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STUDIES ON ION-SOLVENT INTERACTIONS V. NOTE ON THE CHLORIDE ION-SOLVENT INTERACTIONS IN ACETYLACETONE

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Abstract: The free energies of transfer (ΔG°_{tr}) of the chloride ion from water to such alcohols (ROH) as methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 2-propanol (2-PrOH), and 1-butanol (1-BuOH) have been determined potentiometrically at 25°C by using a silver-silver chloride electrode as an indicator electrode. The reference electrode used was a siver-silver perchlorate (0.01 mol dm^{-3} in acetylacetone (Hacac)) electrode and the salt bridge was the 0.1 mol dm^{-3} tetraethylammonium picrate solution of Hacac. Acetylacetone was a less basic and less acidic amphiprotic solvent and was used as the solvent for the reference electrode and salt bridge. It was also used as the reference solvent in the complexing of the chloride ion with water and alcohols. The ΔG°_{tr} (Cl^- : $H_2O \rightarrow$ ROH) values in kcal mol^{-1} (1 cal=4.184 J) were 3.4 for MeOH, 5.4 for EtOH, 5.9 for 1-PrOH, 7.1 for 2-PrOH, and 7.0 for 1-BuOH. The ΔG°_{tr} (Cl^- : $H_2O \rightarrow$Hacac) value was estimated to be 8.4 kcal mol^{-1} by using the values of ΔG°_{tr} (Ag^+ : $H_2O \rightarrow$ Hacac) and the solubility products of silver chloride in water and Hacac. The complex formation through hydrogen bonding of the chloride ion with water and alcohols have also been studied in Hacac by potentiometry. The maximum coordination numbers of the chloride ion were detected to be 6 for water, 5 for MeOH, 4 for EtOH, 3 for 1- and 2-PrOH, and 2 for 1-BuOH, respectively. The solvent effect on the solvent transfer and the complexing of the chloride ion was discussed in connection with the solvent acidity.

INTRODUCTION

In the previous paper[1] was reported the complex formation of silver and sodium ions in acetylacetone (2, 4-pentanedione, Hacac) with other solvents, and was discussed the solvent effect on the complexing from the standpoint of the solvent basicity. In this communication have been determined potentiometrically the free energies of transfer (ΔG°_{tr}) of the chloride ion from water to Hacac, acetone, and such alcohols (ROH) as methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 2-propanol (2-PrOH), and 1-butanol (1-BuOH). The complexing of the chloride ion with water and alcohols through hydrogen bonding has also been studied in Hacac, and the

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solvent effect on the solvent transfer and the complexing of the chloride ion is discussed in connection with the solvent acidity. In the present study, Hacac was used as the solvent for the reference electrode and salt bridge, and was also used as the reference solvent in the complexing of the chloride ion, because Hacac is a less basic and less acidic amphiprotic solvent and it can be reasonably considered that the interactions of Hacac with the chloride ion and other solvents are relatively weak.

RESULTS AND DISCUSSION

Free energies of transfer of the chloride ion

The free energies of transfer of the chloride ion were determined potentiometrically at 25°C by measuring the emf of the following cell (1) with a digital potentiometer (Orion Research model 701 A) to ± 0.1 mV. In the cell (1), S denotes Hacac and other solvents.

Ag	0.01 mol dm^{-3} $AgClO_4$ (Hacac)	0.1 mol dm^{-3} Et_4N-Picrate (Hacac)	0.001 mol dm^{-3} Bu_4NCl (S)	AgCl	Ag	(1)

The silver-silver chloride indicator electrode was prepared by immersing a silver wire in the molten silver chloride and was kept for more than 24 h before use in the 0.01 mol dm^{-3} Bu_4NCl solution of each solvent S. The emf among the electrodes thus prepared was reproducible ; it was 0 ± 1 mV in the 0.01 mol dm^{-3} Bu_4NCl solution of

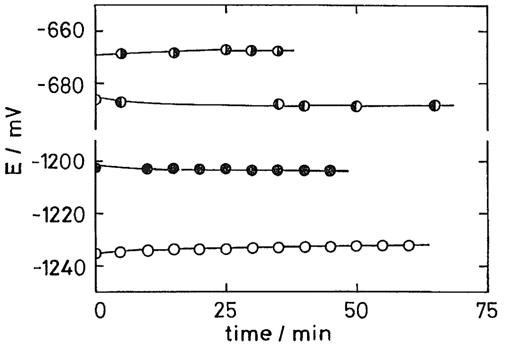

Fig. 1 Emf *vs.* time curve

Ag	0. 01 mol dm^{-3} $AgClO_4$ (Hacac)	0. 1 mol dm^{-3} Et_4N-Picrate (Hacac)	Bu_4NCl solution (S)	AgCl	Ag

Hacac; acetylacetone. Concentrations (in mol dm^{-3}) of Bu_4NCl in solvent S are as follows.

(○) ; 5.9×10^{-4} in acetone,
(●) ; 3.8×10^{-3} in Hacac,
(◑) ; 9.8×10^{-4} in EtOH,
(◐) ; 9.6×10^{-4} in1-PrOH.

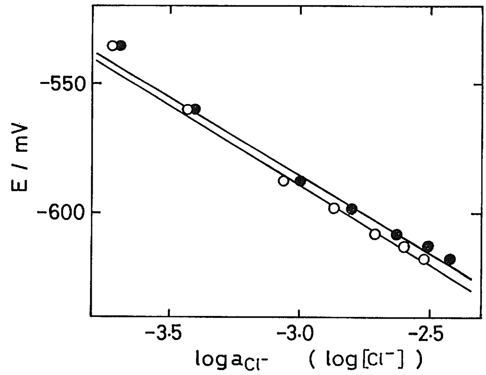

Fig. 2 Nernst response of a silver-silver chloride electrode in methanol

Ag	0. 01 mol dm^{-3} $AgClO_4$ (Hacac)	0. 1 mol dm^{-3} Et_4N-Picrate (Hacac)	Bu_4NCl solution (MeOH)	AgCl	Ag

Hacac ; acetylacetone, MeOH ; methanol,
Slope ;
(○) -61 mV/pa_{Cl^-} and (●) -58 mV/p[Cl^-].

Hacac. The Ag^+/Ag reference electrode and the salt bridge were freshly prepared before measurement in order to avoid the unnecessary mixing of solutions between the cell compartments. The emf measurement was carried out untill the shift of emf had become less than 0.1 mV/10 min. Generally, the emf became constant within 1 h as typically shown in Fig. 1. The liquid junction potential in the cell (1) between the salt bridge solution of 0.1 mol dm^{-3} Et_4N-Picrate in Hacac and a 0.001 mol dm^{-3} Bu_4NCl solution in the solvent S was assumed to be negligibly small$^{2)}$. Thus, the chloride ion free energies of transfer can be estimeted from the emf of the cell (1) so long as the silver-silver chloride electrode responds to the chloride ion according to the Nernst equation.

The response of the silver-silver chloride electrode to the chloride ion in the solvent S was studied in the concentration range of 3×10^{-4} to 3×10^{-3} mol dm^{-3}. The slopes of the response to the concentration of the chloride ion were -60 mV in water, -58 mV in MeOH (see Fig. 2), -70 mV in EtOH, -59 mV in 1-PrOH, -63 mV in 2-PrOH, -51 mV in 1-BuOH, -69 mV in acetone and -74 mV in Hacac. Here, the complete dissociation of Bu_4NCl in these solvents has been tacitly assumed. However, this holds true only in water and MeOH$^{3)}$, and the ion association constants (in mol^{-1} dm^3) of Bu_4NCl have been reported to be 39 in EtOH$^{4)}$, 149 in 1-PrOH$^{4)}$, 670 (or 734) in 2-PrOH$^{5)}$, 640 in 1-BuOH$^{6)}$, 430 in acetone$^{7)}$, and 38 in Hacac$^{8)}$, respectively.

Table 1. Free energies of transfer of the chloride ion from water to other solvents (ΔG^o_{tr} /kcal mol^{-1}, 1 cal=4.184 J) at 25 °C

Solvent	(AN, A)	E/mV	ΔE/mV	ΔG^o_{tr}*1	ΔG^o_{tr}*2	ΔG^o_{tr}*3
H_2O	(54.8, 1.00)	−441.4	0	0	0	0
MeOH	(41.3, 0.76)	−588.6	−147.2	3.4	3.0	3.2
EtOH	(37.1, 0.67)	−673.8	−232.4	5.4	4.4	4.8
1-PrOH	(——, 0.63)	−697.6	−256.2	5.9	4.9	6.2
2-PrOH	(33.5, 0.60)	−750.6	−309.2	7.1	—	—
1-BuOH	(——, 0.61)	−744.0	−302.6	7.0	—	—
Hacac	(——, ——)	−1166.7	−725.3	16.7*4	8.4	—
Acetone	(12.5, 0.25)	−1256.9	−815.5	18.8*4	13.7	13.6

AN ; Gutmann's acceptor number (Ref. 9).

A ; A values (anion-solvating tendency) of Swain *et al.* (Ref. 10).

E ; emf of the cell (1).

cell (1) ; Ag | 0.01 mol dm^{-3} $AgClO_4$ (Hacac) || 0.1 mol dm^{-3} Et_4N-Picrate (Hacac) || 0.001 mol dm^{-3} Bu_4NCl (S) | AgCl | Ag

ΔE ; E(S)-E(H_2O) (Both E and ΔE were corrected for a_{Cl^-}.)

Hacac ; acetylacetone.

* 1 ; $\Delta G^o_{tr} = -F\Delta E$.

* 2 ; calculated from $\Delta G^o_{tr}(Ag^+)$ and pKsp(AgCl) values. The detail will be reported soon.

* 3 ; Ref. 11.

* 4 ; maybe overestimated.

Other abbreviations and symbols have their usual meanings.

The incomplete dissociation of Bu_4NCl, which is not taken into account in this study, may apparently cause the deviation from the Nernstian response. The values of transfer energies and complex formation constants reported below may be affected by the uncertainty of the electrode response, especially for EtOH, 1-BuOH, acetone and Hacac.

The $\Delta G^o_{tr}(Cl^- : H_2O \rightarrow S)$ values obtained from the emf of the cell (1) are summarized in Table 1 together with the $\Delta G^o_{tr}(Cl^- : H_2O \rightarrow S)$ (S=Hacac, acetone, MeOH,EtOH and 1-PrOH) values estimated by using the values of $\Delta G^o_{tr}(Ag^+ : H_2O \rightarrow S)$ and the solubility products (K_{sp}) of silver chloride in water and S. The stabilities of the chloride ion decrease in the order of $H_2O >$ MeOH > EtOH > 1-PrOH > 2-PrOH, 1-BuOH > Hacac > acetone. This order is consistent with that of the solvent acidity (see the Gutmann's acceptor number[9] and the A values (anion-solvating tendency) of Swain *et al.*[10] as presented in Table 1). The large discrepancy exists between the $\Delta G^o_{tr}(Cl^- : H_2O \rightarrow S)$ (S=Hacac, acetone) value obtained from the emf of the cell (1) and that estimated by using the $\Delta G^o_{tr}(Ag^+)$ and the $K_{sp}(AgCl)$ values. This may be attributed in part to the above-mentioned uncertainty of the silver-silver chloride electrode response in Hacac and acetone; the further reason for this has not been elucidated. In Table 1, some of the $\Delta G^o_{tr}(Cl^-)$ values reported in literatures[11] are compared with the results in this study; the agreement is fairly good.

Complex formation of the chloride ion

The emf of the following cell (2) was measured at 25°C to study the complexing through hydrogen bonding of the chloride ion in Hacac with water and alcohols.

$$\mathrm{Ag}\ \left|\ \begin{array}{l} 0.01\ \mathrm{mol\ dm^{-3}} \\ \mathrm{AgClO_4} \\ \quad (\mathrm{Hacac}) \end{array}\ \right\|\ \begin{array}{l} 0.1\ \mathrm{mol\ dm^{-3}} \\ \mathrm{Bu_4NClO_4} \\ \quad (\mathrm{Hacac}) \end{array}\ \left\|\ \begin{array}{l} 0.001\ \mathrm{mol\ dm^{-3}} \\ \mathrm{Bu_4NCl} \\ (\mathrm{Hacac+S}) \end{array}\ \right|\ \mathrm{AgCl}\ |\ \mathrm{Ag} \qquad (2)$$

Here, S denotes water and alcohols added little by little to a 0.001 mol dm^{-3} Bu_4NCl-Hacac solution. Maximum concentrations (in mol dm^{-3}) of S added to the cell (2) were 1.7 for water, 0.7 for MeOH, 0.5 for EtOH, 0.4 for 1-PrOH and 2-PrOH, and 0.3 for 1-BuOH. The liquid junction potential between the Bu_4NCl solution and the salt bridge solution of 0.1 mol dm^{-3} Bu_4NClO_4 in Hacac was assumed to change only negligibly upon the addition of a solvent S. Without a solvent S, the emf of the cell (2) was reproducible; it was 1145 ± 5 mV.

The complexing of the chloride ion in Hacac with other solvents S is expressed in eqns. (3) and (4).

$$Cl^- + nS \overset{\beta_n}{\rightleftharpoons} Cl^-(S)_n \qquad (3)$$

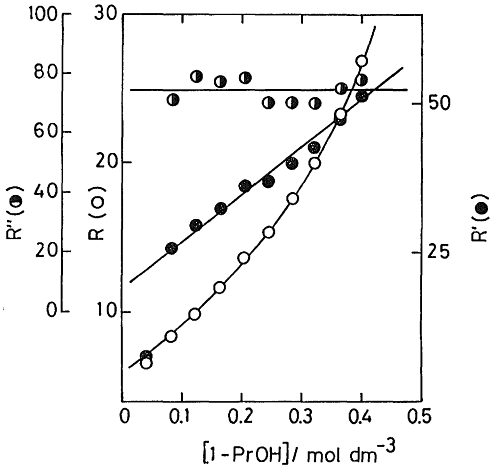

Fig. 3 R, R′ and R″ *vs.* [1-PrOH] plots in the complexing of the chloride ion with 1-PrOH in acetylacetone
R is given in eqns. (5) and (6) in the text, $R' = (R - \beta_1)/[\text{1-PrOH}]$ and $R'' = (R' - \beta_2)/[\text{1-PrOH}]$.

$$\beta_n = [Cl^-(S)_n]/([Cl^-][S]^n)$$
$$= K_1K_2 \cdots\cdots\cdots\cdots K_n \qquad (4)$$

where Cl^- is the chloride ion solvated only by Hacac, n the number of solvating S molecule(s), β_n the over-all complex formation constant, and K_i the successive one. The complexing of Bu_4N^+ with S is considered to be negligible. $[Cl^-]$, $[Cl^-(S)_n]$ and [S] are the molar concentrations of the corresponding chemical species, and the activity coefficient of Cl^- is assumed to be equal to that of $Cl^-(S)_n$. It is also assumed that the solvent S is monomeric in Hacac+S mixtures and the activity of S is equal to the analytical concentration, and that the activity of Hacac does not change upon the addition of S and is equal to unity. As is constant the total concentration of the chloride ion, the next relation holds.

$$R \equiv ([Cl^-]_{Hacac}/[Cl^-]_{Hacac+S} - 1)/[S]$$
$$= \beta_1 + \beta_2[S] + \cdots\cdots\cdots + \beta_n[S]^{n-1} \qquad (5)$$

In eqn. (5), $[Cl^-]_{Hacac}$ and $[Cl^-]_{Hacac+S}$ denote the molar concentrations of the chloride ion solvated only by Hacac in pure Hacac and that in Hacac+S mixtures, respectively. On the assumption that the activity coefficient of the chloride ion solvated only by Hacac is equal in pure Hacac and Hacac +S mixtures, the R values can be calculated from the emf (in mV) of the cell (2) in pure Hacac (E_{Hacac}) and that in Hacac+S mixtures ($E_{Hacac+S}$) as presented in eqn. (6).

$$R[S] + 1 = [Cl^-]_{Hacac}/[Cl^-]_{Hacac+S}$$
$$= 10^{(E_{Hacac+S} - E_{Hacac})/59} \qquad (6)$$

Thus, the β_n values can be obtained from eqns. (5) and (6). The typical applications of the graphical analysis for eqn. (5) are shown in Fig. (3). The β_n values are summarized in Table 2. Only mono- and di-solvated chloride ion were formed for 1-BuOH, while tri-solvated species were detected for 1- and 2-PrOH. Tetra- and penta-solvated ions were also formed for EtOH and MeOH, respectively. For water, six water molecules solvate the chloride ion in Hacac. Though the maximum concentration of water (1.7 mol dm^{-3}) added to the cell (2) was higher than that of other alcohols as described above, the β_n values for water were determined from the emf

Table 2. Over-all complex formation constants (β_n) of the chloride ion in acetylacetone with water and alcohols at 25 °C

Solvent	(AN, A)	β_1	β_2	β_3	β_4	β_5	β_6
H_2O	(54.8, 1.00)	10	26	100	140	80	840
MeOH	(41.3, 0.76)	13	64	220	370	1500	
EtOH	(37.1, 0.67)	7.0	31	78	300		
1-PrOH	(——, 0.63)	6.3	20	75			
2-PrOH	(33.5, 0.60)	2.2	7.4	19			
1-BuOH	(——, 0.61)	1.0	23				

AN ; Gutmann's acceptor number (Ref. 9).

A ; A values (anion-solvating tendency) of Swain *et al.* (Ref. 10).

change up to *ca.* 0.6 mol dm^{-3}. In connection with the present study, Chantooni, Jr. *et al.* studied the hydration of the chloride ion in acetonitrile by conductometry[12] and obtained the values of $\beta_1=9$ and $\beta_2=20$. Cogley *et al.* also detected the mono-hydrated chloride ion ($\beta_1=6.2$) in propylene carbonate by nuclear magnetic resonance spectroscopy[13]. The hydration of the chloride ion was further studied[14,15] in dipolar aprotic solvents by methods such as nuclear magnetic resonance spectroscopy, solubility and vapor pressure measurements, and calorimetry. In general only mono-hydrated and at best di-hydrated chloride ions have been detected in these investigations. The potentiometric method seems to be more convenient than other methods to determine the successive complex formation constants as presented by Izutsu *et al.*[16] in the complexing of alkali metal, thallium (I) and ammonium ions in acetonitrile with other solvents.

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

Figure 4 shows the correlation between the $\Delta G^\circ_{tr}(Cl^- : H_2O \rightarrow ROH)$ values and the solvent acidity for water, MeOH, EtOH, 1-PrOH, 2-PrOH and 1-BuOH. The Gutmann's acceptor number and the A values (anion-solvating tendency) of Swain *et al.* of the solvents are taken as the solvent acidity. The $\Delta G^\circ_{tr}(Cl^- : H_2O \rightarrow ROH)$ values decrease with the increase of solvent acidity, indicating that the solvent with larger value of acidity is a better solvent for the chloride ion. As for aprotic solvents, a similar correlation between the $\Delta G^\circ_{tr}(Cl^- :$ acetonitrile$\rightarrow$other aprotic solvents$)$ values and the

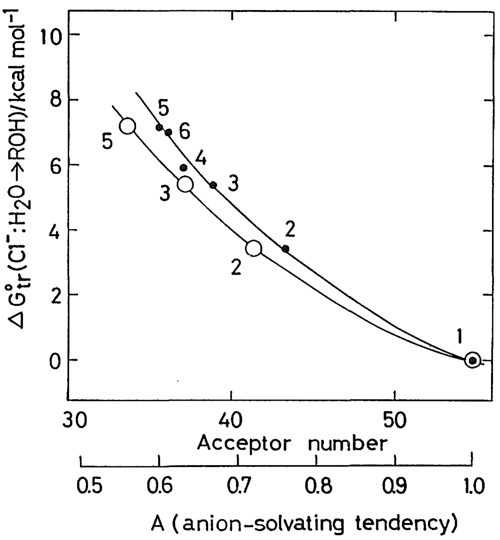

Fig. 4 Correlation between the free energies of transfer of the chloride ion (ΔG^o_{tr}) and the solvent acidity
(○) ; ΔG^o_{tr} *vs.* acceptor number (Ref. 9) plots,
(●) ; ΔG^o_{tr} *vs.* A values (Ref. 10) plots.

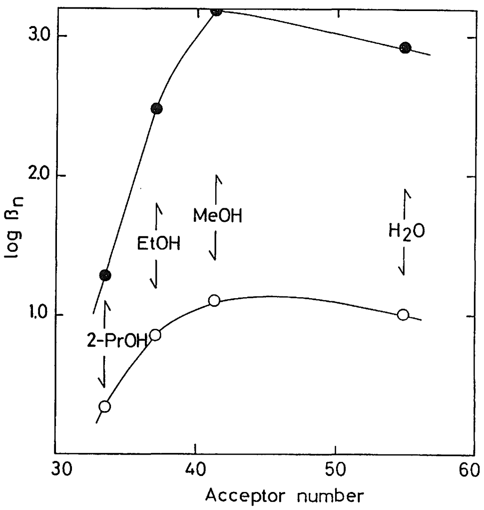

Fig. 5 log β_n *vs.* acceptor number (Ref. 9) plots
(○) ; n=1, (●) ; n=maximum coordination numbers (n=3 for 2-PrOH, 4 for EtOH, 5 for MeOH and 6 for water).

acceptor number of the solvents has already been reported[17].

In Fig. 5, log β_1 and log β_n values for water, MeOH, EtOH and 2-PrOH are plotted against the acceptor number. Here, the subscript n means the maximum number of the solvent molecules bound to the chloride ion as detected by potentiometry. Both log β_1 and log β_n values increase with the increase of the solvent acidity in the order of 2-PrOH<EtOH<MeOH, and then slightly decrease towards water which is the best solvent for the chloride ion as shown in Fig. 4. This discrepancy for water, however, is considered to be only an apparent phenomenon; log β_n values are related to the free energy changes for the reaction in eqn. (3) and they are not equal to the solvent transfer energies as discussed below. It must be noted here that the maximum numbers of the solvent molecules bound to the chloride ion increase with increasing solvent acidity; 3 for 2-PrOH, 4 for EtOH, 5 for MeOH and 6 for water.

Cox *et al.*[18] have proposed an idealized coordination model of ionic solvation in which the free energies of transfer of ions between different solvents are considered to result entirely from differences in the energy of complex formation between the ions and solvent molecules, and in which the interactions of the ion with solvent molecules beyond its primary coordination sphere are assumed to be independent of the medium. According to this model, the free energy of transfer of M^+ ion from one solvent S_1 to another solvent S_2, which is the difference in the standard free energy changes for the following equilibria (7) and (8), is equal to the standard free energy change for equilibrium (9) and is given by eqn. (10).

$$M^+(g)+nS_1 \overset{K(S_1)}{\rightleftharpoons} M^+(S_1)_n \qquad (7)$$

$$M^+(g)+nS_2 \overset{K(S_2)}{\rightleftharpoons} M^+(S_2)_n \qquad (8)$$

$$M^+(S_1)_n+nS_2 \overset{\beta_n'}{\rightleftharpoons} M^+(S_2)_n+nS_1 \qquad (9)$$

$$\begin{aligned}\Delta G^{\circ}_{tr}\,(M^+ : S_1\rightarrow S_2)\\ &=-RT\ \ln\ K(S_2)/K(S_1)\\ &=-RT\ \ln\ \beta_n'\\ &=-RT\ \ln\ ([M^+(S_2)_n]/[M^+(S_1)_n])\{\Phi(S_1)/\Phi(S_2)\}^n \qquad (10)\end{aligned}$$

In eqns. (7) to (10), $M^+(g)$ represents the unsolvated ion in a vacuum, n is the coordination number of M^+, $\Phi(S_1)$ and $\Phi(S_2)$ are the volume fractions of solvents S_1 and S_2, and β_n' is the over-all complex formation constants of M^+ by S_2 in solvent S_1, expressed in terms of the volume fraction concentration scale. All other symbols have their usual meanings. Assuming the ideal volume fraction, the values of β_n' are related to those of β_n expressed in the molar concentration scale (see eqns. (3) and(4)) by eqn. (11),

$$\beta_n'=\beta_n\{1000\rho(S_2)/M(S_2)\}^n \qquad (11)$$

where $\rho(S_2)$ and $M(S_2)$ are the density and molecular weight of solvent S_2. On the

Table 3. Observed and calculated values of the free energies of transfer of the chloride ion from water to alcohols ($\varDelta G^o_{tr}$/kcal mol^{-1}, 1cal=4.184 J)

Solvent	(AN, A)	n	β_n	β_n'	$\varDelta G^o_{tr}$(calcd.)	$\varDelta G^o_{tr}$(obsd.)
H_2O	(54.8, 1.00)	6	840	2.4×10^{13}	0	0
MeOH	(41.3, 0.76)	5	1500	1.3×10^{10}	4.4	3.4
EtOH	(37.1, 0.67)	4	300	2.5×10^{7}	8.2	5.4
1-PrOH	(——, 0.63)	3	75	1.8×10^{5}	11.1	5.9
2-PrOH	(33.5, 0.60)	3	19	4.2×10^{4}	12.0	7.1
1-BuOH	(——, 0.61)	2	23	2.8×10^{3}	13.6	7.0

AN; Gutmann's acceptor number (Ref. 9).

A; A values (anion-solvating tendency) of Swain *et al.* (Ref. 10).

n; maximum coordination numbers of the chloride ion detected by potentiometry.

β_n, β_n'; over-all complex formation constants of the chloride ion in acetylacetone. Concentration of S in mol dm^{-3} for β_n and that in volume fraction for β_n'.

$\varDelta G^o_{tr}$ (calcd.); calculated from the relation,

$$\varDelta G^o_{tr}\text{ (calcd.)} = RT \ln \beta_n'(H_2O)/\beta_n'(ROH)$$

on the basis of the Cox *et al.*'s (Ref. 18) coordination model of ionic solvation.

basis of this coordination model of ionic solvation, Cox *et al.*[18,19] and Clune *et al.*[20] studied and discussed successfully in detail the free energies of transfer of cations between different solvents including solvent mixtures.

Now, the above-mentioned coordination model has been applied to the interactions of the chloride ion with water and alcohols, and the results are summarized in Table 3. The $\varDelta G^o_{tr}(Cl^- : H_2O \rightarrow ROH)$ values were calculated by eqn. (12),

$$\varDelta G^o_{tr}(Cl^- : H_2O \rightarrow ROH) = RT \ln \beta_n'(H_2O)/\beta_n'(ROH) \qquad (12)$$

where $\beta_n'(ROH)$ are the complex formation constants of the chloride ion with ROH in acetylacetone. Referring to Table 3, the calculated values of $\varDelta G^o_{tr}(Cl^- : H_2O \rightarrow ROH)$ increase in the order $H_2O <$ MeOH $<$ EtOH $<$ 1-PrOH $<$ 2-PrOH $<$ 1-BuOH. Though this order is in good agreement with that of the observed values of $\varDelta G^o_{tr}(Cl^- : H_2O \rightarrow ROH)$, the calculated values are always larger than the observed values, especially for 1-PrOH, 2-PrOH and 1-BuOH. The disagreement between the calculated and observed values may be partly due to the uncertainty involved in the determination of the β_n values; for example, the uncertainty of the silver-silver chloride electrode response in acetylacetone, and the assumption that water and alcohols are monomeric and the activities are equal to their analytical concentrations, and so on. Another reason may be found in the coordination model itself applied in the calculation. The potentiometrically detected maximum coordination numbers of the chloride ion are 6 for water, 5 for MeOH, 4 for EtOH, 3 for 1- and 2-PrOH, and 2 for 1-BuOH. On the application of the coordination model, these maximum numbers of solvent molecules are considered to be included in the primary coordination sphere in each solvent. According to the recent studies[21] on the clustering reactions in the gas phase of the chloride ion with water and some alcohols, the numbers of n in the cluster $Cl^-(ROH)_n$ are reported to be 7 for water, 11 for MeOH, 10 for EtOH and 8 for 1-PrOH, respectively. Except for water, these n values are much larger than the corresponding maximum coordination numbers. This fact may suggest that the interactions outside the first coordination sphere may also play an important role in the solvation of the chloride ion in these solvents. The solvation phenomena of anions, especially in hydrogen bonding solvents, seem to be more complicated than those of cations. It is necessary to elucidate anion-solvent interactions to a great extent, and the above discussion will be extended later in detail.

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