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The Complexing of the Sodium Ion in Acetonitrile with Other Solvents. Investigation by the Use of a Cation-sensitive Glass Electrode

Kosuke Izutsu, Toshiaki Nomura, Toshio Nakamura,
Hidetoshi Kazama, and Shigeo Nakajima
Chemistry Department, Faculty of Science, Shinshu University, Asahi, Matsumoto 390

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The complexing of the sodium ion in acetonitrile (AN) with such solvents as methanol, water, DMF, DMA, DMSO, HMPA, and pyridine has been studied potentiometrically by using a monovalent cation-sensitive glass electrode. The reference electrode of Ag-0.005 M $AgNO_3$(AN) and the salt bridge of 0.1 M Et_4NPi(AN) were used. Mono- and di-solvated ions were formed for methanol, water, and pyridine. For DMF, DMA, DMSO, and HMPA, tri-solvated species were also formed. The formation constants for the mono-solvated sodium ion were 0.7 for pyridine, 1 for methanol, 1.8 for water, 2.5 for DMF, 5 for DMA, 6 for DMSO, and 30 for HMPA.

The hydration constants of alkali metal ions and several monovalent anions in acetonitrile(AN) have been determined by Chantooni and Kolthoff.1) This was done by measuring conductometrically the ionic solubility of a slightly soluble salt in AN in the presence of a known concentration of water.

In the present paper, we investigated the complexing of the sodium ion in AN with such solvents as methanol, water, dimethylformamide(DMF), dimethylacetoamide (DMA), dimethylsulfoxide(DMSO), hexamethylphosphoramide(HMPA), and pyridine by using a monovalent cation-sensitive glass electrode. The emf of the following cell was measured:

Ag|0.005 M $AgNO_3$(AN)||0.1 M Et_4NPi(AN)||
(A) (B)
10^{-3} M $NaClO_4$+0.01 M Et_4NClO_4(AN+D)|Glass electrode
(C)

Cell I

where D denotes a solvent added to the AN solution in the compartment (C). The liquid junction potential between the salt bridge (B) and the solution in the compartment (C) was assumed to change only negligibly upon the addition of a solvent (D). The salt bridge of the 0.1 M tetraethylammonium picrate (Et_4NPi) in AN was used because Parker *et al.*2,3) reported that the junction potential between this salt bridge and a 0.01 M $AgClO_4$ solution in other dipolar solvents is usually relatively small. The Nernstian response of the cation-sensitive glass electrode towards alkali-metal ions has been verified in several nonaqueous solvents.4,5) We found, in the present study, that the glass electrode can also be used to measure the difference in the activity of the sodium ion in various solvents, provided that a suitable reference electrode system is employed.

In the mixture of AN and D, the following equilibrium is attained between sodium ions solvated only by AN (denoted by Na_s^+) and those which are solvated also by D (denoted by Na_{xD}^+, where x is the number of solvating D molecule(s)):

$$Na_s^+ + xD = Na_{xD}^+ \tag{1}$$

$$K_x = \frac{[Na_{xD}^+]}{[Na_s^+][D]^x} \tag{2}$$

where K_x is the corresponding formation constant. If we denote the activity of Na_s^+ in pure AN by $[Na_s^+]_{AN}$, and that in the mixture of AN and D by $[Na_s^+]_{AN-D}$, the following relations hold:

$$R \equiv \left\{\frac{[Na_s^+]_{AN}}{[Na_s^+]_{AN-D}} - 1\right\}/[D] = K_1 + K_2[D] + K_3[D]^2 + \cdots \tag{3}$$

and

$$(R-K_1)/[D] = K_2 + K_3[D] + \cdots \tag{4}$$

Here, the values of $[Na_s^+]_{AN}/[Na_s^+]_{AN-D}$ can be obtained from the potentials of the glass electrode in pure AN and an AN–D mixture as follows:

$$[Na_s^+]_{AN}/[Na_s^+]_{AN-D} = 10^{(E_{AN}-E_{AN-D})/59} \tag{5}$$

where E_{AN} and E_{AN-D} are in mV. By plotting the relations between R and [D] and between $(R-K_1)/[D]$ and [D], we can obtain the values of the formation constants of Reaction (1).

In the determination of formation constants, the following assumptions are made: (i) the solvent (D) in AN–D mixtures is monomeric, and the activity of D is equal to the analytical concentration; (ii) the activity of AN does not change upon the addition of D and is equal to unity; and (iii) the salt-effect activity coefficient of the sodium ion, calculated by the Debye-Hückel equation, is equal in pure AN and in AN–D mixtures. We also assume that the amount of the solvent(D) consumed by the solvation of the ions of an indifferent electrolyte is negligible. The last assumption seems to be justified when the indifferent electrolyte is 0.01 M Et_4NClO_4 if we consider that the hydration constant of perchlorate ion in AN has been reported to be 0.7.1)

Apparatus and Reagents

Apparatus. The assembly of Cell I is shown in Fig. 1. In each experiment, the solution in the compartment (C) was initially composed of 50 ml of the AN solution which was 10^{-3} M in $NaClO_4$ and 0.01 M in Et_4NClO_4; from the solvent inlet, the solvent (D) was titrated with a microsyringe. The maximum volume of D added to the cell was 0.85 ml for water, 1.25 ml for methanol, 1.8 ml for HMPA, and 2.5 ml for DMF, DMA, DMSO, and pyridine. After each addition of solvent, the solution was stirred with a magnetic stirrer. The emf was measured with the expanded scale of a Hitachi-Horiba pH meter, model F-7ss, to ±0.1 mV. The mono-

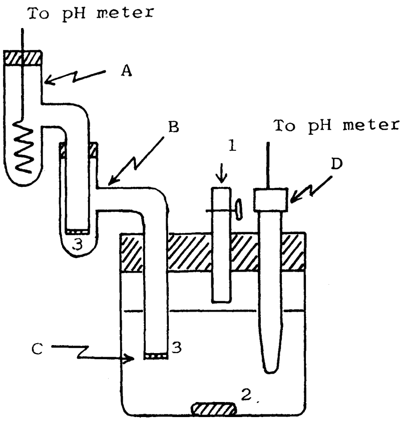

Fig. 1. Diagram of cell assembly.
A: reference electrode, B: salt bridge, C: cell for test solution, D: cation-sensitive glass electrode, 1: solvent inlet, 2: magnetic stirrer, and 3: fine porosity sintered glass. The cell is kept in a bath at 25±0.1 °C.

valent cation-sensitive glass electrode was a Beckman 39047. The reference electrode of Ag-0.005 M $AgNO_3$ in AN was connected to the solution in (C) through a salt bridge of 0.1 M Et_4NPi in AN. The reference electrode and the salt bridge were prepared every day before measurement in order to avoid mixing of solutions between compartments. When the reference electrode and the salt bridge were too fresh, however, the emf of the cell changed with the time. Therefore, the titration was carried out after the shift of emf had become less than 0.5 mV/hr. The emf of the cell of the initial AN solution was reproducible; it was 75±1 mV. Polarograms were measured with a three-electrode polarograph, Yanagimoto P8-PS. All the experiments were carried out at 25±0.1 °C.

Reagents. Unhydrated sodium perchlorate was dried before use at 130 °C under a vacuum. The tetraethylammonium picrate was prepared by the method of Coetzee and Padmanabhan.[6] The tetraethylammonium perchlorate was prepared and dried by the conventional method. Acetonitrile was purified by distilling it three times using an adiabatic vacuum fractional distillation column, first from P_2O_5, next from CaH_2, and finally without any addition.[7] The purified AN was used within a day after distillation. The pyridine was used after the purification of the spectrophotometric product by fractional crystallization. The other solvents were of an analytical reagent grade and were used without further purification.

Results

Response of the Glass Electrode to the Activity of Sodium Ion in Different Solvents. The slope of the response of the glass electrode to the concentration of the sodium ion in AN has been reported to be 56 mV in the presense of 0.1 M Bu_4NClO_4.[4] The glass electrode used in the present study showed a slope of 58 mV to the sodium ion between 10^{-4} and 10^{-2} M in AN–0.01 M Et_4NClO_4. If corrected for the change in the salt-effect activity coefficient, the response towards pa_{Na^+} is very near to the Nernstian slope of 59 mV.

For the present study, it is also necessary for the electrode to respond to the difference in the activity of the sodium ion between solvents of different species or compositions. This was verified by comparing the emfs of the following cell with the polarographic half-wave potentials of the sodium ion, which are considered to make a Nernstian response to the solvent effect on the activity of the sodium ion:

$$\text{Ag}|0.005\text{ M AgNO}_3(\text{AN})\|0.1\text{ M Et}_4\text{NPi(AN)}\|$$
$$10^{-3}\text{ M NaClO}_4 + 0.01\text{ M Et}_4\text{NClO}_4(\text{D})|\text{Glass electrode}$$

(D denotes AN, MeOH, H_2O, DMF, and DMSO)

Cell II

The half-wave potentials were measured in a solution of 10^{-3} M $NaClO_4$+0.01 M Et_4NClO_4 by using a reference electrode and salt bridge similar to those in Cell II.

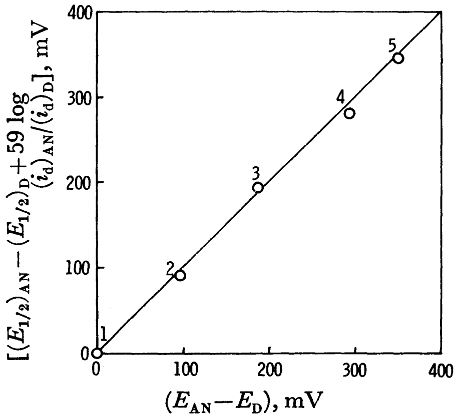

Fig. 2. Relations between the emf of Cell II and the half-wave potential of sodium ion in various solvents. Referred to the values in AN. Circle 1 is in AN, 2 in MeOH, 3 in H_2O, 4 in DMF, and 5 in DMSO.

The results in Fig. 2 show that the emf and the half-wave potential (corrected for the change in diffusion current) in each solvent, both referred to the values in AN, agree quite well, suggesting that the glass electrode can respond to the activity of the sodium ion in different solvents.

Complexing of the Sodium Ion in AN with Other Solvents. From the emf measurement of Cell I, the values of the formation constants of Reaction (1) were calculated by using the relations of Eqs. (3) to (5). The results are summarized in Table 1. Figures 3 to 6 show some

TABLE 1. COMPLEX FORMATION CONSTANTS OF SODIUM ION IN AN WITH OTHER SOLVENTS

Solvent	K_1	K_2	K_3
H_2O	1.8	1.8	
	1.8	1.8	
	1.8	1.9	
MeOH	$1._0$	0.4	
	$1._2$	0.4	
DMF	2.4	$2._1$	$1._1$
	2.5	$2._0$	$1._2$
DMA	5.3	10	$7._6$
	5.2	12	$5._2$
DMSO	5.8	10	$1._3\times 10$
	6.2	12	$1._5\times 10$
HMPA	28	$3._2\times 10^2$	$1._4\times 10^3$
	30	$3._1\times 10^2$	$1._2\times 10^3$

examples of R-[D] and $(R-K_1)/[D]$-[D] relations.

By the addition of water, mono- and di-hydrated sodium ions are formed, with K_1 and K_2 equal to 1.8 and 1.8 respectively. These values are in fairly good agreement with those of 2 and 3 respectively obtained by Chantooni and Kolthoff from the conductometric measurement of the solubility.[1)] The solvation of methanol is weaker than hydration, and K_1 and K_2 are 1 and 0.4 respectively. The solvation becomes easier with the increase in the solvent basicity in the order: MeOH<H_2O<DMF<DMA~DMSO<HMPA. For DMF, DMA, DMSO, and HMPA, a complexing up to three solvent molecules is observed. It is interesting, however, that pyridine, which is strongly basic, solvates only weakly with a K_1 of approximately 0.7. The weak solvation of pyridine to the sodium ion is consistent with the results of the calorimetric investigation in acetone.[8)]

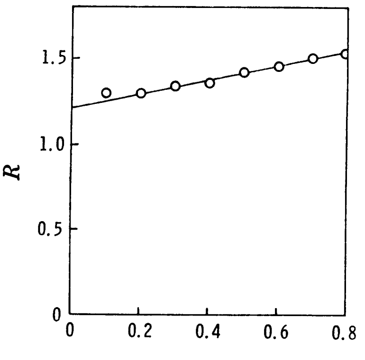

Fig. 3. R-[MeOH] relation.

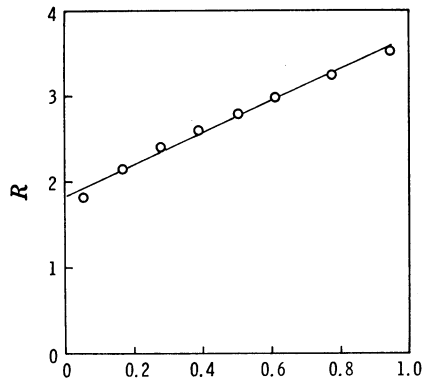

Fig. 4. R-[H_2O] relation.

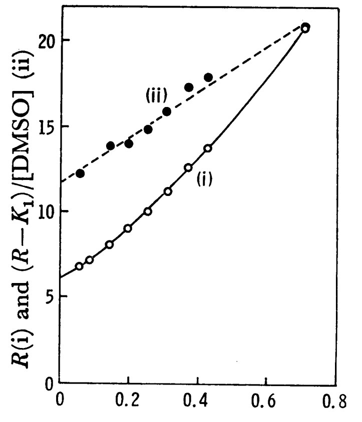

Fig. 5. R-[DMSO] (Curve i) and $(R-K_1)/[DMSO]$ -[DMSO] (Curve ii) relations.

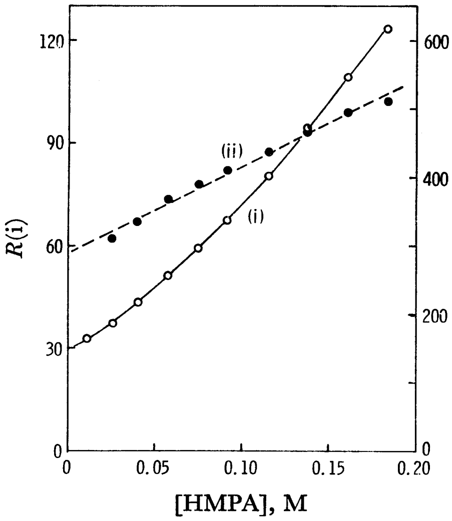

Fig. 6. R-[HMPA] (Curve i) and $(R-K_1)/[HMPA]$–[HMPA] (Curve ii) relations.

Discussion

From the results in Fig. 2, the glass electrode may be considered to respond with a Nernstian slope to the solvent effect on the activity of the sodium ion.

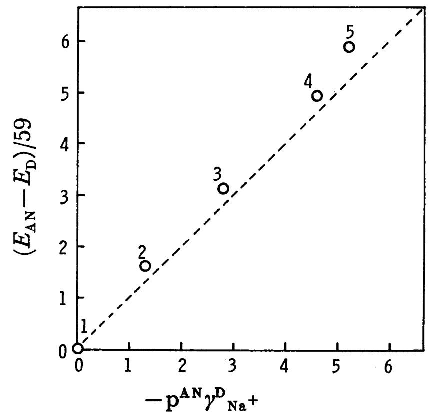

Fig. 7. Relations between the emf of Cell II and the solvent activity coefficient of sodium ion in various solvents. Referred to the values in AN. Circle 1 is in AN, 2 in MeOH, 3 in H_2O, 4 in DMF, and 5 in DMSO. E_{AN} and E_D are in mV.

Figure 7 shows the relation between the emfs of Cell II and the solvent activity coefficients of the sodium ion in several solvents, all referred to the values in AN. As the solvent activity coefficients, the values reported by Kolthoff and Chantooni ($p^{H_2O}\gamma^{MeOH}=1.5$, $p^{H_2O}\gamma^{AN}=2.8$, $p^{H_2O}\gamma^{DMF}=-1.8$, and $p^{H_2O}\gamma^{DMSO}=-2.4$)[9)] were used. As is apparent from this figure, the values of $(E_{AN}-E_D)/59$ and $p^{AN}\gamma^{D}_{Na^+}$ for each solvent are in fairly good agreement. This may support the consideration that the solvent activity coefficients quoted here are reasonable values and allow us to speculate that the junction potentials between the salt bridge and the solutions in these different solvents are relatively small, as has been reported by Cox *et al.*[3]

In the determination of formation constants, the junction potential between the salt bridge and the solution in (C) of Cell I was assumed to change only negligibly upon the addition of the solvent (D). According to Cox *et al.*,[3] the junction potential between the salt bridge of 0.1 M Et_4NPi(AN) and an aqueous 0.01 M $AgClO_4$ solution is approximately 10 mV (Fig. 1, Ref. (3)). If this is correct, the change in the junction potential in the present study, in which water up to *ca.* 1 M (1.7 v/v%) is added to the AN solution, is expected to be small (probably less than 1 mV) and it will tend to decrease the apparent value of $(E_{AN}-E_{AN-D})$. On the contrary, if a salt bridge of 0.1 M Et_4NPi in acetone is used instead of 0.1 M Et_4NPi in AN, the junction potential may be expected, according also to Cox *et al.*, to change to the opposite direction and to increase the apparent value of $(E_{AN}-E_{AN-D})$ (Fig. 1, Ref. (3)). The values of K_1 and K_2 for the hydration of the sodium ion, obtained by using a salt bridge of 0.1 M Et_4NPi in acetone, are 1.8 and 1.9 (Table 2) respectively, in good agreement with the values of 1.8 and 1.8 respectively obtained with Cell I. This seems to support the assumption that the change in the junction potential by the addition of water is negligibly small. For the addition of methanol, however, the change in the junction potential may be somewhat larger than for water (Fig. 1, Ref. (3)). For other aprotic solvents, the change in the junction potential seems to be smaller than in the case of water.[3]

TABLE 2. EFFECT OF SALT BRIDGE ON HYDRATION CONSTANTS OF SODIUM ION IN AN

Salt bridge	K_1	K_2
0.1 M Et_4NPi in AN	1.8	1.8
	1.8	1.8
	1.8	1.9
0.1 M Et_4NPi in Acetone	1.7	2.0
	1.8	1.9
	1.8	1.9

In the present study, the solution of the sodium ion usually contained 0.01 M Et_4NClO_4 as an indifferent electrolyte. According to the conductance measurement,[10] sodium ions in AN associate with perchlorate ions with an association constant of *ca.* 11. The hydration constants of the sodium ion in Table 3, determined in the presence of the indifferent electrolyte of 0, 0.01 and 0.1 M Et_4NClO_4 are, however, in good agreement with each other, suggesting that the effect of ion association is small in this case.

TABLE 3. EFFECT OF CONCENTRATION OF INDIFFERENT ELECTROLYTE ON HYDRATION CONSTANTS OF SODIUM ION IN AN

Concn. of Et_4NClO_4(M)	K_1	K_2
0	1.7	1.7
	1.8	1.8
	1.7	1.9
0.01	1.8	1.8
	1.8	1.8
	1.8	1.9
0.1	1.8	1.7
	1.8	1.8
	2.0	1.7

In addition to the factors considered above, the values of formation constants may also be affected by such factors as follows: (i) Some part of the solvent added may be self-associated, and the activity of the solvent may be less than the concentration. (ii) Both the activity of AN and the medium character may change upon the addition of other solvent. Because the effect of these factors increases with the increase in the amount of solvent added, the deviation of the values of K_2 and K_3 from the true values may be larger than the deviation of K_1. The values of K_1 in Table 1 seem to be reliable within ±10%, except for the case of methanol, in which the reliability is somewhat less.

Due to the importance of solvation phenomena in the mechanism of various chemical reactions, the solvation of the sodium ion has recently been studied extensively by a variety of experimental techniques, among which infrared[11] and NMR[12] spectroscopies, conductometry[1] and calorimetry[8] are most significant. The present potentiometric method, however, seems to be superior to these techniques in the point that the activity of the sodium ion is directly measured.

The complexing of the lithium ion in AN with other solvents is now under investigation by using a similar method.

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