

Development and Application of Ion-Selective Electrodes in Nonaqueous Solutions

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The potentiometric response of electrodes is described, including: (1) Nernstian response to activity change due to an altered concentration of the analyte ion, and (2) Nernstian response to activity change caused by different solvents. In order to ensure the reliability of the data obtained in this study, the following three steps were taken: (i) a comparison of electrode potentials between a monovalent cation-sensitive glass electrode and amalgam electrodes; (ii) a comparison of the data with those obtained by other methods; and (iii) a comparison of the data obtained by employing different reference solvents. This review also describes the development of electrodes, including the synthesis of host compounds by esterification and amide bonding with poly(acrylamide), thermodynamic application results obtained by the developed electrodes, and brief discussions about the response mechanism and an establishment site of the membrane potential.

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1 Introduction and Background

Most chemical reactions proceed in solution, and solvation has a strong effect on the reactivity of compounds. Using dipolar aprotic solvents instead of aqueous systems results in significant differences in both the solubility of hydrophobic compounds and the dissociation of electrolytes, and also in both the activities and Gibbs energies of ions. Since thermodynamic data obtained from ion-solvent complex formation are very important for estimating and predicting such effects as those mentioned above, many investigations¹⁻¹⁰ have been carried out by means of analytical methods, such as IR, NMR, Raman spectroscopy, conductometry, potentiometry, and calorimetry. Among these methods, the potentiometric method is preferable because of its preciseness. Ion-selective electrodes can be used to directly trace activity changes of ions in solution. The application of

ion-selective electrodes in nonaqueous and mixed solvents to thermodynamic studies was reviewed by Pungor *et al.*¹¹ Coetzee *et al.*¹² reviewed their application of a commercial lanthanide-based fluoride ion-selective electrode to the measurement of F^- activity in aprotic solvents, and to the simultaneous determination of impurities. But none of these reports have contained data concerning alkali or alkaline-earth metal ions, although the solubility of alkali-metal salts in propylene carbonate (PC) using ion-selective electrodes has been reported.¹³ A number of other studies¹⁴⁻¹⁸ have been carried out to increase our understanding of both the potential response mechanism and the detection limit of ion sensors. A study of a potential establishment site has also been reported.¹⁹ Previous papers²⁰⁻²² are available for understanding certain kinds of chemical and physical properties of a hydrophilic poly(acrylamide) (PAA) membrane. In these reports, voltammetric investigations concerning the response time²⁰ and the micro array arrangement²¹ of electrodes and conductometric characterization about the properties of ion-transport across a

PAA membrane²² were described.

Studies that aimed to determine the successive complex formation constants between a monovalent cation and solvent molecules using a monovalent cation sensitive glass electrode (Beckman Co. Ltd.) were reported.^{23,24} Also, the thermodynamic response ability of the electrode not only to activity change due to an alteration in its concentration, but also to that due to a change of the solvent was confirmed.²⁵ These studies certified the effectiveness of an ion-selective electrode for investigating ion-solvent complex formation reactions. At that stage thermodynamic data concerning divalent cations, especially Mg^{2+} , Ca^{2+} , and Ba^{2+} , were very scarce. Therefore, an investigation to develop ion-selective electrodes for use to those metal ions in nonaqueous solutions was projected.

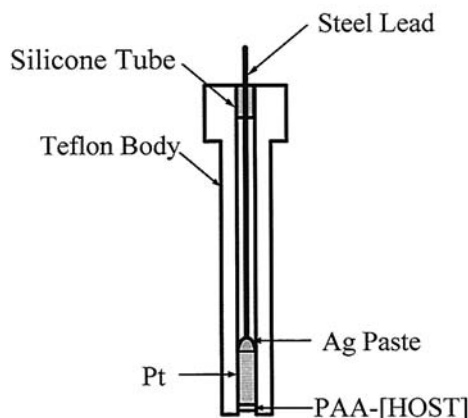
This review describes the development of these electrodes, including the synthesis of host compounds bound with PAA, and the potentiometric response of the electrodes. The polymer membrane ion-selective electrodes developed, which are described later, were used to trace the fundamental physical properties of ions in solution, including the determination of successive complex formation constants of ions with some dipolar aprotic solvent molecules, the solubility products of electrolytes in dipolar aprotic solvents, and the standard molar Gibbs energies of ion transfer. Investigations of the response mechanism and the establishment site of the membrane potential by means of potentiometric and spectrophotometric methods were carried out.

The experimental results confirm the response ability of the ion-selective electrodes developed here in terms of the following two categories. One is the Nernstian response of the electrodes to activity changes due both to concentration change of the analyte ion and to a different solvent; the other is the reliability of data obtained in the experiment. For these categories, the following three were described: (i) a comparison of electrode potentials between a monovalent cation-sensitive glass electrode and amalgam electrodes, (ii) a comparison of the data obtained with those obtained by other methods, and (iii) a comparison of the data obtained by employing different reference solvents.

2 Construction of the Electrodes

Cyclic polyethers have been synthesized and studied since the 1960's, and many of them have been used as neutral carriers of liquid-membrane ion-selective electrodes, *e.g.*, a poly(vinyl chloride) (PVC) membrane electrode. In order to study the thermodynamic properties of ions, including the relatively weaker metal-ligand complex formation reaction between ion-solvent molecules and the solubility of solutes in nonaqueous solutions, ten kinds of ion-selective electrodes based on a non-plasticized PAA membrane were developed. The construction and application of the electrodes were partly reviewed previously.²⁶

The matrices of the ion sensors of divalent cations developed for use in nonaqueous solutions had generally been constructed with solid state materials: for example, ceramics consisting of sulfide compounds and halogenized silver containing silicon rubber-based, so-called Pungor-type electrodes. On the contrary, we proposed using organic polymer matrix electrodes in nonaqueous solvent systems. The construction of the electrode was similar to that for a liquid-membrane electrode consisting of PVC, except that PAA was not cross-linked, and it was not plasticized, and host compounds (HOSTs) were chemically bound with the polymer matrix. PAA is quite stable as a thin membrane on a platinum disk in dipolar aprotic



Scheme 1 Schematic diagram of the PAA-[HOST] electrode.

solvents, such as acetonitrile (AN), PC, γ butyrolactone (GBL), *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMA), and hexamethylphosphoric triamide (HMPA). Carboxyl-modified PAA was used to bind chemically with various HOSTs, which formed selective and reversible complexes with the ions under investigation in nonaqueous solutions.

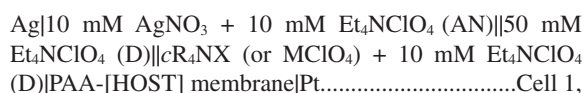
2.1 Synthesis of PAA-[crown ether], PAA-[acyclic polyether], PAA-[Cryp222B], and PAA-[M(pc)]

The HOSTs, except for acyclic polyethers, tetraethylene glycol monododecyl ether (POE4) and hexaethylene glycol monododecyl ether (POE6), which were chemically bound with PAA by esterification, were converted to the amines (HOST-NH₂) *via* the respective nitro derivative (HOST-NO₂), and then bound at the carboxyl group of carboxyl-modified PAA by a reaction in DMF similar to that used by Bauminger and Wilchek²⁷ to obtain the final products. The HOSTs were covalently bound with PAA: PAA-COOH + NH₂-HOST → PAA-CO-NH-HOST + H₂O.

2.2 Potentiometric measuring systems

PAA modified with chemically bound HOST compounds (abbreviated as PAA-[HOST]) was dissolved in water, and then spread on the end of a platinum disk with a 2 mm diameter housed in a Teflon body. A schematic diagram of the electrode construction is shown in Scheme 1. The electrode was stored in a silica-gel desiccator, and a thin membrane (thinner than 50 μ m) formed on the surface. The electrode was conditioned in an examined aprotic solvent containing the analyte ion, the concentration of which ranged from 5 to 0.5 mmol and 10 mM Et₄NClO₄, for durations ranging from several hours to two days before use. It should be noted that the PAA membrane becomes almost solid-state due to dehydration caused by dry aprotic solvents during its conditioning.

The potentiometric responses of the electrodes to various cations and anions were investigated by measuring Cell 1. The emfs were measured with an electrometer. All compartments of Cell 1 were freshly prepared each time. Steady state potentials were read to ± 0.1 mV.



where D is the solvent; R₄N⁺ is tetraethylammonium ion (Et₄N⁺)

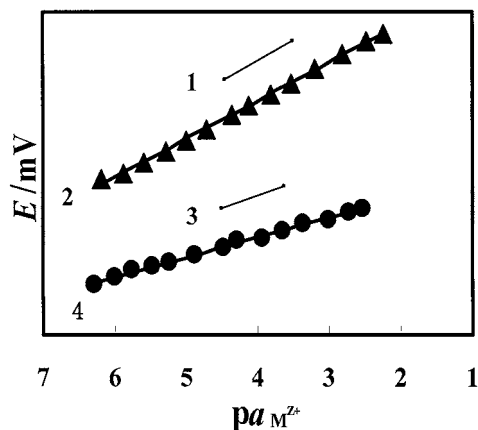


Fig. 1 Typical calibration curves for cations in propylene carbonate at a PAA-[B12C4] electrode (25°C). Lines 1 and 3 are theoretical slopes for a singly charged cation (59.2 mV/pa_M⁺) and for a doubly charged cation (29.6 mV/pa_M^z), respectively; 2 and 4 are for Li⁺ (slope, 58.6 mV/pa_{Li}⁺; *r*² = 0.9975) and Mg²⁺ (slope, 29.1 mV/pa_{Mg}²⁺; *r*² = 1.000), respectively.

Table 1 Response for some cations at a PAA-[B12C4] electrode in aprotic solvents at 25°C

Ion	Solvent	Slope mV/pa _M ^z	Linear range/ pa _M ^z
Li ⁺	AN	+59.7 ± 0.2	3.2 - 5.2
Ca ²⁺	AN	+27.1 ± 0.2	4.1 - 6.7
Li ⁺	PC	+58.9 ± 0.3	2.2 - 6.2
Ma ²⁺	PC	+29.1 ± 0.2	2.4 - 6.3
Ca ²⁺	PC	+31.2 ± 0.2	2.0 - 6.0
Ma ²⁺	GBL	+26.3 ± 0.3	3.0 - 5.5

or tetrabutylammonium ion (Bu₄N⁺), and the counter ion is trifluoromethane sulfonate when M is Ca²⁺; X and M are, respectively, the anion and cation under investigation; *c* is the concentration in mol dm⁻³ of R₄NX (or MClO₄), which was added by a microburet. The change in the liquid-junction potentials of Cell 1 during emf measurements was negligible in the experiment.²⁸

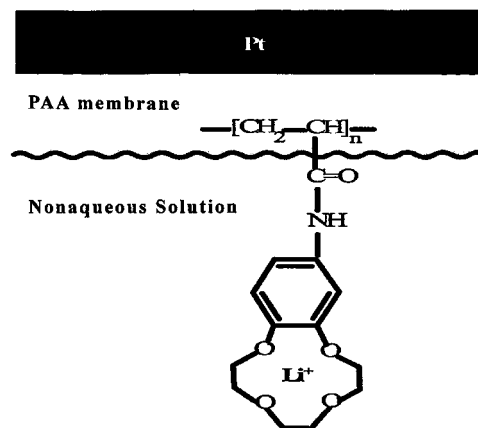
3 Nernstian Response to the Activity Change Caused by the Concentration Change of the Analyte Ion

Ion-selective polymer membrane electrodes for alkali and alkaline earth metal ions and two kinds of anions have been developed. The experimental results, which to confirm the response ability of the ion-selective electrodes to the activity changes due to the concentration change of the analyte ion, are summarized below.

3-1 Nernstian response

3-1-1 PAA-[crown ether] and PAA-[acyclic polyether] electrodes

Electrodes modified with PAA coupled with crown ethers and poly(oxyethylene)s, PAA-[crown ether] and PAA-[acyclic polyether] electrodes, showed Nernstian or near-Nernstian responses to cations such as alkali and alkaline-earth metal ions (Li⁺,^{23,24,29-31} Na⁺,^{24,32,34} and K⁺,^{24,35} Mg²⁺,^{29,30,32} Ca²⁺,^{29,30,32,34} and



Scheme 2 Imaginary configuration diagram at the membrane-nonaqueous solution interface of a PAA-[B12C4] electrode.

Table 2 Responses of a PAA-[B15C5] electrode to Ca²⁺ and Na⁺ in some aprotic solvents at 25°C

Ion	Solvent	Slope mV/pa _M ^z	Linear range/ pa _{Mg} ^z
Ca ²⁺	AN	+29.7 ± 0.3	4.74 - 3.25
Ca ²⁺	PC	+28.6 ± 0.3	5.22 - 2.10
Ca ²⁺	NMP	+30.1 ± 0.3	3.07 - 1.92
Na ⁺	AN	+60.2 ± 0.5	4.40 - 2.40
Na ⁺	PC	+58.6 ± 0.5	5.22 - 2.74

Ba²⁺,^{29,30,32,35}). Examples of the typical calibration curves for Li⁺ and Mg²⁺ in PC at a PAA-[B12C4] electrode³⁰ are shown in Fig. 1. The electrode response results at the PAA-[B12C4] electrode are also displayed in Table 1.³⁰

Generally speaking, the PAA-[B12C4] electrode should respond in a Nernstian way to both Li⁺ and Mg²⁺, due to the best fit between the crystallographic radii of the ion and a hole size half that of the HOST used.³⁶ As can be seen in Table 1, however, the electrode also exhibits a Nernstian response to Ca²⁺ in AN and PC. Such a response may be possible when Ca²⁺ forms a sandwich-type complex with B12C4. An imaginary configuration diagram at the membrane-nonaqueous solution interface of the PAA-[B12C4] electrode is shown in Scheme 2. As can be seen in the scheme, the crown, a hydrophobic compound, may withdraw into a nonaqueous solution, so it becomes possible to make a sandwich-type complex with Ca²⁺. On the other hand, the HOSTs, which exist at an inner site of a solid-state PAA membrane, can never move to construct a sandwich-type complex. Given that the PAA membrane coated on a metal disk is in a solid state, as mentioned above, it is clear that a steric reconstruction to form a sandwich-type complex in the solid state membrane could never occur. This fact confirms that such complex formation occurs at the solution/membrane interface, and the potential establishment site of the electrode should therefore be at the interface of the membrane and the solution.

Examples of the responses to Ca²⁺ in AN, PC, and NMP obtained at the PAA-[B15C5] electrode are given in both Table 2^{32,34} and Fig. 2 (line 1).

3-1-2 PAA-[M(pc)] electrodes

Electrodes of a Pt disk coated with PAA coupled with a metal phthalocyaninates; PAA-[M(pc)] electrode (M = Co(II),^{37,38} VO,³⁹ Sn(II),⁴⁰ Ga(III)⁴¹) were developed. All of these electrodes

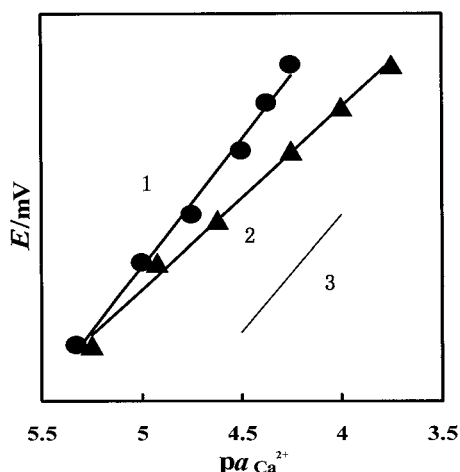


Fig. 2 Calibration curve for Ca^{2+} in acetonitrile at a PAA-[B15C5] electrode. Lines 1 and 2 show the relations between potentials vs. $\text{pa}_{\text{Ca}^{2+}}$ after (●) and before (▲) a correction for the effect of Ca^{2+} - CF_3SO_3^- association; and 3 shows the theoretical slope for a divalent cation ($29.6 \text{ mV}/\text{pa}_{\text{M}^{2+}}$).

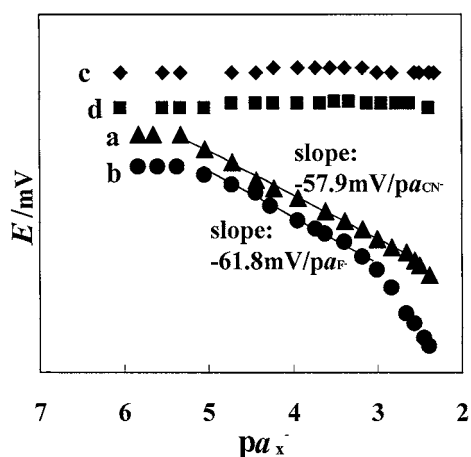


Fig. 3 Potentiometric calibration curves for ions in acetonitrile at a PAA-[Ga(pc)] electrode. Lines a, b, c, and d denote CN^- , F^- , Cl^- , and Br^- , respectively.

showed peculiar responses, *i.e.*, they responded in a Nernstian or near-Nernstian way only for anions, such as F^- ³⁷⁻⁴⁰ and CN^- ^{38,39,41} in AN, PC, DMA, and DMF. However, they showed a very poor response to other anions, such as Cl^- , Br^- , I^- , CF_3SO_3^- , NO_2^- , SCN^- , BPh_4^- , PF_6^- , and ClO_4^- . Typical examples⁴¹ at the PAA-[Ga(pc)] electrode are shown in Fig. 3 for F^- , CN^- , Cl^- , and Br^- in AN. Similar response phenomena observed in spite of differences of the center atoms, such as Co(II), VO, Sn(II), and Ga(III), are mentioned above in connection with phthalocyanine complexes. The quite different response results obtained between F^- and CN^- and Cl^- and Br^- are difficult to interpret. To understand the peculiar selective response ability of the electrode, UV-VIS spectrophotometric investigations in AN and DMA were carried out.^{38,41} A solution of $\text{Bu}_4\text{NF}\cdot 3\text{H}_2\text{O}$, Et_4NCN , or Bu_4NBr in AN or DMA, for example, was titrated by stepwise addition to a [Ga(pc)] saturated AN or DMA solution.⁴¹ Typical spectra are shown in Fig. 4 and, as can be seen in the figure, a dramatic difference was obtained in the spectra after the addition of F^- and Br^- to a [Ga(pc)] saturated DMA solution. The differences in the spectra

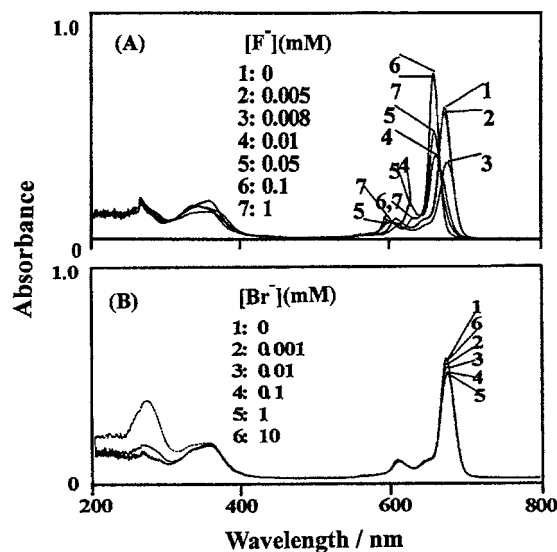


Fig. 4 UV-VIS spectra for (A) (phthalocyaninato)Ga(III) ([Ga(pc)]) saturated *N,N*-dimethylacetamide diluted by a factor of five, containing various concentrations of F^- and (B) (phthalocyaninato)Ga(III) ([Ga(pc)]) saturated *N,N*-dimethylacetamide diluted by a factor of five containing various concentrations of Br^- , respectively. The original concentration of [Ga(pc)] is lower than 0.01 mM. The reference was *N,N*-dimethylacetamide.

obtained at AN and DMA are discussed in detail in Ref. 41 from the viewpoint of the selective complex formation of F^- and Br^- with [Ga(pc)] in AN and DMA. Almost the same behavior was observed in the case of CN^- and Cl^- .

The ligand field theory, although not very applicable in the case of non-transition metals, gives complex formation ability on the order of $\text{CN}^- \gg \text{F}^- \gg \text{Cl}^- > \text{Br}^-$. It is thus reasonable to assume that Ga^{3+} reacts strongly with F^- and CN^- , and that, as a result, they coordinate to [Ga(pc)] at the axial site by a ligand-exchange reaction between the originally bonded solvent molecules or water molecule(s) at the sensor membrane-solution interface.

The imaginary configuration diagram at the membrane-nonaqueous solution interface of the PAA-[M(pc)] electrode is similar to that shown in Scheme 2. The reactions may also be promoted by the very weak acidity of DMA,^{3,6} in which F^- and CN^- have a more active status compared with that in water. This resulted in a strong complex formation reaction of the ions with [Ga(pc)]. These results indicate that [Ga(pc)] interacts strongly with F^- and CN^- , but weakly with Cl^- and Br^- . It is reasonable to consider that the experimental observations of Nernstian or near-Nernstian responses to F^- and CN^- indicated that stable complex formation and ion-distribution between the sensor membrane and the solution may occur. While, a non-Nernstian response to Cl^- and Br^- were due to the weak interaction with HOSTs in all of the above solvents.^{38,40,41}

3-2 Relation between ion-association and the Nernstian slope

Generally, a complete dissociation of the electrolyte compound used for a basic thermodynamic investigation may be preferable, because the ion association would produce side effects concerning the activity change along with both the ion concentration and the chemical reactions, such as complex formation reactions. For these reasons, metal perchlorates were usually used, except for $\text{Ca}(\text{CF}_3\text{SO}_3)_2$, since we could not obtain a completely unhydrated calcium perchlorate. When $\text{Ca}(\text{CF}_3\text{SO}_3)_2$ was used, an activity correction due to the

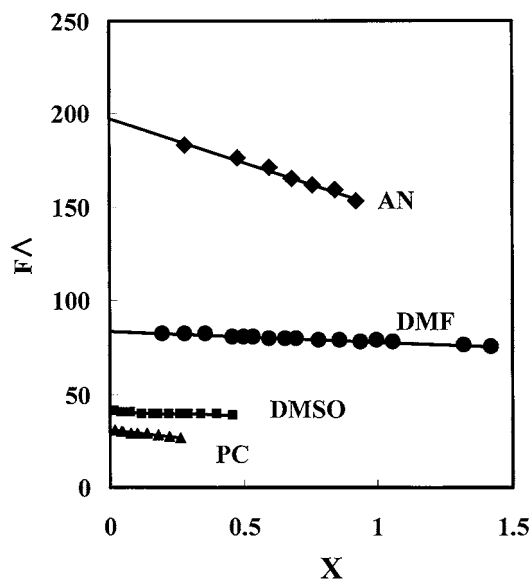
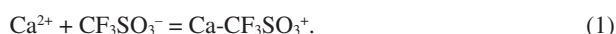


Fig. 5 Modified Fuoss-Edelson plots for $\text{Ca}(\text{CF}_3\text{SO}_3)_2$ in some aprotic solvents at 25°C.

ion-association had to be performed. A slope correction of the calibration curve was only made in the case of the compound. As shown in Fig. 2 (line 1), the PAA-[B15C5] electrode responded in a Nernstian way to Ca^{2+} in AN.³¹ However, this was realized only after a correction of its activity. Before this correction, the calibration slope was only 22.6 mV/ $\text{pa}_{\text{Ca}^{2+}}$ (line 2 in Fig. 2), and the slope was estimated by considering the effect of ion-association on the concentration of Ca^{2+} . When the association constant of the analyte electrolyte is less than 20, there is no need to consider the association effect on the activity change due to its concentration change.

3-2-1 Determination of the molar conductivity of $\text{Ca}(\text{CF}_3\text{SO}_3)_2$ in some aprotic solvents

A conductometric measurement was carried out to determine the association constant, K_1 , in the following chemical reaction (1):



The constant was obtained by using the Modified Fuoss-Edelson method to analyze the conductometric data, as shown in Fig. 5; a $K_{1(\text{AN})}$ was calculated to be 1.02×10^4 ($\text{dm}^3 \text{mol}^{-1}$).³⁴

3-2-2 Correction of ion-activity of non-completely dissociated compounds

The variation of the calcium ion activity, $a_{\text{Ca}^{2+}}$, due to ion association with CF_3SO_3^- , was estimated by using equations described in a previous report.³⁴

As a result, the slope of the calibration curve (22.6 mV/ $\text{pa}_{\text{Ca}^{2+}}$ in concentration) was corrected to 29.7 mV/ $\text{pa}_{\text{Ca}^{2+}}$ (line 1 in Fig. 2).³⁴ The method described here could be used both to estimate the ion activities and to confirm the response of the electrodes in a solvent of low dielectric constant, in which the ion activities of the electrolytes are affected by the ion association.

4 Nernstian Response to an Ionic Activity Change Caused by Different Solvents

Because of its accuracy and convenience, potentiometric titration has been widely used in studying various types of

Table 3 Comparison of β_1 for the complex formation of some univalent cations in AN obtained by various methods at 25°C

Method	Ion and ligand		
	β_1 (Na^+ , H_2O)	β_1 (Na^+ , CH_3OH)	β_1 (Li^+ , CH_3OH)
Potentiometry ^a	1.8 ± 0.3	1.1 ± 0.2	4.5 ± 0.7
IR ^{a,b} (at 35°C)	1.3 ± 0.3	—	3.4 ± 0.7
Conductometry ^{a,c}	2 ± 0.4	—	—
NMR ^{a,d}	2.5 ± 0.1	1.5 ± 0.2	5.6 ± 0.1

a. Refers to values obtained by a Beckmann monovalent cation-sensitive glass electrode (Ref. 24).

b. Refs. 24 and 42.

c. Refs. 24 and 43.

d. Refs. 24 and 44.

reactions, e.g. precipitation, complex formation, and redox reactions in nonaqueous solutions. In order to study the thermodynamic properties of ions and nonaqueous solvents, a number of ion-selective electrodes based on a PAA membrane were developed, and have been successfully used as indicator electrodes in ion-solvent molecule complex formation and precipitation reactions. The ion solvation energies of electrolytes are important for quantitative predictions of the behaviors of ions and electrolytes in different kinds of solutions.⁶

The experimental results, which have confirmed the response ability of the ion-selective electrodes to the activity changes due to the change of solvents and the reliability of the data, are summarized below.

In one previous study, a commercial monovalent cation-sensitive glass electrode (Beckmann Co. Ltd.) was compared with corresponding metal amalgam electrodes.²⁵ A close correlation between the changes in the electrode potential due to the difference of solvents was found. From those results, we could deduce that the commercial electrode responded thermodynamically to the activity change of an analyte ion due to the difference of solvents.

Next, a comparison is given of the data obtained with those obtained by other methods. In Table 3, some of the constants, β_1 in $\text{dm}^3 \text{mol}^{-1}$, determined by using the electrode (Beckmann Co. Ltd.) are compared with constants obtained by other methods. It should be noted that the values are not logarithmic.

As can be seen in Table 3, these values are in close agreement with each other, and we can confirm the thermodynamic response ability of the glass electrode.

4-1 Successive complex formation constants of ions with some dipolar aprotic solvent molecules

Data concerning relatively weaker ion-solvent molecule interactions in nonaqueous solutions were very scarce, especially in the case of magnesium and alkaline earth metal ions. The electrodes presented in this review had been successfully used as the indicator electrodes to obtain stepwise complex formations of the ion with solvent molecules. The constant of ion, β_1 in a reference solvent, R, was defined in the same way in previous papers.³⁰⁻³² The emf change, ΔE , which was the potential difference between the initial and steady potentials obtained at each addition of a quite small volume of other solvents, D, was analyzed by a method proposed by Cox *et al.*⁴⁵ Here, it should be noted that the electrode potential, ΔE , used for obtaining constants is the value of the net potential change due to activity change caused by proceeding chemical reactions.

Successive complex formation constants, β_1 in $\text{dm}^3 \text{mol}^{-1}$ at

Table 4 Successive constant, β_1 , of the complex formation reaction of Ca^{2+} in AN and PC with some basic solvent molecules obtained by using a PAA-[B15C5] electrode at 25°C

	Solvent				
	DMF	NMP	DMA	DMSO	HMPA
Donor number	26.2	27.3	27.8	29.8	38.8
Log β_1 in AN ^a	1.88	2.53	2.60	2.72	3.81
Log β_1 in PC ^b	1.47	1.56	1.60	1.86	2.78

a. Ref. 34.

b. Ref. 32.

25°C, of ions in PC with some basic solvent molecules, D, were determined by using the developed electrodes.^{29,30,32,33} Examples of $\beta_1(\text{Mg}^{2+})$ at PAA-[B12C4] electrode³⁰ are 2.21 (DMF), 2.45 (dimethylsulfoxide (DMSO)), and 3.96 (HMPA). The stabilities of ion-solvent complexes increase with the solvent basicity (which was predicted by Gutmann's donor number; DN).

For a comparison of the data obtained by employing different reference solvents, successive complex formation constants of Ca^{2+} in reference solvents PC and AN with several basic solvents determined by using the PAA-[B15C5] electrode are summarized in Table 4.

From these results, we can see that the ability of Ca^{2+} with other solvents increases with the solvent basicity, as predicted by DN. Here, we can also recognize in each case that the stability of the complex of Ca^{2+} with other solvents in PC is weaker than in AN, which has a lower basicity than PC. These results are reasonable when we consider that the difference in basicity between AN and other solvents is larger than that between PC and other solvents. Hence, it is reasonable to consider that the PAA-[B15C5] electrode responds thermodynamically to the activity change in the ions due to the difference of the solvents.

4.2 Solubility products of electrolytes in dipolar aprotic solvents

Solubility and solubility products are basic data for determining the thermodynamic properties of solvents, including nonaqueous solutions, and many investigations have been carried out using both analytical methods and chemical systems. Wynn *et al.*, for example, reported on the solubility data of alkali-metal fluorides in nonaqueous solvents,⁴⁶ and Emsley *et al.*⁴⁷ on the solubility of several metal fluorides, including NaF in acetic acid and glacial acetic acid.

The PAA-[B15C5] electrode was successfully used as a Na^+ indicator electrode for the chemical reaction of Na^+ with CH_3COO^- in PC solutions (Fig. 6).⁴⁸ As can be seen in the inset of Fig. 6, the potential response after each addition of $\text{CH}_3\text{COOBu}_4\text{N}$ to NaClO_4 in PC was fairly fast, and a steady state potential was achieved. From the titration, the solubility products were obtained by using the relations described in a reported paper.⁴⁸ With this method the initial concentration of the titrant or the titrate must be known (if only one of their concentrations is known, the exact concentration of the other can be determined by the obtained titration curve). The solubility products of NaF in PC, $pK_{\text{sp}}(\text{NaF})$, and CH_3COONa in PC, $pK_{\text{sp}}(\text{CH}_3\text{COONa})$, obtained by this method using the PAA-[B15C5] electrode were 12.6 and 10.4, respectively.⁴⁸ The method reported here can be easily applied to other systems, *e.g.*, Ca^{2+} , Mg^{2+} , Ba^{2+} , and so forth, when we use the corresponding electrodes described above, and can also be used to obtain various solubility products and Gibbs energies of transfer.

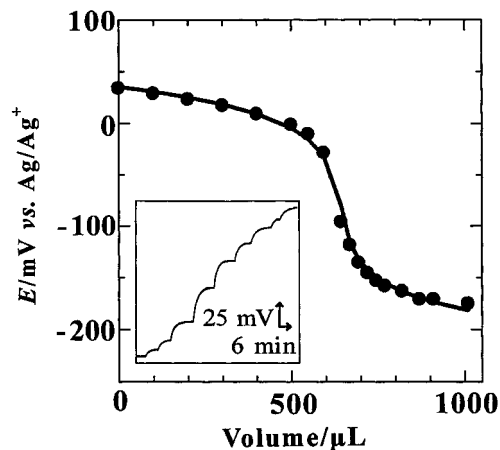


Fig. 6 Titration curve for 10 mL of 2 mM NaClO_4 versus 25 mM $\text{CH}_3\text{COOBu}_4\text{N}$ in a propylene carbonate solution with a PAA-[B15C5] electrode. (●) and (—) show the measured and calculated values, respectively. The inset shows the dynamic response curve. One step on the curve corresponds to one drop of the titrant.

4.3 Standard Gibbs energy of transfer and transfer activity coefficients

The Gibbs energy of transfer of an ion, Y, from a reference solvent, R, to another solvent, D, was defined, and detailed descriptions have been given in previous papers.^{6,34} The emf change, ΔE , which is the potential difference between the initial and steady potentials obtained at each addition of quite a small volume of other solvents, were analyzed by a method proposed by Cox *et al.*⁴⁵ Some examples of the Gibbs energy of transfer,³² $\Delta G_{\text{tr}(2)}$ in kJ mol^{-1} (see Ref. 32 - 34), of Ca^{2+} from PC to some other solvents, such as DMF, NMP, DMA, DMSO, and HMPA at 25°C were determined to be 48.5, 54.8, 52.7, 62.8, and 79.5, respectively.

The difference between the solvation energy of a chemical species, i, in a reference solvent, R, and other solvent D, $\Delta G_{\text{t}}^\circ(\text{i}, \text{R} \rightarrow \text{D})$,⁴⁵ is also expressed as follows:⁶

$$\Delta G_{\text{t}}^\circ(\text{i}, \text{R} \rightarrow \text{D}) = RT \ln(K_{\text{sp}}^{\text{R}}/K_{\text{sp}}^{\text{D}}). \quad (2)$$

When chemical species i are single ions, however, the value of $\Delta G_{\text{t}}^\circ(\text{i}, \text{R} \rightarrow \text{D})$ cannot be obtained by purely thermodynamic means. Various extra-thermodynamic assumptions have been proposed.^{6,7} On the basis of these assumptions, a number of standard molar Gibbs energy of ion transfer from water to other solvents D, $\Delta G_{\text{t}}^\circ(\text{i}, \text{W} \rightarrow \text{D})$, have been obtained, and many data have been compiled by Marcus.⁷ Also, if $\Delta G_{\text{t}}^\circ(\text{M}, \text{W} \rightarrow \text{D})$ or $\Delta G_{\text{t}}^\circ(\text{X}, \text{W} \rightarrow \text{D})$ is known for electrolyte MX_n , the standard molar Gibbs energy of transfer of the counter ion, $\Delta G_{\text{t}}^\circ(\text{X}, \text{W} \rightarrow \text{D})$ or $\Delta G_{\text{t}}^\circ(\text{M}, \text{W} \rightarrow \text{D})$, can be calculated.

An example of $\Delta G_{\text{t}}^\circ(\text{NaF}, \text{R} \rightarrow \text{D})$ from water (the solubility of NaF in water is 4.1 g/100 ml at 25°C and the solubility product of NaF in water, K_{sp}^{W} , is 0.31,⁴⁸ which agrees with the datum of Ref. 49) to PC at 25°C was calculated to be 69.0 kJ mol^{-1} . From pK_{sp} of CH_3COONa in PC obtained by using a PAA-[B-15-C-5] electrode, $\Delta G_{\text{t}}^\circ(\text{CH}_3\text{COONa}, \text{W} \rightarrow \text{PC})$ was determined to be 70.5 kJ mol^{-1} .⁴⁸ Given that the Gibbs energy of F^- transfer from water to PC, $\Delta G_{\text{t}}^\circ(\text{F}^-, \text{W} \rightarrow \text{PC})$, is 56 kJ mol^{-1} , as shown in Ref. 7, the Gibbs energy of Na^+ transfer from water to PC can be calculated to be 13.0 kJ mol^{-1} , and thus the transfer activity coefficient of Na^+ from water to PC, $\log \gamma_{\text{t}}(\text{Na}^+, \text{W} \rightarrow \text{PC})$, can be calculated to be 2.3. Here, the transfer activity coefficient is defined using the following equation (shown below and in Ref. 6):

Table 5 Successive complex formation constants, β_1 , and the Gibbs energy of transfer, $\Delta G_{tr(2)}(i,R \rightarrow D)$ in kcal mol⁻¹, of Na⁺ in AN and PC with some basic solvent molecules at 25 °C

Complex formation solvent	Ref. solvent	PAA-[B15C5] electrode		Monovalent cation-sensitive glass electrode	
		$\log \beta_1$	$\Delta G_{tr(2)}(i,R \rightarrow D)$	$\log \beta_1$	$\Delta G_{tr(2)}(i,R \rightarrow D)$
DMF	AN	0.42 ^c	4.6 ^c	0.40 ^a	—
DMA	PC	0.6 ^b	5.8 ^b	0.57 ^b	6.0 ^b
DMSO	AN	0.77 ^c	6.0 ^c	0.78 ^a	—
DMSO	PC	0.78 ^b	7.4 ^b	0.74 ^b	7.3 ^b

a. Ref. 24.

b. Refs. 32 and 34.

c. Ref. 33.

$$\log \gamma(i,R \rightarrow S) = \Delta G_t^\circ(i,R \rightarrow D)/2.3RT, \quad (3)$$

and the result agrees well with the datum (2.5) given in Ref. 7. The Gibbs energy of CH₃COO⁻ transfer from water to PC, $\Delta G_t^\circ(\text{CH}_3\text{COO}^-, \text{W} \rightarrow \text{PC})$, was similarly calculated to be 57.5 kJ mol⁻¹. Data for CH₃COO⁻ were reported for the first time. The transfer activity coefficient of CH₃COO⁻ from water to PC, $\log \gamma(\text{CH}_3\text{COO}^-, \text{W} \rightarrow \text{PC}; 10.1)$, can then be calculated.⁴⁸ Data, such as $\log \gamma(\text{CH}_3\text{COO}^-, \text{W} \rightarrow \text{AN}; 9.03)$ and $\log \gamma(\text{CH}_3\text{COO}^-, \text{W} \rightarrow \text{GBL}; 8.40)$, were also obtained.⁵⁰ The $\Delta G_t^\circ(\text{NaF})$ from water to PC was obtained potentiometrically from the result for the solubility product of NaF in PC,⁴⁸ which agreed with data from the literature,⁷ suggesting that the proposed method may be applicable to other systems.

4.4 Comparison of data with those obtained by other methods

For a comparison of the data with those obtained by other methods, successive complex formation constants, β_1 , and Gibbs energy of transfer, $\Delta G_{tr(2)}(i,R \rightarrow D)$, for Na⁺ in AN and PC with some basic solvent molecules are displayed in Table 5. From these results we can conclude that the PAA-[B15C5] electrode responded to activity change caused by the selective solvation.

5 Conclusions

PAA-[HOST] membrane-based ion-selective electrodes for use in nonaqueous solution were reviewed. These electrodes have been satisfactorily used to trace ion activity changes due to changes in both their concentrations and solvents, and they have been successfully applied to determining the thermodynamic parameters of ions. The electrochemical selectivity and Nernstian response ability of the electrodes have been confirmed to be the result of heterogeneous selective complex formation reactions between the analyte ion in the solution and HOSTs immobilized at the membrane.

6 References

1. W. R. Fawcett, "Liquids, Solution, and Interfaces; From Classical Macroscopic Descriptions to Modern Microscopic Details", 2004, Oxford University Press, New York.
2. S. Ahrand, "The Chemistry of Nonaqueous Solvents," ed. J. J. Lagowski, 1978, Vol. VA, Chap. 1, Academic Press, New York.
3. V. Gutmann (ed.), "The Donor-Acceptor Approach to

Molecular Interactions", 1978, Plenum Press, New York and London.

4. K. Burger (ed.), "Solvation, Ionic and Complex Formation Reactions in Nonaqueous Solvents", 1983, Elsevier Scientific Publishing Company, Amsterdam-Oxford-New York.
5. G. Mamantov and A. I. Popov (ed.), "Chemistry of Nonaqueous Solutions", 1994, VCH Publishers, Inc., New York.
6. K. Izutsu, "Electrochemistry in Nonaqueous Solutions", 2002, Wiley-VCH, Weinheim.
7. Y. Marcus (ed.), "Ion Solvation", 1985, Wiley & Sons, New York.
8. Y. Marcus (ed.), "Ion Properties", 1997, Marcel Dekker, New York.
9. Y. Marcus (ed.), "The Properties of Solvents", 1998, Wiley & Sons, New York.
10. G. Gritzner, *Pure Appl. Chem.*, 1988, 60, 1743.
11. E. Pungor, K. Toth, P. G. Klatsmanyi, and K. Izutsu, *Pure Appl. Chem.*, 1983, 55, 2029.
12. J. F. Coetzee, B. K. Deshmukh, and C. C. Liao, *Chem. Rev.*, 1990, 90, 827.
13. P. K. Muhuri, S. K. Ghosh, and D. K. Hazra, *J. Chem. Eng. Data*, 1993, 38, 242.
14. R. L. Solsky, *Anal. Chem.*, 1990, 62, 21R - 33R.
15. E. Bakker, P. Buhlmann, and E. Pretsch, *Electroanalysis*, 1999, 13, 11.
16. B. Johan, I. Ari, and L. Andrzej, *Electroanalysis*, 2003, 15(5 - 6), 366.
17. T. Sokalski, A. Ceresa, T. Zwickl, and E. Pretsch, *J. Am. Chem. Soc.*, 1997, 119, 11347.
18. E. Bakker, P. Buhlmann, and E. Pretsch, *Talanta*, 2004, 62, 834.
19. E. Pungor, *Talanta*, 1997, 44, 1505; *Anal. Sci.*, 1998, 14, 249.
20. T. Nakamura, Y. Nakamura, T. Kojima, and K. Izutsu, *Bull. Chem. Soc. Jpn.*, 1990, 63, 2615.
21. X. Ji, B. Jin, J. Ren, J. Jin, and T. Nakamura, *J. Electroanal. Chem.*, 2005, 579, 25.
22. T. Nakamura, T. Ueda, and K. Fujimori, *Bull. Chem. Soc. Jpn.*, 1992, 65, 19.
23. T. Nakamura, *Bull. Chem. Soc. Jpn.*, 1975, 48, 1447.
24. K. Izutsu, T. Nakamura, and K. Iwata, *Anal. Chim. Acta*, 1980, 117, 329.
25. T. Nakamura, *Bull. Chem. Soc. Jpn.*, 1975, 48, 2967.
26. J. Ren and T. Nakamura, *Rev. Polarogr.*, 2005, 51, 3.
27. S. Bauminger and M. Wilcheck, *Methods Enzymol.*, 1980, 70, 151.
28. K. Izutsu, T. Nakamura, M. Muramatsu, and Y. Aoki, *J. Electroanal. Chem.*, 1991, 297, 49.
29. T. Nakamura, H. Higuchi, and K. Izutsu, *Bull. Chem. Soc. Jpn.*, 1988, 61, 1020.
30. T. Nakamura, K. Makino, M. Yanagisawa, and T. Miyasaka, *Bull. Chem. Soc. Jpn.*, 1999, 72, 2459.
31. T. Nakamura, M. Komai, S. Hosono, and K. Izutsu, *Anal. Chim. Acta*, 1990, 238, 351.
32. T. Nakamura, C. Hayashi, and K. Izutsu, *Anal. Chim. Acta*, 1994, 292, 305.
33. G. Clune, W. E. Waghorne, and B. G. Cox, *J. Chem. Soc. Faraday Trans. I*, 1976, 72, 1294; B. G. Cox, W. E. Waghorne, and C. K. Pigott, *J. Chem. Soc. Faraday Trans. I*, 1979, 75, 227.
34. T. Nakamura and H. Mongi, *Bull. Chem. Soc. Jpn.*, 1997, 70, 2449.
35. T. Nakamura and G. A. Rechnitz, *Anal. Chem.*, 1985, 57, 393.

36. C. J. Pedersen, *J. Am. Chem. Soc.*, **1967**, 89, 7017.
 37. T. Nakamura, Y. Tsukamoto, and K. Izutsu, *Bunseki Kagaku*, **1990**, 39, 689.
 38. T. Nakamura, C. Hayashi, and T. Ogawara, *Bull. Chem. Soc. Jpn.*, **1996**, 69, 1555.
 39. T. Nakamura, T. Ueda, T. Yanagisawa, and H. Watanabe, *Bull. Chem. Soc. Jpn.*, **1999**, 72, 235.
 40. T. Nakamura, J. Ren, T. Hinoue, and K. Umemoto, *Anal. Sci.*, **2003**, 19, 991.
 41. J. Ren, H. Watanabe, S. Yamamura, and T. Nakamura, *Anal. Chim. Acta*, **2004**, 525, 105.
 42. I. D. Kuntz, Jr. and C. J. Cheng, *J. Am. Chem. Soc.*, **1975**, 97, 4852.
 43. M. K. Chantooni, Jr. and I. M. Kolthoff, *J. Am. Chem. Soc.*, **1967**, 89, 1582.
 44. G. W. Stockton and J. Martin, *J. Am. Chem. Soc.*, **1972**, 94, 6921; R. L. Benoit and S. Y. Lam, *J. Am. Chem. Soc.*, **1974**, 96, 7385.
 45. B. G. Cox, A. J. Parker, and W. E. Waghorne, *J. Phys. Chem.*, **1974**, 78, 1731.
 46. D. A. Wynn, M. M. Roth, and B. D. Pollard, *Talanta*, **1984**, 31, 1036.
 47. J. Emsley, *J. Chem. Soc. (A), Inorg. Phys. Theor.*, **1971**, 2511.
 48. J. Ren, J. Nakamshima, and T. Nakamura, *Bull. Chem. Soc. Jpn.*, **2006**, 79, 291.
 49. W. J. Harmer and Y. C. Wu, *J. Phys. Chem. Ref. Data*, **1972**, 1, 1047.
 50. J. Nakashima and T. Nakamura, Abstract of papers, the 67th Symposium on Analytical Chemistry, Akita University, **2006**, 27.
 51. M. M. Shultz, O. K. Stefanova, S. B. Mokrov, and K. N. Mikhelson, *Anal. Chem.*, **2002**, 74(3), 510.
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