The Response Behavior of PAA–B12C4 Electrode to Li^+, Mg^{2+}, and Ca^{2+} in Some Aprotic Solvents and Its Thermodynamic Application

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The potentiometric response behavior of an electrode, which consists of a non-plasticized carboxyl-modified polyacrylamide polymer (PAA) coupled to benzo-12-crown-4 (PAA–B12C4) to Li^+, Mg^{2+}, and Ca^{2+} in such aprotic solvents as acetonitrile (AN), propylene carbonate (PC), and γ-butyrolactone (GBL), were examined. The electrode showed a Nernstian response to Li^+ and Ca^{2+} in AN, and Li^+, Mg^{2+}, and Ca^{2+} in PC and a near-Nernstian response to Mg^{2+} in GBL. From the response to Ca^{2+} it could be confirmed that the membrane potential was mainly established at the polymer membrane–solution interface. The electrode was applied to a study of their complexing with such other basic aprotic solvent molecules (D) as *N*,*N*-dimethylformamide, dimethyl sulfoxide, and hexamethylphosphoric triamide. The successive complex formation constants (β_i) and Gibbs energies of transfer ($\Delta G_{tr(j)}$) of Li^+ in AN and Mg^{2+} in PC in relation to such D were obtained.

Information concerning the specific solvation of cations is significant, and books compiled by Marcus[1] concerning ion solvation are effective for dealing with such data. The theory about response mechanism of ion-selective electrodes was reported by Pungor.[2] Ion sensors have been widely used for thermodynamic studies in nonaqueous solutions owing to their advantage of getting precise information easily about ion-solvent interactions by a handy-type apparatus. Ion sensors for use of alkaline earth metal ions in aprotic solvents, however, had not existed, except for one developed by Nakamura et al.;[3—5] some sensors based on a hydrophilic polymer coupled to neutral carriers have been successfully applied studies of the ionic solvation reactions of alkali metal ions, Ca^{2+}, and Ba^{2+} in acetonitrile (AN) and propylene carbonate (PC) with basic aprotic solvent (D) molecules. The Gibbs energies of transfer both from AN and PC to D and AN and PC to AN–D and PC–D mixtures were obtained at the same time. Similar kinds of sensors based on metal phthalocyanine complexes for F^- and CN^- in aprotic solvents have also been developed[6,7] and applied to thermodynamic studies. An ion sensor for the use of Mg^{2+} in aprotic solvents, however, has not existed, except for one developed by Nakamura et al.[3] Thermodynamic data concerning to the ionic solvation of Mg^{2+} with other solvents are very rare. Mg^{2+} sometimes called a forgotten ion in the field of ion sensors, even in an aqueous solution system. Spichiger[8] reported from the view point of thermodynamic aspects that much fewer examples of ion sensors for Mg^{2+} compared with Ca^{2+} had been developed because of the tendency of a weaker stability of Mg^{2+} complexes than Ca^{2+}. Generally speaking, if the potential of a sensor could be established based on host–guest complexation on the electrode surface, a stable and rapid complex formation reaction between them must proceed. Also, when the electrode is used in order to obtain thermodynamic parameters, it must exhibit a precise Nernstian response to ions at interest in the solvents. In this paper we first report on the development of ion-sensitive electrode consisting of a non-plasticized carboxyl-modified polyacrylamide polymer (PAA) coupled to synthesized benzo-12-crown-4 (B12C4) for use to Li^+, Mg^{2+}, and Ca^{2+} in such aprotic solvents as AN, PC, and γ-butyrolactone (GBL). The site of the membrane potential establishment is discussed concerning to the response behavior for Ca^{2+} at a PAA–B12C4 electrode. Secondly, the determination of successive complex formation constants (β_i) of Li^+ in AN and Mg^{2+} in PC with some other basic aprotic solvent D molecules as *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and hexamethylphosphoric triamide (HMPA) is carried out. The Gibbs energies of transfer ($\Delta G_{tr(j)}$) of Li^+ in AN and Mg^{2+} in PC both to D and to AN–D mixtures are also reported.

Experimental

Reagents and Apparatus. Lithium and magnesium perchlorates were purchased from Wako (No. 128-02712 and No. 133-00323, respectively) and were dried at 130 °C for 2 h under a high vacuum. Catechol and 1,2-bis(2-chloroethoxy)ethane were purchased from Wako (No. 034-13752) and Fluka (No. 533-06361), respectively. GBL was a purified product of Mitsubishi Yuka Co., Ltd. (F-GBL). Other chemicals and solvents used in the study were prepared in the same way as that reported in a previous paper,[5] if not otherwise mentioned. The emfs were measured with a pH meter equipped with a Hitachi-Horiba-type F-8 AT and recorded on a Yokokawa Denki Co. type 3056.

Preparation of Polymer-Ionophore Conjugate. B12C4 was obtained from catechol and 1,2-bis(2-chloroethoxy)ethane by a method of Pacey et al.,[9] i.e., the reaction in DMSO under the coexistence of lithium perchlorate and sodium hydroxide for 24 h at 110 °C. After it was converted to amines, aminobenzo-12C4, via the nitro derivative, the modified ionophore was conjugated at the carboxyl group of the carboxyl-modified polyacrylamide (PAA) by a reaction in DMF following a procedure reported in a previous paper[10] to obtain the final polymer-neutral ionophore conjugate (PAA–B12C4).

Indicator Electrode. A PAA–B12C4 electrode was constructed in the same way as that reported in a previous paper,[5] and was conditioned for more than 7 h in an AN-solution containing 0.5 mM analyte ion and 10 mM indifferent electrolyte shown in Cell 1 (described later). The thickness of the membrane on the platinum disk was less than 0.2 mm.

Potentiometric Measurement. The response behavior of some cations in some aprotic solvents (D) at a PAA–B12C4 electrode was investigated by next measuring Cell 1. All compartments of Cell 1 were prepared freshly every time.

Ag|10 mM $AgNO_3$ + 10 mM Et_4NClO_4 (AN)||50 mM Et_4NClO_4 (D)||*c* M $N^{z+}(X^-)_z$ + 10 mM Et_4NClO_4 (D)|PAA–B12C4|Pt ···· Cell 1

where D = AN, PC, and GBL, $N^{z+} = Li^+$, Mg^{2+}, or Ca^{2+}, and $X^- = ClO_4^-$ or $CF_3SO_3^-$. M = mol dm^{-3} and *c* means concentration. To obtain a calibration curve, the standard addition method was used. The steady-state potential was obtained within 2—5 min and the emf of the Cell 1 was recorded to 0.1 mV.

Determination of the Complex Formation Constants and Gibbs Energy of Transfer. The emfs of Cell 2 were measured,

Ag|10 mM $AgNO_3$+10 mM Et_4NClO_4 (AN)||50 mM Et_4NX (AN or PC)|| 5×10^{-4} M $N^{z+}(X^-)_z$ +10 mM Et_4NClO_4 (AN+D or PC+D)|PAA–B12C4|Pt ···· Cell 2

where D denotes DMF, DMSO, and HMPA. AN and PC were used in the experiments as reference solvents (R). X^- was the same as that in Cell 1. The change in the junction potentials of Cell 2 during emf measurements was considered based on the results of an experiment,[11] and was used later to estimate the reliability of the obtained data. Small amounts of solvent D were added stepwise into the cell to obtain successive complex formation constants. The steady-state potential was obtained within 1—2 min and the emf change was recorded to 0.1 mV.

Results and Discussion

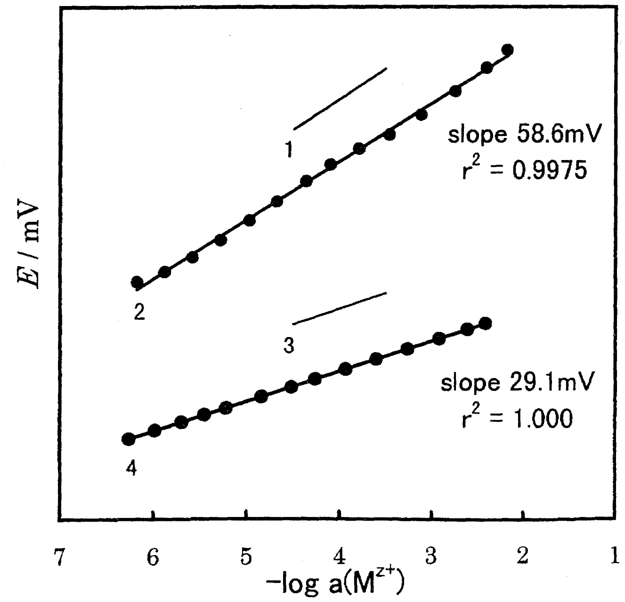

Fig. 1. Typical calibration curves for cations in propylene carbonate at the PAA–B12C4 electrode (25 °C). Lines 1 and 3: a theoretical slope for a singly charged cation (59.2 mV/log a_{M^+}) and for a doubly charged cation (29.6 mV/log $a_{M^{2+}}$); 2 and 4: Li^+ and Mg^{2+}, respectively.

Responses of the PAA–B12C4 Electrode. The potentiometric response behavior of an electrode consisting of a non-plasticized carboxyl-modified PAA coupled to B12C4 to Li^+, Mg^{2+}, and Ca^{2+} in such aprotic solvents as AN, PC, and GBL were examined. Typical calibration curves for Li^+ and Mg^{2+} in PC at the PAA–B12C4 electrode are shown in Fig. 1. The response results obtained by measuring the emf change of Cell 1 are summarized in Table 1. The linear ranges of the slopes in the Nernstian equation are also given in the table. The activities of the cations ($a(N^{z+})$), were calculated by the Debye–Hückel equation used in a previous report.[12] In the case of Ca^{2+} in AN, the slope was corrected with the variation of $a(Ca^{2+})$ due to an ion association of Ca^{2+} in AN with $CF_3SO_3^-$ according to that described in a previous paper.[5] The association constant, $1.0_2 \times 10^4$, had been reported previously[5] and the correction led ca. a 23% higher slope to be 27.1 mV/activity decade, as can be seen in the table. From the table we can find that the electrode showed a Nernstian response to Li^+ and Ca^{2+} in AN, and Li^+, Mg^{2+}, and Ca^{2+} in PC, and a near-Nernstian response to Mg^{2+} in GBL. Generally speaking, because crown ethers and their derivatives are apt to make more stable complexes with the ions being expected from the so-called "hole size rule", we used a kind of derivative of 12-crown-4 as an ionophore for Li^+ and Mg^{2+}. It is interesting that the electrode can respond in a Nernstian way to not only Li^+ and Mg^{2+}, but also to Ca^{2+} in AN and PC in spite of the deviated crystallographic radii of Ca^{2+} from that of the 12-crown-4 ethers. The Nernstian response to Li^+ and Mg^{2+} are quite reasonable, but the thermodynamic response to Ca^{2+} is indeed beyond our expectations. This unusual Nernstian response to Ca^{2+} in AN and PC may be explained by considering a sandwich-type complexation of Ca^{2+} with B12C4; the molecular ratio should be 1 : 2. The sandwich-type complexation of B12C4 coupled to a PAA membrane with Ca^{2+} proposed here is acceptable when we consider that the potential was established not at an inner site of the membrane, but at the membrane–solution interface because the chemically bounded B12C4 to PAA may not arrange its three-dimensional conformation to make a complex with Ca^{2+} at an inner phase of the membrane. The PAA membrane matrix on the platinum disk is very rigid, and seemed not to be liquid, but solid. We had proposed an idea in previous reports[6,13] that the potential of PAA-coated platinum electrodes is mainly established at the polymer membrane–solution interface by the complexing equilibrium between host compounds coupled to PAA and analyte ions in a solution. It had also been reported that a host compound conjugated with PAA at a vicinity close to the solution-membrane interface is considered to be in the aprotic

Table 1. The Response for Some Cations at PAA–B12C4 Electrode in Some Aprotic Solvents at 25 °C.

Solvents	Ions	Slope (mV/log $a_{M^{z+}}$)	Linear range (p$a_{M^{z+}}$)
AN	Li^+	$+59.7 \pm 0.2$	3.2—5.2
	Ca^{2+}	$+27.1 \pm 0.2$	4.1—6.7
PC	Li^+	$+58.9 \pm 0.3$	2.2—6.2
	Mg^{2+}	$+29.1 \pm 0.2$	2.4—6.3
	Ca^{2+}	$+31.2 \pm 0.2$	2.0—6.0
GBL	Mg^{2+}	$+26.3 \pm 0.3$	3.0—5.5

solution, since the compound is fond of an organic solvent rather than a hydrophilic PAA membrane. The Nernstian response of Ca^{2+} in AN and PC of the electrode by the sandwich-type complexing described here firmly supports that the potential-established site is not an inner site of the PAA membrane, but is a polymer membrane–solution interface. The broader ranges of the Nernstian response of PAA–B12C4 to Ca^{2+} in AN and PC than those of PAA–B15C5 to Ca^{2+} [5] suggest the formation of a more stable complex in the case of the Ca^{2+}–(B12C4)$_2$ complex than that of Ca^{2+}–B15C5. The sandwich-type complexation of cations with crown ethers, e.g., Li^+–(derivatives of 12C4)$_2$, had been considered to develop a Li^+ sensor by Kimura et al.[14] An improvement in selectivity was established. A Nernstian response, not only Mg^{2+}, but also Ba^{2+} in AN, had been reported in the case of PAA–POE4.[15] A magnesium ion sensor is quite rare, and we have none for use in aprotic solvent systems, except for one previously developed at our laboratory.[15] The electrode developed here has a wider range of Nernstian response than did the previous one.

Successive Complex Formation Constants and Gibbs Energies of Transfer for Li^+ and Mg^{2+}. From the Nernstian response of the electrode mentioned above it has been found that the electrode has the necessary condition to proceed with the experiment in order to obtain the successive complex formation constants (β_i) and the Gibb's energies of transfer ($\Delta G_{tr(j=1,2,3)}$), which are estimated by the same method described previously.[5] The electrode was applied to determine the β_i of Li^+ in AN and Mg^{2+} in PC with such D as DMF, DMSO, and HMPA. The β_i of the next reaction (1) for the complex formation reaction of cations M^{z+} in a reference solvent R, (R = AN and PC), with solvent molecules D was defined as follows:

$$M_R^{z+} + iD = M_{iD}^{z+}, \tag{1}$$

$$\beta_i = a(M_{iD}^{z+})/\{a(M_R^{z+})(D)^i\}. \tag{2}$$

Here, M_R^{z+} and M_{iD}^{z+} mean Li^+ and Mg^{2+} solvated only by reference solvent molecules and those solvated by D, respectively; $a(M_R^{z+})$ and $a(M_{iD}^{z+})$ denote the activities of Li^+ and Mg^{2+} before and after the addition of D, respectively; i shows the number of solvating D molecules. The results of the β_i of Li^+ in AN with DMF and the $\Delta G_{tr(j=1,2,3)}$ of Li^+ from AN to DMF and AN–DMF mixtures obtained by the PAA–B12C4 electrode are summarized in Table 2. As can be seen from the table, the values between $\Delta G_{tr(1)}$ and $\Delta G_{tr(3)}$ well agreed with each other. The obtained complex formation constants are summarized in Table 3. The β_1 in the table seem to be reliable within ±10% and other β_i and $\Delta G_{tr(j)}$, to be within ±20%. In the case of log β_i of Li^+ in AN with DMF, the values had been reported previouly[16] to be 1.20, 2.04, and 1.82 as β_1, β_2, and β_3, respectively. The monovalent cation-sensitive glass electrode used there had been confirmed to respond satisfactorily in a Nernstian way for Li^+, and could be used to monitor both the activity change of Li^+ caused by a variation of its concentration in AN and that by the solvent effect.[17] Since we can see that the constants agreed fairly well with each other, the electrode developed here worked well to obtain these constants. Clune et al.[18] reported the log β_i of

Table 2. The Complex Formation Constants of Lithium Ion in Acetonitrile with *N,N*-Dimethylformamide and Gibbs Energies of Transfer $\Delta G_{tr(j=1,2,3)}$ from Acetonitrile to *N,N*-Dimethylformamide and Their Mixtures at 25 °C

φ (DMF)[a]	0.003	0.007	0.010	0.030	0.040	0.060	0.0090	0.17	0.23
$-\Delta G_{tr(1)}$	0.29	0.75	1.19	2.06	2.38	2.87	3.51	4.54	5.18
$-\Delta G_{tr(3)}$	0.21	0.76	1.18	2.07	2.38	2.87	3.47	4.55	5.17
$-\Delta G_{tr(2)} = 8.52 \pm 1.70$ ($\varphi = 1.0$)									

a) φ (DMF) denotes the volume fraction of DMF.

Table 3. The Complex Formation Constants of Some Cations in Some Aprotic Solvent with Other Basic Aprotic Solvent Molecules, D, and Gibbs Energies of Transfer, ($\Delta G_{tr(2)}$), of Cations from Acetonitrile and Propylene Carbonate to D at 25 °C

Ion	R[a]	D (DN)	logβ_1	logβ_2	logβ_3	logβ_4	$-\Delta G_{tr(2)}$/kcal mol^{-1}
Li^+	AN	DMF (26.6)	1.14	2.20	1.66	1.75	8.52 ± 1.70
Mg^{2+}	PC	DMF	2.21	3.29	3.57	3.72	11.1 ± 2.2
		DMSO (29.8)	2.45	3.67	4.96	5.13	13.3 ± 2.7
		HMPA (38.8)	3.96	5.05	6.36	7.60	14.5 ± 2.9
Ba^{2+} [b]	PC	DMF	0.76	1.90	2.25		7.6 ± 1.5
		DMSO	1.63	1.99	2.31	2.59	9.79 ± 1.96

a) "R" denotes a reference solvent. b) The data obtained with PAA–POE4 electrode (cf. Refs. 12 and 15).

Na^+ in PC with DMSO obtained by using monovalent cation-sensitive glass electrode; $\beta_1 = 0.74$, $\beta_2 = 0.92$, and $\beta_3 = 0.9$. The values agreed very well with our data, which was obtained with the PAA–B15C5 electrode; $\beta_1 = 0.78$, $\beta_2 = 0.94$, and $\beta_3 = 0.92$.[4] We have no such data concerning the divalent-cations listed in Table 3, which make it possible to compare with the constants obtained in the experiment. We have no effective method for a practical certification of the data for the divalent cations obtained in Table 3 at this stage; however, it should be noted that the same PAA–B12C4 electrode developed in the experiment was used to obtain such data for both Li^+ and Mg^{2+}. It might have some efficiency in order to certify the reliability of the electrode that one compares the changes in the relative stability with such parameters as solvent basicity and charge densities of ions. The stability of the complexes obtained here increase with their cationic charge, their basicity of the complexing solvents D, and decreasing of their crystallographic radii. The $\log \beta_1$ for Ca^{2+} in AN at DMF, NMP, DMA, DMSO, and HMPA were from 3- to 10-times larger than those in PC, as can be seen in Ref. 5. This is expected from the fact that AN is a less-basic solvent than PC; Gutmann's donor number (DN) of AN and PC are 14.1 and 15.1, respectively. Concerning the solvent basicity, Izutsu et al. reported in their paper[19] that PC was about a 10-times stronger base than AN. We can find that when an ion is solvated by lesser complexing molecules the $\Delta G_{tr(2)}$ become smaller in spite of its larger β_1. As can be seen in Table 3, for example, the $\Delta G_{tr(2)}$ of Mg^{2+} in PC for DMF, DMSO, and HMPA are 11.1, 13.3, and 14.5, respectively, the solvation number of which is four; on the other hand, those of Ca^{2+} in PC are 11.6, 15.0, and 19.0, respectively, the solvation number of which is five under each experimental condition, as can be seen in previous paper.[4] Here, the β_1 of Ca^{2+} in PC[4] for DMF, DMSO, and HMPA are 1.47, 1.86, and 2.78, respectively.

Conclusion

An electrode consisting of a non-plasticized carboxyl-modified PAA coupled to B12C4 showed a Nernstian response to Li^+ and Ca^{2+} in AN, and Li^+, Mg^{2+}, and Ca^{2+} in PC, and a near-Nernstian response to Mg^{2+} in GBL. An unexpected Nernstian response of the PAA–B12C4 electrode to Ca^{2+} in AN and PC was used to deduce the conclusion that the site of the potential establishment of the electrode was not at an inner site of the polymer membrane, but at the polymer membrane–solution interface. The electrode was confirmed to be applicable for obtaining the successive complex formation constants and the Gibbs energies of transfer of Li^+ in AN and Mg^{2+} in PC in relation to some other basic aprotic solvent molecules, which were very rare.

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References

1 Y. Marcus, "Ion Solvation," John Willey & Sons Ltd., New York (1985); "Ion Properties," Marcel Dekker, Inc., New York (1997); "The Properties of Solvents," John Willey & Sons Ltd., New York (1998).

2 E. Pungor, *Anal. Sci.*, **14**, 249 (1998).

3 T. Nakamura, H. Higuchi, and K. Izutsu, *Bull. Chem. Soc. Jpn.*, **61**, 1020 (1988).

4 T. Nakamura, C. Hayashi, and K. Izutsu, *Anal. Chim. Acta*, **292**, 305 (1994).

5 T. Nakamura and H. Mongi, *Bull. Chem. Soc. Jpn.*, **70**, 2449 (1997).

6 T. Nakamura, C. Hayashi, and T. Ogawara, *Bull. Chem. Soc. Jpn.*, **69**, 1555 (1996).

7 T. Nakamura, T. Ueda, T. Yanagisawa, and H. Watanabe, *Bull. Chem. Soc. Jpn.*, **72**, 235 (1999).

8 U. E. Spichiger, *Electroanalysis*, **5**, 739 (1993).

9 G. E. Pacey, Y. P. Wu, and B. P. Bubnis, *Synth. Commun.*, **11**, 323 (1981).

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

11 K. Izutsu, T. Nakamura, M. Muramatsu, and Y. Aoki, *J. Electroanal. Chem.*, **297**, 49 (1991).

12 T. Nakamura, M. Komai, S. Hosono, and K. Izutsu, *Anal. Chim. Acta*, **238**, 351 (1990).

13 T. Nakamura, Y. Nakamura, T. Kojima, and K. Izutsu, *Bull. Chem. Soc. Jpn.*, **63**, 2615 (1990).

14 K. Kimura, H. Yano, S. Kitazawa, and T. Shono, *J. Chem. Soc., Perkin Trans. 2*, **1986**, 1945.

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

16 K. Izutsu, T. Nakamura, and K. Iwata, *Anal. Chim. Acta*, **117**, 329 (1980).

17 T. Nakamura, *Bull. Chem. Soc. Jpn.*, **48**, 2967 (1975).

18 G. Clune, W. E. Waghorne, and B. G. Cox, *J. Chem. Soc., Faraday Trans. 1*, **72**, 1294 (1976).

19 K. Izutsu, I. M. Kolthoff, T. Fujinaga, M. Hattori, and M. K. Chantooni, Jr., *Anal. Chem.*, **49**, 503 (1977).