The Pressure Effect on the Activity Coefficient of Sodium Chloride and Bromide Ions

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A new paraffin salt bridge was developed for the concentration cell in high pressure system. The emf values of the concentration cells were measured to calculate the activity coefficients of the electrolytic ions depending upon the pressure of the system. The activity coefficients of sodium, chloride and bromide ions increase with the temperature of the cell and decreased, nearly halfed at 2500 bars, 20°C, with the pressure. These results can be explained to be attributed to the volume change of the hydrated ion due to the electrostriction. The volume change decreased with pressure due to an increase in the degree of the hydration.

Introduction

It has been very interesting and important to know the colligative properties of the polyelectrolyte solutions by measuring the activity of the counter ions under the atmospheric pressure.[1-4] Therefore, to study the pressure dependence of the polyelectrolyte we have to investigate the activities of the counter ions of the polyelectrolytes in the solution at high pressure.

Until now, most of the electrochemical studies for the activities of simple and polyelectrolytes in a concentration cell have been achieved at the atmospheric pressure because the conventional salt bridge was not sustainable under high pressure system.[5-11] Accordingly, the study for the measurement of the electromotive force from which is calculated the activities of the ions has been succeeded only in the electrochemical cell in which the salt bridge was not required under high pressure.[12,13]

In this work, we devised a paraffin salt bridge which is available in the concentration cell for the high pressure system. The emf values of the concentration cells were used to calculate the activity coefficients of sodium, chloride and bromide ions. The pressure dependence of the activity coefficients of these ions was investigated to understand the behavior of the ions in the solution at high pressure system. In addition to the paraffin salt bridge, a sodium amalgam

bridge was designed to obtain the activity coefficient of a single ion under the high pressure.

This study might contribute to understand the soluble and structural behavior of polyelectrolytes in the high pressure system.[1,2]

The concentration cell with the sodium amalgam bridge which we call it Cell A was Ag/AgCl/ NaCl(m(H))/ Hg(Na)/ NaCl(m(L))/ AgCl/Ag, where the m(H) and m(L) stand for the high and low molality of NaCl respectively.

The novel concentration cell with the paraffin salt bridge which we called it Cell B was Ag/AgX/ NaX(m(H))/ Paraffin(KX)/ NaX(m(L))/ AgCl/Ag, where X is halide ion; chloride or bromide.

The emf of the Cell A can be expressed by

$$E = (RT/F) \ln (a_{Na^+}(H)/a_{Na^+}(L))$$
$$- (RT/F) \ln (\gamma_{Na^+}(H) m_{Na^+}(H)/\gamma_{Na^+}(L) m_{Na^+}(L)) \qquad (1)$$

where the subscripts H and L were mentioned above and the other parameters have conventional meanings. Assuming the value of the activity coefficient of sodium ion in the low molality $(\gamma_{Na^+}(L))$ unity, we derive the following equation from Eqn(1).

$$\gamma_{Na^+}(H) = (m_{Na^+}(L)/m_{Na^+}(H)) \exp(FE/RT) \qquad (2)$$

Similarly, the next equation can be obtained for the Cell B.

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$$\gamma_{\pm}(NaX) = ((\gamma_{Na}^{+}(H)\,\gamma_{X^{-}}(H))^{1/2}$$

$$= (m_{NaX}(L)/m_{NaX}(H))\,\exp(FE/RT) \qquad (3)$$

where $\gamma_{\pm}(NaX)$ represent the mean activity coefficient of NaX.

From Eqn (2) and (3), we obtain the next equation.

$$\gamma_{X}^{-}(H) = (1/\gamma_{Na}^{+}(H))\,(m_{NaX}(L)/m_{NaX}(H))\,\exp(FE/RT) \quad (4)$$

Taking the natural logarithm to the both sides of Eqn (2) and then differentiating the result with pressure at a constant temperature and molality, we can get the following equation.

$$\Delta V_{Na}^{+} = -F(\partial E/\partial P)_{T,m} = -RT(\partial \ln \gamma_{Na}^{+}/\partial P)_{T,m} \qquad (5)$$

where $\Delta G = -FE$ (for 1 – 1 electrolytes) were used. The Eqn (5) represents that the volume change of sodium ion in Cell A is closely related to the pressure dependence of the activity coefficient of the ion.

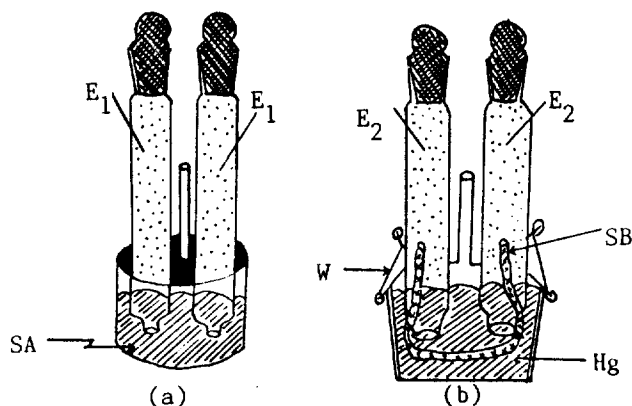Similarly, the next equations can also be derived from Eqn (3).

$$\Delta V_{NaX} = \Delta V_{Na}^{+} + \Delta V_{X}^{-}$$

$$= -RT(\partial \ln \gamma_{Na}^{+}/\partial P)_{T,m} - RT(\partial \ln \gamma_{X}^{-}/\partial P)_{T,m} \qquad (6)$$

From this equation, we can know that the volume change of a single ion can be obtained from the pressure dependence of its activity coefficient at constant temperature and molality of NaX.

Experimental

Mercury and water purified by the three consecutive distillations were used for the experiment. Sodium chloride and sodium bromide of guaranted reagents were used. The sodium amalgam, which was cathodically prepared, contains about 0.2% of sodium.

Cell A was made of pyrex glass and had a sodium amalgam pool with the two branched cylinders as shown in Figure 1(a). The hand operated pressure pump and the pressure vessel, in which Cell A was suspended, were described in the previous paper.[14] The sodium amalgam in the pool attached to the cell were functioned as a pressure transmitting fluid.

Cell B was made by replacing the sodium amalgam bridge of Cell A with the potassium chloride bridge sealed with paraffin. Mercury was added as the pressure transmitting fluid in place of sodium amalgam. The cotton bundle which is consisted of 10 strings of cotton thread were inserted into 50 ml of the potassium chloride solution and then boiled it for about 5 minutes. The agar powder of 0.1 g was added to this boiling solution and then it had been boiling with stirring for 5 minutes. Taking the cotton bundle out from this solution and twisting it by hand, we put it into a boiling paraffin solution for about one minute. This cotton bundle was retwisted by hand and then inserted it into a polyethylene tube of which inner diameter and length were 3mm and 70mm, respectively. At that time the polyethylene tube was densely packed with the strings of the cotton bundle in order to prevent the passing of the solutions through the both cell compartments. This tube was solidified in the air and then dipped in distilled water for one day before its use. We called it a paraffin salt bridge.

We checked the reliability of the cells prepared by com-

Figure 1. Schematic diagram of the cell used for the high pressure system; (a) Cell A: Ag/AgCl/NaCl(1.607×10^{-2}m)/Hg(Na)/NaCl (1.603×10^{-4}m) AgCl/Ag; (b) Cell B: Ag/AgX/NaX(H)/Paraffin(KX)/ NaX(L)/AgX/Ag NaX(H) = 1.000×10^{-2}m, NaX(L) = 1.000×10^{-4}m. E_1: Ag/AgCl electrode, E_2:Ag/AgX (X = Cl or Br) electrode. SA: Sodium amalgam, SB: Paraffin salt bridge. W: Connecting wire.

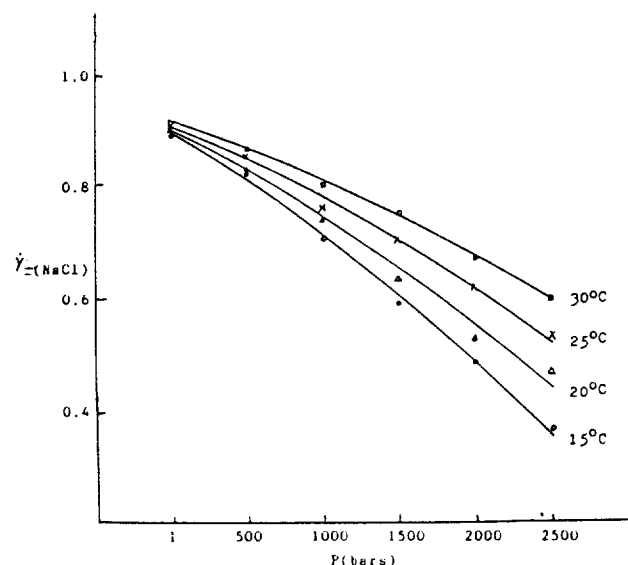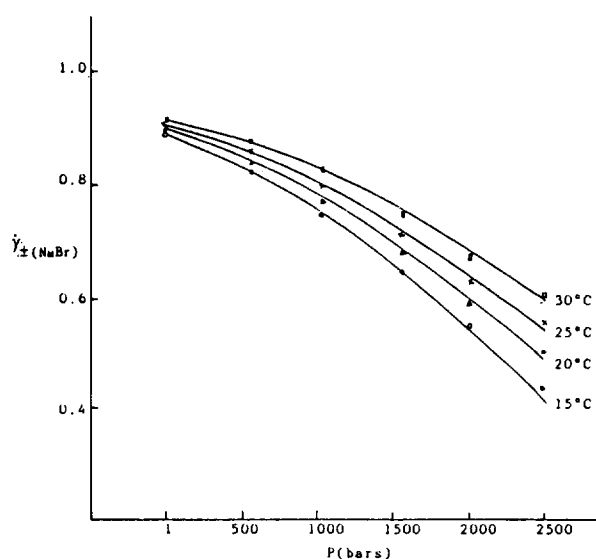**Figure 2.** Mean activity coefficient of sodium chloride as a function of pressure at various temperature.

Figure 3. Mean activity coefficient of sodium bromide as a function of pressure at various temperature.

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paring the emf between measured and calculated from Eqn (1). The asymmetry potential of the paraffin bridges were less than one milivolt and although it change slightly with age, in any particular experiment it reached a nearly steady value after one pressure cycle and was then independent of the pressure to within 0.5 mV between 1 and 2500 bars.

The silver–silver bromide electrode, instead of the silver–silver chloride electrode of Cell A was used in Cell B as shown in Figure 1 (b).

Controlling the high molality, m(H) to be about 10^{-2}m and the low molality, m(L) about 10^{-4}m in the Cell A and B, we made the factor of m(H)/m(L) be 100 before the measurement of the emf them.

The measurement of the emf for the cells was carried out in the temperature range of 15 - 30°C ($\pm$0.1°C). The pressure of the system was varied from 1 to 2500 bars($\pm$1 bar). The cell voltage was measured with a DC potentiometer (Yokogawa Electric Works, type 2727, Japan).

Results and Discussion

The values of the emf measured from the three different cells of one Cell A and two Cell B's were listed in Table 1, 2, and 3. These data indicate the average emf values obtained from three or four measurements. The emf values decrease

Table 1. The emf (V) of the cell (Ag/AgCl/NaCl(1.067 x 10⁻²m)/ Hg(Na)/Nacl(1.063 x 10⁻⁴m)/AgCl/Ag) at the Various Pressure and Temperature

T(°C)	P(bars)					
	1	500	1,000	1,500	2,000	2,500
15	0.1120	0.1090	0.1055	0.1020	0.0980	0.0931
20	0.1140	0.1110	0.1078	0.1040	0.1013	0.0969
25	0.1160	0.1139	0.1109	0.1075	0.1040	0.0998
30	0.1181	0.1165	0.1136	0.1108	0.1059	0.1021

Table 2. The emf (V) of the cell (Ag/AgCl/NaCl(1.000 x 10⁻²m)/ Paraffin(KCl)/NaCl(1.000 x 10⁻⁴m)/AgCl/Ag) at Various Pressure and Temperature

T(°C)	P(bars)					
	1	500	1,000	1,500	2,000	2,500
15	0.1090	0.1051	0.0973	0.0886	0.0786	0.0722
20	0.1110	0.1073	0.1016	0.0938	0.0840	0.0796
25	0.1131	0.1109	0.1050	0.1007	0.0947	0.0866
30	0.1151	0.1130	0.1093	0.1056	0.0994	0.0940

Table 3. The emf (V) of the Cell (Ag/AgBr/NaBr(1.000 x 10⁻²m)/ Paraffin(KBr)/NaBr(1.000 x 10⁻⁴m)/AgBr/Ag) at Various Pressure and Temperature

T(°C)	P(bars)					
	1	500	1,000	1,500	2,000	2,500
15	0.1091	0.1051	0.1000	0.0935	0.0856	0.0768
20	0.1113	0.1076	0.1025	0.0961	0.0896	0.0820
25	0.1135	0.1110	0.1066	0.1036	0.0932	0.0860
30	0.1156	0.1137	0.1102	0.1054	0.0997	0.0940

with pressure but increase with temperature for all of the cell.

The activity coefficient of sodium ion present in 1.067×10^{-2}m sodium chloride solution was calculated from Eqn (2) at various temperature and pressure and listed in Table 4. These data can be used for the estimation of the activity coefficient of the halide ions in the polyelectrolyte solutions corressponding pressure. The mean activity coefficients calculated from Eqn (3) of sodium chloride and bromide ions are shown in Figure 2 and 3 respectively. The activity coefficients of chloride and bromide ions calculated from Eqn (6) are listed in Table 5 and 6 respectively.

From Table 4, 5 and 6, the pressure dependence of the activity coefficient of ion can be expressed by using the linear regression method.

$$\ln \gamma_{Na^+} (H) = -2.692 \times 10^{-8} P^2 - 2.011 \times 10^{-4} P - 9.631 \times 10^{-2} \quad (7)$$

$$\ln \gamma_{Cl^-} (H) = -5.982 \times 10^{-8} P^2 - 6.555 \times 10^{-4} P - 0.1160 \quad (8)$$

$$\ln \gamma_{Br^-} (H) = -5.812 \times 10^{-8} P^2 - 5.436 \times 10^{-4} P - 0.1004 \quad (9)$$

All of the activity coefficient described above decrease with pressure. This phenomenon can be explained as follows. First

Table 4. The Activity Coefficient of Sodium Ion in 1.067 x 10⁻²m NaCl Solution at Various Pressure and Temperature

T(°C)	P(bars)					
	1	500	1,000	1,500	2,000	2,500
15	0.907	0.803	0.695	0.606	0.516	0.422
20	0.909	0.807	0.711	0.612	0.550	0.462
25	0.911	0.839	0.747	0.654	0.571	0.484
30	0.916	0.862	0.771	0.693	0.574	0.496

Table 5. The Activity Coefficient of Chloride Ion in 1.000 x 10⁻²m NaCl Solution at Various Pressure and Temperature

T(°C)	P(bars)					
	1	500	1,000	1,500	2,000	2,500
15	0.888	0.857	0.704	0.654	0.458	0.400
20	0.890	0.865	0.784	0.669	0.564	0.519
25	0.895	0.891	0.796	0.769	0.696	0.599
30	0.896	0.896	0.850	0.821	0.782	0.635

Table 6. The Activity Coefficient of Bromide Ion in 1.000 x 10⁻²m NaBr Solution at Various Pressure and Temperature

T(°C)	P(bars)					
	1	500	1,000	1,500	2,000	2,500
15	0.881	0.858	0.805	0.712	0.609	0.522
20	0.899	0.877	0.812	0.734	0.631	0.554
25	0.909	0.895	0.847	0.761	0.657	0.588
30	0.910	0.900	0.880	0.805	0.689	0.636

Table 7. The Volume Change of Sodium, Chloride, and Bromide Ions by Varying Pressure at 20°C

P(bars)	1	500	1,000	1,500	2,000	2,500
V_{Na^+} (cm³/mol)	-4.90	-5.56	-6.21	-6.78	-7.52	-8.18
V_{Cl^-}		-1.60	-3.06	-4.51	-5.97	-7.43	-8.89
V_{Br^-}		-1.33	-2.74	-4.16	-5.57	-6.99	-8.41

the mobility of the ions in the ionic solution is accelerated by increasing pressure so that the average distance between the opposite ions decreases. This fact explains the decrease of the ionic charge, which results the decrease in the ionic activity. Second, the degree of hydrogon bonding of water molecules can be increased with pressure, which decreases the ionic charge to give a decrease in ionic activity.[15]

From the equations of (1), (2), and (5), we derived the next equations.[16]

$$\Delta V_{Na}^{+} - \Delta V_{Na}^{+}(L) - \Delta V_{Na}^{+}(H)$$
$$= -RT(\partial \ln \gamma_{Na}^{+}(L)/\partial P)_{T,\pi} + RT(\partial \ln \gamma_{Na}^{+}(H)/\partial P)_{T,\pi} \quad (10)$$

Assuming that the activity coefficients of ions in the dilute concentration is not dependent on pressure, we can obtain the Eqn (11) from the Eqn (10).

$$\Delta V_{Na}^{+} - RT(\partial \ln \gamma_{Na}^{+}(H)/\partial P)_{T,\pi} \quad (11)$$

Similarly we can get the next equations.

$$\Delta V_{Cl}^{-} - RT(\partial \ln \gamma_{Cl^{-}}(H)/\partial P)_{T,\pi} \quad (12)$$
$$\Delta V_{Br}^{-} - RT(\partial \ln \gamma_{Br^{-}}(H)/\partial P)_{T,\pi} \quad (13)$$

The volume changes of the sodium, chloride, and bromide ions which had been calculated from these equations were listed in Table 7. The ΔV_{ion} values are negative and decrease with pressure. This fact is attributed to the electrostriction between the ion and water molecules. It can be also illustrated that the hydration of the ions increases with pressure to diminish the ionic charge of the ions and so the activity of the ions decreases.

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Synthesis of a Conformationally-rigid Etorphine Analogous

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In order to synthesize conformationally rigid etorphine analogues having potentially interesting pharmacological activities, synthesis of compound **3** by the reaction of compound **4** and compound **5** via intramolecular Diels–Alder reaction has been attempted. However, the reaction did not go well and the compound **3** would not be isolated. Therefore, intermolecular Diels–Alder reaction using dimethyl acetylene dicarboxylate was attempted. As shown in scheme 2, Diels–Alder adduct **9** was converted into the target molecule **14** containing the new [2,2,2] bicyclo octane ring in good yields.

Introduction

Many morphine derivatives possess analgesic activities. Most of these compounds are converted into the compounds with good antagonist activity by the simple substitution of N-methyl group. For example, the agonist morphine **1** is converted into the antagonist nalorphine **2** by changing the methyl group.