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Studies on Ion-solvent Interactions Ⅵ.

The Complexing of the Cadmium Ion in Acetylacetone with Other Solvents and Its Gibbs Free Energy of Transfer

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Abstract: The complex formation constants (β_n) of the cadmium ion in acetylacetone (2, 4-pentanedione, Hacac) with other solvents S and its Gibbs free energies of transfer ($\Delta G^o{}_{tr}$) have been determined polarographically. The values of $\Delta G^o{}_{tr}$ (Cd^{2+}: Hacac → S) (in kJ mol^{-1}) and β_n, where n is the maximum coordination number detected, are as follows; −9.7 and log β_4 = 2.53 for acetone, −45.5 and log β_6 = 4.63 for water, −24.3 and log β_5 = 3.20 for EtOH, −85.3 and log β_5 = 7.63 for N, N-dimethylformamide, −83.7 and log β_6 = 8.22 for N, N-dimethylacetamide, and −110.0 and log β_8 = 12.7 for dimethyl sulfoxide. The correlation between the $\Delta G^o{}_{tr}$ and β_n values is discussed on the basis of the coordination model of ionic solvation. The results for the cadmium ion are shortly discussed in comparison with those for the silver and sodium ions.

INTRODUCTION

Relatively weak interactions of metal ions in less basic solvents such as acetonitrile (AN) and propylene carbonate, for example, with other donor solvents have widely been studied [1-6] because these investigations are effective in fact to elucidate the relative solvation ability of solvents. Izutsu et al. [1, 2] studied the complexing of alkali metal, thallium and ammonium ions in AN with other solvents by potentiometry using a univalent cation-sensitive glass electrode, and discussed in detail the solvent effect on complexing. Cox et al. [3-5] proposed the coordination model of ionic solvation where the interactions of ions in the first coordination sphere with solvent molecules are considered to play the most important role to decide the solvation energies, and applied this model successfully to the solvation of

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some univalent cations. In the previous studies, we also reported the interactions of silver [7], sodium [8] and chloride [9] ions in acetylacetone (2, 4-pentanedione, Hacac) with other solvents, where the Gibbs free energies of transfer ($\Delta G^{o}{}_{tr}$) of these ions and their complex formation constants (β_n) with other solvents were determined potentiometrically and correlated with each other. Acetylacetone is a less basic and less acidic amphiprotic solvent and has been chosen as the reference solvent in our studies [9]. In comparison with these studies of univalent ions, data concerning divalent ions in non-aqueous solvents are very scarce [6], which may be due to some difficulties involved in electroanalytical measurements. In this regard, by potentiometry using a polyacrylamide-tetraethylene glycol monododecyl ether membrane ion-sensitive electrode, Nakamura et al. [10] recently studied the complexing of the magnesium and barium ions in AN with N, N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and hexamethylphosphoric triamide. In this communication, we discussed the solvent effect on the complexing of the cadmium ion in Hacac with other solvents and its Gibbs free energies of transfer on the basis of the data obtained polarographically.

EXPERIMENTAL

Reagents

Cadmium trifluoromethanesulfonate Cd $(CF_3SO_3)_2$ was prepared by the reaction of cadmium carbonate with an aqueous solution of trifluoromethanesulfonic acid and recrystallized from acetone. The product was dried by heating at 120 °C on phosphorus pentoxide under vacuum for 24 h. Ferrocene was the analytical reagent grade product of Nakarai Chemicals, Ltd. Ferricinium picrate was prepared and purified according to the method of Kolthoff and Thomas [11]. Other reagents and solvents used in this experment were the same as those reported in the previous papers [12-16].

Apparatus

The dc polarograms were recorded with a Huso three-electrode polarograph system

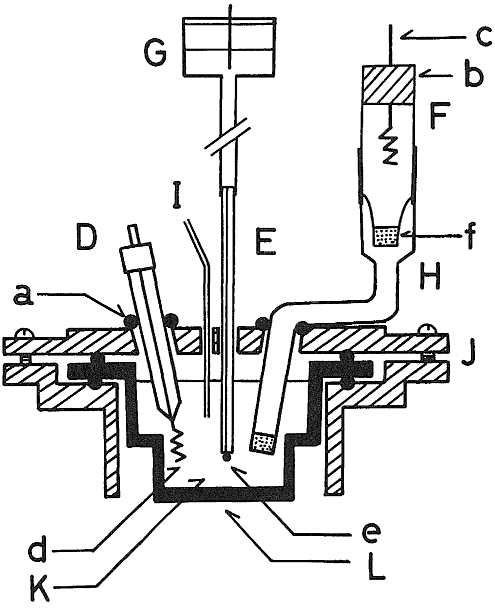

Fig. 1. Diagram of cell assembly.

D: Pt counter electrode, E: dropping mercury electrode, F: Ag^+/Ag reference electrode, G: Hg pool, H: salt bridge, I: N_2 gas inlet and outlet, J: teflon cell stand, K: test solution, L: glass cell, a: viton rubber o-ring, b: silicon rubber stopper, c: Ag wire, d: Pt wire, e: Hg drop, and f: fine porosity sintered glass.

which was composed of a potentiostat model 1100M, a multi-sweep unit model 1104, a drop control unit model 1102 and a Graphtec X-Y recorder model WX1100. The typical cell assembly was shown in Fig. 1. A complexing solvent was added to the cell with a micrometer burrete Gilmont model S-1200A, by 100 μl in each step untill its volume fraction became ca. 0.04. The half-wave potentials $E_{1/2}$ were determied from the $-E$ vs. log $i/(i_d-i)$ plot analysis. All measurements were carried out at 25 ± 0.1 °C.

RESULTS AND DISCUSSION

The complexing of the cadmium ion

Equation (1) represents the cell diagram for the determination of the complex formation constants of the cadmium ion in Hacac with other solvents.

	0.01 mol dm^{-3}	0.1 mol dm^{-3}		Dropping mercury	
Ag	$AgClO_4$	Bu_4NClO_4	Sample	electrode	(1)
	(Hacac)	(Hacac)	(Hacac + S)	(DME)	

Here, S denotes the complexing solvent added to a sample solution of 1 x 10^{-3} mol dm^{-3} $Cd(CF_3SO_3)_2$ with 0.02 mol dm^{-3} Bu_4N-CF_3SO_3 in Hacac. The maximum concentrations (in mol dm^{-3}) of S were 0.8 for acetone, 2.5 for water, 0.7 for ethanol (EtOH), 0.6 for DMF, 0.5 for N, N-dimethylacetamide (DMA) and 0.6 for DMSO. The liquid junction potential between the sample solution and the salt bridge solution of 0.1 mol dm^{-3} Bu_4NClO_4 in Hacac was assumed to change only negligibly upon addition of S.

The complexing of the cadmium ion Hacac with other solvent S is expressed by the following equations:

$$Cd^{2+} + nS \xrightleftharpoons{\beta_n} Cd^{2+}(S)_n \qquad (2)$$

$$\beta_n = [Cd^{2+}(S)_n] \,/\, ([Cd^{2+}][S]^n) \qquad (3)$$

where Cd^{2+} is the cadmium ion solvated only by Hacac, n is the number of solvating S molecules, and β_n is the overall complex formation constant. The complexing of Bu_4N^+ and $CF_3SO_3^-$ with S is considered to be negligible. $[Cd^{2+}]$, $[Cd^{2+}(S)_n]$ and $[S]$ are the molar concentrations of the corresponding chemical species, and the activity coefficient of Cd^{2+} is assumed to be equal to that of $Cd^{2+}(S)_n$. It is also assumed that the solvent S is monomeric in Hacac + S mixtures, that the activity of S is equal to the analytical concentration, and that the activity of Hacac does not change upon addition of S and is equal to unity. The β_n values were determined from the shift of $E_{1/2}$ (Cd^{2+}) upon addition of S according to the method of Deford and Hume [17]. The results are presented in Table 1.

Judging from the values of n and β_n, it is found that the complexing of the cadmium ion in Hacac becomes easier with the increase of the basicity of the solvent added in the order

TABLE 1

Overall complex formation constants (β_n) of the cadmium ion in acetylacetone (Hacac) with other solvents (S) at 25 °C[a]

Complexing solvent (DN)	[Solvent] /mol dm^{-3}	$-\Delta E_{1/2}$ /mV	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	$\log \beta_5$	$\log \beta_6$	$\log \beta_7$	$\log \beta_8$
Acetone	0.089	15	1.31	1.59	1.94	2.53				
(17.0)	0.177	24								
	0.263	34								
	0.433	52								
	0.599	57								
	0.761	67								
Water	0.724	15	2.59	2.81	3.02	3.65	3.36	4.63		
(18.0)	1.08	144								
	1.43	152								
	1.78	186								
	2.12	199								
	2.46	230								
Ethanol	0.112	10	1.41	2.05	2.58	2.80	3.20			
(20.0)	0.223	38								
	0.332	50								
	0.440	60								
	0.547	70								
	0.652	80								
DMF	0.085	91	3.43	4.64	5.67	6.99	7.63			
(26.6)	0.169	126								
	0.252	148								
	0.334	162								
	0.415	174								
	0.494	186								
	0.573	194								
DMF*	0.017	34	2.68	4.14	5.21	6.63	7.63			
(26.6)	0.034	47								
	0.052	63								
	0.069	73								
	0.086	83								
	0.103	90								
	0.119	100								
	0.136	107								
	0.153	114								
	0.170	117								
DMA	0.071	80	2.91	4.38	5.40	6.45	8.02	8.22		
(27.8)	0.141	119								
	0.210	142								
	0.278	160								
	0.345	175								
	0.412	184								
	0.477	198								
DMSO	0.092	184	6.05	7.72	8.97	9.71	11.4	11.9	12.1	12.7
(29.8)	0.184	237								
	0.274	265								
	0.363	289								
	0.450	308								
	0.537	321								
	0.622	334								

[a] The β_n values were obtained polarographically in a 0.02 mol dm^{-3} $Bu_4N\text{-}CF_3SO_3$ solution by the Deford and Hume method [17]. [Solvent] : concentration of complexing solvents added in cell (1) in the text. The half-wave potential ($E_{1/2}$) of the cadmium ion in Hacac in cell (1) was reproducible; it was − 902 ± 4 mV. $\Delta E_{1/2}$: $E_{1/2}$ (S) − $E_{1/2}$ (Hacac). DN: Gutmann's donor number [18]. DMF: N,N-dimethylformamide. DMA: N,N-dimethylacetamide. DMSO: dimethyl sulfoxide. *: second run.

TABLE 2

Overall complex formation constants (β_n) of sodium, silver and cadmium ions in acetylacetone with N, N-dimethylformamide (DMF) and N, N-dimethylacetamide (DMA)[a]

log β_n	Na^+ (r_c = 0.97)		Ag^+ (r_c = 1.26)		Cd^{2+} (r_c = 0.97)	
	DMF	DMA	DMF	DMA	DMF	DMA
log β_1	0.98	1.15	1.26	1.58	3.43	2.91
log β_2	1.30	1.69	1.56	2.49	4.64	4.38
log β_3	1.68	2.19	2.15	3.26	5.67	5.40
log β_4					6.99	6.45
log β_5					7.63	8.02
log β_6						8.22

[a] Values for Na^+ and Ag^+ ions were obtained potentiometrically. r_c: crystallographic ionic radius in Å (1Å = 10nm) [20] .

acetone < EtOH < H_2O < DMF, DMA << DMSO. Hydration is stronger than expected from the donor number [18] of water. The same phenomenon was observed in the hydration of the silver [7] and sodium [8] ions in Hacac as reporetd before. This may be partly due to the smaller molecule size of water which enables its molecules to approach the cadmium ion more closely. Therefore hexa-solvated ions were formed for water: the number of solvating molecules for water (n = 6) is larger than that for DMF (n = 5) and is equal to that for DMA. As for DMSO, which is the most basic solvent used here, even octa-solvated species were detected. In this connection, the cadmium ion is considered to exist in the form $Cd^{2+}(S)_6$ in the pure dipolar aprotic solvents S as reported in AN [19] . So it may be concluded that the cadmium ions in Hacac easily become almost the same species as those in pure solvents S upon addition of a small amount of S. In Table 2 are summarized the β_n values of the silver [7] , sodium [8] and cadmium ions in Hacac with DMF and DMA. The silver ion, in spite of its larger ionic radius, has a stronger complex formation ability than the sodium ion. This may be attributed to the formation of coordinate bond between the silver ion and solvent molecules of DMF and DMA. The ion-solvent interaction to form the coordinate bond is stroger than the mainly electrostatic interaction between the sodium ion and solvent molecules. Much stronger complex formation ability of the cadmium ion is reasonably explained by its larger positive-charge density.

However, as apparently shown in the complexing of the cadmium ion with DMSO (see Table 1), for example, there remain some problems that the abnormal coordination number has been observed and that the relation among the successive complex formation constants is unusual: it is necessary to study further the complexing of the cadmium ion by another method like potentiometry.

Gibbs free energies of transfer of the cadmium ion

The Gibbs free energies of transfer of the cadmium ion from Hacac to other solvents S ΔG°_{tr} (Cd^{2+}: Hacac → S) were determined polarographically according to the negligible liquid junction assumption [21] as follows:

$$\mathrm{Ag}\left|\begin{matrix}0.01\ \mathrm{mol\ dm^{-3}} \\ \mathrm{AgClO_4\ (Hacac)}\end{matrix}\right\vdots\begin{matrix}0.1\ \mathrm{mol\ dm^{-3}} \\ \mathrm{Et_4\ N\text{-}picrate\ (Hacac)}\end{matrix}\vdots\ \mathrm{Sample\ (S)}\ \Big|\ \mathrm{DME} \qquad (4)$$

The sample is a solution of 1 x 10^{-3} mol dm^{-3} Cd $(CF_3\ SO_3)_2$ with 0.02 mol dm^{-3} $Et_4\ NClO_4$ except for water (Et_4 N-CF_3 SO_3) and Hacac (Bu_4 N-CF_3 SO_3). The results are summarized in Table 3. The stability of the cadmium ion decreases in the order DMSO > DMF, DMA > H_2O > EtOH > acetone > AN > Hacac. This order is consistent with the order of the β_n values as described above. In Table 3, some values of ΔG°_{tr} (Cd^{2+}) reported in the literatures [22, 23] are compared with those obtained in this study. Both are in fairly good agreement as a whole: the value of ΔG°_{tr} (Cd^{2+}: DMF → EtOH) [23] should be more positive in comparison with our data. The ΔG°_{tr} (Cd^{2+}) values obtained according to the neglilible liquid junction assumption are also compared in Fig. 2 with those based on the ferrocene / ferricinium assumption: except for Hacac and EtOH, the agreement among dipolar aprotic solvents is good. The comparison in Fig. 2 is only relative, as a matter of course, and it seems that the invalidity of the ferrocene / ferricinium assumption [24] especially in hydrogen bonding solvents such as water and alcohols caused the deviation for Hacac and EtOH.

TABLE 3

Polarographic data for the cadmium ion and its Gibbs free energies of transfer (ΔG°_{tr}) from acetylacetone (Hacac) to other solvents (S) at 25 °C[a]

Solvent (DN)	Hacac (−)	AN (14.1)	Acetone (17.0)	H_2O (18.0)	EtOH (20.0)	DMF (26.6)	DMA (27.8)	DMSO (29.8)
$E_{1/2}$ (Cd^{2+}) / mV	−878	−899	−928	−1114	−1004	−1320	−1312	−1448
Slope / mV	−29	−29	−32	−30	−36	−30	−29	−34
$\Delta E_{1/2}$ / mV	0	−21	−50	−236	−126	−442	−434	−570
ΔG°_{tr} (Cd^{2+})[b] / kJ mol^{-1}	0	−4.1	−9.7	−45.5	−24.3	−85.3	−83.7	−110.0
ΔG°_{tr} (Cd^{2+})[c] / kJ mol^{-1}	−	42.3	−	0	−	−33.5	−	−53.6
ΔG°_{tr} (Cd^{2+})[d] / kJ mol^{-1}	−	64.7	74.3	−	18.9	0	0.6	−20.5

[a] DN: Gutmann's donor number [18] . AN: acetonitrile. DMF: N, N-dimethylformamide. DMA: N, N-dimethylacetamide. DMSO: dimethyl sulfoxide. $E_{1/2}$ (Cd^{2+}): half-wave potential of Cd^{2+} ion of the cell Ag | 0.01 mol dm^{-3} $AgClO_4$ (Hacac) ‖ 0.1 mol dm^{-3} Et_4 N-picrate (Hacac) ‖ 1 x 10^{-3} mol dm^{-3} Cd $(CF_3\ SO_3)_2$, 0.02 mol dm^{-3} $Et_4\ NClO_4$ (S) | DME. The supporting electrolytes are Et_4 N-CF_3 SO_3 for water and Bu_4N-CF_3 SO_3 for Hacac. Slope: slope of − E vs. log i/ (i_d − i) plots. $\Delta E_{1/2}$: $E_{1/2}$ (Cd^{2+}: S) − $E_{1/2}$ (Cd^{2+}: Hacac).

[b] $\Delta G^{\circ}_{tr} = 2F\Delta E_{1/2}$.

[c] Obtained potentiometrically according to the negligible liquid junction assumption [22] .

[d] Obtained polarographically according to the bis(biphenyl)chromium assumption [23] .

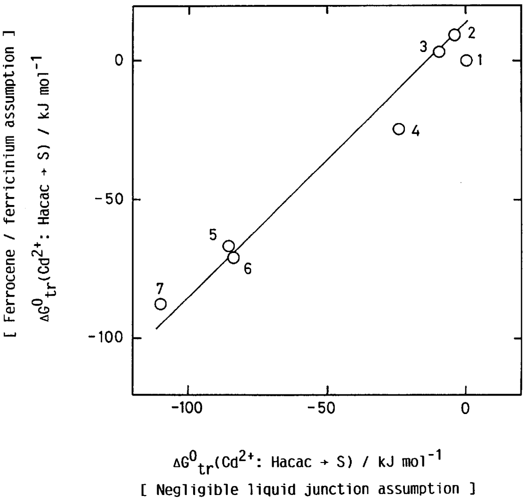

Fig. 2. Comparison of Gibbs free energies of transfer (ΔG^o_{tr}) of cadmium ion from acetylacetone (Hacac) to other solvents S based on the ferrocene/ferricinium assumption with those based on the negligible liquid junction assumption.

1: Hacac, 2: acetonitrile, 3: acetone, 4: EtOH, 5: N, N-dimethylformamide, 6: N,N-dimethylacetamide, and 7: dimethyl sulfoxide. Slope = 1.

The values of $E_{1/2}$ (Cd^{2+}) based on the negligible liquid junction assumption are presented in Table 3. These values in mV versus ferricinium/ferrocene as reference redox system are as follows: −673 in solvent 1, −625 in 2,. −657 in 3, −802 in 4, −1019 in 5, −1041 in 6, and −1129 in 7.

Solvent effect on the complexing and solvent transfer of the cadmium ion

Figure 3 shows the correlation between the log β_n and ΔG^o_{tr} (Cd^{2+}) values and the solvent basicity. The β_n values increase and the ΔG^o_{tr} (Cd^{2+}) values decrease, as a whole, with increasing solvent basicity, indicating that a solvent with a stronger basicity is a better solvent for the cadmium ion. In this connection, based on a considerable larger set of data, it was found that the Gibbs free energies of transfer for the cadmium ion depend linearly on the donor numbers of the solvents [23] .

The theoretical and quantitative relationship between the complexing of an ion i in one solvent S_1 with another S_2 and its solvent transfer has been proposed by Cox et al. [3] as the following equation:

$$\Delta G^o_{tr}(i: S_1 \rightarrow S_2) = -RT \ln \beta_n' \qquad (5)$$

where β_n' is the overall complex formation constant of i in S_1 with S_2, expressed in terms of

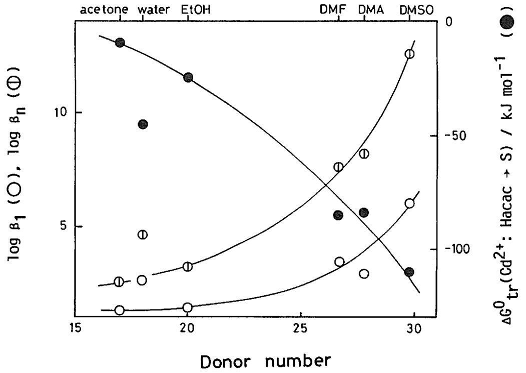

Fig. 3. Log β_n and ΔG^o_{tr} (Cd^{2+}: Hacac → S) vs. donor number (DN) [18] plots.

(○) log β_1 vs. DN plots. (⦶) log β_n vs. DN plots. n = maximum coordination number (n=4 for acetone, 5 for EtOH and N,N-dimethylformamide (DMF), 6 for water and N,N-dimethylacetamide (DMA), and 8 for dimethyl sulfoxide (DMSO)). (●) ΔG^o_{tr} vs. DN plots.

the volume fraction concentration scale. In this coordination model of ionic solvation, only the difference in ion-solvent interactions inside the primary coordination sphere is taken into account as a factor to decide the Gibbs free energy of transfer. According to this model, the ΔG^{o}_{tr} (Cd^{2+}) values were calculated and compared with the observed values in Table 4. It can be seen that the calculated values of ΔG^{o}_{tr} (Cd^{2+}: Hacac → S) decrease, except water, with the increase of solvent basicity in the order acetone > EtOH > DMF > DMA > DMSO. This

TABLE 4

Observed and calculated values of Gibbs free energies of transfer (ΔG^{o}_{tr}) of cadmium ion from acetylacetone to other solvents[a]

Solvent	DN	n	log β_n	log β_n'	ΔG^{o}_{tr} (calcd.) / kJ mol^{-1}	ΔG^{o}_{tr} (obsd.) / kJ mol^{-1}
Acetylacetone	–	–	–	–	0	0
Acetone	17.0	4	2.53	7.06	−40.3	−9.7
Water	18.0	6	4.63	15.1	−86.2	−45.5
Ethanol	20.0	5	3.20	9.36	−53.6	−24.3
N, N-Dimethylformamide	26.6	5	7.63	13.2	−75.3	−85.3
N, N-Dimethylacetamide	27.8	6	8.22	14.4	−82.4	−83.7
Dimethyl sulfoxide	29.8	8	12.7	21.8	−124.7	−110.0

[a] DN: Gutmann's donor number [18] . n: maximum coordination number of cadmium ion detected by polarography. β_n, β_n': overall complex formation constants of cadmium ion in acetylacetone with other solvent S. Concentration of solvent in mol dm^{-3} for β_n, and that in volume fraction for β_n'. $\beta_n' = \beta_n \{1000\rho (S) / M (S)\}^{n}$, where ρ (S) and M (S) are the density (ing cm^{-3}) and the molar mass of solvent S. ΔG^{o}_{tr} (calcd.): calculated on the basis of Cox et al.'s [3] coordination model. ΔG^{o}_{tr} (obsd.): observed polarographically according to the negligible liquid junction assumption.

TABLE 5

Overall complex formation constants (β_n) of some divalent metal ions in acetonitrile (AN) with other solvents and their ionic Gibbs free energies of transfer (ΔG^{o}_{tr}) from AN at 25°C

Ion	Ba^{2+}	Pb^{2+}		Mn^{2+}	Co^{2+}	Cd^{2+}			
Complexing solvent	DMF	H_2O	DMF	H_2O	DMF	H_2O	MeOH	DMF	DMSO
log β_1	1.4	1.3	3.0	1.7	2.4	0.8	0.2	1.9	2.2
log β_2	2.9	1.7	4.6	2.7	4.2	1.3	1.4	3.3	3.8
log β_3	3.3	2.3	5.8	3.2	5.2	1.5		4.5	4.8
log β_4	5.5	2.8	7.3	3.5	5.9	2.1		5.8	5.9
log β_5				4.3	7.0				7.6
log β_6					8.2				
log β_7					9.2				
log β_8					10.7				
ΔG^{o}_{tr} (obsd.)	−92	−51	−54	−65	*	−49	*	−71	−98
ΔG^{o}_{tr} (calcd.)	−57	−56	−67	−74	−112	−52	−24	−58	−76

ΔG^{o}_{tr} (M^{2+}: AN → S) values in kJ mol^{-1}. Obsd.: polarographically observed values using a Ag/0.01 mol dm^{-3} $AgClO_4$ (AN)//0.1 mol dm^{-3} Et_4N-picrate (AN)// reference electrode. Calcd.: calculated values based on the coordination model. * :not obtained. DMF: N, N-dimethylformamide. MeOH: methanol. DMSO: dimethyl sulfoxide.

order is in good agreement with that of the observed values. Especially, the good agreement between the calculated and observed values for DMF, DMA and DMSO indicates that the ion-solvent interactions in the primary coordination sphere play a dominant role to decide the Gibbs free energies of transfer of the cadmium ion as well as in the case of the silver and sodium ions [7, 8] . However, the large discrepancy between the calculated and observed values for acetone, water and EtOH can not be explained well from the coordination model. It may be attributed to the uncertainty involved in the polarographic determination by the Deford and Hume method for the β_n values. Moreover, in spite of the addition of other complexing solvents to Hacac, some specific solvent-solvent interaction which may exist was ignored in this study, and the change of the reduction mechanism of the cadmium ion which may occur was not taken into account either.

In connection with this study in Hacac, the complexing of some divalent metal ions in AN with other solvents and the solvent transfer of these ions from AN have been studied polarographically, and the results are summarized in Table 5. It can be seen that the complexing of the cadmium ion in AN becomes weaker than that in Hacac because AN is a more basic solvent than Hacac. Including the ionic transfer from AN to water, the ΔG^{o}_{tr} values calculated on the coordination model agree well with the observed values. In order to clarify further the divalent ions-solvent interactions, we will study more synthetically the complexing and solvent transfer of divalent ions.

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