1020 © 1988 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 61, 1020—1022 (1988) [Vol. 61, No. 3

The Complexing of the Magnesium and Barium Ions in Acetonitrile with Other Solvents. Investigation by the Use of a Polyacrylamide-Tetraethylene Glycol Monododecyl Ether Membrane Ion-Selective Electrode

Toshio NAKAMURA,* Hisakazu HIGUCHI, and Kosuke IZUTSU
Department of Chemistry, Faculty of Science, Shinshu University, Asahi, Matsumoto 390

(Received July 1, 1987)

Synopsis. The complexations of magnesium and barium ions in acetonitrile with DMF, DMSO, and HMPA were studied potentiometrically by the use of an organic polymer membrane electrode. The formation constants for 1 : 1 complexes of magnesium and barium ions, respectively, were 2.1×10^2 and 19 with DMF, 4.5×10^2 and 41 with DMSO, and $(5._5\times10^3)$ and 1.6×10^3 with HMPA. The roles of the basicity of the complexing solvent, crystallographic radius, and charge of the cations are discussed briefly.

Some types of ion-selective electrodes have been successfully used in physicochemical as well as in analytical studies of nonaqueous solutions.[1] Univalent cation-sensitive glass electrodes have been used in the studies of the complex formations of alkali metal ions in acetonitrile(AN)[2] and propylene carbonate[3] with other donor solvents and macrocyclic polyethers as well as in solvation studies of alkali metal ions in mixed nonaqueous solvents. The solid state copper sulfide electrode for copper(II)[4] and lanthanum fluoride electrode for fluoride ion[5] have also been used in solvation studies.

Recently, we have developed alkaline earth metal ion-sensitive electrodes for use in dipolar aprotic solvents. One was constructed by coating a platinum disk with polyacrylamide(PAA) coupled to a crown ether[6] and the other with PAA polymer coupled to acyclic polyether neutral carriers.[7] In the present report, the latter was used for a study of the complexing of magnesium and barium ions in AN with such solvent molecules as *N,N*-dimethylformamide(DMF), dimethyl sulfoxide(DMSO), and hexamethylphosphoric triamide(HMPA).

The emf of the following cell was measured: Ag/0.01 M $AgNO_3$+0.01 M Et_4NClO_4(AN)//0.05 M Et_4NClO_4(AN)//10^{-4} M $M^{2+}(ClO_4^-)_2$+0.01 M Et_4NClO_4 (AN+D)/PAA-POE4/Pt···Cell I where D denotes DMF, DMSO, or HMPA, M^{2+} the magnesium or barium ion to be investigated, and M is in mol dm^{-3}. POE4 is an abbreviation for tetraethylene glycol monododecyl ether. From the emf measurements of Cell I, the complex formation constants for the reaction of Eq. 1 were obtained by using Eqs. 2 to 4.

$$M_s^{2+} + xD = M_{xD}^{2+} \tag{1}$$

$$\beta_x = a(M_{xD}^{2+})/a(M_s^{2+})[D]^x \tag{2}$$

$$R_1 \equiv \{10^{(E_{AN}-E_{AN-D})/29.6} - 1\}/[D] = \sum_{i=1} \beta_i[D]^{i-1} \tag{3}$$

$$R_j \equiv (R_{j-1} - \beta_{j-1})/[D] = \sum_{i=j} \beta_i[D]^{i-j}, \tag{4}$$

where M_s^{2+} is M^{2+} solvated only by AN and M_{xD}^{2+} is M^{2+} cosolvated by x molecules of D; $a(M_s^{2+})$ and $a(M_{xD}^{2+})$ represent the activities of the respective species. [D] is the molar concentration of D. E_{AN} and E_{AN-D} represent the emfs of Cell I(in mV) in pure AN and AN-D, respectively.

Experimental

Apparatus. The construction of the electrodes, the cell assembly, and the potentiometric measurements were the same as those in a previous report.[7] A complexing solvent D was added to the cell with a microburette(Gilmont instruments, Inc. S1100A or S1200A), 5 μl in each step until its volume percent became 1%. In each step, the steady state potential was digitally read to ±0.1 mV. Analyses of the potentiometric data were carried out with a personal computer, NEC PC-9801 or Hewlett-Packard 86.

Reagents. Reagent grade magnesium and barium perchlorates were obtained from Wako Pure Chemical Industries, Ltd. Barium metal was the product of Kanto Chemical Co., Inc. Other reagents and solvents used in this experiment were the same as those in the previous report.[7]

Results

As shown by the typical potential-time curves in Fig. 1, a steady potential was quickly established after each addition of D to Cell I. Figure 2 shows an example of the relation between R_1, defined by Eq. 3, and [D] for the case in which D and M^{2+} were DMF and the magnesium ion, respectively. From the intercept and the slope of the straight line, $\beta_1=1.9\times10^2$ and $\beta_2=2.2\times10^3$ were obtained. For Mg^{2+}–DMSO and Ba^{2+}–DMF the formation constants, β_1 and β_2, were obtained in the same way. For Ba^{2+}–DMSO and Ba^{2+}–HMPA the relations between R_1 and [D] were not linear and a R_2–[D] relation defined by Eq. 4 was also used to determine the formation constants, β_2 and

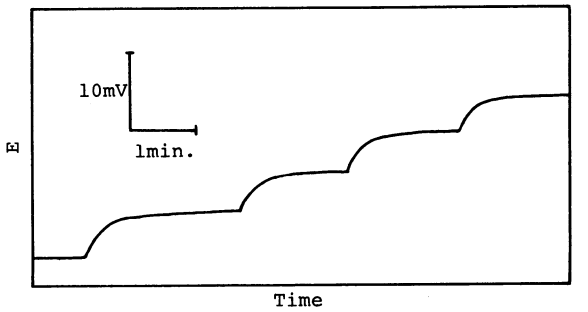

Fig. 1. Typical time vs. potential curve for titration of the barium ion(1×10^{-4}) M) in AN with DMSO. Ten μl DMSO was added to 10 ml of 0.01 M Et_4NClO_4-AN solution at each step.

Table 1. Complex Formation Constants of M^+ and M^{2+} in Acetonitrile with Other Solvent Molecules (at 25 °C)

Ion / Solvent	Li^+(r_c: 0.60)[a]		Mg^{2+}(r_c: 0.65)		K^+(r_c: 1.33)[a]		Ba^{2+}(r_c: 1.35)	
	β_1	β_2	β_1	β_2	β_1	β_2	β_1	β_2
DMF	16	1.1×10^2	2.1×10^2	2.2×10^3	1.5	1.1	19	57
DMSO	49	9.8×10^2	4.5×10^2	5.3×10^3	2.9	2.3	41	3.2×10^2
HMPA	2.1×10^3	3.2×10^5	(5.5×10^3)	(2.2×10^6)[b]	6.9	10	1.6×10^3	3.1×10^4

r_c: crystallographic ionic radius (Å). a) See Ref. 2. b) See text.

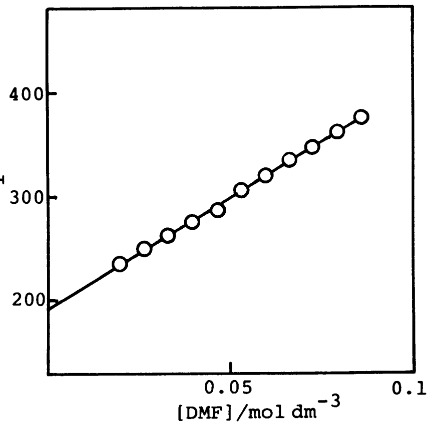

Fig. 2. The relation between R_1 vs. [DMF] for the magnesium ion in AN.

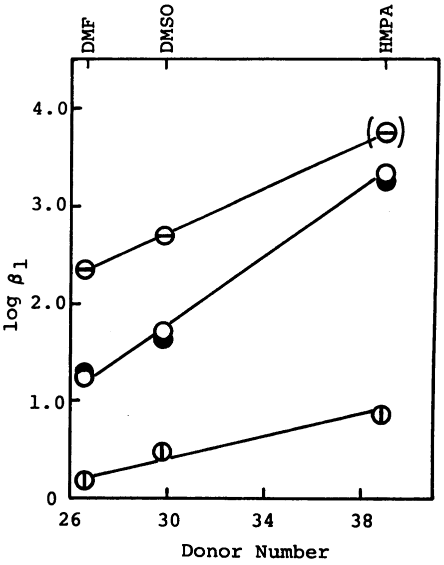

Fig. 3. The relation between log β_1 and donor numbers of solvents: (⊖) Mg^{2+}, (●) Ba^{2+}, (○) Li^+, (⦶) K^+.

β_3. In Table 1, however, only β_1 and β_2 are listed, since the reliability of β_3 was not sufficient in this experiment. A small amount of D was added to the solution in order to suppress any change of the organic membrane phase by the solvent effect. For D of DMF, DMSO, and HMPA, the maximum molar fraction of D added to Cell I was about 0.005, except if otherwise mentioned. The results are summarized in Table 1. The value of β_1 for the Ba^{2+}–DMF complex was also obtained by using a barium amalgam electrode instead of the PAA-POE4 electrode in Cell I. The barium metal was dissolved in mercury in order to construct the electrode; its concentration was about 0.33M for 1×10^{-3} M of the barium ion in Cell I. The experiment was carried out under oxygen-free conditions. The obtained β_1-value agreed with the value in Table 1 within the reliability of the experiment. The formation constants for the Mg^{2+}–HMPA complex in Table 1 were obtained in a somewhat different way since the potential after the addition of HMPA to the Mg^{2+}–AN solution gradually became ill-defined. The interaction of the magnesium ion with HMPA was so strong that the magnesium ion trapped by POE4 in the organic membrane phase seemed to become unstable; the electrode potential may be irreproducible. The method was as follows: To a 1×10^{-3} M solution of magnesium ion in Cell I was added twice equivalent of HMPA to the magnesium ion (the potentials before and after the addition were measured). The values of β_1 and β_2 were obtained from the potential jump by assuming that K_1/K_2(ratio of the stepwise formation constants) was the same as that for the Li^+–HMPA complexes in AN(i.e., $K_1:K_2=14:1$).

Discussion

From Table 1 the stabilities of the complexes of both the magnesium and barium ions in AN with DMF, DMSO, and HMPA increase in the order: DMF(26.6)<DMSO(29.8)≪HMPA(38.8). The figures in the parentheses show the Gutmann's donor number.[8] These orders are the same as those for the lithium and potassium ions. When the formation constants for the magnesium ion with DMF and DMSO are compared with those for the lithium ion, which has a crystallographic ionic radius very close to the magnesium ion, the former has β_1 and β_2 that are about one order larger than those of the latter. The situation is approximately the same for the case in which the ions are potassium and barium ions, although the stability of the HMPA complex with the barium ion is much larger than expected. These results may be attributed to the difference in the ionic charge. On the other hand, the larger complex formation abilities of the magnesium ion compared with those of the barium ion may be reasonably explained if we considered that the crystallographic radius of the magnesium ion is smaller than that of

the barium ion. Except for the complex of Mg^{2+}–HMPA, the values of β_1 in Table 1 seem to be reliable within ±10%, while those of β_2 within ±20%. The relations between the donor numbers of the complexing solvents and log β_1 are plotted in Fig. 3. It is interesting that in each case a linear relation was obtained. Complex formations of the barium ion occur with almost the same stability as those of the lithium ion.

Recently, we have plenty of thermodynamic and kinetic data concerning cation-macrocyclic ligand interactions in nonaqueous solvents.[9] However data concerning relatively weaker metal–ligand interactions, such as ion-solvent molecule interactions in the present study, are very scarce. The information obtained using the present electrode may effectively be used for a comparison of the relative strength of the solvation phenomena and specific interactions[8] between metal cations and dipolar aprotic solvent molecules.

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

References

1) E. Pungor, K. Toth, P. G. Klatsmanyi, and K. Izutsu, *Pure Appl. Chem.*, **55**, 2029 (1983).

2) K. Izutsu, T. Nakamura, and K. Iwata, *Anal. Chim. Acta,* **117**, 329 (1980); T. Nakamura, Y. Yumoto, and K. Izutsu, *Bull. Chem. Soc. Jpn.*, **55**, 1850 (1982).

3) B. G. Cox, W. E. Waghorne, and C. K. Pigott, *J. Chem. Soc., Faraday Trans. 1,* **75**, 227 (1979).

4) L. F. Heerman and G. A. Rechnitz, *Anal. Chem.* **44**, 1655 (1972).

5) J. F. Coetzee and W. K. Martin, *Anal.Chem.*, **52**, 2412 (1980).

6) T. Nakamura and G. A. Rechnitz, *Anal. Chem.*, **57**, 393 (1985).

7) T. Nakamura, K. Ogiwara, K. Izutsu, and G. A. Rechnitz, *Bull. Chem. Soc. Jpn.*, **58**, 3409 (1985).

8) V. Gutmann; "The Donor-Acceptor Approach to Molecular Interactions," Plenum Press, New York (1978).

9) R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen, and D. Sen, *Chem. Rev.*, **85**, 271 (1985).