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The Complexing of the Ammonium Ion in Acetonitrile with Other Solvents. Investigation Using a Cation-sensitive Glass Electrode

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As a part of potentiometric studies of the complexing of univalent cations in acetonitrile with other solvents by the use of a cation-sensitive glass electrode, investigations were carried out of the complexing of the ammonium ion in acetonitrile with such solvents as water, methanol, *N*-methylformamide, *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, dimethyl sulfoxide, 1-methyl-2-pyrrolidone, and hexamethylphosphoric triamide, and also with dibenzo-18-crown-6. Prior to the study of the complexing, the cation-sensitive glass electrode was confirmed to respond in a Nernstian way to the change in the ammonium-ion activity which occurs due to the change of the solvent (solvent effect). The ammonium ion in acetonitrile formed complexes of mono- and di-solvated species with methanol and water. Formations of up to tri-solvated species were formed with DMF, DMA, and DMSO, and up to tetra-solvated species with 1-methyl-2-pyrrolidone and NMF. With HMPA, even penta-solvated species were formed. The complex formation constants of the mono-solvated ammonium ion, β_1 (mol^{-1} dm^3), were $1._7$ with methanol, 5.6 with DMF, 14 with DMSO, 17 with DMA, 31 with 1-methyl-2-pyrrolidone, 3.0×10^2 with NMF, and 1.2×10^3 with HMPA. The association constant of ammonium perchlorate in acetonitrile was determined conductometrically to be 25 mol^{-1} dm^3.

Recently, the complexing of univalent cations with other solvents has been investigated in acetonitrile (AN) by using such techniques as nuclear magnetic resonance,[1] infrared spectroscopy,[2] conductometry,[3] and potentiometry,[4–6] but few reports have appeared concerning the complexing of the ammonium ion in acetonitrile. In the present paper, we have studied the complexing of the ammonium ion in acetonitrile with other dipolar solvents, such as water, methanol, *N*-methylformamide (NMF), *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), 1-methyl-2-pyrrolidone, and hexamethylphosphoric triamide (HMPA), and with dibenzo-18-crown-6, by using a potentiometric method similar to that used in the previous reports.[4–6] The emf of the following cell was measured:

$$\begin{gathered}\mathrm{Ag|0.005\ M\ AgNO_3,\ 0.01\ M\ Et_4NClO_4(AN)\,\|}\\ \mathrm{0.1\ M\ Et_4NClO_4(AN)\,\|\,10^{-3}\ M\ NH_4ClO_4,}\\ \mathrm{0.01\ M\ Et_4NClO_4(AN+D)\,|\,Cation\text{-}sensitive}\\ \mathrm{Glass\ Electrode}\cdots\mathrm{Cell\ I}\end{gathered}$$

where D denotes the solvents added and where M=mol dm^{-3}. The formation constants, β_x in (mol^{-1} dm^3)^x, for Reaction 1 were obtained by analyzing the emf data under assumptions similar to those in the previous reports.[4–6]

$$\mathrm{NH_4{}^+{}_s} + x\mathrm{D} = \mathrm{NH_4{}^+{}_{\mathit{x}D}} \tag{1}$$

$$\beta_x = \frac{(\mathrm{NH_4{}^+{}_{\mathit{x}D}})}{(\mathrm{NH_4{}^+{}_s})[\mathrm{D}]^x} \tag{2}$$

In Eq. 1, $\mathrm{NH_4{}^+{}_s}$ shows ammonium ions solvated only with acetonitrile and $\mathrm{NH_4{}^+{}_{\mathit{x}D}}$ those complexed by molecules of D in AN+D. In Eq. 2, ($\mathrm{NH_4{}^+{}_s}$) and ($\mathrm{NH_4{}^+{}_{\mathit{x}D}}$) are the activities, and [D], the concentration, of the respective species in the molar scale.

Experimental

Apparatus. Most of the apparatus and experimental techniques used for the potentiometric determination of the complex formation constants were the same as those in the previous reports.[4–6] A Horiba No. 1826A-05T glass electrode was used to determine the acid dissociation constant of the pyridinium ion in acetonitrile. The conductance was measured with a universal bridge model 4255A of the Yokogawa-Hewlett-Packard Co., Ltd. Polarograms were measured with a three-electrode polarograph, Yanagimoto P8-PS. All these measurements were carried out at 25 °C.

Reagents. The ammonium perchlorate was prepared by introducing ammonia into a solution of perchloric acid, purified by recrystallizing from water, and dried *in vacuo* at 110 °C. The pyridinium perchlorate was prepared by passing evaporated pyridine into an aqueous solution of perchloric acid and purified by recrystallizing it from ethanol. It was dried at room temperature under a high vacuum with P_2O_5. The dibenzo-18-crown-6, which has been prepared by the method of Pedersen,[7] was recrystallized from chloroform. The 1-methyl-2-pyrrolidone was a product of Wako Chemicals Co., Ltd., and was purified according to the method of Sears *et al.*[8] The DMA[9] was purified by distillation, first from BaO, next from CaH_2, and finally without any additives. The other solvents and reagents used in this experiment were the same as those described in the previous reports.[4–6]

Results

Response of the Cation-sensitive Glass Electrode to the Activity of the Ammonium Ion. The cation-sensitive glass electrode used in this study showed a response of a slope of 56 mV for the ammonium-ion concentration between 10^{-2} and 10^{-4} M in acetonitrile-0.01 M Et_4NClO_4. If correction is made for the change in the salt-effect activity coefficient, which is calculated by using the Debye-Hückel equation: $\log f = -AI^{1/2}/[1+BaI^{1/2}]$, assuming $A=1.64$ mol$^{-1/2}$ dm$^{3/2}$, $B=4.86\times10^8$ mol$^{-1/2}$ dm$^{1/2}$, and $a=5\times10^{-8}$ cm, the slope of the response to $\mathrm{p}a_{\mathrm{NH_4^+}}$ becomes 58.5 mV, which is very near to the Nernstian slope of 59.16 mV.

In order to confirm that the glass electrode also responds to the change in the activity of the ammonium ion due to the solvent effect, the emfs of Cell II were measured in various solvents, D, and were compared with the polarographic half-wave potentials of the ammonium ion, which were measured in 10^{-3} M NH_4ClO_4–0.01 M Et_4NClO_4(D) by using a salt bridge and a reference electrode similar to those in Cell II.

Ag|0.005 M $AgNO_3$, 0.01 M Et_4NClO_4(AN)||
0.1 M Et_4NClO_4(AN)||10^{-3} M NH_4ClO_4,
0.01 M Et_4NClO_4(D)|Cation-sensitive Glass
Electrode ⋯ Cell II

(D denotes AN, DMF, DMA, and DMSO)

The results are shown in Fig. 1. For D solvents such as acetonitrile, DMF, DMA, and DMSO, the values on the abscissa agree fairly well with the values on the coordinate. Because the polarographic behavior of the ammonium ion is nearly reversible in these solvents, these results can be considered to confirm the Nernstian response of the glass electrode to the effect of the solvent on the activity of the ammonium ions. For other solvents, the polarographic behavior of the ammonium ion was not reversible or did not give a well-defined wave, and so a comparison as in Fig. 1 was impossible. However, it would be reasonable to assume that even in these solvents the glass electrode can respond in a Nernstian way to the effect of the solvent on the ammonium-ion activity.

Complexing of the Ammonium Ion in Acetonitrile with Other Solvents. From the emf measurement of Cell I, the values of the complex formation constants of the ammonium ion in acetonitrile with other solvents, such as water, methanol, NMF, DMF, DMA, DMSO, 1-methyl-2-pyrrolidone, and HMPA, were obtained by the method used in the previous papers.[4–6] The results are summarized in Table 1. The values of β_1 in Table 1 seem to be reliable within ±10% for aprotic solvents. However, for β_1 in the cases in which D was a protic solvent and for β_2 to β_5, the reliability seems to be somewhat less because of the deviations from the ideal conditions assumed in calculating these values.[4] The formation constants with water are shown in parentheses

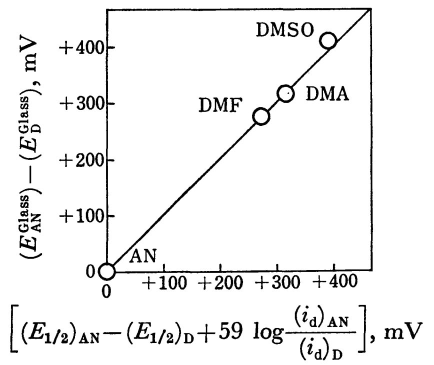

Fig. 1. Relation between the emf of Cell II and the half-wave potential of the ammonium ion in different solvents. Both referred to the values in acetonitrile.

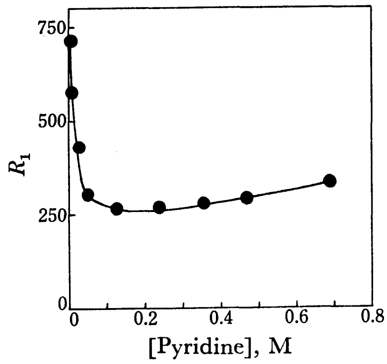

Fig. 2. The exceptional relation of R_1-[D] for the case in which D=pyridine (see text).

TABLE 1. COMPLEX FORMATION CONSTANTS, β_x IN $(mol^{-1}\ dm^3)^x$, OF THE AMMONIUM ION IN ACETONITRILE WITH OTHER SOLVENTS AND A CROWN ETHER (at 25 °C)

Ligand	Max. concn of ligand added (M)	β_1	β_2	β_3	β_4	β_5
Methanol	0.7	$1._7$	$0._4$			
	0.7	$1._8$	$0._3$			
DMF	0.7	5.3	6.8	$8._7$		
	0.7	5.9	6.9	$7._6$		
H_2O	1.1	$(5._5)$[a)]	$(4._2\times10)$[a)]			
	0.5	$(5._6)$[a)]	$(4._6\times10)$[a)]			
DMSO	0.7	14	31	$7._1\times10$		
	0.7	14	30	$8._4\times10$		
DMA	0.7	16	41	$5._7\times10$		
	0.7	17	40	$5._1\times10$		
1-Methyl-2-pyrrolidone	0.5	30	1.7×10^2	$2._8\times10^2$	7×10^2	
	0.6	31	1.7×10^2	$3._0\times10^2$	6×10^2	
NMF	0.7	2.9×10^2	1.7×10^3	$3._6\times10^3$	9×10^3	
	0.5	3.0×10^2	1.9×10^3	$3._3\times10^3$	8×10^3	
HMPA	0.2	1.2×10^3	2.1×10^5	3.5×10^6	$5._8\times10^7$	2×10^8
	0.2	1.2×10^3	2.0×10^5	3.9×10^6	$4._7\times10^7$	2×10^8
Dibenzo-18-crown-6	0.03	4.9×10^3	1.1×10^5			
	0.03	5.0×10^3	8.7×10^4			

a) See text for the values in parentheses.

in Table 1. This is because the potential of the glass electrode was not stable enough when water was titrated in Cell I. When pyridine was used as the D solvent, the relation between R_1** and the concentration of pyridine added to Cell I (Fig. 2) was peculiar and an extremely big R_1 value was obtained at a small concentration of pyridine. The complex formation constants of the ammonium ion in acetonitrile with dibenzo-18-crown-6 were determined by adding a solution of 6.25×10^{-2} M crown ether to a solution of 5×10^{-3} M NH_4ClO_4 in acetonitrile–5×10^{-2} M Et_4NClO_4. These results are also shown in Table 1.

The Acid Dissociation Constant of the Pyridinium Ion. The acid dissociation constant of the pyridinium ion (pyH^+) in acetonitrile was determined by measuring the emf of Cell III:

$$\begin{array}{l} \mathrm{Ag}|0.005\ \mathrm{M\ AgNO_3},\ 0.01\ \mathrm{M\ Et_4NClO_4(AN)}\| \\ 0.1\ \mathrm{M\ Et_4NClO_4(AN)}\|4\times10^{-3}\ \mathrm{M\ pyHClO_4}, \\ x\ \mathrm{M\ pyridine(AN)}|\text{Glass Electrode} \cdots \text{Cell III} \end{array}$$

The Horiba 1826A-05T glass electrode in Cell III was calibrated in a 5×10^{-3} M picric acid–5×10^{-3} M tetraethylammonium picrate buffer solution in acetonitrile by using the pK_a value of 11.0[10] for picric acid. The pyridine concentration added to Cell III was varied from 2.00×10^{-4} to 2.74×10^{-2} M. The pa_{H^+} value was calculated by assuming a response of 59.16 mV/pa_{H^+} and the pK_a value (K_a in mol dm^{-3}) was obtained from the simple Henderson equation by making a correction for the change in the activity coefficient according to the Debye-Hückel limiting law, $-\log f=1.64\{I/(\mathrm{mol\ dm^{-3}})\}^{1/2}$. As is shown in Table 2, a pK_a value of 12.60 ± 0.01 was obtained. The pK_a value was also determined in the presence of an indifferent electrolyte of 1.0×10^{-2} M Et_4NClO_4 in Cell III, a pK_a value of 12.53 was thus obtained, which is in fairly good agreement with the literature data of 12.33.[11]

TABLE 2. THE DISSOCIATION CONSTANTS OF THE PYRIDINIUM ION FROM THE GLASS ELECTRODE MEASUREMENTS

[pyH^+] M × 10^3	[Pyridine] M × 10^3	E mV	log f	pa_{H^+}	p$K_a^{pyH^+}$
4.00	0.200	17.5	-0.10_4	11.40	12.60
4.00	0.500	−5.9	-0.10_4	11.80	12.60
4.00	0.959	−22.0	-0.10_4	12.07	12.59
3.99	1.92	−39.7	-0.10_4	12.37	12.59
3.99	2.87	−50.7	-0.10_4	12.56	12.60
3.99	3.83	−57.5	-0.10_4	12.67	12.59
3.98	4.78	−63.2	-0.10_4	12.77	12.59
3.98	5.73	−68.5	-0.10_3	12.86	12.60
3.97	6.68	−73.2	-0.10_3	12.94	12.61
3.97	7.65	−76.4	-0.10_3	12.99	12.60
3.95	11.5	−87.1	-0.10_3	13.17	12.61
3.92	19.2	−101.2	-0.10_3	13.41	12.62
3.89	27.4	−110.8	-0.10_2	13.57	12.62

Determination of the Association Constant of the Ammonium Perchlorate. The conductometric measurements of the ammonium perchlorate in acetonitrile were carried out at (25±0.01) °C at ammonium-perchlorate concentrations from 4.20×10^{-4} to 3.33×10^{-2} M. The association constant and the molar conductivity of ammonium perchlorate, obtained with the Schedolovsky equation, were 25 mol^{-1} dm^3 and $200._6$ S cm^2 mol^{-1} respectively. By using the molar ionic conductivity, $\lambda_0(ClO_4^-)$, of 103.7 S cm^2 mol^{-1} [12] in acetonitrile, $\lambda_0(NH_4^+)$ can be calculated to be $96._9$ S cm^2 mol^{-1}, which is between the λ_0 (H^+) value of 99 S cm^2 mol^{-1} [13] and the $\lambda_0(Me_4N^+)$ value of 94.5 S cm^2 mol^{-1}.[12]

Discussion

From the results in Fig. 1, it may be considered that the cation-sensitive glass electrode can respond well to the activity of the ammonium ion in solvents of different species or compositions.

The ammonium ion in acetonitrile behaves as a Lewis acid, and the complex formation constant, β_1, increases with the solvent basicity. The values in Table 1 show that the complexing of the ammonium ion in acetonitrile with other solvents is generally more extensive than in the cases of the sodium and thallium(I) ions and that it is roughly comparable to the case of the lithium ion[5]. Kolthoff and Coetzee[14] indicated, as the results of their polarographic measurements, that the free energy of the solvation of the ammonium ion is considerably larger in water than in acetonitrile. Coetzee and Padmanabhan reported similar results.[11] The complex formation constants of the ammonium ion with water are, as is shown in Table 1, fairly large and are comparable to the complex formation constants with DMF. For sodium and thallium(I) ions, on the other hand, the formation constants with water are smaller than those with DMF.[4,6]

The formation constants of the ammonium ion with dibenzo-18-crown-6 (Table 1) are considerably larger than the polarographic results of Angelis *et al.*[15] They obtained the formation constant of 3.1×10^2 in a 0.1 M tetrabutylammonium perchlorate–acetonitrile solution, but they mentioned that the validity of their value may be somewhat in doubt since the electrode-reaction kinetics of the ammonium ion may be influenced by the adsorption of the polyether complex. The existence of the 2:1 crown ether–NH_4^+ complex seems to be reasonable if we consider the fact that the Pauling crystal diameter of the ammonium ion (2.96 Å) and the diameter of the cavity of dibenzo-18-crown-6 (2.6 Å according to Corey-Pauling-Koltun atomic models and 3.2 Å according to Fisher-Hirschfelder-Taylor atomic models).[16]

When pyridine was used as the D solvent in Cell I, a peculiar change in the glass electrode potential was observed, as is shown by the R_1 value in Fig. 2. Because the acid dissociation constants of the ammonium and pyridinium ions in acetonitrile are, as pK_a values, 16.5[11] and 12.6 respectively, the $NH_4^+ + py \rightarrow NH_3 + pyH^+$ reaction should occur to some extent. However our attempt to explain the behavior of the glass-electrode potential in terms of the above reaction was unsuccessful.

** R_1 is obtained by the use of the relation $R_1=\{10^{(E_{AN}-E_{AN-D})/59.16}-1\}/[D]$, where E_{AN} and E_{AN-D} are the emfs of Cell I in the absence and in the presence respectively of the D solvent. In ordinary cases, the following relation holds: $R_1=\beta_1+\beta_2[D]+\beta_3[D]^2+\cdots$.[4]

More complicated phenomena, including homo- and hetero-conjugations between ammonium ions and pyridine, may be occurring.[11]

The association of the univalent cation under investigation with the perchlorate ion may affect, at least theoretically, the complex formation constants of the cation with other solvents.[4–6] The association constant of the ammonium perchlorate in acetnitrile, which was determined conductometrically, was *ca.* 25 $\mathrm{mol^{-1}\,dm^3}$, somewhat smaller than that of the thallium(I) perchlorate.[17] We determined the complex formation constant of the ammonium ion in acetonitrile with DMSO in the presence of varing concentrations of Et_4NClO_4 from 0 to 0.1 M. However no appreciable change in the formation constant was observed with the change in the concentration of Et_4NClO_4. These results suggest that the association of the ammonium ion with the perchlorate ion, which was detected by conductometric measurement, does not significantly affect the potentiometric results of the formation constants of complexes between the ammonium ion and solvent molecules.

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