Effects of Pressure, Temperature, and Concentration on the Viscosity of Aqueous Ammonium Bromide Solution

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Dedicated to Prof. Hitoshi Ohtaki on the occasion of his 60th birthday

The viscosity of aqueous ammonium bromide solutions is measured at 0.1–1.0 mol kg^{-1}, 278.2–323.2 K, and 0.1–375 MPa, using a high-pressure rolling-ball viscometer. The activation energy (E_v) for viscous flow and Jones-Dole's B coefficient are estimated. E_v against pressure yields a concave curve with a minimum and B yields a convex one with a maximum. These phenomena are attributed to pressure, temperature, and concentration effects on the water-structure.

Key words: Viscosity, High pressure, Ammonium bromide, Activation energy, Jones-Dole's B coefficient

1. Introduction

It is well known that the viscosity curve at low temperature of water against pressure exhibits a minimum, e.g. at 100 MPa for an isothermal curve at 283 K [1]. The reduction of the viscosity with increasing pressure up to the minimum has been ascribed to breaking of the bulky water-structure by compression [2] and the increase of the viscosity after the minimum has been reached to stuffing. The minimum shifts to lower pressure with increasing temperature and disappears at ca. 310 K because of the breaking of the hydrogen-bonding [1].

Another type of reduction of the viscosity of water is known to be caused by addition of an electrolyte whose Jones-Dole's B coefficient is negative, suggesting breaking of water-structure at atmospheric pressure [3]. A typical electrolyte showing this effect is ammonium bromide (NH_4Br). We are interested in the viscosity phenomena of aqueous NH_4Br solutions at high pressure where the water structure is broken. In the present work we have measured the viscosity of aqueous NH_4Br solutions as a function of pressure, temperature, and concentration. The results are compared with those of NaCl [4], whose B coefficients is slightly positive.

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To estimate the viscosity, the density of the solution is needed [4]. Therefore the high-pressure density of the solution was also measured.

2. Experimental Section

NH_4Br purchased from Nakarai Tesque, Inc. (extra pure grade) was recrystallized twice from water and dried in a vacuum desicator over P_2O_5. The purity of the salts was checked to be better than 99.8% by titration with 0.1 mol dm^{-3} $AgNO_3$. The concentrations of the sample solutions were 0.100, 0.300, 0.500, 0.700, and 1.000 ($\pm$ 0.0002) mol kg^{-1}. They were passed through a membrane filter (d = 25 mm, pore size 0.1 μm), to remove dust, and then put into viscometers or pycnometers.

The viscosity at 0.1 MPa was measured using an Ubbelohde-type viscometer and that at high pressure was done using a rolling-ball type viscometer designed by us [6]. The viscosity, η, was estimated from the rolling time, t:

$$\eta = K(d_b - d)\,t, \tag{1}$$

where K is a constant for the equipment and d_b and d are the density of the ball and solution, respectively. The density of the solution at 0.1 MPa was measured using an Ostwald's pycnometer (25 cm^3). To estimate the high-pressure density, the compression k, defined by

$$k = (d - d_0)/d) \tag{2}$$

Table 1. Compression of aqueous NH_4Br solution.

p/MPa	T/K					
	278.2	283.2	288.2	298.2	313.2	323.2
	0.100 mol kg^{-1}					
50	0.0220	0.0217	0.0221	0.0205	0.0195	0.0200
100	0.0412	0.0401	0.0396	0.0388	0.0365	0.0372
150	0.0577	0.0572	0.0553	0.0537	0.0510	0.0510
200	0.0720	0.0707	0.0696	0.0679	0.0648	0.0656
250	0.0854	0.0844	0.0833	0.0801	0.0770	0.0772
300	0.0975	0.0964	0.0962	0.0912	0.0913	0.0887
	0.300 mol kg^{-1}					
50	0.0237	0.0222	0.0209	0.0204	0.0185	0.0177
100	0.0403	0.0396	0.0395	0.0387	0.0370	0.0357
150	0.0573	0.0553	0.0544	0.0521	0.0507	0.0490
200	0.0712	0.0699	0.0691	0.0680	0.0671	0.0651
250	0.0839	0.0828	0.0817	0.0795	0.0761	0.0759
300	0.0983	0.0963	0.0952	0.0934	0.0899	0.0860
	0.500 mol kg^{-1}					
50	0.0243	0.0222	0.0203	0.0201	0.0179	0.0166
100	0.0399	0.0392	0.0392	0.0382	0.0370	0.0348
150	0.0570	0.0543	0.0537	0.0510	0.0502	0.0479
200	0.0706	0.0692	0.0685	0.0674	0.0674	0.0643
250	0.0829	0.0816	0.0806	0.0786	0.0752	0.0748
300	0.0981	0.0957	0.0942	0.0935	0.0875	0.0869
	0.700 mol kg^{-1}					
50	0.0235	0.0218	0.0202	0.0197	0.0177	0.0168
100	0.0397	0.0390	0.0386	0.0376	0.0362	0.0345
150	0.0566	0.0541	0.0533	0.0505	0.0495	0.0476
200	0.0702	0.0686	0.0679	0.0662	0.0657	0.0633
250	0.0823	0.0809	0.0799	0.0776	0.0742	0.0738
300	0.0967	0.0944	0.0931	0.0914	0.0862	0.0853
	1.000 mol kg^{-1}					
50	0.0219	0.0210	0.0202	0.0190	0.0184	0.0182
100	0.0404	0.0340	0.0376	0.0356	0.0345	0.0342
150	0.0563	0.0546	0.0529	0.0503	0.0488	0.0483
200	0.0704	0.0684	0.0666	0.0635	0.0618	0.0609
250	0.0829	0.0808	0.0790	0.0754	0.0735	0.0724
300	0.0943	0.0920	0.0903	0.0864	0.0843	0.0829

where d_0 is the density of the solution at 0.1 MPa, was measured using an Adams-type piezometer [7]. The detail for these measurements were previously described [4–6, 8].

3. Results and Discussion

3.1. *Density of Aqueous NH_4Br Solution*

The obtained compression of the solution is listed in Table 1. It is well known that the modified Tait's equation

$$k = E \log_{10} [(F + p)/(F + 0.1)], \quad (3)$$

Table 2. Density at 0.1 MPa and parameters of modified Tait's equation.

$\frac{T}{\mathrm{K}}$	$\frac{m}{\mathrm{mol\ kg^{-1}}}$	$\frac{d_0}{\mathrm{g\ cm^{-3}}}$	E	$\frac{F}{\mathrm{MPa}}$
278.2	0.100	1.00548	0.3031	273.8
	0.300	1.01649	0.2971	268.8
	0.500	1.02737	0.2914	263.9
	0.700	1.03811	0.2856	258.9
	1.000	1.05399	0.2773	251.5
283.2	0.100	1.00514	0.3135	291.5
	0.300	1.01604	0.3065	286.7
	0.500	1.02682	0.2999	281.9
	0.700	1.03746	0.2929	277.2
	1.000	1.05323	0.2841	269.9
288.2	0.100	1.00455	0.3201	305.7
	0.300	1.01539	0.3128	301.4
	0.500	1.02608	0.3061	297.1
	0.700	1.03663	0.2993	292.8
	1.000	1.05221	0.2894	286.3
298.2	0.100	1.00246	0.3243	323.0
	0.300	1.01321	0.3203	322.4
	0.500	1.02379	0.3143	319.3
	0.700	1.03421	0.3078	316.2
	1.000	1.04956	0.2984	311.5
313.2	0.100	0.99768	0.3203	330.0
	0.300	1.00831	0.3156	328.6
	0.500	1.01876	0.3096	326.1
	0.700	1.02902	0.3042	323.7
	1.000	1.04400	0.2957	320.1
323.2	0.100	0.99357	0.3187	331.8
	0.300	1.00409	0.3112	327.9
	0.500	1.01449	0.3025	322.8
	0.700	1.02477	0.2941	317.7
	1.000	1.03980	0.2816	310.1

where E and F are constants and p is the pressure (MPa), is applicable to many compression data of liquids, such as organic solvents and water, as a function of pressure [9]. Our compression data in Table 1 are fitted to this equation, and E and F values are obtained as listed in Table 2. To estimate the high-pressure density, we did not use the compression data in Table 1 but those calculated from (3), using the E and F values in Table 2. The densities at 0.1 MPa are also listed in Table 2.

3.2. *Pressure Dependence of the Viscosity*

The viscosities are listed in Table 3 and plotted in Figure 1. The solid curves in Fig. 1 are fitting curves.

$$\eta = f_0 + f_1 p + f_2 p^2, \quad (4)$$

where f_0, f_1, and f_2 are coefficients and the numerical values are tabulated in Table 4. The deviation of the

Table 3. Viscosity (η/mPa s) of aqueous NH_4Br solution

p/MPa	T/K					
	278.2	283.2	288.2	298.2	313.2	323.2
	0.100 mol kg^{-1}					
0.1	1.4983	1.2904	1.1305	0.8858	0.6505	0.5444
25	1.465	1.267	1.117	0.878	0.654	0.550
50	1.445	1.251	1.112	0.877	0.662	0.555
75	1.429	1.242	1.109	0.880	0.670	0.563
100	1.418	1.237	1.108	0.883	0.679	0.570
125	1.412	1.238	1.110	0.887	0.688	0.580
150	1.409	1.243	1.114	0.892	0.697	0.589
175	1.411	1.251	1.121	0.899	0.706	0.599
200	1.418	1.263	1.129	0.906	0.716	0.606
225	1.429	1.278	1.141	0.915	0.727	0.617
250	1.444	1.296	1.155	0.921	0.738	0.628
275	1.464	1.316	1.171	0.936	0.749	0.640
300	1.488	1.339	1.190	0.948	0.760	0.650
325	1.516	1.364	1.211	0.962	0.772	0.665
350	1.549	1.391	1.234	0.976	0.785	0.675
375	1.594	1.420	1.260	0.992	0.797	0.690
	0.300 mol kg^{-1}					
0.1	1.4694	1.2706	1.1159	0.8791	0.6495	0.5463
25	1.445	1.256	1.102	0.871	0.655	0.555
50	1.425	1.249	1.096	0.871	0.663	0.561
75	1.409	1.244	1.092	0.873	0.671	0.567
100	1.398	1.242	1.090	0.876	0.680	0.574
125	1.392	1.242	1.091	0.880	0.689	0.585
150	1.389	1.245	1.094	0.885	0.698	0.594
175	1.391	1.250	1.099	0.892	0.705	0.603
200	1.398	1.258	1.107	0.899	0.717	0.613
225	1.409	1.268	1.118	0.908	0.728	0.626
250	1.424	1.281	1.130	0.918	0.739	0.636
275	1.444	1.296	1.145	0.929	0.750	0.646
300	1.468	1.313	1.162	0.941	0.761	0.656
325	1.496	1.338	1.182	0.955	0.773	0.670
350	1.529	1.356	1.204	0.969	0.786	0.684
375	1.574	1.381	1.229	0.985	0.798	0.699
	0.500 mol kg^{-1}					
0.1	1.4423	1.2517	1.1022	0.8731	0.6490	0.5466
25	1.422	1.222	1.094	0.866	0.652	0.558
50	1.415	1.215	1.088	0.857	0.667	0.564
75	1.411	1.209	1.087	0.856	0.672	0.572
100	1.410	1.207	1.086	0.857	0.685	0.582
125	1.411	1.208	1.101	0.868	0.689	0.592
150	1.414	1.212	1.101	0.878	0.705	0.601
175	1.421	1.220	1.103	0.881	0.718	0.613
200	1.429	1.231	1.120	0.890	0.722	0.624
225	1.441	1.246	1.134	0.900	0.738	0.635
250	1.454	1.263	1.142	0.926	0.744	0.647
275	1.466	1.285	1.161	0.940	0.755	0.660
300	1.500	1.309	1.174	0.956	0.767	0.672
325	1.522	1.337	1.192	0.973	0.780	0.685
350	1.546	1.369	1.212	0.991	0.792	0.701
375	1.584	1.403	1.233	1.011	0.805	0.720

Table 3. Continued.

p/MPa	T/K					
	278.2	283.2	288.2	298.2	313.2	323.2
	0.700 mol kg^{-1}					
0.1	1.4168	1.2336	1.0893	0.8678	0.6488	0.5474
25	1.396	1.210	1.082	0.857	0.653	0.559
50	1.394	1.201	1.074	0.851	0.657	0.570
75	1.396	1.197	1.071	0.848	0.662	0.580
100	1.399	1.198	1.070	0.849	0.675	0.590
125	1.400	1.204	1.074	0.852	0.679	0.600
150	1.416	1.215	1.082	0.859	0.695	0.610
175	1.436	1.232	1.094	0.868	0.708	0.620
200	1.451	1.253	1.109	0.881	0.712	0.631
225	1.460	1.280	1.128	0.897	0.728	0.641
250	1.490	–	1.151	0.916	0.734	0.655
275	1.515	–	1.178	0.938	0.745	0.665
300	1.533	–	–	0.963	0.757	0.680
325	1.575	–	–	0.992	0.770	0.695
350	1.610	–	–	–	0.782	0.712
375	1.635	–	–	–	0.795	0.730
	1.000 mol kg^{-1}					
0.1	1.3861	1.2125	1.0716	0.8616	0.6505	0.5497
25	1.380	1.190	1.064	0.851	0.652	0.564
50	1.373	1.181	1.056	0.845	0.667	0.572
75	1.384	–	1.053	0.842	0.672	0.582
100	1.386	–	1.052	0.843	0.685	0.591
125	1.400	–	1.056	0.846	0.689	0.603
150	1.424	–	1.064	0.854	0.705	0.615
175	1.434	–	1.084	0.862	0.718	0.626
200	1.468	1.260	1.113	0.875	0.722	0.637
225	1.490	1.290	1.138	0.901	0.738	0.650
250	1.520	1.321	1.161	0.919	0.744	0.663
275	1.551	1.358	1.188	0.941	0.755	0.675
300	1.590	1.400	1.219	0.967	0.768	0.690
325	1.622	–	1.254	0.996	0.780	0.705
350	1.650	–	1.292	1.042	0.792	0.725
375	1.699	–	1.335	1.080	0.805	0.740

dots from the curves is at most ±1%. The curves at zero concentration are cited from [1]. The viscosity curve of water at zero concentration at lower temperatures than 298.2 K shows a minimum in Figure 1. The curve is deformed by addition of NH_4Br, but the minimum is kept even at 1 mol kg^{-1}. This means that addition of NH_4Br up to 1 mol kg^{-1} does not completely break the water structure at 0.1 MPa.

3.3. Temperature Dependence of the Viscosity

Temperature dependence of the viscosity has been represented by the activation energy, E_v, for viscous flow [10] defined by

$$[\partial \ln \eta / \partial (1/T)]_p = E_v/R\,. \tag{5}$$

E_v is an important parameters for the understanding the structure of ionic hydration [11]. $\ln \eta$ vs. $1/T$ for the solutions at 0.5 mol kg^{-1} is plotted in Fig. 2 as an example. The curves are estimated from Table 4 using (4) and are fitted to the second polynomial of $1/T$. E_v is estimated from the slope of (5). The pressure dependence of the E_v at 298.2 K is shown in Figure 3. The

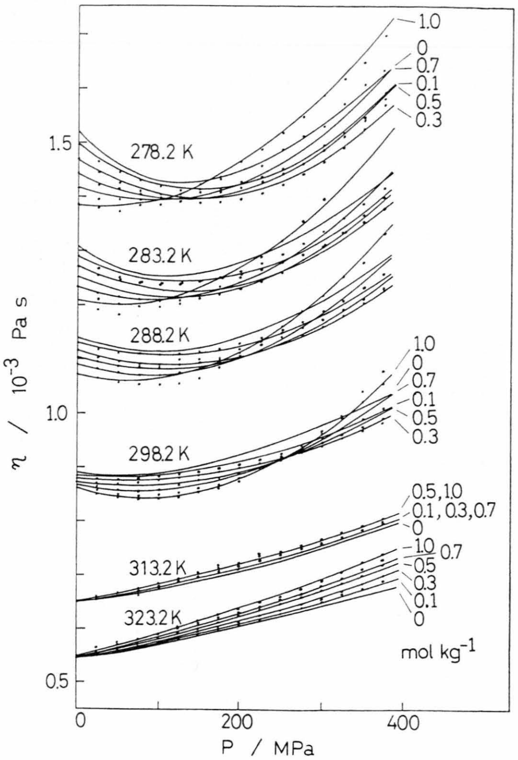

Fig. 1. Pressure dependence of the viscosity for aqueous NH_4Br solution.

Table 4. Coefficients of f_0, f_1, and f_2 in (4) for aqueous NH_4Br solution.

T / K	m / mol kg^{-1}	f_0 / 10^{-3} Pa s	f_1 / 10^{-12} s	f_2 / 10^{-21} Pa^{-1} s
278.2	0.100	1.496	−1.063	3.555
	0.300	1.468	−0.936	3.166
	0.500	1.442	−0.755	3.064
	0.700	1.418	−0.530	2.900
	1.000	1.383	−0.096	2.650
283.2	0.100	1.289	−0.695	2.964
	0.300	1.271	−0.708	2.701
	0.500	1.251	−0.636	2.751
	0.700	1.232	−0.504	2.802
	1.000	1.208	−0.244	2.802
288.2	0.100	1.131	−0.434	2.021
	0.300	1.116	−0.455	2.015
	0.500	1.102	−0.418	2.120
	0.700	1.088	−0.430	2.522
	1.000	1.070	−0.325	2.766
298.2	0.100	0.885	−0.091	1.104
	0.300	0.878	−0.119	1.102
	0.500	0.872	−0.184	1.425
	0.700	0.867	−0.273	1.860
	1.000	0.860	−0.402	2.477
313.2	0.100	0.651	0.221	0.391
	0.300	0.650	0.240	0.366
	0.500	0.649	0.272	0.311
	0.700	0.649	0.297	0.259
	1.000	0.651	0.296	0.297
323.2	0.100	0.544	0.267	0.281
	0.300	0.546	0.274	0.350
	0.500	0.547	0.306	0.349
	0.700	0.547	0.341	0.335
	1.000	0.550	0.387	0.308

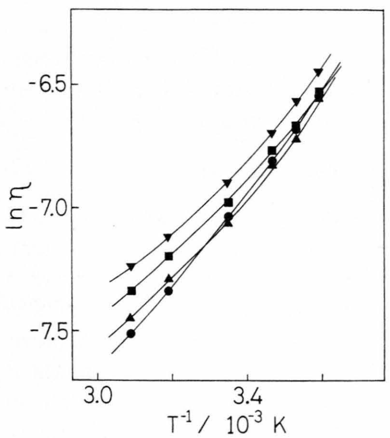

Fig. 2. $\ln \eta$ vs. $1/T$ for 0.500 mol kg^{-1} NH_4Br solution. ●: 0.1 MPa, ▲: 100 MPa, ■: 250 MPa, ▼: 375 MPa.

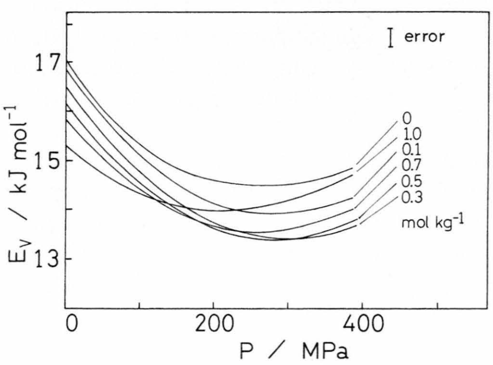

Fig. 3. Pressure dependence of the activation energy for the viscosity of aqueous NH_4Br solution and water at 298.2 K.

E_v's at all concentrations diminish with increasing pressure up to 200–300 MPa and then increase, as similar minimum has been observed for 0–2 mol kg^{-1} NaCl solution in the same pressure region [4]. The minimum of E_v for water has been ascribed to competition between the decrease of E_v accompanying water-structure breaking by compression and increase of E_v by stuffing of water molecules. The E_v at 0.1 MPa decreases with addition of NH_4Br, as shown in Figure 3. This has been attributed to the water-structure breaking effect of NH_4Br. At high pressure, this effect is thought to become weak because the water structure is already broken by pressure. Therefore E_v at 375 MPa increases with increasing concentration after the reduction from zero to 0.3 mol kg^{-1}.

3.4. Concentration Dependence of the Viscosity

In Fig. 4 the viscosity is plotted against concentration. Our results at 0.1 MPa and 298.2 K coincide with the data by Getman [12]. This viscosity at 0.1 MPa decreases with increasing concentration at low temperature between 278.2 K and 298.2 K. A similar reduction of the viscosity has been observed for several aqueous electrolyte solutions, and at high concentration the viscosity increased, resulting in a minimum [3]. For NH_4Br solution the minimum is known to be at 2–3 mol dm^{-3} [12]. This reduction of the viscosity has been ascribed to breaking of water-structure by addition of electrolyte, and the electrolyte has been classified as a structure breaker [3]. Because the water structure at high temperature is already broken by heat, the viscosity at high temperature does not decrease by addition of the electrolyte, as shown in Figure 4.

With increasing pressure up to 375 MPa, the viscosity minimum shifts to low concentrations and appears at 278.2–298.2 K in Figure 4. This seems to suggest that the water-structure breaking effect of NH_4Br is weakened by pressure. On the other hand, the slope of the curve at zero concentration at 375 MPa is steeper than that at 0.1 MPa, suggesting that the water-structure breaking effect of NH_4Br is enhanced by pressure. To make the situation clear, it is reasonable to estimate the Jones-Dole's B coefficient [3]. Because the concentration range in Fig. 4 is wide, we use an extended Jones-Dole's equation [13]:

$$\eta/\eta_0 = 1 + A\sqrt{c} + Bc + Dc^2, \tag{6}$$

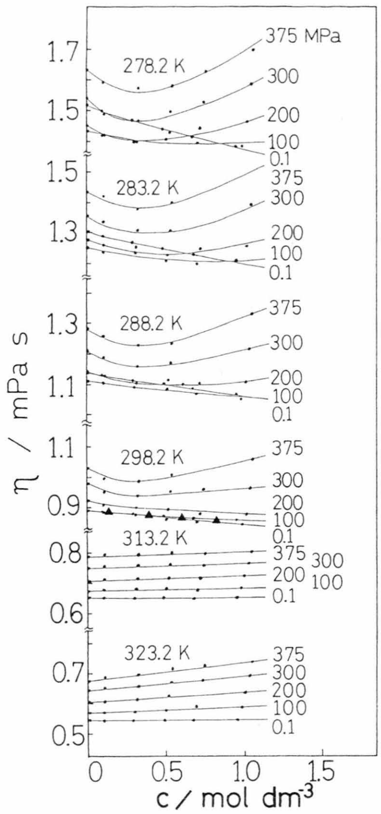

Fig. 4. Concentration dependence of the viscosity for aqueous NH_4Br solution. ▲: Getman [12] at 298.2 K and 0.1 MPa.

where η_0 is the viscosities of water and c is the molarity (mol dm^{-3}) of the electrolytes. This equation can be changed into a linear function of c:

$$(\eta/\eta_0 - 1 - A\sqrt{c})/c = B + Dc. \tag{7}$$

The A value can be estimated to be 0.0050 mol$^{-1/2}$ dm$^{3/2}$ [14, 15]. Its pressure and temperature dependences may be negligible because A itself is small. Therefore we applied this value of A in (7) at all temperatures and pressures. Figure 5 shows linear relations of $(\eta/\eta_0 - 1 - A\sqrt{c})$ vs. c. Our data at 0.1 MPa are in good agreement with those by Getman [12]. The B value at 0.1 MPa is obtained to be -0.065 mol^{-1} dm^3 by extrapolation of the line to zero concentration. It is compared with -0.049 mol^{-1} dm^3 calculated from the B values of NH_4^+ and Br^- ions by Nightingale [3]. These facts support the validity of our estimation of B using (7). The pressure dependence of the B of NH_4Br in water is shown in Figure 6. The B's

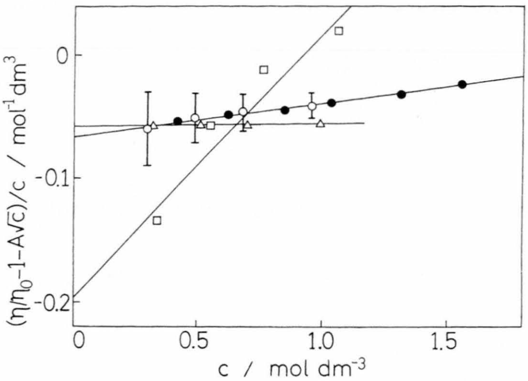

Fig. 5. $(\eta/\eta_0 - 1 - A\sqrt{c})$ vs. c for aqueous NH_4Br solution at 298.2 K. ○: 0.1 MPa, △: 100 MPa, □: 300 MPa, ●: Getman [12] at 0.1 MPa.

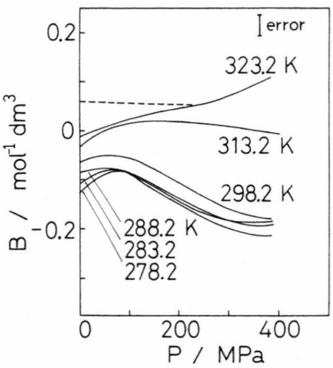

Fig. 6. Pressure dependence of Jones-Dole's B coefficient of NH_4Br in water. ······: theoretical (see text).

are negative at 0.1 MPa, increase with increasing pressure up to ca. 100 MPa, and decrease after having a maximum except for the B at 323.2 K. A similar maximum has been observed for NaCl in water at ca. 100 MPa at 283.2, 298.2, and 323.2 K [4]. The dotted line was estimated by Ibuki and Nakahara's method based on a Hubbard and Onsager's dielectric friction theory [16] using high pressure properties of the viscosity [1], dielectric constant [17], and dielectric relaxation time of water [18]. This line is for electrolytes whose ionic radius is 0.1 – 0.2 nm, including both NH_4Br and NaCl. It decreases with increasing pressure without any maximum because the theory does not take any water structure into account. The reduction of B for NaCl with increasing pressure at higher pressure than 100 MPa was ascribed to this effect [4]. On the other hand, the increasing of B for NaCl up to 100 MPa has been ascribed to an apparent enhancement of B accompanying the structure-breaking in bulk water by pressure [4]. The maximum of B for NH_4Br in Fig. 6 may be ascribed to competition of these two effects, though the increase of B at 323.2 K higher pressure than 100 MPa can not be ascribed to these effects, suggesting an other interaction between NH_4Br and water because this increase has not been observed for NaCl in water at the same temperature. The matter needs further consideration.

4. Conclusion

In the present work, two high-pressure phenomena were observed; (1) the activation energy of viscous flow for aqueous NH_4Br solution decreases with increasing concentration at 0.1 MPa and increases at high pressure, (2) the Jones-Dole's B coefficient of NH_4Br in water has a maximum at ca. 100 MPa. Similar phenomena have been observed for NaCl in water [4]. Supposing two types of water, that is, bulk water and hydrated water around an ion, the phenomena are ascribed to breaking of the former structure with increasing pressure, implying that the latter structure does not change (or change less) by pressure. As the hydrated water is strongly attracted by ions, it is reasonable that the structure of hydrated water does not change or change less by pressure than that of bulk water.

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