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The Response Behavior of a Polyacrylamide–Benzo-15-C-5 Electrode to Sodium and Calcium Ions in Acetonitrile and Its Application to the Study of Their Complexing with Other Basic Aprotic Solvent Molecules

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The response behaviors of an ionophore-conjugated polymer-based ion sensor, which consists of a polyacrylamide (PAA) coupled to benzo-15-crown-5 (B15C5), for Na^+ and Ca^{2+} in acetonitrile (AN) and *N*-methylpyrrolidinone (NMP) were studied. The PAA–B15C5 electrode showed a Nerstian response to Na^+ in AN and Ca^{2+} in AN and NMP. The electrode was then applied to investigate the complexation of Na^+ in AN with such other solvent molecules (D) as *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO); the successive complex formation constants and Gibbs energies of transfer of Na^+ in AN to DMF or DMSO and AN to AN–D mixtures were obtained. Reasonable responses of the electrode to an activity change of Na^+ due to the solvation of the basic solvent molecules could be certified. The complex formation constant of Ca^{2+} in AN with such D as DMF, NMP, *N*,*N*-dimethylacetamide (DMA), DMSO and hexamethylphosphoric triamide could be obtained by the electrode. The association constants of Ca^{2+} with $CF_3SO_3{}^-$ in AN, propylene carbonate, DMF, and DMSO were determined conductometrically and the constant in AN ($K_1^{\mathrm{AN}} = 1.0_2 \times 10^4$ $\mathrm{dm^3\,mol^{-1}}$) was used for correcting the variation of calcium ion-activity due to a concentration change of $Ca(CF_3SO_3)_2$ in AN.

Ion sensors have been widely used for both thermodynamic and analytical studies in nonaqueous solutions.[1] Some of them have been successively applied to the study of ionic solvation.[2] Recently, some new types of ion sensors for use in aprotic solvents based on a polymer coupled to neutral carriers[3] or metal phthalocyanine complexes[4] were developed; one of them was used to obtain the successive complex formation constants of Mg^{2+}, Ca^{2+}, and Ba^{2+} in acetonitrile (AN)[5] and propylene carbonate (PC) with some basic aprotic solvent molecules (D) and Gibbs energies of transfer from PC to D and from PC to PC–D mixtures.[6,7]

The thermodynamic parameter concerning the complexing of alkaline earth metal ion-aprotic solvent molecules is rare, especially in the case of Ca^{2+}. Usually, perchlorates have been used as salts for thermodynamic studies in nonaqueous solvents due to their high ability of dissociation; however, anhydrous calcium perchlorate is not available. Here, we used the calcium trifluoromethanesulfonate $Ca(CF_3SO_3)_2$, as a calcium salt. Firstly, a conductometric study of the association of Ca^{2+} with $CF_3SO_3{}^-$ in some aprotic solvents is reported. Secondly, the potentiometric responses to Na^+ in AN and Ca^{2+} in AN and *N*-methylpyrrolidinone (NMP) of the electrode prepared by coating a platinum disk with a membrane of polyacrylamide (PAA) coupled to benzo-15-crown-5 (B15C5) are described. The association constants in AN obtained by a conductometric measurement is used to correct the variation of calcium-ion activity ($a(Ca^{2+})$) due to a concentration change of $Ca(CF_3SO_3)_2$ in AN. As a result, the slope of the measured potential vs. p$a(Ca^{2+})$ curve is corrected. Finally, the electrode is applied to obtain the successive complex formation constants of Na^+ in AN with *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The constants are used to calculate the Gibbs energies of transfer of Na^+ from AN to D and AN to AN–D mixtures. The complex formation constants of Ca^{2+} in AN with such D as DMF, NMP, *N*,*N*-dimethylacetamide (DMA), DMSO, and hexamethylphosphoric triamide (HMPA) are also reported.

Experimental

Conductivity Measurement. A meter and an electrode for the conductivity of Horiba Model ES-14 and 3551-10D were used, respectively. A $Ca(CF_3SO_3)_2$ solution of known concentration was added to the conductometric cell with a digital syringe of Gilmont Instruments, Inc., S4200.

Potentiometric Measurement. The apparatus and reagents used in the potentiometric measurement were similar to those mentioned previously.[3—5] Both the construction and preparation of the electrode were also the same as those used in a previous study.[5—7] The response of the electrode was tested in the following cell I:

$$\begin{aligned}&\mathrm{Ag/10\ mM\ AgNO_3{+}10\ mM\ Et_4NClO_4\ (D)}\\&\qquad\qquad\qquad\qquad\mathrm{//50\ mM\ Et_4NClO_4\ (D)}\\&\mathrm{//}C\ \mathrm{MX_z{+}10\ mM\ Et_4NClO_4\ (D)/PAA\text{–}B15C5/Pt\cdots\cdot Cell\ I,}\end{aligned}$$

where MX_z were such salts as $NaClO_4$ and $Ca(CF_3SO_3)_2$ to be tested and D was AN and NMP (1 M=1 $\mathrm{mol\,dm^{-3}}$). All of the solutions were freshly prepared daily. To obtain calibration graphs, the concentration (C in $\mathrm{mol\,dm^{-3}}$) was usually increased by the standard addition method with a microburette. The other conditions were the same as those in a previous study.[7]

Determination of the Complex Formation Constants and Gibbs Energies of Transfer. The emfs of Cell II were measured.

$Ag/10\,mM\ AgNO_3 + 10\,mM\ Et_4NClO_4\ (AN)//$
$50\,mM\ Et_4NClO_4\ (AN)//$
$5\times10^{-4}\,M\ NaClO_4$ or $Ca(CF_3SO_3)_2$
$+10\,mM\ Et_4NClO_4\ (AN+D)/PAA\text{–}B15C5/Pt$····Cell II.

Here, D denotes DMF, NMP, DMA, DMSO, and HMPA. In order to determine the complex formation constants of Na^+ and Ca^{2+} in AN with D, each of them was added stepwise to the cell, and the steady-state potential at each step was recorded to ± 0.1 mV.

Results and Discussion

Conductometry. A conductometric measurement was carried out to determine the association constant of $Ca(CF_3SO_3)_2$ in AN, PC, DMF, and DMSO. The Modified Fuoss–Edelson method[3,8] was used to analyse the experimental data; the symbols used in the report have the same meaning as in the literature.[3,8,9] The ionic equilibrium of first-step association was considered,

$$Ca^{2+} + CF_3SO_3{}^- = CaCF_3SO_3{}^+ \qquad (1)$$

and the constant was defined as follows under the assumption of $f(CaCF_3SO_3{}^+) = f(CF_3SO_3{}^-)$:

$$K_1 = [CaCF_3SO_3{}^+]/\{f_{Ca^{2+}}[Ca^{2+}_{AN}][CF_3SO_3{}^-]\}. \qquad (2)$$

Here, $f_{ca^{2+}}$ denotes the activity coefficient of Ca^{2+}, being similarly calculated by the Debye Hückel equation used in a previous report.[5] Then, the following equation based on Onsager limiting law is derived:

$$\Lambda F = \Lambda_0 - XK_1/\Lambda_0,$$

where

$$X = cf_{Ca^{2+}}\Lambda F(\Lambda F - \Lambda_0/2),$$
$$F = [\{1 - \delta c^{1/2}/(1 + BaI^{1/2})\}^{-1} + (\Lambda_0 - \lambda_1^\circ)/2\Lambda]/\{1 + (\Lambda_0 - \lambda_1^\circ)/2\Lambda_0\}.$$

Here, Λ and Λ_0 are molar and limiting molar conductances of $1/2Ca(CF_3SO_3)_2$, respectively. λ_1° and c are the limiting molar conductance of $CF_3SO_3{}^-$ and the analytical total concentration of $CF_3SO_3{}^-$, respectively. Using the intercept with the ordinate and the slope of the straight line in Fig. 1, Λ_0 and the 1 : 1 association constant (K_1) in Eq. 2 were obtained. The values of λ_1° from Ref. 9 were used to calculate those of the limiting molar conductance of Ca^{2+} (λ_2°). The result, summarized in Table 1, and the K_1 in AN suggests that the activity change of Ca^{2+} by changing the $Ca(CF_3SO_3)_2$ concentration should be taken into account. The ion association of Ca^{2+} with $CF_3SO_3{}^-$ occurs higher in AN compare with that in other solvents because of its weak basicity and lower dielectric constant than other solvents.

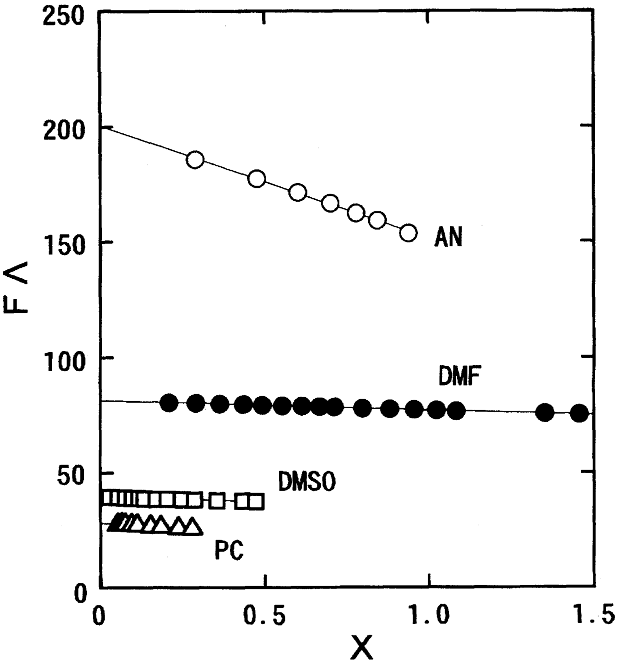

Fig. 1. Modified Fuoss Edelson plots for $Ca(CF_3SO_3)_2$ in some aprotic solvents at 25 °C.

Table 1. Limiting Molar Conductances of Ca^{2+} and the 1 : 1 Ion Association Constants, K_1, between Ca^{2+} and $CF_3SO_3{}^-$ in Some Aprotic Solvents at 25 °C

Solvents	Λ_0[a)]	$\lambda_2^\circ/S\ cm^2\ mol^{-1}$	$K_1/dm^3\ mol^{-1}$
AN	201.4	105.1	$1.0_2\times10^4$
DMF	81.2	37.6	$3.4_1\times10^2$
DMSO	39.4	17.7	$1.7_3\times10^2$
PC	28.2	11.3	$2.8_2\times10^2$

a) $\Lambda_0\{1/2Ca(CF_3SO_3)_2\}=\lambda_2^\circ+\lambda_1^\circ=\lambda^\circ(1/2Ca^{2+})+\lambda^\circ(CF_3SO_3{}^-)$.

Responses of the PAA–B15C5 Electrode. Generally speaking, crown ether B15C5 is apt to make a more stable complex with Na^+ because of the coinsidence of the crystalographic radii. More stable complexation of crown ethers with cations in low basic aprotic solvents, such as AN and PC, are usual. Considering the radii of the Ca^{2+}, stable complexation of the ion with B15C15 is also expected in AN. The responses of the PAA–B15C5 electrode to Na^+ in AN and Ca^{2+} in AN and NMP were investigated. The electrode usually reached a steady state potential within five to seven minutes after changes in the ion concentrations. The results of the response of the PAA–B15C5 electrode to Na^+ in AN are listed in Table 2 together with the result of the case in PC.[7] $Ca(CF_3SO_3)_2$ had been used as an ion source of Ca^{2+} in PC,[7] just like in this experiments. Line 2 in Fig. 2 shows the typical calibration curve of the PAA–B15C5 electrode for Ca^{2+} in AN: the slope is 22.6 mV/activity decade. The activity coefficient of Ca^{2+} was calculated similarly by the Debye Hückel equation used in a previous report.[5] The constant K_1 between Ca^{2+} and $CF_3SO_3{}^-$ in AN was found to be $1.0_2\times10^4$; thus, a smaller apparent potential change might be observed than that expected due to a change in increasing the analytical Ca^{2+} concentration (cf. Fig. 2). The variation of $a(Ca^{2+})$ due to the ion association of Ca^{2+} in AN with $CF_3SO_3{}^-$ was estimated as follows: the total concentration

Table 2. The Response of PAA–B15C5 Electrode to Ca^{2+} and Na^{+} in Some Aprotic Solvents at 25 °C

Ions	Solvents	Slope	Linear range
		mV/log a_{M}^{z+}	mol dm^{-3}
Ca^{2+}	AN	+29.7±0.3	$1.8\times10^{-5} \sim 5.6\times10^{-4}$
	PC[a)]	+28.6±0.3	$6.0\times10^{-6} \sim 8.0\times10^{-3}$
	NMP	+30.1±0.3	$8.5\times10^{-4} \sim 1.2\times10^{-2}$
Na^{+}	AN	+60.2±0.5	$4.0\times10^{-5} \sim 4.0\times10^{-3}$
	PC[a)]	+58.6±0.5	$6.0\times10^{-6} \sim 1.8\times10^{-3}$

a) See Ref. 7.

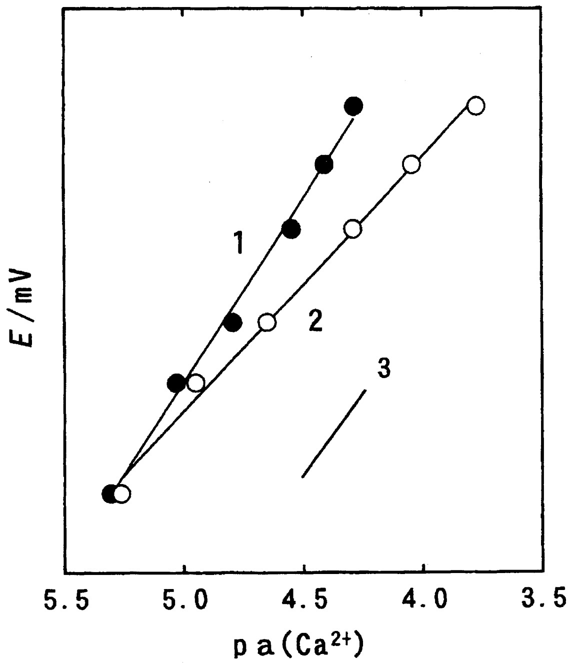

Fig. 2. The calibration curve for Ca^{2+} in acetonitrile at PAA–B15C5 elecrode, 1 and 2 : Relations between potentials vs. pa(Ca^{2+}) after and before correction of the effect of Ca^{2+}–$CF_3SO_3^-$ association, and 3 : the theoretical slope for divalent cation (29.6 mV/pa(M^{2+})).

of Ca^{2+} (C) is

$$C = [Ca^{2+}] + [CaCF_3SO_3^{+}] + [Ca(CF_3SO_3)_2].$$

Here, the relative concentration of next each species is defined by

$$[Ca^{2+}] = C\gamma_1,\quad [CF_3SO_3^{-}] = C\gamma_2,\ \text{and}\ [CaCF_3SO_3^{+}] = C\gamma_3 \quad (3)$$

and

$$[Ca(CF_3SO_3)_2] = C - [Ca^{2+}] - [CaCF_3SO_3^{+}] = C(1-\gamma_1-\gamma_3).$$

From the condition of electric neutrality,

$$2\gamma_1 + \gamma_3 = \gamma_2.$$

Here, since we assume $K_1 \gg K_2 \simeq 0$, the concentration of $Ca(CF_3SO_3)_2$ may be nearly equal to zero. K_2 means the second-step association constant between Ca^{2+} and $CF_3SO_3^-$. From these,

$$\gamma_3 = 1-\gamma_1 \quad \text{and} \quad \gamma_2 = 1+\gamma_1. \quad (4)$$

Also, we can obtain Eq. 5 from Eqs. 2, 3, and 4,

$$K_1 f_{\mathrm{Ca^{2+}}} C\gamma_1^2 + (1 + K_1 f_{\mathrm{Ca^{2+}}} C)\gamma_1 - 1 = 0. \quad (5)$$

The γ_1 can be obtained from Eq. 5. By substitutings it into the relation of Eq. 3, the concentration of Ca^{2+} is obtained. Line 1 in Fig. 2 shows the result after a correction of the variation of a(Ca^{2+}) due to the ion association obtaining a slope of 29.7 mV/activity decade. The method described here could be used both to estimate the ion activities and to confirm the responses of the electrodes in a solvent of low dielectric constant, in which the ion activities of the electrolytes are affected by the ion association. The result of the response of the PAA–B15C5 electrode to Ca^{2+} in AN is listed in Table 2 as the value of the corrected slope for the effect of ion association, together with the results of the case in PC.[7)] As can be seen in the Table 2, the electrode was confirmed to respond in a Nernstian way to Na^+ in AN and to Ca^{2+} in AN and NMP.

Successive Complex Formation Constants and Gibbs Energies of Transfer for Na^+. For verifying the response of the PAA–B15C5 electrode, the successive complex formation constants (β_i) of Na^+ in AN with DMF and DMSO were determined by the electrode. The β_i, of the reaction (6) is defined by Eq. 7 (see Refs. 6 and 7),

$$\mathrm{M}_{\mathrm{AN}}^{z+} + i\mathrm{D} = \mathrm{M}_{i\mathrm{D}}^{z+}, \quad (6)$$

$$\beta_i = a(\mathrm{M}_{i\mathrm{D}}^{z+})/\{a(\mathrm{M}_{\mathrm{AN}}^{z+})[\mathrm{D}]^i\}. \quad (7)$$

Here, $\mathrm{M}_{\mathrm{AN}}^{z+}$ and $\mathrm{M}_{i\mathrm{D}}^{z+}$ mean the sodium ion solvated only by AN and that solvated by D, respectively; $a(\mathrm{M}_{\mathrm{AN}}^{Z+})$ and $a(\mathrm{M}_{i\mathrm{D}}^{z+})$ denote the activity of Na^+ in AN before and after the addition of D, respectively; i shows the number of solvating D molecules. Next, the relation is described according to Cox et al.,[2)]

$$-\Delta G_{\mathrm{tr}(1)} = zF\Delta E = nRT\ln\phi_{\mathrm{AN}} + RT\ln\{1 + \Sigma\beta_i'(\phi_{\mathrm{D}}/\phi_{\mathrm{AN}})^i\} \quad (8)$$

Where, ΔE is the difference between the potentials before and after the addition of D to Cell II, ϕ_{D} and ϕ_{AN} are the volume fractions of D and AN, and n is the coordination number; β_i' is calculated using

$$\beta_i' = \beta_i(1000\rho_{\mathrm{D}}/M_{\mathrm{D}})^i, \quad (9)$$

where ρ_{D} is the density of D and M_{D} is its molecular weight. Then, we express P as

$$P = (1000\rho_{\mathrm{D}}/M_{\mathrm{D}})(\phi_{\mathrm{D}}/\phi_{\mathrm{AN}}),$$

and Q_1 is defined as follows:

$$Q_1 = [\exp\{zF\Delta E - nRT\ln\phi_{\mathrm{AN}})/RT\} - 1]/P$$
$$= \beta_1 + \beta_2 P + \beta_3 P^2 + \cdots$$

and

$$Q_j = (Q_{j-1} - \beta_{j-1})/P = \sum_{i=j} \beta_i P^{i-j}.$$

We can obtain β_i by plotting Q_1 and Q_j against P. When the relation-ship between Q_1 and P on a graph shows the curvature, the intercept with the ordinate is β_1. From the relations Q_j and P, β_i is obtained similarly. If the relation becomes a straight line, the slope shows the highest successive complex formation constant obtained under the experimental conditions. From the constants (β_i) the Gibbs energies of transfer of Na^+ from AN to AN–D mixtures ($\Delta G_{tr(1)}$) and those from AN to D ($\Delta G_{tr(2)}$) are calculated by Eqs. 8 and 10, respectively,

$$-\Delta G_{tr(2)} = RT\ln\beta_n'. \tag{10}$$

The Gibbs energies of transfer of Na^+ from AN to AN–D, $\Delta G_{tr(3)}$, were also calculated directly by the next equation and the emf change (ΔE) in the equation was the same as that obtained from each steady state potential recorded at each addition of D at Cell II:

$$-\Delta G_{tr(3)} = zF\Delta E. \tag{11}$$

Prior to the experiment the electrode was conditioned in a 0.5 mmol $NaClO_4$–AN solution over night. The electrode usually reached a steady state potential within three minutes after the addition of D. The obtained Gibbs energies of transfer of Na^+ are listed in Table 3 together with the values which

Table 3. Complex Formation Constants of Na^+ in AN with Some Other Basic Solvent Molecules, D and Gibbs Energies of Transfer, ΔG_{tr} in kcal mol^{-1}, of Na^+ from AN to D and AN–D Mixtures at 25 °C

D=DMF	log β_1=0.42 log β_2=0.48 log β_3=0.02									
	(log β_1=0.38 log β_2=0.32 log β_3=0.04)$^{a)}$									
ϕ(DMF)	0.003	0.007	0.011	0.015	0.021	0.031	0.049	0.067	0.092	0.116	0.167
$-\Delta G_{tr(1)}$	0.06	0.13	0.20	0.27	0.37	0.53	0.78	1.02	1.30	1.53	1.95
$-\Delta G_{tr(3)}$	0.06	0.13	0.18	0.24	0.38	0.54	0.80	1.01	1.28	1.54	1.97
$-\Delta G_{tr(2)}$	4.6±0.9 (4.8±1.0)$^{b)}$										
D=DMSO	log β_1=0.77 log β_2=0.92 log β_3=0.93										
	(log β_1=0.76 log β_2=1.00 log β_3=1.11)$^{a)}$										
ϕ(DMSO)	0.002	0.006	0.010	0.015	0.020	0.029	0.057	0.091	0.167	0.231	0.375
$-\Delta G_{tr(1)}$	0.09	0.25	0.40	0.56	0.71	0.97	1.58	2.14	3.00	3.51	4.30
$-\Delta G_{tr(3)}$	0.09	0.25	0.38	0.54	0.70	0.99	1.61	2.12	2.99	3.51	4.32
$-\Delta G_{tr(2)}$	6.0±1.0 (6.2±1.2)$^{b)}$										

a) See Ref. 10. b) Calculated values obtained by the use of the constants in Ref. 10.

Table 4. Complex Formation Constants of Ca^{2+} in AN with Some Basic Solvent Molecules at 25 °C

Solvents	DMF	NMP	DMA	DMSO	HMPA
logβ_1	1.88±0.18	2.53±0.25	2.60±0.26	2.72±0.27	3.81±0.38
logβ_1	1.47$^{a)}$	1.56$^{a)}$	1.60$^{a)}$	1.86$^{a)}$	2.78$^{a)}$

a) See Ref. 7.

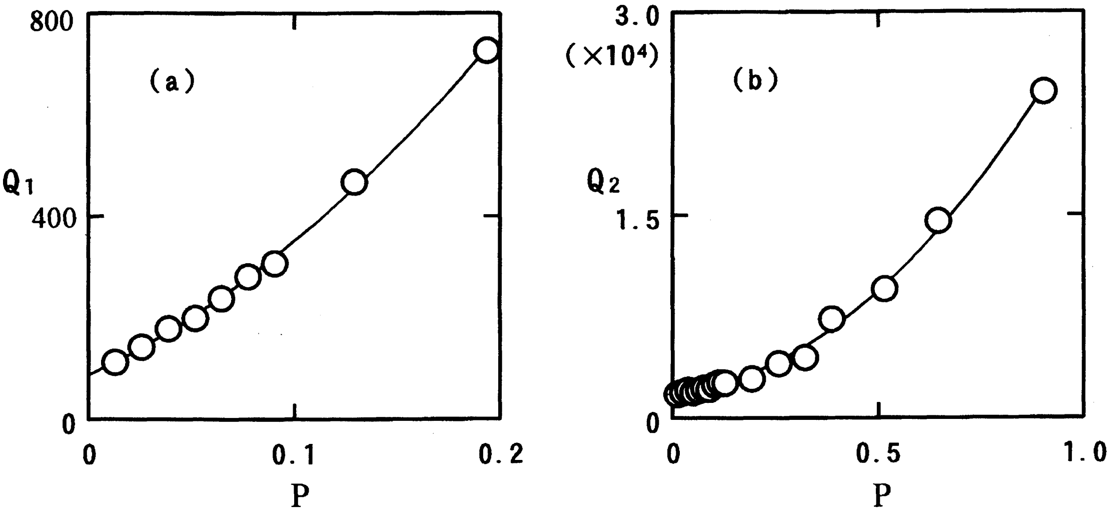

Fig. 3. The relations between Q_1 vs. P; (a) and between Q_2 vs. P; (b) for the complex formation of Ca^{2+} in acetonitrile with DMF. See text for Q and P.

were obtained before.[10] The β_1 in Table 3 seem to be reliable within ± 10% and $\beta_{2,3}$, $\Delta G_{tr(1)}$, and $\Delta G_{tr(3)}$ to be within ± 20%. The cation-sensitive glass electrode used in the experiment had been proven to work thermodynamically.[11] That the values of $\log \beta_i$ and $\Delta G_{tr(2)}$ of Na^+ in AN are comparable to each other means that the electrode used in this experiment could be expected to work thermodynamically.

Successive Complex Formation Constants of Ca^{2+}. The electrode developed here was applied to a study of the complexing of Ca^{2+} in AN with such D as DMF, NMP, DMA, DMSO, and HMPA. Prior to the experiment the electrode was conditioned in a 0.5 mmol $Ca(CF_3SO_3)_2$–AN solution for two days. From the emf change obtained by the stepwise addition of D to Cell II the complex formation constants (β_i) of Ca^{2+} were calculated similarly by using the equations described before. Examples of the relations between $Q_{i(i=1 \text{ and } 2)}$ and P are shown in Fig. 3. From the intercept with the ordinate in Fig. 3(a) the value of β_1 could be obtained. The higher values of β_i and the Gibbs energies of transfer for Ca^{2+} were not determined because the change of $a(Ca^{2+})$ should be affected as the addition of D at Cell II according to the dissociation of Ca^{2+}–$CF_3SO_3^-$. On the other hand, β_1 is the value obtained at zero D content. The values are summarized in Table 4 along with the values obtained in PC.[7] From the table we find the following two results; one is that the complexing ability of Ca^{2+} in both AN and PC, which have a relative close donor number of Gudmann (DN) compared with other solvents (D) used in the experiment, increase with the basicity of D expected by the DN; the other is that the ability of Ca^{2+} in AN with D is stronger than that in the case in PC. From the former result, we deduce that the complexing of Ca^{2+} with D is effected only by the term of enthalpy, which is reasonable if we take into account that the reaction occur along with a smaller conformational change. From the latter we conclude that the relative smaller stability in PC than that in AN seems to be introduced by a much higher dielectric constant of PC than AN and a larger DN of PC than that of AN. The response ability of the electrode to a variation of $a(Ca^{2+})$ due to a change in the Gibbs energy of transfer of the ion from AN to D could not be clarified because of a lack of such thermodynamic data as the activity coefficients concerning to Ca^{2+} transfer from AN into D.

Conclusions

The limiting molar conductances of Ca^{2+} and the association constants of $Ca(CF_3SO_3)_2$ in AN, PC, DMF, and DMSO were determined. The PAA–B15C5 electrode was confirmed to respond in a Nernstian way to Na^+ in AN and Ca^{2+} in AN and NMP. The successive complex formation constants of Na^+ with DMF and DMSO were determined and the electrode was confirmed to be used for obtaining thermodynamic parameters of complexing of Na^+ with other basic aprotic solvent molecules. The electrode was applied to obtain the complex formation constant of Ca^{2+} in AN with several other basic aprotic solvent molecules.

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