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Thermodynamic Studies of Halogenocadmium Complexes in Nonaqueous Solvents

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Synopsis. The thermodynamic constants for the formation of halogenocadmium complexes in *N,N*-dimethylformamide (DMF) and propylene carbonate (PC) were calculated by potentiometric titration. The differences in the order of the stability among the halide ions (X^-) for CdX_4^{2-} in nonaqueous solvents and water were found to be dependent mainly on the enthalpy changes of transfer from water to DMF and PC for the formation of CdX_4^{2-}.

Earlier studies on the stability of metal halide complexes (halogenocadmium, -lead and -copper complexes[1–3]) proved that the classification of metals by Ahrland[4] according to their complexation with halide ions in water was different from that in dipolar aprotic solvents. In the nonaqueous solvents the stability of the halogeno complexes on the metals described above decreases in the order of $Cl^- > Br^- > I^-$, which is the reversed order in water.

The purpose of the present paper is to investigate from the thermodynamic constants of the formation of halogenocadmium complexes the difference of the stability on metal halide complexes in *N,N*-dimethylformamide, propylene carbonate and water.

Experimental

Materials. The purification of *N,N*-dimethylformamide (DMF) and propylene carbonate (PC), the preparation and purification of tetraehylammonium perchlorate, tetraethylammonium halides, and the preparation of the saturated cadmium amalgam have been described elsewhere.[2,5] As a cadmium salt, cadmium perchlorate (Found: C, 28.8 ; H, 5.6 ; N, 11.2%. Calcd for $Cd(ClO_4)_2 \cdot 6DMF$: C, 28.3; H, 6.2; N, 11.5%.) obtained by twice recrystallization of the commercial reagent [$Cd(ClO_4)_2 \cdot 6H_2O$) in DMF was used. The $Cd(ClO_4)_2 \cdot 6DMF$ was dried in a vacuum oven for two days at 30 °C.

Procedure. The experimental device for measuring the potential was described in the previous papers.[6,7] A solution of 10^{-3} mol dm^{-3} of $Cd(ClO_4)_2 \cdot 6DMF$ was titrated with a solution of 5×10^{-2} mol dm^{-3} of tetraethylammonium halides in 0.1 mol dm^{-3} tetraethylammonium perchlorate. Each temperature was controlled to an accuracy of 0.1 °C.

Results and Discussion

The titration curves for Cd^{2+} with Cl^- in PC at 15, 20, and 25 °C are shown in Fig. 1. The higher-order halogenocadmium complexes produced in DMF and PC are found to be CdX_4^{2-}, as shown in the previous paper.[2] The method for calculating the overall formation constants (β_4) of CdX_4^{2-} is described elsewhere.[2,8] The enthalpy changes ($\Delta H^\circ_{(CdX_4^{2-})}$) for the formation of CdX_4^{2-} were obtained graphically from the slope of the log β_4 *vs.* $1/T$ plot (Vant Hoff plot, Eq. 1).

$$\log\beta_4 = -\frac{\Delta H^\circ_{(CdX_4^{2-})}}{2.303R}\frac{1}{T} + \text{const.} \tag{1}$$

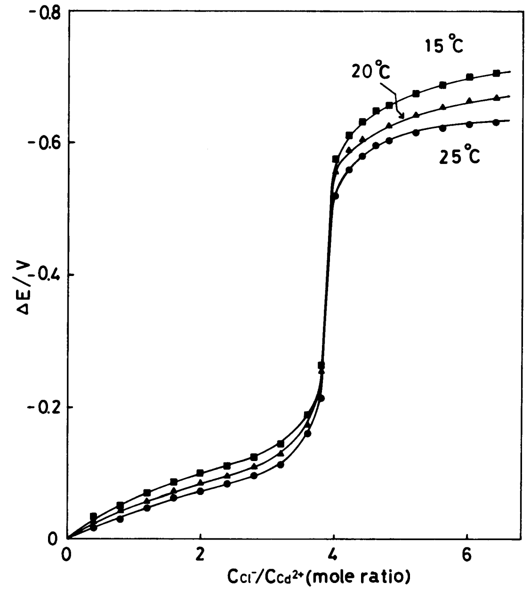

Fig. 1. Potentiometric titration curves for Cd^{2+} with Cl^- in PC at 15, 20 and 25 °C.
ΔE : potential shift caused by addition of Cl^-.

The free energy changes ($\Delta G^\circ_{(CdX_4^{2-})}$) for the formation of CdX_4^{2-} can be correlated to log β_4 with the temperature in Eq. 2, and

$$\Delta G^\circ_{(CdX_4^{2-})} = -2.303RT\log\beta_4 \tag{2}$$

the entropy changes ($T\Delta S^\circ_{(CdX_4^{2-})}$) were calculated from the $\Delta H^\circ_{(CdX_4^{2-})}$ and $\Delta G^\circ_{(CdX_4^{2-})}$. These thermodynamic constants in water have already been reported by many authors.[9] The overall formation constants in 0.1 mol dm^{-3} tetraethylammonium perchlorate and these thermodynamic constants in DMF, PC, and water at 25 °C are given in Table 1. These data in water were quoted from the literature.[9–12] The formation of $CdCl_4^{2-}$ in water is recognized polarographically by Marple.[10] However, its formation is not observed by calorimetric measurement.[11,12] In Table 1, the order of the stability of CdX_4^{2-} with $\Delta G^\circ_{(CdX_4^{2-})}$ in DMF and PC is found to be $CdCl_4^{2-} > CdBr_4^{2-} > CdI_4^{2-}$, while it is the reversed order in water. These thermodynamic constants in DMF were compared with those in dimethyl sulfoxide (DMSO).[13,14] The values of $-\Delta G^\circ_{(CdX_4^{2-})}$ in DMF are larger than those values in DMSO. It seems reasonable to consider that donicity of DMF is smaller than that of DMSO. The values of $\Delta H^\circ_{(CdX_4^{2-})}$ and $T\Delta S^\circ_{(CdX_4^{2-})}$ in DMF differ fairly from those in DMSO. The difference in $\Delta H^\circ_{(CdX_4^{2-})}$ and $T\Delta S^\circ_{(CdX_4^{2-})}$ in these solvents will be based on that of the measurements, because the calorimetric measurement takes account of the

Table 1. Thermodynamic constants for formation of halogenocadmium complexes(CdX_4^{2-}) in DMF, PC, and water at 25 °C

Solvent	CdX_4^{2-}	$\log \beta_4$	$\Delta G^\circ{}_{(CdX_4^{2-})}$ / kJ mol^{-1}	$\Delta H^\circ{}_{(CdX_4^{2-})}$ / kJ mol^{-1}	$T\Delta S^\circ{}_{(CdX_4^{2-})}$ / kJ mol^{-1}
DMF	$CdCl_4^{2-}$	21.3±0.4	−121	−288	−167
	$CdBr_4^{2-}$	17.7±0.3	−101	−206	−105
	CdI_4^{2-}	14.1±0.1	−81	−129	−48
PC	$CdCl_4^{2-}$	32.3±0.6	−184	−400	−216
	$CdBr_4^{2-}$	29.9±0.8	−171	−306	−135
	CdI_4^{2-}	26.6±0.5	−152	−269	−117
Water	$CdCl_4^{2-}$ [a]	1.7	−9.4		
	$CdBr_4^{2-}$ [b,c]	3.7	−21.0	+2.0	+23.0
	CdI_4^{2-} [b,c]	6.5	−37.1	−29.3	+7.8

a) Ref. 10. b) Ref. 11. c) Ref. 12.

Table 2. Thermodynamic constants for formation of halogenocadmium complexes(CdX_4^{2-}) of transfer from water to DMF and PC at 25 °C

Transfer	CdX_4^{2-}	$\Delta G^\circ_{tr(CdX_4^{2-})}$ / kJ mol^{-1}	$\Delta H^\circ_{tr(CdX_4^{2-})}$ / kJ mol^{-1}	$T\Delta S^\circ_{tr(CdX_4^{2-})}$ / kJ mol^{-1}
From water to DMF	$CdCl_4^{2-}$	−112		
	$CdBr_4^{2-}$	−80	−208	−128
	CdI_4^{2-}	−44	−100	−56
From water to PC	$CdCl_4^{2-}$	−175		
	$CdBr_4^{2-}$	−150	−308	−158
	CdI_4^{2-}	−115	−240	−125

state of the bulk in solution and the potentiometric titration considers the state of the vicinity of the electrode. However, considering the fact that the difference in the enthalpy changes for free Cd^{2+} in DMF and DMSO is very small,[15] and that the difference in solvation of X^- is not so large between DMF and DMSO,[16] it is difficult to elucidate the reason of the large difference for $\Delta H^\circ{}_{(CdX_4^{2-})}$ in DMF and DMSO.

The thermodynamic constants for the formation of CdX_4^{2-} of the transfer from water to DMF and PC are listed in Table 2. From the values of $\Delta G^\circ{}_{tr(CdX_4^{2-})}$ it is manifest that $CdCl_4^{2-}$ becomes the most stable complex for transfer among the CdX_4^{2-} complexes. The difference in $\Delta H^\circ{}_{tr(CdX_4^{2-})}$ between the $CdBr_4^{2-}$ and CdI_4^{2-} complexes is larger than that in $T\Delta S^\circ{}_{tr(CdX_4^{2-})}$ as shown in Table 2. Therefore, it was found that the enthalpy changes in transfer from water to DMF and PC contribute much to the free-energy changes of the transfer. It may be concluded that the differences in the order of the stability for metal halogeno complexes in DMF, PC, and water depend mainly on the enthalpy changes ($\Delta H^\circ{}_{tr(CdX_4^{2-})}$) for the formation of CdX_4^{2-} complexes.

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