General paper

EFFECTS OF PRESSURE AND TEMPERATURE ON THE VISCOSITY *B* COEFFICIENT FOR POTASSIUM CHLORIDE IN WATER

Takehiro NAKAI*, Seiji SAWAMURA*, Yoshihiro TANIGUCHI*

and Takashi KUBOYAMA**

*Department of Chemistry, Faculty of Science and Engineering, Ritsumeikan University,
1-1-1 Nojihigashi, Kusatsu, Shiga 525-77, Japan.
**Japan Space Utilization Promotion Center,
Nishiwaseda, Shinjyuku, Tokyo 169, Japan.

Abstract: Viscosity of aqueous potassium chloride (KCl) solution was measured at temperatures of 283.2 and 323.2 K and pressures up to 375 MPa by means of a rolling-ball viscometer. The Jones-Dole *B* coefficient of KCl at both temperatures increased with increasing pressure and then decreased after passing over a maximum as well as previously observed one at 298.2 K. The maximum became more pronounced at lower temperatures. In comparison with the dielectric friction theory, the observation of the maximum is ascribed to a balance between two contributions; pressure breaks any water structure (*B* increases) and reduces the dielectric friction between ion and solvent (*B* decreases). The temperature coefficient $\partial B/\partial T$ was observed to be positive at all pressures and decreases with increasing pressure. The fact suggests that the structure-breaking effect of KCl for water reduces with increasing pressure, and the reduction of the effect may be ascribed that the water structure which should be broken by addition of the electrolyte is already broken by pressure.

Key words: *Viscosity, Potassium chloride, Aqueous solution, Jones-Dole B coefficient, High pressure*

1. INTRODUCTION

It is important to study the effects of pressure and temperature on the properties of aqueous electrolyte solutions from the viewpoint of understanding the interaction between ions and water. So far, the viscosity *B* coefficient of the Jones-Dole equation [1] for electrolyte solutions has provided a useful information about ion-solvent interaction from both macroscopic and dynamical viewpoints:

$$\eta / \eta_0 = 1 + Ac^{1/2} + Bc , \qquad (1)$$

where η and η_0 are the viscosities of solutions and pure solvent, respectively, and c the molarity (mol dm^{-3}) of the solution. *A* is theoretically ascribed to the interionic interaction and fundamentally positive [2]. *B* is associated with the ion-solvent interaction. Special interest has been received to not only *B* but also the temperature coefficient $\partial B/\partial T$ which has been used to classify the property of ions for water structure. For example, it is suggested that the positive $\partial B/\partial T$ value for the ion breaks water structure [3]. While attention has been paid to *B* for electrolyte in water for a long time, its pressure effect is almost ignored and therefore measurements of viscosity of aqueous electrolyte solution under high pressure have hardly been done.

We have previously measured the high-pressure viscosity of aqueous solutions of NaCl [4] and CsCl [5,6], and examined the pressure effects on the *B* coefficients for these electrolytes in water. It was found that the *B* for these electrolytes increased initially and then decreased after passing over a maximum and pressure at the maximum depended on temperature. For a better understanding of the cation effect on these phenomena, we extend a series of our works to aqueous solution of KCl in this report.

2. EXPERIMENTAL

2.1. Sample

Potassium chloride (extra pure grade) obtained from Nacalai Tesque Inc. was recrystallized from distilled water, and dried over P_2O_5 under vacuum for more than one week. Experimental details for sample preparation were described elsewhere [7]. The measurements were performed for five species the concentrations of which is 0.5, 1.0, 2.0, 3.0, and 4.0 (±0.0001) mol kg^{-1}.

2.2. Measurement of Viscosity

The viscosity at 0.1 MPa was measured using a Ubbelohde-type viscometer, and high-pressure viscosity measurement was done by means of a rolling-ball viscometer constructed in our laboratory [8]. The basic equation to estimate the viscosity η for the latter case is given by

$$\eta = K (\rho_b - \rho_s) t , \qquad (2)$$

where ρ_b and ρ_s are the densities of ball of the viscometer and the sample solution, respectively, t is the time which is required for a ball passing through a fixed distance in a

sloped tube filled with a sample solution, and K is a cell constant which is calibrated from the viscosity of water [9] at each pressure and temperature. t can be detected with an accuracy of ±0.01 s. The viscometer was located in a water bath regulated within ±0.01 K. The pressure was monitored with a Brudon-type pressure gauge (Heise Co.) of 700 MPa in full scale with an accuracy of ±0.5 MPa.

2.3. Measurement of Compression

The ρ_S (at high pressure) in Eq. (2) is estimated by the following equation:

$$\rho_S = \rho_S^0 / (1-k),\qquad(3)$$

where ρ_S^0 is the density at 0.1 MPa and k is the compression of sample solution defined as

$$k = (V^0 - V^p) / V^0,\qquad(4)$$

where V^0 and V^p are the molar volumes of the sample solution at 0.1 MPa and high pressures, respectively, and the latter was measured using a mercury-trapped type piezometer with 7 cm³ inner volume [7]. The pressure was monitored with a Bourdon-type gauge (Heise Co.) of 400 MPa in full scale with a precision of ±0.5 MPa, and the temperature was controlled within ±0.1 K. ρ_S^0 was measured using an Ostwald-type pycnometer with 10 cm³ inner volume.

3. RESULTS AND DISCUSSION

3.1. Compression and Density

The values of k for aqueous KCl solution are listed in Table 1. These values are fitted to the Tait's equation as a function of pressure p (MPa):

$$k = \alpha \log [(\beta + p) / (\beta + 0.1)],\qquad(5)$$

within a standard deviation of 5×10^{-3}. The fitted parameters α and β and the density ρ_S^0 are summarized in Table 2. The k in Eq. (3) was estimated using α and β in Table 2 and Eq. (5).

3.2. Viscosity

The viscosity data are listed in Table 3 and plotted in Fig. 1 up to 50 MPa where the reference data [10-13] are also plotted in comparison. The data by Kestin et al. are larger than the others at 0.1 MPa and 298.2 K though the values at 323.2 K do not differ each other. The deviation is inevitable because the aim of their study is to get the viscosity at higher temperatures than 298.2 K. At high pressure the viscosity has been published only by Kestin et al. presenting it as a linear function of pressure up to 35 MPa. On the other hand, our data are fitted to the third polynomials within a standard deviation of 2×10^{-3}:

$$\eta = a_0 + a_1 p + a_2 p^2 + a_3 p^3.\qquad(6)$$

Table 1. Compression k (%) of aqueous KCl solution.

Pressure	Molality m, mol kg⁻¹				
p, MPa	0.5	1.0	2.0	3.0	4.0
			283.2 K		
50	2.02	1.85	1.67	1.48	1.38
100	3.77	3.55	3.29	2.83	2.70
150	5.23	4.92	4.60	4.22	3.89
200	6.52	6.24	5.93	5.43	5.18
250	7.89	7.55	7.02	6.44	6.12
300	8.94	8.67	8.18	7.54	7.16
350	10.15	9.67	9.13	8.37	7.95
			298.2 K [a]		
50	1.93	1.80	1.65	1.56	1.39
100	3.56	3.40	3.15	2.87	2.65
150	5.09	4.80	4.47	4.18	3.89
200	6.49	6.11	5.70	5.32	4.98
250	7.62	7.26	6.78	6.35	5.94
300	8.82	8.31	7.78	7.30	6.84
350	9.83	9.30	8.67	8.11	7.69
			323.2 K		
50	1.85	1.66	1.50	1.38	1.25
100	3.42	3.08	2.79	2.63	2.50
150	4.84	4.41	4.01	3.81	3.62
200	6.05	5.70	5.28	4.97	4.70
250	7.20	6.88	6.35	6.08	5.70
300	8.35	8.00	7.43	7.02	6.68
350	9.47	8.97	8.47	8.03	7.62

[a] Ref. [7].

Table 2. Density at 0.1 MPa and parameters of Tait's equation for aqueous KCl solution.

	Molality m, mol kg⁻¹				
	0.5	1.0	2.0	3.0	4.0
			283.2 K		
ρ_S^0, g cm⁻³	1.0233	1.0454	1.0864	1.1236	1.1579
α	0.3148	0.3302	0.3351	0.3545	0.3601
β, MPa	321.1	362.5	400.0	479.5	521.9
			298.2 K		
ρ_S^0, g cm⁻³	1.0198	1.0414	1.0814	1.1183	1.1520
α	0.3155	0.2981	0.2861	0.2796	0.3004
β, MPa	333.1	332.7	345.2	365.5	434.4
			323.2 K		
ρ_S^0, g cm⁻³	1.0103	1.0314	1.0708	1.1070	1.1402
α	0.3211	0.3890	0.4703	0.4610	0.4657
β, MPa	364.2	497.8	682.4	709.8	765.4

The fitted parameters of the equation are listed in Table 4. Figure 2 shows the viscosity surfaces of aqueous KCl solution against pressure and molality at 283.2-323.2K.

3.3. Jones-Dole B Coefficient

The viscosity of electrolyte solution can be fitted to the following extended Jones-Dole equation [14] as a function of molarity c (mol dm⁻³):

$$\eta / \eta_0 = 1 + Ac^{1/2} + Bc + Dc^2.\qquad(7)$$

This equation can be changed to Eq. (8) as a linear

205

Takehiro NAKAI, Seiji SAWAMURA, Yoshihiro TANIGUCHI and Takashi KUBOYAMA

function of c :

$$(\eta / \eta_0 - 1 - Ac^{1/2}) / c = B + Dc \quad . \tag{8}$$

The value of A can be usually calculated from the method by Falkenhagen et al. [2] using some high-pressure properties, i.e., the limiting molar conductances of ions [15-17], the viscosity [9] and the static dielectric constant

Table 3. The viscosity for aqueous KCl solution.

| Pressure	Molality m, mol kg^{-1}				
p, MPa	0.5	1.0	2.0	3.0	4.0
			283.2 K		
0.1	1.2760	1.2546	1.2357	1.2340	1.2503
25	1.263	1.246	1.233	1.232	1.251
50	1.253	1.242	1.233	1.233	1.257
75	1.250	1.243	1.240	1.244	1.267
100	1.248	1.246	1.248	1.258	1.278
125	1.250	1.251	1.256	1.267	1.294
150	1.256	1.259	1.270	1.286	1.310
175	1.264	1.270	1.282	1.300	1.328
200	1.277	1.282	1.296	1.318	1.348
225	1.295	1.301	1.315	1.338	1.367
250	1.313	1.320	1.336	1.361	1.387
275	1.335	1.340	1.356	1.382	1.412
300	1.357	1.364	1.383	1.408	1.438
325	1.377	1.383	1.403	1.432	1.462
350	1.405	1.407	1.426	1.455	1.489
375	1.431	1.435	1.451	1.478	1.512
			298.2 K [a]		
0.1	0.8887	0.8882	0.8950	0.9117	0.9372
25	0.886	0.889	0.900	0.919	0.946
50	0.886	0.892	0.905	0.926	0.955
75	0.890	0.895	0.913	0.935	0.966
100	0.896	0.902	0.920	0.945	0.977
125	0.901	0.910	0.928	0.955	0.988
150	0.907	0.915	0.938	0.966	1.001
175	0.918	0.925	0.948	0.979	1.015
200	0.927	0.936	0.959	0.990	1.031
225	0.941	0.948	0.972	1.007	1.047
250	0.954	0.960	0.985	1.020	1.062
275	0.968	0.975	1.001	1.037	1.079
300	0.981	0.988	1.015	1.052	1.096
325	0.998	1.004	1.030	1.068	1.112
350	1.014	1.019	1.045	1.084	1.128
375	1.031	1.037	1.063	1.101	1.146
			323.2 K		
0.1	0.5565	0.5658	0.5864	0.6124	0.6410
25	0.562	0.571	0.592	0.618	0.645
50	0.567	0.577	0.598	0.622	0.650
75	0.573	0.583	0.604	0.629	0.655
100	0.580	0.590	0.611	0.635	0.662
125	0.588	0.597	0.619	0.643	0.671
150	0.596	0.604	0.627	0.651	0.680
175	0.604	0.612	0.635	0.659	0.689
200	0.612	0.620	0.643	0.666	0.698
225	0.622	0.629	0.652	0.676	0.708
250	0.631	0.638	0.661	0.686	0.719
275	0.641	0.648	0.670	0.695	0.730
300	0.649	0.656	0.680	0.705	0.741
325	0.660	0.667	0.690	0.716	0.753
350	0.669	0.677	0.699	0.726	0.765
375	0.679	0.686	0.709	0.737	0.778

[a] Ref. [7].
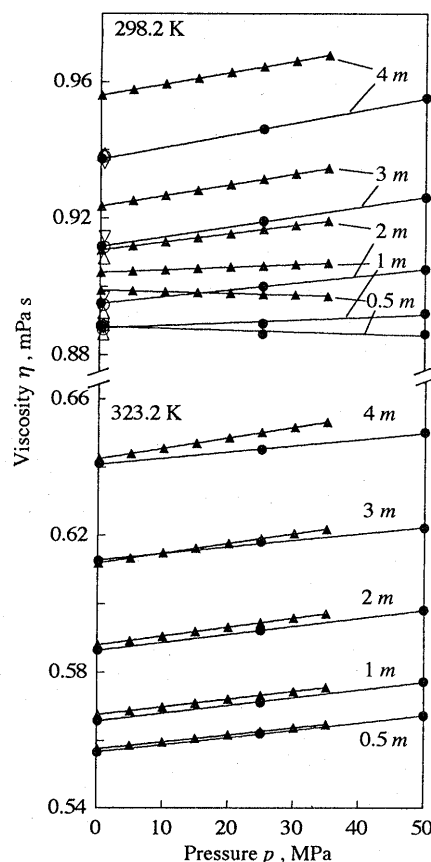
Fig. 1. Pressure dependence of the viscosity for aqueous KCl solution at 298.2 and 323.2 K up to 50 MPa. ●: This work, ▲: Kestin et al. [10], O: Isono [11], ∇: Ostroff et al. [12], △: Kume et al. [13].

Table 4. Parameters of Eq. (6) for aqueous KCl solution.

| m, mol kg^{-1}	a_0, 10^{-3} Pa s	a_1, 10^{-12} s	a_2, 10^{-21} Pa^{-1}s	a_3, 10^{-30} Pa^{-2}s
		283.2 K		
0.5	1.277	-0.664	3.95	-2.88
1.0	1.255	-0.393	3.17	-2.25
2.0	1.235	-0.134	2.66	-2.04
3.0	1.232	-0.035	2.93	-2.88
4.0	1.249	-0.072	2.53	-2.26
		298.2 K		
0.5	0.888	-0.103	1.79	-1.33
1.0	0.888	0.012	1.27	-0.66
2.0	0.895	0.154	0.92	-0.37
3.0	0.912	0.226	1.01	-0.71
4.0	0.938	0.281	1.14	-1.09
		323.2 K		
0.5	0.556	0.180	0.63	-0.64
1.0	0.566	0.196	0.44	-0.28
2.0	0.586	0.207	0.46	-0.38
3.0	0.613	0.181	0.53	-0.33
4.0	0.641	0.146	0.84	-0.68

206

HIGH PRESSURE VISCOSITY OF KCl IN H_2O
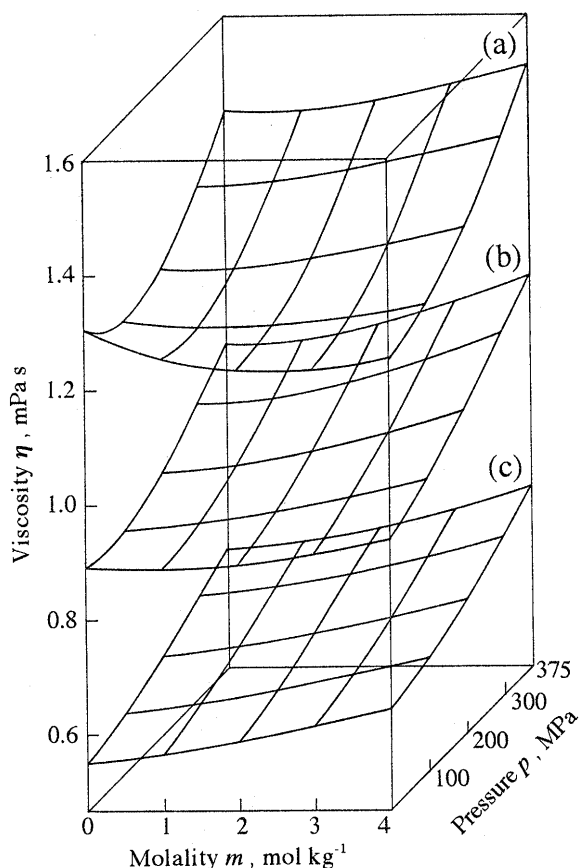
Fig. 2. Isothermal viscosity surface of aqueous KCl solutions as a function of pressure and concentration at (a) 283.2 K, (b) 298.2 K [7], and (c) 323.2 K.

of water [18]. The calculated A values for KCl in water at 0.1-200 MPa are listed in Table 5. These values decrease only by 0.0002-0.0005 $dm^{3/2}mol^{-1/2}$ with increasing pressure up to 200 MPa. As the reductions are negligibly small, A values at 0.1 MPa are used as those at high pressures. We plotted $(\eta/\eta_0-1-Ac^{1/2})/c$ against c in Fig. 3, where c (mol dm^{-3}) was translated from m (mol kg^{-1}) using the compression data in Table 2. At all pressures and temperatures, linear relations were observed. Therefore, in Fig. 3, the intercept at zero concentration corresponds to B. The B value at 0.1 MPa is estimated to be -0.058 dm^3mol^{-1} at 283.2 K, -0.015 dm^3mol^{-1} at 298.2 K [7], and 0.024 dm^3mol^{-1} at 323.2 K, respectively. The value of -0.015 dm^3mol^{-1} at 298.2 K is in good agreement with reference data of -0.014 dm^3mol^{-1} [3,19] and -0.015 dm^3mol^{-1} [11]. Figure 4 shows pressure dependence of B for KCl in water. The B coefficient increases with increasing pressure and then decreases after passing over a maximum. The pressure at the maximum B decreases with increasing temperature from 200 MPa at 283.2 K to 50 MPa at 323.2 K. Similar decreasing of the pressure has been also observed for NaCl [4] and CsCl [6] in water.

A theoretical expression for B has been derived by Ibuki and Nakahara [20] based on the continuum dielectric friction theory of Hubbard-Onsager(HO) [21,22]. In their expression, B is written as a function of the solvent parameter R_{HO} defined in the HO theory, i.e.,

$$B_{theor} = f(u) R_{HO}^3 N / 1000 , \qquad (9)$$

$$u = R/R_{HO} , \qquad (10)$$

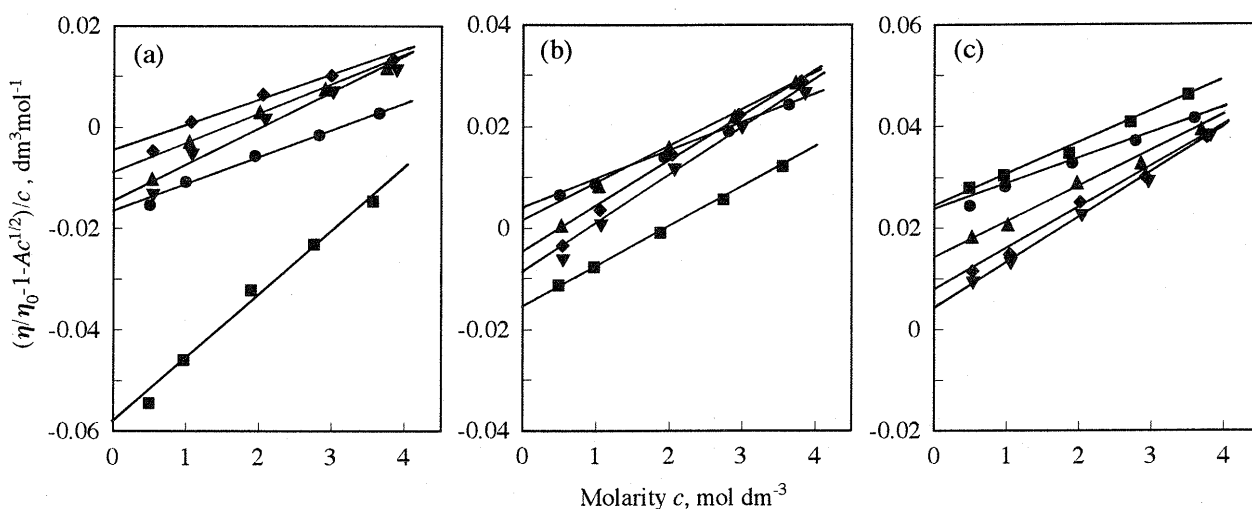$$R_{HO} = [e^2 (\varepsilon_0 - \varepsilon_\infty) \tau_D /16\pi \eta_0 \varepsilon_0^2]^{1/4} , \qquad (11)$$

Fig. 3. $(\eta/\eta_0-1-Ac^{1/2})/c$ against c for aqueous KCl solution at (a) 283.2 K, (b) 298.2 K [7], and (c) 323.2 K.
■: 0.1 MPa, ●: 100 MPa, ▲: 200 MPa, ◆: 300 MPa, ▼: 375MPa.

207

Takehiro NAKAI, Seiji SAWAMURA, Yoshihiro TANIGUCHI and Takashi KUBOYAMA

Table 5. The calculated Jones-Dole A coefficient of KCl in water.

Pressure	A coefficient, $dm^{3/2}mol^{-1/2}$ [a]		
p , MPa	283.2 K	298.2 K	323.2 K
0.1	0.0047	0.0050	0.0055
50	0.0047	0.0049	0.0053
100	0.0046	0.0048	0.0052
150	0.0046	0.0047	0.0051
200	0.0045	0.0047	0.0050

[a] The coefficients A at 283.2 and 323.2 K were obtained from those at 278.2, 298.2, and 318.2 K, using the limiting molar conductances by Ueno et al. [15-17], and then extrapolating to 283.2 and 323.2K, respectively.

where R is the ionic radius [23], N the Avogadro's number, e the protonic charge, η_0 the solvent viscosity [9], τ_D the dielectric relaxation time of the solvent [24], and ε_0 and ε_∞ are the static [18] and high-frequency dielectric constants [25] of the solvent. Using these solvent properties at high pressures, B_{theor} of KCl were calculated and also depicted in Fig. 4 as broken lines supposing that the ionic radii do not depend on pressure. The theoretical curves monotonously decrease with increasing pressure without any maximum. As the B coefficient depend on the difference between η and η_0 in Eq. (1), the pressure dependence of B can be influenced by the difference in any structural change of both water in the hydration shell and bulk water. Therefore, the decrease in the η_0 accompanying a breaking of bulky water structure may contribute to an increase of B. On the other hand, several recent computer simulations for aqueous solutions of LiI [26], NaCl [27], and Cs^+ [28] at high pressures suggest that the structure of hydration water is much less

sensitive against pressure than that of pure water. Therefore, main contribution to the positive slope of B in low pressure side of the maximum in Fig. 4 is thought to be a breaking of bulky water structure by compression. Such contribution should be considerable at low temperatures where the water structure is more pronounced. In the high pressure side in Fig. 4, the degree of the negative slope is similar to that for B_{theor}.
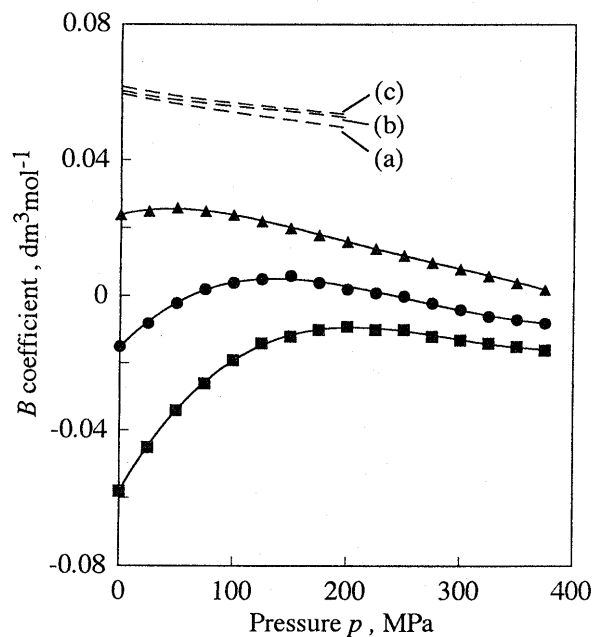

Fig. 4. Pressure dependence of B for KCl in water at 283.2 K(■), 298.2 K(●) [7], and 323.2 K(▲).
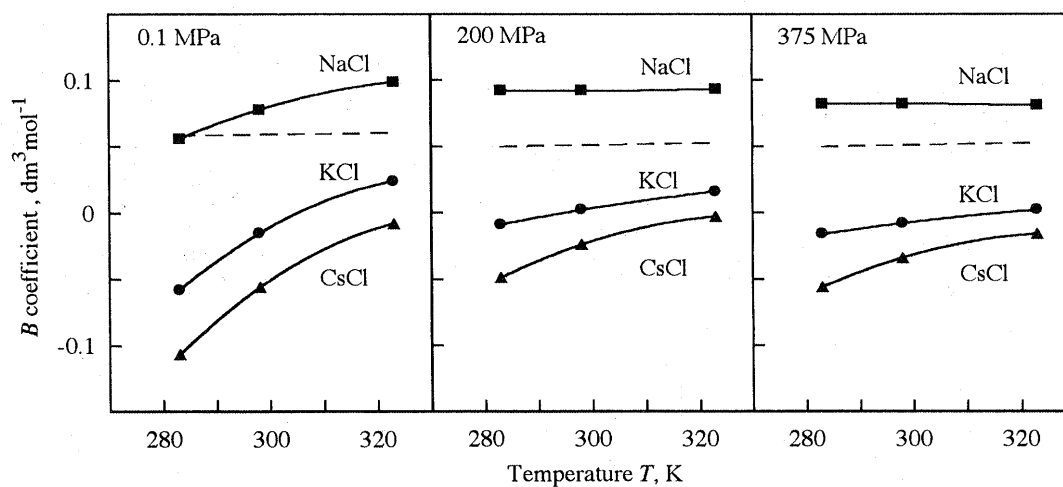----: B_{theor} at (a) 283.2 K, (b) 298.2 K, and (c) 323.2 K.

Fig. 5. Temperature dependence of B for alkali chloride in water at several pressures.
■: NaCl [4], ●: KCl, ▲: CsCl [6], ----: B_{theor} for KCl.

208

HIGH PRESSURE VISCOSITY OF KCl IN H_2O

This fact implies that the water structure is broken by pressure and approaches to a continuum fluid supposed by Ibuki and Nakahara. Consequently, the observation of the maximum of B in Fig. 4 is ascribed to a balance between these two contributions; (1) pressure breaks any water structure (B increases) and (2) pressure reduces the dielectric friction between ion and water (B decreases).

Figure 5 shows the temperature dependence of B for KCl in water at each pressure including those for other alkali chlorides of NaCl [4] and CsCl [6]. All of the B increase with increasing temperature at 0.1 MPa. These phenomena can be ascribed to breaking of hydrogen-bonded structure of bulk water by heating. This contribution of the breaking is similar to that by pressure shown above. Because of such temperature effects of the B, these electrolytes have been classified to structure-breaker [3]. Broken lines in Fig. 5 show theoretical values by Ibuki and Nakahara [29]. They hardly depend on temperature. It means that the slope of B is almost zero in a continuum fluid which does not have any structure such as water. The slope of B in Fig. 5 decreases with increasing pressure. It suggests that the strength as a breaker of these electrolytes weakens with increasing pressure. This conclusion is the same as that described in Fig. 4, but the water structure appears to be not completely destroyed because the slope for KCl and CsCl are still positive at 375 MPa in Fig. 5.

In conclusion, the enhancement of B with increasing pressure or temperature is thought to be caused by breaking of bulk-water structure by pressing or heating. This contribution is inevitably weakened at high pressures and temperatures, hence another contribution of the dielectric friction becomes predominant.

REFERENCES

1. G. Jones and M. Dole, J. Am. Chem. Soc., **51** (1929) 2950.
2. H. Falkenhagen and E. L. Vernon, Phil. Mag., **14** (1932) 537.
3. M. Kaminsky, Discuss. Faraday Soc., **24** (1957) 171.
4. S. Sawamura, Y. Yoshimura, K. Kitamura, and Y. Taniguchi, J. Phys. Chem., **96** (1992) 5526.
5. T. Nakai, S. Sawamura, and Y. Taniguchi, J. Mol. Liq., **65/66** (1995) 365.
6. T. Nakai, S. Sawamura, Y. Taniguchi, and Y. Yamaura, Mater. Sci. Res. Int., **2** (1996) 143.
7. T. Nakai, S. Sawamura, and Y. Taniguchi, J. Soc. Mater. Sci. Japan, **45** (1996) 280.
8. S. Sawamura, N. Takeuchi, K. Kitamura, and Y. Taniguchi, Rev. Sci. Instrum., **61** (1990) 871.
9. The IAPS Formulation 1985 for the Viscosity of Ordinary Water Substance, International Association for the Properties of Stream (1985).
10. J. Kestin, H. E. Khalifa, and R. J. Correia, J. Phys. Chem. Ref. Data, **10** (1981) 57.
11. T. Isono, Rikagaku-Kenkyusho Houkoku, **61** (1985) 53.
12. A. G. Ostroff, B. S. Snowden, Jr., and D. E. Woessner, J. Phys. Chem., **73** (1969) 2784.
13. T. Kume and M. Tanaka, Nippon Kagaku Kaishi (J. Chem. Soc. Japan), **81** (1960) 534.
14. G. Jones and H. J. Fornwalt, J. Am. Chem. Soc., **58** (1936) 619.
15. M. Nakahara, M. Zenke, M. Ueno, and K. Shimizu, J. Chem. Phys., **83** (1985) 280.
16. M. Ueno, A. Yoneda, N. Tsuchihashi, and K. Shimizu, J. Chem. Phys., **86** (1987) 4678.
17. M. Ueno, N. Tsuchihashi, and K. Shimizu, J. Chem. Phys., **92** (1990) 2548.
18. K. R. Srinivasan and R. L. Kay, J. Chem. Phys., **60** (1974) 3645.
19. G. Jones and S. K. Talley, J. Am. Chem. Soc., **55** (1933) 624.
20. K. Ibuki and M. Nakahara., J. Chem. Phys., **85** (1986) 7312.
21. J. Hubbard and L. Onsager, J. Chem. Phys., **67** (1977) 4850.
22. J. Hubbard, J. Chem. Phys., **68** (1978) 1649.
23. L. Pauling, The Nature of the Chemical Bond, Cornell University Press, New York (1960) p. 514.
24. R. Pottel, E. Asselborn, R. Eck, and V. Tresp, Ber. Bunsenges. Phys. Chem., **93** (1989) 676.
25. J. B. Hasted, Water, Vol. 1 (ed. by F. Franks), Plenum, New York (1972) p. 277.
26. G. I. Szász and K. Heinzinger, Earth and Planetary Sci. Lett., **64** (1983) 163.
27. G. Jansćo, K. Heinzinger, and P. Bopp, Z. Naturforsch, **40a** (1985) 1235.
28. M. R. Reddy and M. Borkowitz, J. Sol. Chem., **17** (1988) 1183.
29. K. Ibuki and M. Nakahara., J. Chem. Phys., **89** (1988) 5015.