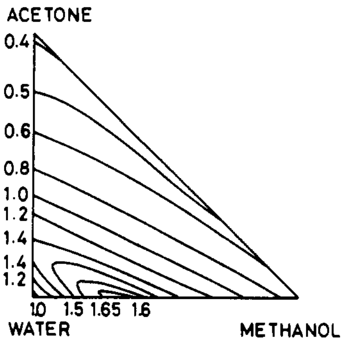

Figure 2. Lines of constant kinematic viscosity ($\mu m^2\ s^{-1}$) for methanol–acetone–water system at 298.15 K.

$$\begin{aligned}\ln \nu_{mix} = {} & x_1^4 \ln \nu_1 + 4x_1^3x_2 \ln \nu_{1112} + 6x_1^2x_2^2 \ln \nu_{1122} + \\ & 4x_1x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln (x_1 + x_2M_2/M_1) + \\ & 4x_1^3x_2 \ln [(3 + M_2/M_1)/4] + \\ & 6x_1^2x_2^2 \ln [(1 + M_2/M_1)/2] + \\ & 4x_1x_2^3 \ln [(1 + 3\ M_2/M_1)/4] + x_2^4 \ln (M_2/M_1)\end{aligned} \quad (1)$$

where ν_i and M_i are the kinematic viscosity and the molecular mass of pure component i, respectively, and ν_{ijkl}'s are constants based on the four-body approach.

On the other hand, it is difficult to predict the viscosities for the ternary systems (*6*). Ternary McAllister equations are discussed by Kalidas and Laddha (*7*) and Heric (*8*). However, these are based on the three-body interaction equation and cannot apply to complex systems. Therefore, eq 1 is expanded and used for ternary systems. This equation has three adjustable parameters and is given by

$$\begin{aligned}\ln \nu_{mix} = {} & \sum_{i}^{3} x_i^4 \ln (\nu_i M_i) + 4\sum_{i}^{3} \sum_{\substack{j \\ (i \neq j)}}^{3} x_i^3x_j \ln [\nu_{iiij}(3M_i + \\ & M_j)/4] + 6\sum_{i}^{3} \sum_{\substack{j \\ (i<j)}}^{3} x_i^2x_j^2 \ln [\nu_{iijj}(M_i + M_j)/2] + \\ & 12\sum_{i}^{3} \sum_{\substack{j \\ (i \neq j,\ i \neq k,\ j<k)}}^{3} \sum_{k}^{3} x_i^2x_jx_k \ln [\nu_{iijk}(2M_i + M_j + M_k)/4] - \\ & \ln \left(\sum_{i}^{3} x_i M_i\right)\end{aligned} \quad (2)$$

where ν_{1123}, ν_{2213}, and ν_{3312} are the ternary adjustable parameters.

To evaluate each set of adjustable parameters from experimental data, a least-squares method is used. Table IV presents the parameters and the root mean square deviations in relative kinematic viscosities. Figures 1 and 2 show the calculated values of the viscosities for the binary and ternary systems. The experimental data are also shown in Figure 1.

From Table IV and Figure 1, the McAllister equation of the four-body interactions can be seen to correlate the data in the case of the ternary complex system.

Table IV. Parameters and the Root Mean Square Deviations in Relative Kinematic Viscosity

	methanol (*i*) + water	acetone (*i*) + water	methanol (*i*) + acetone		methanol (1) + acetone (2) + water (3)
ν_{iiij}	1.3072	0.6988	0.4975	ν_{1123}	0.9711
ν_{iijj}	1.1651	0.2961	0.3993	ν_{2213}	0.7629
ν_{ijjj}	3.4233	4.8559	0.4558	ν_{3312}	0.6427
rms[a]	0.0057	0.0294	0.0085		0.0190

[a] $\mathrm{rms} = [\sum_{i=1}^{K} \{(\nu_{calcd} - \nu_{exptl})/\nu_{exptl}\}_i^2/K]^{1/2}$.

Glossary

K	number of data
M	molecular mass, kg mol^{-1}
x	liquid mole fraction
ν	kinematic viscosity, μm^2 s^{-1}

Subscripts

calcd	calculated
exptl	experimental
i	pure-component property
$iijk$	four-body interaction parameter
mix	mixture property

Literature Cited

(1) McAllister, R. A. *AIChE J.* **1960**, *6*, 427.
(2) Fort, R. J.; Moore, W. R. *Trans. Faraday Soc.* **1966**, *62*, 1112.
(3) Mikhail, S. Z.; Kimel, W. R. *J. Chem. Eng. Data* **1961**, *6*, 533.
(4) Riddick, J. A.; Bunger, W. B. "Organic Solvents"; Wiley-Interscience: New York, 1970; pp 145, 242.
(5) Timmermans, J. "Physico-chemical Constants of Pure Organic Compounds"; Elsevier: Amsterdam, 1965; Vol. 2, pp 252, 271.
(6) Noda, K.; Ishida, K. *J. Chem. Eng. Jpn.* **1977**, *10*, 478.
(7) Kalidas, R.; Laddha, G. S. *J. Chem. Eng. Data* **1964**, *9*, 142.
(8) Heric, E. L. *J. Chem. Eng. Data* **1966**, *11*, 66.

Received for review October 1, 1981. Accepted April 5, 1982.

Diffusion Coefficients and Solubilities of Carbon Dioxide in Binary Mixed Solvents

Masahiro Takahashi* and Yoki Kobayashi
Department of Industrial Chemistry, Suzuka College of Technology, Suzuka 510-02, Japan

Hiroshi Takeuchi
Department of Chemical Engineering, Nagoya University, Nagoya 464, Japan

The diffusion coefficients and the solubilities of carbon dioxide in binary systems of miscible solvents over the full range of liquid compositions were determined simultaneously from the relationship between the transient rate of gas absorption and the contact time in a modified diaphragm cell. The binary mixtures studied were selected from various systems on the basis of their viscosity behavior: *n*-propyl alcohol–ethyl alcohol, carbon tetrachloride–benzene, *n*-propyl alcohol–benzene, *n*-octyl alcohol–carbon tetrachloride, methyl alcohol–water, ethyl alcohol–water, *n*-propyl alcohol–water, and isobutyl alcohol–formamide. The results obtained are also discussed in terms of semiempirical correlations.

Introduction

Liquid-diffusion coefficients of gases have both practical and theoretical importance. In order to determine the liquid-diffusion coefficient by using a liquid-jet column (gas–liquid system) or a conventional diaphragm cell (liquid–liquid system), it is necessary to know the solubility or the concentration of gases in the liquid. However, there are few data on the solubility of gases in mixed solvents, and also it is difficult to evaluate the solubilities for mixed solvents from those for their pure-solvent components (*1*).

According to Takeuchi et al. (*2*), on the other hand, from the relationship between the transient absorption rate and the contact time for gas absorption in a modified diaphragm cell the diffusion coefficient and the solubility of a gas in liquids can be determined simultaneously with an accuracy suitable for engineering purposes. In this work, by means of such a simultaneous determination, the diffusion coefficients and the solubilities of CO_2 in various systems of two miscible solvents were obtained, the results being discussed in terms of semiempirical correlations.

Experimental Section

The experimental apparatus shown schematically in Figure 1 is identical with that described in previous papers (*2*, *3*). The geometric interfacial area of the diaphragm and the volume of the lower compartment of a diaphragm cell (1) are 5.81 cm^2 and 53.5 cm^3, respectively. A Millipore filter (mean pore size: 10.0 μm; thickness: 125 ± 15 μm; porosity: 0.68) made of Teflon (labeled LC) was used as the diaphragm after being wetted well with a mixed solvent as the absorbent. A stirrer (2) was rotated by a magnet (3) at the same 1.33 rotations/s as in the previous works (*2*, *3*).

Carbon dioxide was introduced from a gas cylinder (7) into the upper compartment of the cell through two saturators (8). A U-type glass tube (4) fitted with a mercury bottle (5) was used for measuring the absorption rate of CO_2 into the mixed solvents. All parts of the apparatus were set in a water bath (6), whose temperature was controlled at 298 ± 0.1 K. The experimental procedure has been described elsewhere (*2*, *3*).

Binary mixed solvents were selected from various systems by a classification procedure proposed by Ishikawa (*4*) on the basis of viscosity–composition curves, which has taken the chemical properties of the liquids into consideration, that is, the ideal systems (*n*-propyl alcohol–ethyl alcohol and carbon tetrachloride–benzene), the system with a minimum in the liquid viscosity (*n*-propyl alcohol–benzene), the system with a concave type of viscosity–composition curve (*n*-octyl alcohol–carbon tetrachloride), the systems with a maximum in the liquid viscosity (methyl alcohol–water, ethyl alcohol–water, and *n*-propyl alcohol–water), and the system with a minimum and a maximum in the liquid viscosity (isobutyl alcohol–formamide). The chemicals used were of special grade. Solutions of the binary mixtures studied were prepared and degassed by refluxing at total reflux for 5 h; their compositions were determined by measuring their densities or refractive indexes.

Results and Discussion

For the apparatus, in which the so-called film-theory model is applicable to a process of gas absorption (*3*), the transient absorption rate into the finite volume of liquid is given by

$$N_A a = \frac{a}{l} D_A A_i \exp\left\{-\frac{D_A t}{l^2(V/a - 1)}\right\} \qquad (1)$$