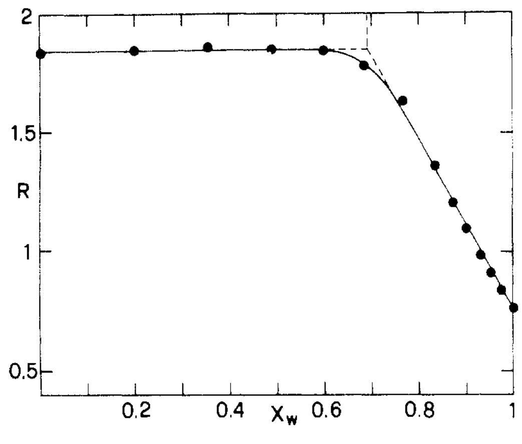

Figure 5. Ratio R (eq 7) for acridine orange in methanol-water solutions X_w = mole fraction of water; dye molality ~ 10^{-4} mol/1000 g.

of equal sign. We may compare K_m in acetic acid (~25, ϵ = 6.2), K_m in N-methylformamide (6.5, ϵ = 177), and K_m in water (1.4 × 10^4, ϵ = 89). On the other hand, the K_m constants of Table I seem to show a possible correlation between the dye stacking tendency and the self-association tendency of the solvent. Particularly interesting is to observe the K_m change along the formamide series (see Figure 4): it increases with the increasing possibility of the solvent molecules associating through hydrogen bonding. No H bonds are expected in dimethylformamide; linear sequences of H bonds are possible in N-methylformamide (as in the alcohol series), while the presence of the NH_2 group in formamide allows for the possible formation of a two-dimensional network of H bonds (*9*, *10*); the same possibility is present in acetic acid.

On the other hand, the peculiar role of water as a dye solvent must be stressed. The AO dimerization constant in water is 2-3 orders of magnitude higher than in other solvents. In this case several authors suggested that hydrophobic interactions give a dominant contribution to the stacking process (*4*, *6*, *11-18*). The evidence that the increasing possibility of H bonding seems to increase the dye stacking tendency suggests that the dye association in nonaqueous medium may be favored by some process similar to the hydrophobic interactions in water.

It is also interesting to observe that the addition of water to methanol and to dimethylformamide increases the K_m value. In the light of our previous suggestion this depends on the possibility of H_2O molecules increasing the net of solvent H bonds and favoring the possibility even of a two- or three-dimensional network. Actually it must be stressed that even in mixed solvents we are always in a "nonaqueous" medium. Water in mixed solvents is in fact far from being "common water". In the water-methanol system it has been observed that the AO stacking increases slightly up to a water-to-methanol ratio ~2:1 (see Figure 5). At higher water concentration the dye association increases drastically. So we may assume that the clusterlike structure of water, responsible for the very high stacking tendency of dyes, starts to organize itself for water-to-methanol ratios higher than 2:1.

Registry No. AO, 65-61-2; formamide, 75-12-7; N-methylformamide, 123-39-7; dimethylformamide, 68-12-2; ethyl alcohol, 64-17-5; n-propyl alcohol, 71-23-8; n-butyl alcohol, 71-36-3; acetic acid, 64-19-7; dimethyl sulfoxide, 67-68-5; water, 7732-18-5; methyl alcohol, 67-56-1.

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Viscosity of Gaseous Chlorotrifluoromethane (R 13) under Pressure

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The viscosity of gaseous chlorotrifluoromethane (R 13) was measured by using an oscillating disk viscometer of Maxwell type at 273.15-373.15 K in the pressure range up to 10.4 MPa. Two empirical equations were obtained for the viscosity as a function of temperature and pressure below 2 MPa and as a function of temperature and density in the whole range of pressure. Also an empirical equation was obtained for the atmospheric viscosity as a function of temperature. The intermolecular force parameters of the Lennard-Jones 12-6 model were determined from the temperature dependence of the atmospheric viscosity as follows: ϵ/k = 204.0 K, σ = 0.4971 nm.

Viscosity data of fluids are needed for the analysis of heat and mass transfer and for the design of related equipment. Also those are important information in determining the intermolecular force parameters available for the prediction of various physicochemical properties.

Many halogenated hydrocarbons are commonly used as refrigerants and expected to be used as working fluids of turbines. However, the experimental data for gas viscosity under pressure are scarce and the reliability of the literature data is uncertain because of the large discrepancies among them. Therefore, the measurement of the gas viscosity of halogenated hydrocarbons under pressure is being continued by us, and the viscosities of chlorodifluoromethane (R 22) and dichlorodi-

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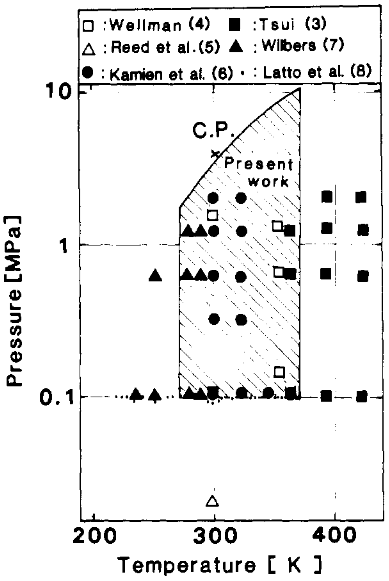

Figure 1. Temperatures and pressures at which the existing R 13 viscosity data were obtained.

fluoromethane (R 12) were reported previously (*1*, *2*). The viscosity of chlorotrifluoromethane (R 13) is described in the present paper.

The viscosity of R 13 has been measured by Tsui (*3*), Wellman (*4*), Reed et al. (*5*), Kamien et al. (*6*), Wilbers (*7*), and Latto et al. (*8*). The literature data cover the pressure range up to 2 MPa, as shown in Figure 1. The present measurement covers the area with oblique lines in Figure 1, that is, the pressure range up to 10.4 MPa. The point C.P. in Figure 1 denotes the critical point. The critical temperature and pressure are 302.3 K and 3.911 MPa, respectively (*9*).

Experimental Section

The viscosity measurement was made with an oscillating disk viscometer of Maxwell type, as described in the previous reports (*10*, *11*). The evaluating method of gas viscosity used in the present study is the same as that used by Iwasaki and Kestin (*12*). The empirical value C_N' for C_N was obtained by using nitrogen as the standard, the viscosity of which was measured by several investigators and represented by an equation (*13*). The average of seven C_N' values obtained at 25 °C in the pressure range from 0.1017 to 3.497 MPa was 1.1227. The average of deviations of each C_N' from the above value was 0.05% and the maximum was 0.10%.

The errors in the temperature and pressure measurements were 0.01 K and 1 kPa, respectively. The error in the viscosity measurement was estimated to be 0.3% from the consideration of the errors in the measurements of the amplitude and period of oscillation, the temperature, and the pressure. The sample, the purity of which was certified to be above 99.9%, was supplied from the Daikin Kogyo Co. and used without further purification.

Results and Discussion

The viscosity values obtained in the present measurement are shown in Table I and Figures 2 and 3. The density values in Table I were calculated from the empirical equation given by Michels et al. (*9*).

Equation 1 was obtained for the present experimental vis-

$$\eta_1 = 5.189 \times 10^{-2}T - 1.279 \times 10^{-5}T^2 \qquad (1)$$

cosity at atmospheric pressure as a function of temperature. This equation is valid in the temperature range from 273.15 to 373.15 K. The average deviation of the present experimental values from eq 1 is 0.05% and the maximum is 0.08%.

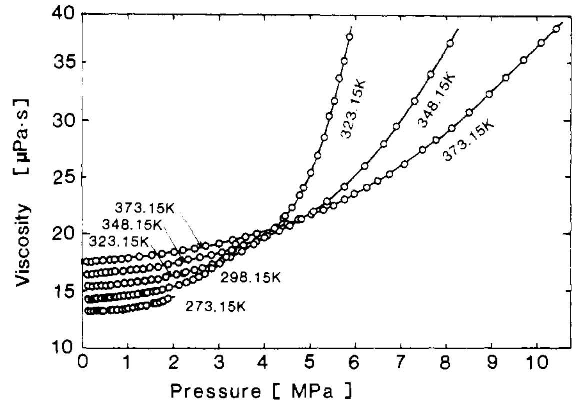

Figure 2. Viscosity of gaseous R 13 vs. pressure plots.

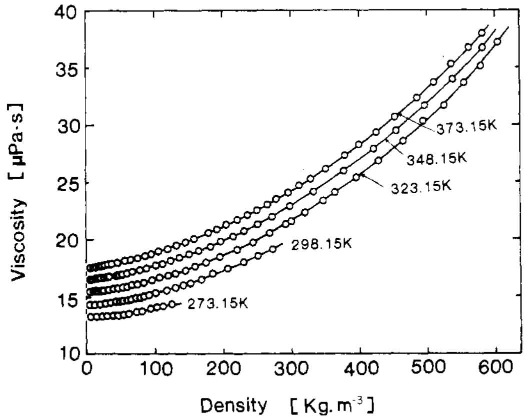

Figure 3. Viscosity of gaseous R 13 vs. density plots.

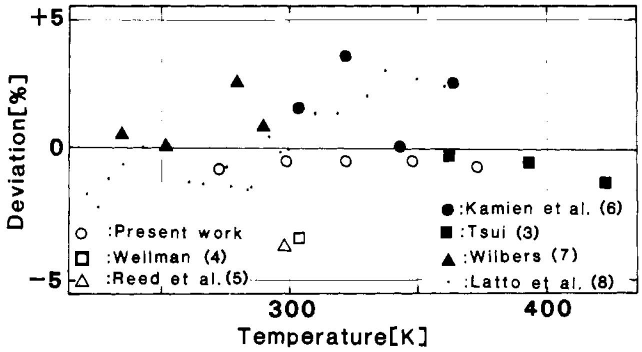

Figure 4. Deviations of experimental atmospheric viscosity from eq 2.

The intermolecular force parameters of the Lennard-Jones 12–6 model were determined by using the theoretical equation given by Hirschfelder et al. (*14*) and the present experimental viscosity values at atmospheric pressure as follows:

$$\epsilon/k = 204.0\ \mathrm{K} \qquad \sigma = 0.4971\ \mathrm{nm}$$

The average deviation of the present experimental values from the above-mentioned theoretical equation with these parameters is 0.14% and the maximum is 0.22%.

Equation 2, showing the relation between the atmospheric

$$\eta_1 = T^{1/2}/(0.41108 + 328.51/T - 27963/T^2) \qquad (2)$$

viscosity and temperature, has been obtained previously (*15*). This equation gives higher viscosity values than the present measurement by 0.5–0.8%. It should be noted that the constants in eq 2 were determined by using the data obtained by

Table I. Viscosity of Chlorotrifluoromethane (R 13)

P, MPa	ρ, kg·m^{-3}	η, μPa·s
	273.15 K	
0.1013	4.718	13.28
0.194	9.143	13.24
0.268	12.75	13.25
0.294	14.05	13.24
0.361	17.39	13.27
0.415	20.15	13.27
0.461	22.52	13.29
0.576	28.61	13.31
0.649	32.59	13.32
0.754	38.43	13.35
0.858	44.60	13.39
0.939	49.41	13.43
1.004	53.44	13.46
1.108	60.10	13.53
1.209	66.88	13.60
1.291	72.60	13.65
1.413	81.60	13.75
1.559	92.20	13.90
1.604	97.00	13.96
1.688	104.4	14.07
1.773	112.4	14.15
1.894	124.8	14.35
	298.15 K	
0.1013	4.309	14.33
0.203	8.718	14.36
0.253	10.92	14.35
0.304	13.18	14.37
0.405	17.74	14.38
0.406	17.79	14.40
0.507	22.44	14.41
0.555	24.69	14.41
0.608	27.19	14.44
0.708	32.05	14.48
0.755	34.30	14.49
0.828	37.92	14.53
0.912	42.16	14.57
1.012	47.80	14.63
1.123	53.22	14.68
1.227	58.90	14.73
1.330	64.69	14.79
1.385	67.86	14.82
1.434	70.72	14.84
1.552	77.79	14.92
1.638	83.01	15.00
1.757	90.73	15.10
1.907	100.8	15.25
2.131	117.0	15.50
2.293	129.8	15.75
2.436	142.0	15.97
2.554	152.8	16.16
2.708	168.2	16.45
2.857	184.4	16.97
3.027	206.7	17.38
3.174	229.5	17.95
3.282	249.8	18.55
3.370	270.0	19.12

P, MPa	ρ, kg·m^{-3}	η, μPa·s	P, MPa	ρ, kg·m^{-3}	η, μPa·s	P, MPa	ρ, kg·m^{-3}	η, μPa·s
	323.15 K			348.15 K			373.15 K	
0.1013	3.967	15.42	0.1013	3.676	16.51	0.1013	3.426	17.59
0.204	8.047	15.44	0.204	7.446	16.53	0.203	6.896	17.60
0.308	12.24	15.48	0.322	11.83	16.57	0.304	10.37	17.61
0.405	16.21	15.49	0.418	15.44	16.62	0.456	15.66	17.67
0.507	20.45	15.52	0.522	19.40	16.63	0.612	21.17	17.71
0.609	24.76	15.57	0.639	23.91	16.66	0.713	24.78	17.75
0.761	31.31	15.61	0.722	27.15	16.72	0.861	30.12	17.80
0.916	38.15	15.69	0.892	33.88	16.76	1.016	35.80	17.85
1.062	44.77	15.73	1.056	40.51	16.83	1.257	44.79	17.97
1.212	51.75	15.80	1.191	46.08	16.87	1.536	55.47	18.14
1.364	59.02	15.89	1.329	51.86	16.96	1.754	64.01	18.23
1.513	66.35	16.00	1.479	58.28	17.05	2.025	74.90	18.38
1.665	74.06	16.03	1.660	66.19	17.17	2.263	84.73	18.55
1.839	83.19	16.23	1.898	76.90	17.31	2.480	93.89	18.70
2.071	95.90	16.42	2.114	86.96	17.47	2.722	104.4	18.92
2.243	105.8	16.58	2.395	100.5	17.69	3.017	117.5	19.16
2.262	106.9	16.62	2.597	110.7	17.88	3.313	131.1	19.44
2.464	119.1	16.82	2.836	123.1	18.12	3.598	144.7	19.73
2.635	130.0	17.01	3.077	136.2	18.39	3.846	156.9	20.01
2.855	144.8	17.29	3.322	150.0	18.68	4.263	178.2	20.55
3.050	158.7	17.60	3.553	163.6	18.99	4.490	190.2	20.85
3.260	174.7	17.96	3.834	181.0	19.38	4.742	203.9	21.24
3.512	195.6	18.47	4.066	196.1	19.80	5.040	220.7	21.70
3.783	220.5	19.10	4.335	214.6	20.25	5.312	236.5	22.12
4.003	243.0	19.72	4.559	230.7	20.71	5.524	249.2	22.51
4.225	268.4	20.53	4.820	250.6	21.30	5.771	264.3	23.01
4.414	292.6	21.27	5.082	271.7	21.98	5.990	278.1	23.50
4.452	297.8	21.50	5.391	298.2	22.89	6.263	295.7	24.06
4.471	300.4	21.54	5.772	333.4	24.17	6.514	312.3	24.66
4.606	320.2	22.34	6.210	377.3	25.97	6.760	328.9	25.25
4.778	348.1	23.39	6.629	422.3	27.94	7.088	351.5	26.18
4.872	364.9	24.06	6.922	454.9	29.48	7.481	379.2	27.34
5.030	395.8	25.39	7.304	497.8	31.69	7.777	400.4	28.26
5.173	426.9	26.89	7.668	537.8	33.97	8.135	426.3	29.34
5.315	460.7	28.53	8.085	581.3	36.68	8.508	453.2	30.72
5.447	494.3	30.39				8.958	485.3	32.33
5.541	518.9	31.70				9.315	510.2	33.74
5.656	549.0	33.63				9.711	537.0	35.27
5.752	573.7	35.17				10.08	561.1	36.75
5.875	603.6	37.20				10.41	581.7	37.99

Wellman (*4*), Reed et al. (*5*), Kamien et al. (*6*), Tsui (*3*), and Wilbers (*7*), and the average deviation of these data from eq 2 is 1.5% and the maximum is 3.6%. The deviations of the existing atmospheric viscosity values including the present experimental ones from eq 2 are shown in Figure 4.

Table II. Constants in Eq 3 and 4

$a_{01} = 5.198 \times 10^{-2}$	$b_{01} = 5.221 \times 10^{-2}$
$a_{02} = -1.338 \times 10^{-5}$	$b_{02} = -1.413 \times 10^{-5}$
$a_{10} = -2.053$	$b_{10} = -4.9492 \times 10^{-2}$
$a_{11} = 1.297 \times 10^{-2}$	$b_{11} = 2.7189 \times 10^{-4}$
$a_{12} = -1.780 \times 10^{-5}$	$b_{12} = -3.1048 \times 10^{-7}$
$a_{20} = 2.112$	$b_{20} = 3.16948 \times 10^{-4}$
$a_{21} = -1.112 \times 10^{-2}$	$b_{21} = -1.50944 \times 10^{-6}$
$a_{22} = 1.502 \times 10^{-5}$	$b_{22} = 2.09820 \times 10^{-9}$
	$b_{30} = -1.19748 \times 10^{-7}$
	$b_{31} = 7.66356 \times 10^{-10}$
	$b_{32} = -1.20112 \times 10^{-12}$

An empirical equation for the present experimental viscosity in the whole range of pressure could not be obtained as a function of temperature and pressure with sufficient accuracy, but for the viscosity in the pressure range up to 2 MPa eq 3

$$\eta = a_0 + a_1P + a_2P^2 \qquad (3)$$

$$a_0 = a_{01}T + a_{02}T^2 \qquad (3.1)$$

$$a_1 = a_{10} + a_{11}T + a_{12}T^2 \qquad (3.2)$$

$$a_2 = a_{20} + a_{21}T + a_{22}T^2 \qquad (3.3)$$

was obtained. The numerical values of the constants are given in Table II. The deviations of the present experimental values from eq 3 are shown in Table III. Comparison of the literature values with eq 3 is shown in Figure 5. It should be noted that

Table III. Deviations of Experimental Viscosity from Eq 3

T, K	n^a	P range, MPa	devn,[b] % av	bias	max
273.15	22	~1.894	0.40	−0.24	0.99
298.15	24	~2.131	0.33	−0.27	0.62
323.15	14	~2.071	0.25	−0.18	0.39
348.15	15	~2.114	0.15	−0.05	0.42
373.15	12	~2.025	0.13	−0.10	0.30

[a] n = number of data. [b] Deviation, av = $100\sum\{|\eta_{\text{exptl}} - \eta_{\text{calcd}}|/\eta_{\text{calcd}}\}/n$. Deviation, bias = $100\sum\{(\eta_{\text{exptl}} - \eta_{\text{calcd}})/\eta_{\text{calcd}}\}/n$. Deviation, max = maximum of $100|\eta_{\text{exptl}} - \eta_{\text{calcd}}|/\eta_{\text{calcd}}$.

Table IV. Deviations of Experimental Viscosity from Eq 4

T, K	n^a	P range, MPa	ρ range, kg·m^{-3}	devn,[b] % av	bias	max
273.15	22	~1.894	~124.8	0.08	0.04	0.20
298.15	33	~3.370	~270.0	0.18	−0.12	1.02
323.15	40	~5.875	~603.6	0.14	−0.05	0.45
348.15	35	~8.085	~581.3	0.15	0.10	0.45
373.15	40	~10.41	~581.7	0.13	−0.05	0.51

[a] n = number of data. [b] Definition of deviation is the same as in Table III.

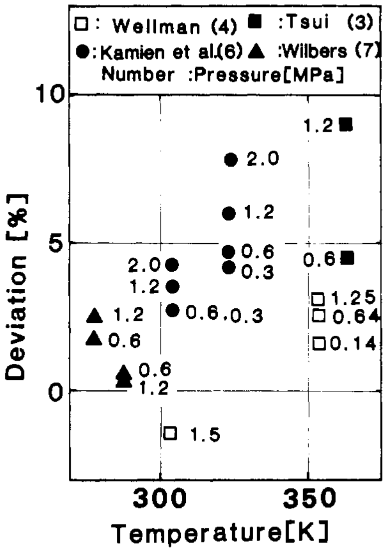

Figure 5. Deviations of experimental viscosity under pressure from eq 3.

Table V. Numerical Values of the Constants in Eq 5

R = 8.31441 cm^3·MPa/(K·mol)
K = 9.5
T_c = 301.96 K
P_c = 3.8686 MPa
V_c = 180.29 cm^3/mol

$A_{11} = 0.1077090772 \times 10$	$A_{41} = 0.2178336850 \times 10$
$A_{12} = -0.2227323512 \times 10$	$A_{42} = -0.3153854967 \times 10$
$A_{13} = -0.5867087008 \times 10^3$	$A_{43} = 0.1140756952 \times 10^5$
$A_{21} = -0.2474508174 \times 10^{-1}$	$A_{51} = -0.1232597677 \times 10$
$A_{22} = 0.3663034097$	$A_{52} = 0.1773160363 \times 10$
$A_{23} = 0.1562490536 \times 10$	$A_{53} = -0.8601302056 \times 10^4$
$A_{31} = -0.1229245837 \times 10$	$A_{61} = 0.2502404069$
$A_{32} = 0.1835156227 \times 10$	$A_{62} = -0.3451651350$
$A_{33} = -0.4075085879 \times 10^4$	$A_{63} = 0.1992322617 \times 10^4$

Table VI. Deviation of the *PV* Values Calculated by Eq 5 from Those Obtained by Michels et al.

temp, °C	n^a	devn, % av	max
0	1	0.11	0.11
25	15	0.10	0.31
30	40	0.12	0.43
30.35	8	0.72	1.22
31.35	8	0.12	1.27
32.35	8	0.10	0.28
50	40	0.05	0.98
75	40	0.06	0.21
100	40	0.04	0.11
125	40	0.03	0.09
150	40	0.11	0.17

[a] n = number of data.

the literature values in Figure 5 were obtained by using the rolling-ball method.

Equation 4 was obtained for the present experimental viscosity in the whole range of pressure as a function of temperature and density.

$$\eta = b_0 + b_1\rho + b_2\rho^2 + b_3\rho^3 \qquad (4)$$

$$b_0 = b_{01}T + b_{02}T^2 \qquad (4.1)$$

$$b_1 = b_{10} + b_{11}T + b_{12}T^2 \qquad (4.2)$$

$$b_2 = b_{20} + b_{21}T + b_{22}T^2 \qquad (4.3)$$

$$b_3 = b_{30} + b_{31}T + b_{32}T^2 \qquad (4.4)$$

The numerical values of the constants are given in Table II. The deviations of the present experimental values from eq 4 are shown in Table IV.

The density in eq 4 is calculated conveniently by the use of the equation of state. Among the three equations of state proposed for R 13 (*16*–*18*), eq 5, given by Kondo et al. (*16*), was found to be the most accurate from the comparison with the experimental data obtained by Michels et al. (*9*),

$$z = 1 + \sum_{l=1}^{6} [(A_{l1} + A_{l2}/T_r + A_{l3}\exp(-KT_r))/V_r^l] \qquad (5)$$

where $z = PV/RT$, $T_r = T/T_c$, and $V_r = V/V_c$. The numerical values of the constants in eq 5 are shown in Table V. The deviations of the PV values calculated by eq 5 from those obtained by Michels et al. (Table XIV in ref *9*) are shown in Table VI.

Acknowledgment

We thank the Daikin Kogyo Co. for supplying the sample.

Glossary

A_{l1}, A_{l2}, A_{l3}	constants in eq 5 (l = 1–6)
a_0, a_1, a_2	constants in eq 3
a_{01}, a_{02}	constants in eq 3.1
a_{10}, a_{11}, a_{12}	constants in eq 3.2
a_{20}, a_{21}, a_{22}	constants in eq 3.3
b_0, b_1, b_2, b_3	constants in eq 4
b_{01}, b_{02}	constants in eq 4.1
b_{10}, b_{11}, b_{12}	constants in eq 4.2
b_{20}, b_{21}, b_{22}	constants in eq 4.3
b_{30}, b_{31}, b_{32}	constants in eq 4.4
C_N	constant which characterizes the effect of the edge of the disk on oscillation
C_N'	empirical value for C_N
K	constant in eq 5
k	Boltzmann's constant
P	pressure, MPa
P_c	critical pressure, MPa
R	gas constant (=8.31141 cm^3·MPa/(K·mol))
T	temperature, K
T_c	critical temperature, K

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T_r	reduced temperature ($=T/T_c$)
V	volume, cm^3/mol
V_c	critical volume, cm^3/mol
V_r	reduced volume ($=V/V_c$)
z	compressibility factor ($=PV/RT$)
ϵ/k	intermolecular force parameter in Lennard-Jones 12-6 model, K
η	viscosity, μPa·s
η_1	atmospheric viscosity, μPa·s
ρ	density, kg/m^3
σ	intermolecular force parameter in Lennard-Jones 12-6 model, nm

Registry No. Chlorotrifluoromethane, 75-72-9.

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Thermodynamics of Aqueous Magnesium and Calcium Bicarbonates and Mixtures with Chloride

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The potential for the cell $Pt,H_2,CO_2|M(HCO_3)_2,MCl_2,CO_2(aq)|AgCl,Ag$ with M = Mg and Ca was measured over a wide range of molalities at 298.15 K. The data were interpreted by the mixed-electrolyte equations of Pitzer and Kim to yield the ion-interaction parameters for Mg^{2+}, HCO_3^-, and for Ca^{2+}, HCO_3^-. The trace activity coefficients of $M(HCO_3)_2$ in MCl_2 and in NaCl are calculated.

Introduction

In many natural waters, including seawater, there are significant molalities of Mg^{2+}, Ca^{2+}, and HCO_3^-, and these ions enter into various reactions of importance. Hence, the thermodynamic properties of $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ in mixed electrolytes are a matter of considerable interest. The mixed-electrolyte equations of Pitzer and Kim (*1*) have been used with great success for complex natural brines, especially by Harvie and Weare (*2*) and Millero (*3*). Thus, it is desirable to determine the pertinent parameters for $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ in these equations which are based on a Debye–Hückel term and a virial expansion including second and third virial coefficients representing short-range interactions between pairs and triplets of ions.

Values for the second virial parameters $\beta^{(0)}$ and $\beta^{(1)}$ for Mg^{2+}, HCO_3^- at 25 °C have been determined by Millero and Thurmond (*4*) from potentiometric titrations in solution with $MgCl_2$ and NaCl. Harvie et al. (*5*) have given values for these parameters for both $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ on the basis of calculations of solid solubilities in brines. The present investigation was designed specifically to yield these parameters as accurately as possible in simple mixtures with minimum uncertainty related to the other parameters required. The method is that used for the alkali bicarbonates $NaHCO_3$ (*6*, *7*) and $KHCO_3$ (*8*, *9*) which were successfully investigated by measurements of mixed solutions with chlorides in electrochemical cells with hydrogen and silver–silver chloride electrodes. We extend this method to magnesium and calcium bicarbonate with the cell

$$Pt,H_2,CO_2|M(HCO_3)_2(m_1),MCl_2(m_2),CO_2(m_3)|AgCl,Ag \quad (A)$$

where M is either Mg or Ca.

Various aqueous carbonate species are at equilibrium in the following reactions

$$CO_2(g) = CO_2(aq) \qquad K_s \quad (1)$$

$$CO_2(aq) + H_2O(l) = H^+ + HCO_3^- \qquad K_1 \quad (2)$$

$$HCO_3^- = H^+ + CO_3^{2-} \qquad K_2 \quad (3)$$

with the indicated equilibrium constants. Two combinations of these reactions are particularly useful.

$$CO_2(g) + H_2O(l) = H^+ + HCO_3^- \qquad K_1K_s \quad (4)$$

$$2HCO_3^- = CO_3^{2-} + H_2O(l) + CO_2(g) \qquad K_2/K_1K_s \quad (5)$$

The reaction for the electrochemical cell is

$$^1/_2H_2(g) + AgCl(s) + HCO_3^- = Cl^- + Ag(s) + H_2O(l) + CO_2(g) \quad (6)$$

with the potential given by

$$E = E_A^\circ - \frac{RT}{F}\left[\ln\left(\frac{m_{Cl}a_{H_2O}f_{CO_2}}{m_{HCO_3}f_{H_2}^{1/2}}\right) + \ln\left(\frac{\gamma_{Cl^-}}{\gamma_{HCO_3^-}}\right)\right] \quad (7)$$

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