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Thermodynamics of complexation of Sr(II) and Ba(II) by 18 crown 6 in water–ethanol binary mixture using titration calorimetry

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ABSTRACT

The thermodynamic parameters for the complexation reaction of Sr(II) and Ba(II) with 18 Crown 6 (18C6) were determined in the binary water–ethanol mixtures as solvent. The stability of both complexes was found to increase with increase in ethanol mole fraction (X_E). The complexation reaction is exothermic with the ΔH value increasing with X_E. The entropy of complexation was found to decrease for X_E up to 0.1 above which it increased monotonically. The complexation process was enthalpically favored but entropically unfavorable. The data have been explained in terms of the solvent effects on metal ion, ligand and complex stabilization in binary mixture. The ab initio calculations were also carried out to investigate the stability of metal ion and ligand in water and ethanol medium.

1. Introduction

Crown ethers are well known for their selectivity towards alkali and alkaline earth metals [1,2]. This property has been extensively used in designing ion selective electrodes, increasing the solubility of salts in low polarity solvent and in the separation of metal ions [3,4]. Macrocyclic crown ethers are also used as models for studying the ion transport in biological membrane due to their structural similarity with abiotic ligands. In complexation process, the metal ion is partially or completely desolvated and fits in the crown ether cavity [5,6].

The stability constants of alkali and alkaline earth metal ions with crown ethers in non-aqueous solvents are known to be much higher than that in water [7–10]. The higher stability of metal ion crown ether complexes in non-aqueous solvents has been explained in terms of the enthalpy and entropy of transfer of metal ion, crown ether and the complex from water to the non-aqueous solvent. In order to investigate the solvent effects in detail it is important to obtain thermodynamic data of complexation in binary mixture of water and the solvent. Rounaghi and Mofazzeli [6] studied the complex formation between alkaline earth metal ions and 18C6 in ethanol–water binary mixtures at three values of ethanol mole fraction (X_E). They used conductometric titration for complexation and found that the $\Delta_c H$ and $\Delta_c S$ of complexation do not vary monotonically with X_E. A detailed study of effect of solvent composition (water–acetonitrile binary mixture) on the complexation of K^+ by 18C6 was carried out by Yingguang and Masaaki [11] and brought out the important role of solvent effects in the enthalpy and entropy of complexation.

In the present paper, we report the results of our study on the complexation of alkaline earth metal ions, namely, Sr^{2+} and Ba^{2+}, by 18C6 in binary ethanol water medium. Various techniques used for such studies are conductometry [12], potentiometry [13], NMR [14], polarography [15], spectrophotometry [16], and calorimetry [17]. We have used isothermal titration calorimetry (ITC) for the present study as it provides the most precise data on thermodynamic quantities ($\log K$ and ΔH), simultaneously. Sr^{2+} and Ba^{2+} were chosen for the present study as these are the important high yield fission products present in the high level radioactive waste and some of the crown ethers are found to be selective for separation of these metal ions. Derivative of 18C6, namely, di-tertiary butyl di-cyclohexano 18C6 has been found to be selective for Sr^{2+} [18], while 18C6 has the highest stability constant for Ba^{2+} among the alkaline earth metals [2]. We chose ethanol water binary mixtures as these systems are known to undergo microscopic phase transition at cluster level in wide range of ethanol mole fraction. In order to understand the stabilization of metal and ligand in the water and ethanol medium, the ab-initio calculations of free energy of Sr^{2+}, Ba^{2+} and 18C6 were also performed in water and ethanol as solvents.

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2. Experimental

18C6 (Fluka) was desiccated for 3 days before the preparation of solution to remove the absorbed water. The concentration was also confirmed by CHNS elemental analysis. $Sr(NO_3)_2$ (99.97%, Merc) and $Ba(NO_3)_2$ (G.R. grade, BDH) were used without any treatment.

2.1. Isothermal titration calorimetry

The calorimetric experiments were conducted with an isothermal titration calorimeter system (Nanocalorimeter TAM-III, Thermometric AB, Sweden). It is a twin thermopile heat conduction type calorimeter and differential power signal measured is dynamically corrected for the thermal inertia of the system [19]. The titration assembly consists of 4 ml reaction vessel and a reference vessel. The heat capacity of reaction vessel and reference vessel was balanced by keeping the same volume of solutions in both sides in order to minimize the short-term noise. The titrant was delivered in the reaction vessel through a stainless steel injection needle (length 1 m and internal diameter 1.5×10^{-4} m) connected to the Hamilton syringe containing titrant. The syringe was driven by Lund Syringe pump. The temperature of the bath was maintained at 25.0000 (±0.0001) °C. Before each experiment the instrument was calibrated electrically and the performance of the instrument was tested by measuring $\log K$ and ΔH for the reaction between $BaCl_2$ and 18C6 in water. The measured heat $Q_i(\text{ex})$ at each injection was corrected for the heat of dilution of titrant $Q_i(\text{dil})$ to obtain the net heat of reaction $Q_i(r)$.

$$Q_i(r) = Q_i(\text{ex}) - Q_i(\text{dil}) \tag{1}$$

The set of $Q_i(r)$ data was analyzed using TAM Assistant program [20] which gives the $\log K$ and ΔH of the reaction investigated.

For all the experiments 2.7 ml of 18C6 solution was taken in reaction vessel and metal nitrate solution was injected into the reaction vessel. The concentrations of the solutions were different for different systems in order to obtain good titration profile and to minimize error.

2.1.1. Mathematical treatment of data

The overall complexation of 18C6 with metal (M^{2+}) is represented by following equation:

$$M^{2+} + nL = [ML_n]^{2+} \tag{2}$$

$$\beta_n = \frac{[ML_n]^{2+}}{[M^{2+}][L]^n} \tag{3}$$

where β_n is the cumulative stability constant of complex ML_n. $\beta_n = K_1, K_2 \ldots K_n$, where $K_1, K_2, \ldots K_n$ are stability constants for ML, $ML_2, \ldots ML_n$ complexes respectively. Using the following mass–balance equations, the concentrations of free metal $[M^{2+}]$ and free [L] can be related to total concentration of metal ($C_{M,i}$), and ligand ($C_{L,i}$)

$$C_{M,i} = [M^{2+}]_i + \sum \beta_n [M^{2+}]_i [L]_i^n \tag{4}$$

$$C_{L,i} = [L]_i + \sum \beta_n n [M^{2+}]_i [L]_i^n \tag{5}$$

The heat $Q_i(r)$ measured at each injection is related to the $[ML_n{}^{2+}]$ species formed and its enthalpy of formation (ΔH_n).

$$Q_i(r) = -\left(V_i \sum \beta_n \Delta H_n [M^{2+}]_i [L]_i^n - V_{i-1} \sum \beta_n \Delta H_n [M^{2+}]_{i-1} [L]_{i-1}^n\right) \tag{6}$$

Nonlinear least square fitting of the $Q_i(r)$ data was carried out using Eq. (6) in conjunction with Eqs. (4) and (5) to obtain the β_n and ΔH_n values. The first data point (Q_1) is ignored due to the diffusion of the solution from capillary to the reaction vessel even before the first injection.

3. Theoretical calculations

The structure of 18C6 was optimized in the gaseous state as well as in water and ethanol medium and the total free energy of metal ion and 18C6 were calculated using Polarized Continuum Model (PCM) [21]. In PCM, the medium is considered as an infinite assembly of molecules that generate an electrostatic field. The electron distribution of solute is determined quantum mechanically in the presence of electrostatic field generated by medium. At the same time the solvent field and its interaction with solute charge distribution is calculated using electrostatics. Theoretical calculations were done using GAMESS electronic structure program [22].

The Gaussian Orbital Valance basis sets were used for Sr and Ba. For Sr the 28 core electrons were described by the effective core potential of Preuss and coworker and the valance electrons by a (6s 6p 5d)/[4s 4p 2d] Gaussian function basis set. For Ba 46 core electrons were described by effective core potential and the valance electrons by a (6s 6p 5d 1f)/[4s 4p 2d 1f] Gaussian function basis set [23,24]. The free energy of the species was calculated taking electrostatic interactions into account.

4. Results and discussion

Fig. 1 shows the typical plot obtained by isothermal titration calorimeter for titration of 18C6 solution by Sr^{2+} solution in pure water. Fig. 2 shows the calorimetric titration curve of [Metal]/[Ligand] vs. $Q_i(r)$/mol (heat measured at each injection per mole of Ba^{2+} added) for Ba^{2+}–18C6 complexation in pure water as well as in water ethanol binary mixture ($X_E = 0.42$). The 1:1 stoichiometry of the complex is reflected in the inflection point of these calorimetric titration curves. Table 1 gives the calorimetric titration data (metal concentration, ligand concentration, volume of titrant added and $Q_i(r)$ at each injection) for Ba^{2+}–18C6 complexation in pure water and in water ethanol binary mixture ($X_E = 0.42$). The n value (≈1) obtained by fitting the ITC data to equation 6 corroborates the formation of Sr^{2+}–18C6 and Ba^{2+}–18C6 complexes with 1:1 stoichiometry at all the water ethanol composition used in present study. The $\log K$ values obtained from the ITC data are given in Table 2. The data for pure water are in agreement with those

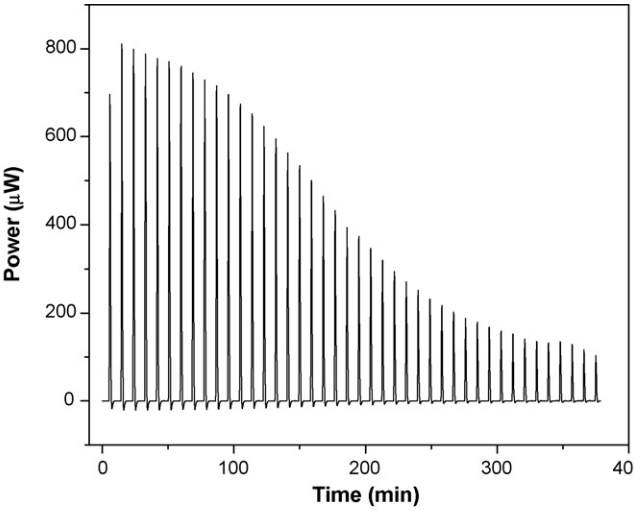

Fig. 1. Calorimetric data (power vs. time) for titration of 18C6 solution by Sr^{2+} solution in pure water. Cup solution: 2.7 ml of 20 mM 18C6 in pure water, titrant: 0.5 M $Sr(NO_3)_2$ in pure water.

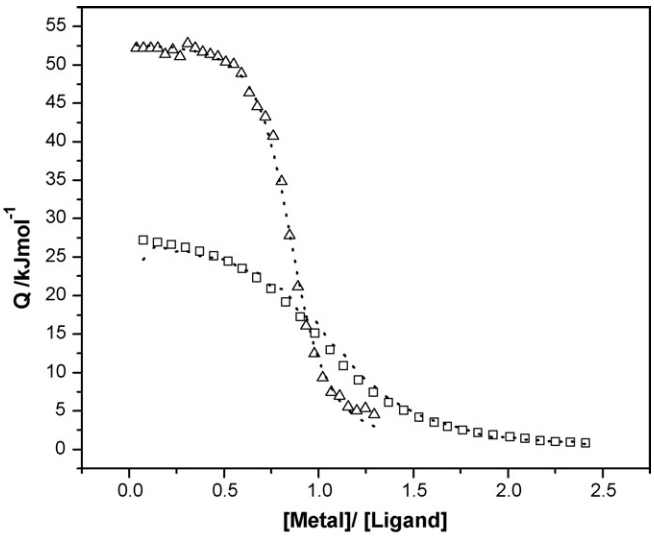

Fig. 2. Calorimetric titration curve for Ba^{2+}-18C6 complexation (a) (symbol: □) cup solution: 2.7 ml of 3.8 mM 18 Crown 6 in pure water, titrant: 5 μl injection of 0.151 M $Ba(NO_3)_2$ solution in pure water (b) (symbol: △) cup solution: 0.986 mM of 18C6, titrant: 10 μl injection of 9.966 mM $Ba(NO_3)_2$ solution in water ethanol binary mixture ($X_E = 0.42$). Dotted line represents the data fitted for K and Δ_cH.

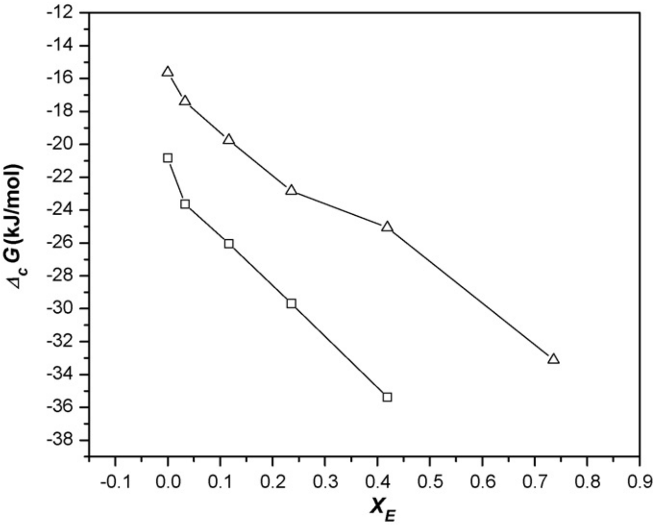

Fig. 3. Gibbs free energy of complexation for Sr^{2+}–18C6 (symbol: △) and Ba^{2+}–18C6 (symbol: □) vs. X_E.

reported by Izatt et al. [2] but are lower than those of Ansarifard and Rounaghi [25]. The same authors also measured log K for complexation of Sr^{2+} by 18C6 in water ethanol binary mixtures at three ethanol mole fractions and observed increase in log K from 3.4 for pure water to 5.0 for 50% ethanol. However, at higher ethanol content (75.4%), log K decreased significantly to 3.2, which is contrary to the observations of the present work. The Δ_cG for complexation reaction was obtained from log K values.

Figs. 3–5 show the plot of thermodynamic parameters of complexation (Δ_cG, Δ_cH and $T\Delta_cS$) of Ba^{2+} and Sr^{2+} by 18C6 as a function of ethanol mole fraction (X_E). The values of Δ_cG, Δ_cH and Δ_cS for Sr^{2+}–18C6 and Ba^{2+}–18C6 complexation in pure water are in good agreement with the reported values in literature [2]. Addition of ethanol favors the complexation process as evident from the trend of Δ_cG vs. X_E. In all the cases, the Sr^{2+} and Ba^{2+} complexation

Table 1
Calorimetric titration data for Ba^{2+}–18C6 complexation (a) titration A—cup solution: 2.7 ml of 3.8 mM 18 Crown 6 in pure water, titrant: 5 μl injection of 0.151 M $Ba(NO_3)_2$ solution in pure water (b) titration B—cup solution: 2.7 ml of 0.986 mM of 18C6, titrant: 10 μl injection of 9.966 mM $Ba(NO_3)_2$ solution in water–ethanol binary mixture ($X_E = 0.42$).

Titration A				Titration B			
[Metal] (mM)	[Ligand] (mM)	Vol. of titrant V_i (μl)	$Q_i(r)$ (mJ)	[Metal] (mM)	[Ligand] (mM)	Vol. of titrant V_i (μl)	$Q_i(r)$ (mJ))
0.279	3.793	5.00	18.61	0.037	0.982	10.00	4.64
0.557	3.786	5.00	20.19	0.0733	0.979	10.00	4.4
0.834	3.779	5.00	19.33	0.110	0.975	10.00	4.79
1.110	3.772	5.00	19.49	0.146	0.972	10.00	5.12
1.385	3.765	5.00	18.98	0.181	0.968	10.00	4.61
1.659	3.758	5.00	18.76	0.217	0.965	10.00	4.45
1.932	3.751	5.00	18.57	0.252	0.961	10.00	4.99
2.204	3.745	5.00	17.59	0.288	0.958	10.00	5.09
2.475	3.738	5.00	17.42	0.322	0.954	10.00	4.77
2.746	3.731	5.00	16.02	0.356	0.951	10.00	4.68
3.015	3.724	5.00	15.66	0.390	0.947	10.00	4.45
3.283	3.717	5.00	13.26	0.424	0.944	10.00	4.77
3.550	3.711	5.00	12.77	0.458	0.941	10.00	4.77
3.816	3.704	5.00.	10.52	0.491	0.937	10.00	4.67
4.081	3.697	5.00	9.42	0.525	0.934	10.00	4.81
4.345	3.691	5.00	7.46	0.558	0.931	10.00	4.00
4.609	3.684	5.00	6.26	0.590	0.928	10.00	3.81
4.871	3.677	5.00	4.99	0.623	0.924	10.00	3.97
5.132	3.671	5.00	4.14	0.655	0.921	10.00	3.97
5.393	3.664	5.00	3.38	0.687	0.918	10.00	3.16
5.652	3.658	5.00	2.81	0.719	0.915	10.00	2.61
5.911	3.651	5.00	2.41	0.751	0.912	10.00	1.58
6.169	3.645	5.00	2.06	0.782	0.909	10.00	1.11
6.426	3.638	5.00	1.52	0.814	0.906	10.00	0.97
6.681	3.632	5.00	1.54	0.845	0.902	10.00	0.78
6.936	3.625	5.00	1.18	0.875	0.899	10.00	0.37
7.191	3.619	5.00	1.23	0.906	0.896	10.00	0.48
7.444	3.613	5.00	0.96	0.936	0.893	10.00	0.37
7.700	3.606	5.00	0.9	0.967	0.890	10.00	0.40
7.947	3.600	5.00	0.71	0.997	0.887	10.00	0.26
8.198	3.594	5.00	0.79	1.026	0.884	10.00	0.24
8.448	3.587	5.00	0.51	0.037	0.982	–	–

Table 2
Stability constant, enthalpy and entropy of complexation enthalpy of Sr^{2+}–18C6 and Ba^{2+}–18C6 in water ethanol binary mixture.

X_E	0	0.03	0.12	0.24	0.42	0.74
Sr^{2+}						
Log K	2.74 ± 0.04	3.05 ± 0.09	3.46 ± 0.05	4.00 ± 0.08	4.39 ± 0.3	5.80 ± 0.09
$-\Delta_c H$ (kJ/mol)	14.50 ± 0.96	16.99 ± 0.12	31.00 ± 0.27	31.70 ± 0.30	32.76 ± 0.50	35.57 ± 0.60
$T\Delta_c S$ (kJ/mol)	1.14 ± 0.96	0.42 ± 0.17	−11.25 ± 0.27	−8.87 ± 0.31	−7.70 ± 0.60	−2.46 ± 0.60
Ba^{2+}						
Log K	3.65 ± 0.09	4.14 ± 0.08	4.56 ± 0.09	5.20 ± 0.09	6.20 ± 0.20	–
$-\Delta_c H$ (kJ/mol)	29.00 ± 0.38	33.10 ± 0.30	43.50 ± 0.35	43.84 ± 0.62	47.9 ± 0.38	–
$T\Delta_c S$ (kJ/mol)	−8.16 ± 0.39	−9.46 ± 0.31	−17.47 ± 0.36	−14.15 ± 0.62	−12.5 ± 0.42	

is favored enthalpically but not entropically except for Sr^{2+}–18C6 complexation in water rich medium where $\Delta_c S$ is slightly positive (Figs. 4 and 5). $\Delta_c G$ decreases monotonically with X_E, while the decrease in $\Delta_c H$ is steep up to $X_E = 0.1$ above which it decreases slowly. $\Delta_c S$ data also show sharp decrease up to $X_E = 0.1$, above which it increases monotonically. This will be discussed in a later section.

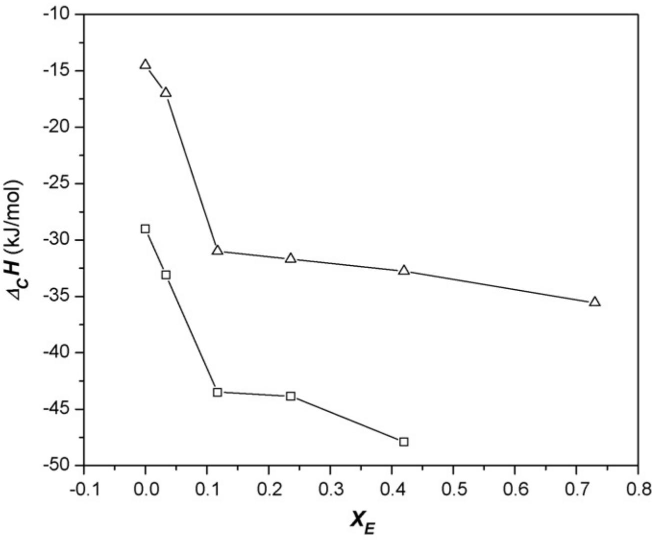

Fig. 4. Enthalpy of complexation of Sr^{2+}–18C6 (symbol: △) and Ba^{2+}–18C6 (symbol: □) vs. X_E.

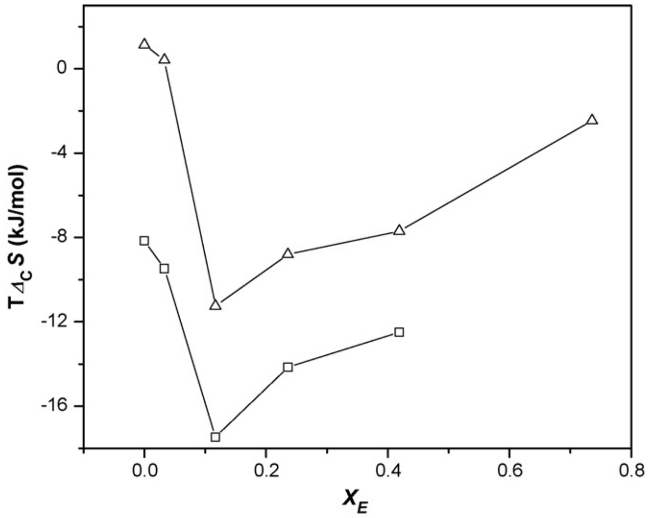

Fig. 5. Entropy of complexation for Sr^{2+}–18C6 (symbol: △) and Ba^{2+}–18C6 (symbol: □) vs. X_E.

Table 3 summarizes free energy of transfer for Sr^{2+}, Ba^{2+} and 18C6 from water to ethanol obtained from theoretical calculations.

4.1. Enthalpy entropy compensation

It is generally observed that in the complexation reaction involving macrocyclic ligands, the decrease in enthalpy is accompanied by decrease in complexation entropy [26]. The decrease in ΔH value is due to stronger interaction between metal ion and ligand which in turn leads to the formation of rigid complex structure. Therefore, part of the decrease in ΔH is compensated by decrease in ΔS. With a view to investigate the enthalpy entropy compensation during complexation reaction, $T\Delta_c S$ was plotted against $\Delta_c H$ for all the systems. It was observed that the linear plot was followed only for X_E values up to 0.1 in the case of Ba^{2+}–18C6 and X_E up to 0.2 in the case of Sr^{2+}–18C6, while the higher X_E data showed wide deviation from linearity (Fig. 6). This shows that the compensation between enthalpy and entropy of complexation is followed only in the dilute ethanol solutions in water, contrary to the observations of Inoue and Hakushi [26]. The deviation of $T\Delta_c S$ vs. $\Delta_c H$ plot from linearity at higher ethanol fraction indicates that factors other than conformation of 18C6 also govern the $\Delta_c S$.

Table 3
Theoretically calculated free energy of transfer Sr^{2+} and Ba^{2+} and 18C6 from water to ethanol.

Species	$\Delta_{tr} G$ (water to ethanol) ($E_E - E_W$) (kJ/mol)
Sr^{2+}	44.2
Ba^{2+}	44.4
18 Crown 6	1.5

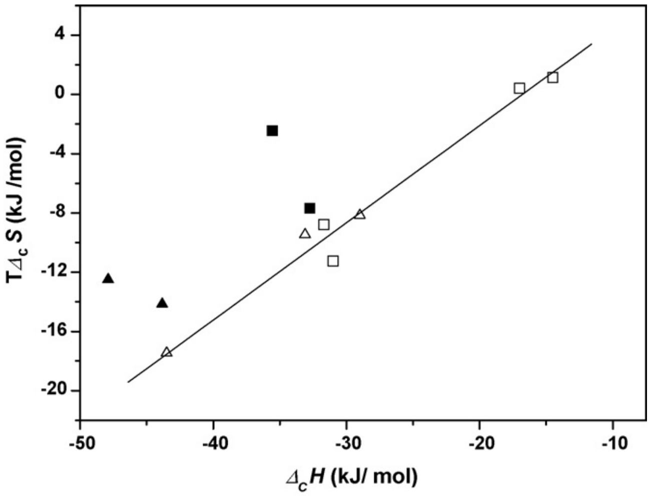

Fig. 6. Enthalpy–entropy compensation during complexation of Sr^{2+} and Ba^{2+} by 18C6 in water–ethanol binary mixture (□: Sr^{2+}–18C6 $X_E \leq 0.2$, ■: Sr^{2+}–18C6 $X_E > 0.2$, △: Ba^{2+}–18C6 $X_E \leq 0.1$, ▲: Ba^{2+}–18C6 $X_E > 0.1$).

4.2. Comparison between Ba^{2+}–18C6 and Sr^{2+}–18C6 complexation

The stability constants of Ba^{2+}–18C6 are higher than those for Sr^{2+}–18C6 at all values of X_E, which is also manifested in the Δ_cH values. The ionic radius of Ba^{2+} (1.34 Å) is larger than that of Sr^{2+} (1.12 Å) and it fits well into the cavity of 18C6 molecule (radius 1.40 Å). Thus Ba^{2+} ion interacts strongly with the oxygen atoms of the 18C6 and has less dehydration enthalpy, which in turn reflects in the more negative Δ_cH compared to Sr^{2+} complexation. The more negative value of Δ_cS for Ba^{2+} complexation also indicates the more rigid structure of Ba^{2+}–18C6 complex compared to Sr^{2+}–18C6. Though Ba^{2+} complexation has less favorable entropy change compared to Sr^{2+} complexation, the more negative, Δ_cH makes the Ba^{2+} complex more stable at all water ethanol compositions. Due to the higher charge to radius ratio, Sr^{2+} is expected to be more solvated than Ba^{2+} in water. Therefore, one expects greater decrease in Δ_cG for Sr^{2+} than Ba^{2+}. Similar trend of Δ_cG, Δ_cH and Δ_cS for Sr^{2+} and Ba^{2+} on the other hand indicates very small difference in free energy of transfer of ions from water to water ethanol binary solvent ($\Delta_{tr}G$) for the two metal ions. The exact data for $\Delta_{tr}G$ for Sr^{2+} and Ba^{2+} are not available. In case of alkali metal ions $\Delta_{tr}G$ follows the order $Na^+ > K^+ > Rb^+ = Cs^+$ [27], that is, the effect of size becomes negligible for heavier metal ions. Our observation also points towards similar $\Delta_{tr}G$ for Sr^{2+} and Ba^{2+} which is supported by theoretical calculations (Table 3). On the other hand the slope for Δ_cG vs. X_E is higher for Ba^{2+} compared to Sr^{2+}. This could be due to more negative $\Delta_{tr}H$ for Ba^{2+}–18C6 compared to Sr^{2+}–18C6. Ohtsu and Ozutsumi [10] observed that $\Delta_{tr}H$ for M^+-complex varied in the order $Na^+ > K^+ > Rb^+ > Cs^+$ in various aprotic solvents. The surface of larger ion inside the cavity interacts more with the water molecules. During the transfer of metal complexes to aprotic solvents, these water molecules go to bulk water and form hydrogen bonds. This partly compensates for the desolvation of metal complex. Similar compensation could be responsible for less $\Delta_{tr}H$ for Ba^{2+}–18C6 compared to Sr^{2+}–18C6.

4.3. Solvent effects on metal ion transfer from water to water ethanol mixture

The donor number (*DN*), which is a measure of Lewis basicity, for water and ethanol are 18 and 19.2, respectively [28]. Generally the solvation of cations is stronger in solvent with high *DN*. Thus on the basis of *DN*, Sr^{2+} and Ba^{2+} are expected to be more solvated in ethanol than in water. The electron donating ability, which is also represented by Kamlet Taft parameter, is 0.44 in pure water and 0.73 in pure ethanol. Despite the more basic nature of water ethanol binary mixture, the positive values of $\Delta_{tr}G$ (water to ethanol) for alkali and alkaline earth metal ions suggest the more stabilization of metal ion in water compared to water ethanol solvent mixture [27].

From the theoretical calculation also Sr^{2+} and Ba^{2+} are predicted to be stabilized more in water compared to ethanol mainly by electrostatic interaction (Table 3). The higher dielectric constant of water (78.5) compared to ethanol (24.3), favors strong interaction between metal ion and water. Sr^{2+} and Ba^{2+} are more stabilized in water compared to ethanol by 44.2 and 44.4 kJ/mol, respectively. The similar $\Delta_{tr}G$ (water to ethanol) of Sr^{2+} and Ba^{2+}reflect in their similar behavior with respect to X_E.

4.4. Solvent effects on ligand transfer from water to water ethanol mixture

The Lewis acidity as represented by acceptor number is 54.8 and 34.1 for water and ethanol, respectively. By virtue of high Lewis acidity water stabilizes 18C6 by forming hydrogen bonds with oxygen atoms of 18C6. This stabilization of 18C6 in water reflects in its large positive $\Delta_{tr}H$ (water to water ethanol binary mixture) as shown in Fig. 2 of Ref. [29]. Another factor, which plays an important role in stabilizing 18C6 is the hydrophobic hydration, that is, the interaction of water molecules with the hydrophobic part [$-CH_2-CH_2-$] of 18C6. Thus the positive value of $\Delta_{tr}H$ of 18C6 (water to water ethanol mixture) appears to be one of the main factors for higher stability of metal crown ether complex in the ethanol rich solvent. The less solvation of both the metal ion and 18C6 in water ethanol binary mixture compared to water make the complexation process favorable with increasing concentration of ethanol.

4.5. Solvent effects on complex transfer from water to water ethanol mixture

The complex formation between metal ion and crown ether results in loss of hydrogen bonding as the oxygen atoms of crown ether are no longer available for hydrogen bonding with water. Further the complexation process makes the molecular structure of the complex more expanded (hydrophobic hydration). Consequently, the free energy of transfer of the complex from water to water ethanol mixture is negative and it becomes more negative with X_E. This is corroborated in the case of K^+–18C6 complex by Yingguang and Masaaki [11].

This shows that the complexation of Sr^{2+} and Ba^{2+} by 18C6 is enthalpically favored. The decrease in dielectric constant of water ethanol binary mixture with X_E also leads to the increase in electrostatic interaction between metal ion and oxygen atoms of 18C6 thereby favoring the complexation process.

4.6. Effect of solvent composition

The Δ_cG for both the metal ions decreases monotonically with X_E. The stability constant for dicyclohexano 18C6 complexation with Tl^+ and Pb^{2+} varies monotonically with the mole fraction of acetonitrile in water–acetonotrile binary mixture [15]. Authors have attributed this behavior to the monotonous change in acid base property of the binary mixture. However, in water ethanol binary system, the Kamlet Taft parameter [27] does not change monotonically. Though the decrease in Δ_cG is monotonous with X_E, the decrease in Δ_cH and Δ_cS is drastic at X_E up to 0.1. The sudden decrease in Δ_cH is partially compensated by decrease in Δ_cS leading to small decrease in Δ_cG. The sudden change in Δ_cH and Δ_cS can be explained by micro-heterogeneity in the water ethanol binary mixture. At $X_E \sim 0.1$ the solvent structure changes drastically due to the break down of bulk water structure while at $X_E > 0.1$, the formation of small clusters of ethanol and water takes place [30].

The water ethanol binary mixtures exhibit minima in excess mixing properties like excess dielectric constant and excess viscosity [31]. The negative excess properties suggest certain interactions between solvent molecules. At molecular level negative values of excess dielectric constant for various systems is a consequence of the formation of polar associates of lower dipole moment. This microscopic phase separation has been observed by number of authors, and has been detected by techniques like low frequency Raman spectroscopy and mass spectroscopy [30]. The micro-heterogeneity affects the hydrogen bonding and hydrophobic interaction of the solvent with solute. Therefore, the drastic increase in $\Delta_{diss}H$ for 18C6 could be the consequence of decrease in hydrogen bonding. Wu and Masaaki have also observed effect of micro-heterogeneity on the thermodynamics of K^+–18C6 complexation in water acetonitrile mixture [11].

The two main factors which affect the Δ_cS are (i) the loss of conformational entropy of 18C6 on complexation and (ii) randomness of solvent molecules in bulk solvent after being released during desolvation of metal ion and 18C6. In pure water 18C6 forms hydrogen bonds with water molecules making its structure rigid-like complexed 18C6. Therefore, loss of conformational entropy due to complexation of 18C6 is less in water. With increase in ethanol composition the ability of solvent to form hydrogen bond decreases. This effect is more prominent at X_E up to 0.1 which is reflected in large increase in $\Delta_{tr}H$ of 18C6 at X_E up to 0.1. At X_E up to 0.1, the increase in ethanol composition makes the 18C6 molecule more flexible and loss in conformational entropy during complexation increases. Jozwiak and Piekarski [32] studied the heat of dissolution ($\Delta_{diss}H$) of 15C5 in water–propan-1-ol and the shape of the curve is similar to the $\Delta_{diss}H$ of 18C6 in water ethanol binary mixture. The strong water–propan-1-ol interaction is suggested in water-rich region. The same groups observed increase in dissolution enthalpy of 15C5 with acetone mole fraction in acetone–water mixtures [33]. The similar interaction in water ethanol mixture might be responsible for the weakening of hydrogen bonds between water and 18C6. The fate of solvent molecules released after desolvation process also affects the $\Delta_c S$. In water, the released water molecules become the part of more ordered three-dimensional hydrogen bonded network where as ethanol is comparatively structure-less solvent. Therefore, $\Delta_c S$ is expected to increase with X_E. These two factors have opposing effect on $\Delta_c S$, and might be responsible for minimum in $T\Delta_c S$ vs. X_E. The observed enthalpy entropy compensation at low X_E values also suggests the dominant role of 18C6 conformation on $\Delta_c S$ in water-rich region.

5. Conclusion

The stability constant of Sr^{2+} and Ba^{2+} complexes with 18C6 increased monotonically with the ethanol mole fraction in the binary mixture of water and ethanol. The complexation process was mainly enthalpically favorable but entropically unfavorable in all the water ethanol compositions studied. The $\Delta_c H$ decreased with X_E whereas a minimum was observed in the plot of $T\Delta_c S$ vs. X_E. Similar behavior in the thermodynamic quantities, viz., $\Delta_c G$, $\Delta_c H$, and $\Delta_c S$ was observed for both the metal ions, indicating very small difference in $\Delta_{tr}G$ (water to binary mixture) which is supported by the ab initio calculations. The ab initio calculation also showed more stabilization of metal ions as well as crown ether in water compared to ethanol.

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References

[1] M. Hiaoka, Crown compounds: Their characteristics and Applications 282, Mir, Moscow, 1986, p. 359.
[2] R.M. Izatt, R.E. Terry, B.L. Haymore, L.D. Hansen, N.K. Dalley, A.G. Avondet, J.J. Christensen, J. Am. Chem. Soc. 98 (1976) 7620–7626.
[3] A. Lewandowski, J. Malinska, J. Chem. Soc., Faraday Trans. 89 (1983) 2015–2016.
[4] N. Rawat, P.K. Mohapatra, D.S. Lakshmi, A. Bhattacharya, V.K. Manchanda, J. Membr. Sci. 275 (2006) 82–88.
[5] G.W. Gokel, Crown ether and Cryptands RSC, Cambridge (1991).
[6] G.H. Rounaghi, F. Mofazzeli, J. Incl. Phenom. Macrocycl. Chem. 51 (2005) 205–210.
[7] K. Ozutsumi, K. Ohtsu, T. Kawashima, J. Chem. Soc., Faraday Trans. 90 (1994) 127–131.
[8] K. Ozutsumi, K. Kohyama, K. Ohtsu, T. Kawashima, J. Chem. Soc., Faraday Trans. 91 (1995) 3081–3085.
[9] K. Ohtsu, T. Kawashima, K. Ozutsumi, J. Chem. Soc., Faraday Trans. 91 (1995) 4375–4380.
[10] K. Ohtsu, K. Ozutsumi, J. Incl. Phenom. Macrocycl. Chem. 45 (2003) 217–224.
[11] W. Yingguang, T. Masaaki, J. Solution Chem. 33 (2004) 777–795.
[12] G. Rounaghi, Z. Eshaghi, E. Ghiamati, Talanta 44 (1997) 275–282.
[13] H.J. Buschmann, E. Schollmeyer, J. Electroanal. Chem. 474 (1999) 188–191.
[14] E. Karkhaneei, M.H. Zebarjadian, M. Shamsipur, J. Solution Chem. 30 (2001) 323–333.
[15] H.G. Rounaghi, A.S. Yazdi, Z. Monsef, J. Incl. Phenom. Macrocycl. Chem. 43 (2002) 231–237.
[16] M. Shamsipur, A. Esmaeli, M.K. Amini, Talanta 36 (1989) 1300–1302.
[17] R.M. Izatt, D.P. Nelson, J.H. Rytting, B.L. Haymore, J.J. Christensen, J. Am. Chem. Soc. 93 (1971) 1619–1623.
[18] P.K. Mohapatra, D.S. Lakshmi, V.K. Manchanda, Desalination 198 (2006) 166–172.
[19] P. Johansson, I. Wadso, Thermochim. Acta 342 (1999) 19–29.
[20] Data analysis program downloaded from http://www.box.net/shared/static/ugmd1nqoss.zip (TAM Assistant CD v1.0.116.37).
[21] J. Tomasi, Persico, Chem. Rev. 94 (1994) 2027–2094.
[22] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, K. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery Jr., J. Comput. Chem. 14 (1993) 1347–1363.
[23] A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, Mol. Phys. 80 (1993) 1431–1441.
[24] H. Kaupp, P.V.R. Schleyer, H. Stoll, H. Preuss, J. Chem. Phys. 94 (1991) 1360–1366.
[25] M. Ansarifard, G. Rounaghi, J. Incl. Phenom. Macrocycl. Chem. 52 (2005) 39–44.
[26] Y. Inoue, T. Hakushi, J. Chem. Soc., Perkin Trans. II (1985) 935–946.
[27] C. Kalidas, G. Hefter, Y. Marcus, Chem. Rev. 100 (2000) 819–852.
[28] V. Gutmann, The Donor–Acceptor Approach to Molecular Interactions, Plenum, NewYork, 1978.
[29] T. Usacheva, S. Leddenkov, V. Sharnin, J. Therm. Anal. Calorim. 70 (2002) 379–385.
[30] A. Wakisaka, K. Matsuura, J. Mol. Liq. 129 (2006) 25–32.
[31] H. Yilmaz, Turk. J. Phys. 26 (2002) 243.
[32] M. Jozwiak, H. Piekarski, J. Therm. Anal. Calorim. 69 (2002) 291–300.
[33] M. Jozwiak, J. Mol. Liq. 141 (2008) 69–72.