ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 3, pp. 571–577. © Pleiades Publishing, Ltd., 2014.

A Complexation Study of 15-Crown-5 with Co^{2+} Cation in Some Pure and Mixed Organic Solvents[1]

Mahshid Sattari, Gholam Hossein Rounaghi, Behjat Deiminiat, and Massoumeh Mohajeri

Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran
e-mail: ghrounaghi@yahoo.com

Received January 9, 2014

Abstract—The stability constant (log K_f) and the thermodynamic parameters (free energies, enthalpies, and entropies) of the complexation of Co^{2+} cation with 15-crown-5 (15C5) in acetonitrile-methanol (AN/MeOH), acetonitrile-nitrobenzene (AN/NB), acetonitrile-dichloromethane (AN/DCM) and acetonitrile-1,2-dichloroethane (AN/DCE) binary solvent solutions were calculated from the experimental conductance data at different temperatures. The complexation behavior of the crown ether used in these media was discussed in view of the estimated parameters. In all solvent systems, 15-crown-5 formed a 1 : 1 complex with Co^{2+} cation. The stability order of $(Co\text{-}15C5)^{2+}$ complex in the binary mixed solvents at 25°C was found to be: AN/NB > AN/DCM ≈ AN/DCE > AN/MeOH. In most cases, a non-linear relationship was observed for changes of log K_f of $(Co\text{-}15C5)^{2+}$ complex versus the composition of the binary mixed solvent systems. The experimental results show that the standard thermodynamic parameters of the complexation process change with the nature and composition of the binary solvent solutions.

DOI: 10.1134/S1070363214030281

INTRODUCTION

Crown ethers are known to be effective macrocyclic ligands capable of binding metal ions with a high selectivity, by inclusion them to the inner cavity of their ring-shaped molecules. This property is the basis of their broad practical applications in various areas of chemistry, biology, pharmacology and medicine [1–6]. Crown compounds prove their advantages when used in the reaction carried out in non-aqueous medium. Many chemical reactions that were traditionally considered difficult or impossible to implement, proceed easily in the presence of crown ethers. This can be explained by unique ability of the latter to perform transfer of ionic reagents from the aqueous or solid phase into organic phase and to change the state of the ion pairs in solutions. With the appearance of these compounds, chemists have a tool for the fine impact on the state of the ion pairs, and hence on the reaction mechanism [7].

The complexation of metal ions and their selective recognition by molecular receptors containing a structure of the crown ether type includes the direct contact between the two chemical species. This process involves in sequential order: desolvation (total or partial) of the cation and ligand, interaction between cation and ligand, and often structural recognition in the ligand [8, 9]. The strength of the complexes formed depends on the cavity size of the ligand, the number of available electron donor atoms within the crown ether, the spatial distribution of ring binding sites, the charge density of the cation and also the cation diameter. Apart from these factors, solvent plays a crucial role in the binding selectivity of the crown ethers for metal ions. The solvents commonly used to study these reactions are water, methanol, acetonitrile, and propylene carbonate [10–14]. The composition of the solvent mixtures has a pronounced influence on the stability of the metal ion−crown complexes [15, 16]. This is mainly caused by the solvation of the metal cation, the ligand, the resulting complex and even the nature of the counter ion. Effect of solvent on the chemical equilibrium, the energy and the reaction rate is due to the change in the solvation state of reactants and reaction products.

In order to achieve appropriate solvent properties, we use a mixture of two solvents. The physicochemical properties of mixed solvents are important from a theoretical and practical point of view, because many chemical and electrochemical reactions may be carried out in such media. Usually mixed solvents do

---

[1] The text was submitted by the authors in English.

not behave as expected from statistical consideration; the solvating ability of solvents in their mixtures can be different from those of neat media [17]. The deviations from ideal behavior are indicative of the extent of preferential solvation and the existence of specific solvent–solute and solvent-solvent intractions [18, 19].

We have studied the effect of the nature and composition of the some solvent systems and the influence of temperature on the complexation of macrocyclic ligand, 15-crown-5, with Co^{2+} metal cation and report the results obtained for the stoichiometry, stability and also the thermodynamic parameters of the formation of the $(Co\text{-}15C5)^{2+}$ complex in some binary solvent solutions of methanol (MeOH), nitrobenzene (NB), dichloromethane (DCM) and 1,2-dichloroethane (DCE) with acetonitrile (AN), at different temperatures using conductometry.

EXPERIMENTAL

Chemicals. 15-crown-5 and cobalt(II) nitrate hexahydrate were purchased from Merck (>99% purity) and used without further purification. The organic solvents: acetonitrile, methanol, nitrobenzene, 1,2-dichloroethane, and dichloromethane all from Merck company were used with > 99% purity.

Apparatus. Conductance measurements were performed using a digital Metrohm conductivity meter (model 712) at a frequency of 1 kHz, with a specially designed water-jacketed cell (150 mL, pyrex) equipped with a magnetic stirrer and connected to a thermostated circulating water bath (Julabo, model F12) with a precision of ±0.1°C and a refrigeration unit. A conductometric cell with a cell constant of $1.004\ \text{cm}^{-1}$ was used throughout the studies.

Method. The experimental procedure to obtain the stability constant of the $(Co\text{-}15C5)^{2+}$ complex is described below: a solution of cobalt(II) salt (1.0×10^{-4} M, 20 mL) was placed in a titration cell and the conductance of the solution was measured. Then a step-by-step increase of the 15C5 solution prepared in the same solvent (2.0×10^{-3} M) was carried out using a pre-calibrated microburette and the conductance of the solution was measured after each step at the desired temperature. In such dilute solutions, in order to keep the electrolyte concentration constant during the titration, both the starting solution and the titrant had the same metal ion concentration.

CALCULATED

The stability constant of complex formation. The reaction for a 1 : 1 complex formation can be expressed by Eq. (1) and the corresponding equilibrium constant, K_f, is given by Eq. (2):

$$M^+ + L \leftrightarrow ML^+, \tag{1}$$

$$K_f = \frac{[ML^+]}{[M^+][L]} \cdot \frac{f_{ML^+}}{f_{M^+} f_L}, \tag{2}$$

where $[ML^{n+}]$, $[M^{n+}]$, [L], and f, represent the equilibrium molar concentrations of the complex, cation, ligand and the activity coefficient of the species indicated, respectively. Under the highly dilute experimental conditions which we used in this study, the activity coefficient of the uncharged ligand, can be reasonably assumed to be unity [20]. The use of Debye-Hьckel limiting law [21] leads to the conclusion that, $f_{M^+} \sim f_{ML^+}$, therefore, the activity coefficients in Eq. (2) could be canceled.

The complex formation constant in terms of the molar conductance can be expressed as [22]:

$$K_f = \frac{[ML^+]}{[M^+][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_M)[L]}, \tag{3}$$

where

$$[L] = c_L - \frac{c_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{obs})}. \tag{4}$$

Here, Λ_M is the molar conductance of the metal nitrate before addition of the ligand, Λ_{obs} is the molar conductance of solution during titration and Λ_{ML} is the molar conductance of the complexed ion. c_L is the analytical concentration of the ligand added and c_M is the analytical concentration of the metal nitrate. The complex stability constant, K_f, was obtained by computer fitting of Eqs. (3) and (4) to the molar conductance-mole ratio data using a non-linear least-squares program GENPLOT [23]. The values of formation constant for the studied complex are given in Table 1.

The thermodynamic parameters of complex formation. The dependence of standard Gibbs free energy (ΔG_c^0) with the complex formation constant (K_f) and standard enthalpy (ΔH_c^0) and standard entropy (ΔS_c^0) are expressed by the following equations:

$$\Delta G_c^0 = -RT \ln K_f, \tag{5}$$

$$\Delta G_c^0 = \Delta H_c^0 - T\Delta S_c^0, \tag{6}$$

where T and R denote the absolute temperature in Kelvin and universal gas constant, respectively. By determining complex formation constant (K_f) at different temperatures and plotting the graph of ln K_f vs. $1/T$ (van't Hoff plot), the standard enthalpy (ΔH_c^0) value can be found [24]:

$$\ln K_f = -\Delta H_c^0/RT + \Delta S_c^0/R, \quad (7)$$

$$\Delta H_c^0 = -\mathrm{R}\cdot\mathrm{slope}. \quad (8)$$

The values of standard Gibbs free energy (ΔG_c^0) and standard entropy (ΔS_c^0) can be obtained from Eqs. (5) and (6), respectively. The thermodynamic data are summarized in Table 2.

RESULT AND DISCUSSION

Conductance studies. The complex formation of the crown ether, 15C5, with Co^{2+} cation was investigated in acetonitrile-methanol (AN/MeOH), acetonitrile-nitrobenzene (AN/NB), acetonitrile-dichloromethane (AN/DCM) and acetonitrile-1,2-dichloroethane (AN/DCE) binary mixtures by molar conductance changes at 15, 25, 35, and 45°C. Some of the resulting molar conductance vs. ligand/cation mole ratio plots ($[L]_t/[M]_t$) are shown in Figs. 1 and 2. As can be seen from these Figures, addition of the ligand to the metal cation solution, results an increase in the molar conductance of the solution which indicates that the complexed cation is more mobile than the free solvated one. Since the $(Co\text{-}15C5)^{2+}$ complex is more bulky than Co^{2+} cation, therefore, it is much less solvated by the solvent molecules, and hence the complex is more mobile than free Co^{2+} solvated cation. Similar behavior was observed in all other solvent systems. As is evident from Fig. 1, the slope of the corresponding molar conductance-mole ratio plot changes sharply at the point where the ligand to cation mole ratio is 1 : 1 which is indicative of the formation of a fairly stable 1 : 1 complex in solution. In the case of AN-MeOH binary mixture (Fig. 2), the gradual increase observed in the molar conductance of the salt solution does not exhibit any significant change in the slope at the mole ratio of about one, emphasizing the formation of a weaker complex in this binary solvent solution.

Effect of solvent composition. The log K_f data in Table 1 show that the stability constant of $(Co\text{-}15C5)^{2+}$ complex is larger in pure acetonitrile than pure methanol which is consistent with the inverse order of their solvating abilities as expressed by the Gutmann donor number. In a solvent with a high solvating ability (high donor number) such as methanol (DN = 20.0), the complex formation tends to be weak, but in a solvent with lower donar number like acetonitrile (DN = 14.1), the relatively poorer solvating ability of

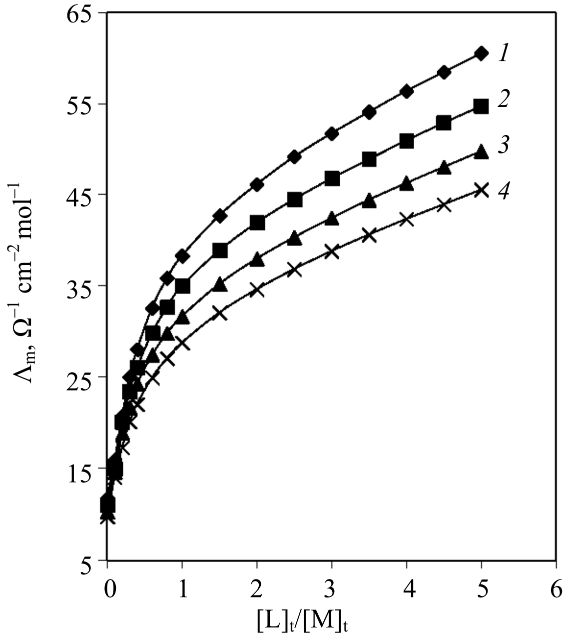

Fig. 1. Molar conductance-mole ratio plots for $(Co\text{-}15C5)^{2+}$ complex in AN-NB binary system (AN = 25 mol %) at different temperatures, °C: (*1*) 15, (*2*) 25, (*3*) 35, and (*4*) 45.

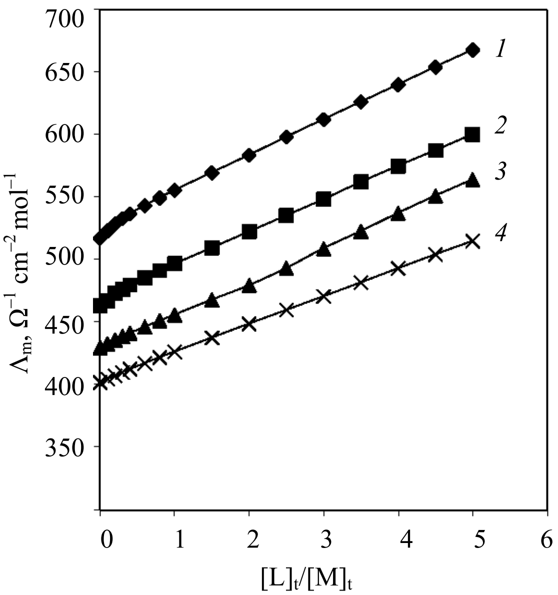

Fig. 2. Molar conductance-mole ratio plots for $(Co\text{-}15C5)^{2+}$ complex in AN-MeOH binary solvent system (AN = 50 mol %) at different temperatures, °C: (*1*) 15, (*2*) 25, (*3*) 35, and (*4*) 45.

Table 1. log K_f values of $(Co\text{-}15C5)^{2+}$ complex in AN-MeOH, AN-NB, AN-DCM, and AN-DCE binary systems at different temperatures

AN, mol %	log K_f ± SD[a]			
	15°C	25°C	35°C	45°C
	AN-MeOH[b]			
100	3.79±0.05	3.71±0.05	3.64±0.04	3.54±0.05
75	3. 08±0.14	2.81±0.09	2.75±0.09	2.76±0.09
50	2.80±0.10	2.77±0.10	2.51±0.24	2.70±0.11
25	2.70±0.11	2.71±0.10	2.70±0.11	2.74±0.10
0	2.56±0.16	2.69±0.11	2.72±0.13	2.68±0.12
	AN-NB[b]			
100	3.79±0.05	3.71±0.05	3.64±0.04	3.54±0.05
75	3.65±0.04	3.67±0.05	3.59±0.05	3.56±0.05
50	3.79±0.06	3.80±0.06	3.78±0.07	3.70±0.06
25	4.17±0.11	4.17±0.12	4.14±0.13	4.09±0.12
0	4.46±0.19	4.53±0.21	4.49±0.21	4.52±0.22
	AN-DCE[b]			
100	3.79±0.05	3.71±0.05	3.64±0.04	3.54±0.05
75	3.44±0.04	3.42±0.04	3.33±0.05	3.28±0.04
50	3.38±0.04	3.37±0.05	3.29±0.04	3.20±0.05
25	3.33±0.05	3.53±0.07	3.45±0.08	3.34±0.06
0	[c]	[c]	[c]	[c]
	AN-DCM[b]			
100	3.45±0.03	3.79±0.05	3.71±0.05	3.64±0.04
75	3.40±0.04	3.47±0.04	3.43±0.04	3.37±0.04
50	3.28±0.04	3.38±0.04	3.32±0.04	3.31±0.04
25	3.42±0.04	3.58±0.07	3.54±0.06	3.52±0.06
0	[c]	[c]	[c]	[c]

[a] Standard Deviation. [b] The composition of binary mixtures is expressed in mol % for each solvent system. [c] The salt is not completely dissolved.

Table 2. Thermodynamic parameters for $(Co\text{-}15C5)^{2+}$ complex in AN-MeOH, AN-NB, AN-DCM, and AN-DCE binary solvent solutions ($T = 25°C$)

AN, mol %	ΔG^0_c±SD[a], kJ/mol	ΔH^0_c±SD[a], kJ/mol	ΔS^0_c±SD[a], kJ/mol
	AN–MeOH[b]		
100	–21.17±0.29	–14.37±0.98	22.82±3.15
75	–16.05±0.56	[c]	[c]
50	–15.85±0.62	[c]	[c]
25	–15.50±0.61	[c]	57.19±2.73
0	–15.40±0.67	[c]	76.55±15.72
	AN–NB[b]		
100	–21.17±0.29	–14.37±0.98	22.82±3.15
75	–20.96±0.32	–6.36±2.47	48.99±8.21
50	–21.69±0.38	–4.98±1.54	56.05±8.44
25	–23.85±0.70	–5.07±1.59	62.99±4.79
10	–25.87±1.24	[c]	95.71±6.96
	AN–DCM[b]		
100	–21.17±0.29	[c]	[c]
75	–19.53±0.26	[c]	59.83±12.13
50	–19.26±0.31	[c]	65.73±13.59
25	–20.15±0.44	[c]	82.61±17.51
	AN–DCE[b]		
100	–21.17±0.29	–14.37±0.98	22.82±3.15
75	–19.53±0.26	–10.11±1.58	31.59±5.25
50	–19.26±0.31	–10.73±2.52	28.60±8.41
25	–20.15±0.44	[c]	67.47±30.35

[a] Standard deviation. [b] The composition of binary mixtures is expressed in mol % for each solvent system. [c] With high uncertainty.

this solvent leads to an increase in the stability constant. It has been shown that the solvating ability of a solvent, as expressed by the Gutmann donocity scale [25], plays a fundamental role in complexation reactions [26]. In addition, since the acceptor number of methanol (AN = 41.3) is bigger than that of acetonitrile (AN = 19.3), therefore, the macrocyclic ligand is more solvated in MeOH than AN which in turn results in the formation of a weaker complex in methanol than in acetonitrile.

The comparison of the data in Table 1 reveals that the stability of $(Co\text{-}15C5)^{2+}$ complex in the binary mixed solvent solutions varies in the order: AN/NB > AN/DCM ≈ AN/DCE > AN/MeOH. In spite of higher donor ability of NB (DN = 4.4) relative to DCM

(DN = 1.0) and DCE (DN = 0.0), the stability of the complex in AN-NB binary mixture is higher than in the other two binary mixed solvent systems. This behavior is due to the typical hydrogen bonds of the DCE and DCM molecules with the donor atoms of crown ether which lead to a much stronger ligand solvation in these solvent systems. Some solvent molecules that contain polar OH and CH bonds are capable of forming hydrogen bonds. Crown ethers, being in an environment of such solvents, shall enter into specific interaction with their molecules with the energy higher than the universal energy of interaction with the environment [7, 27]. This has a significant impact on the solvation energy and reactivity of the macrocycle upon complex formation with the other species. The stability constants ($\log K_f$) of $(Co\text{-}15C5)^{2+}$ complex and some of the complexes of alkali metal cations with 15-crown-5 ligand are given in Table 3. As can be seen from Table 3, the Li^+ , Na^+, and K^+ cations form more stable complexes with 15C5 in pure AN than Co^{2+} cation. Since Co^{2+} cation is a softer acid than these alkali metal cations, therefore, the interaction of this heavy metal cation with the oxygen atoms of 15C5 ligand is weaker than the alkali metal cations in this organic solvent.

Table 3. $\log K_f$ values for complexation reaction of some cations with 15C5 in pure AN at 25°C

Cation	$Li^{+\,a}$	$Na^{+\,a}$	$K^{+\,a}$	$Co^{2+\,b}$
$\log K_f$	5.3	5.3	3.9	3.71

[a] Reference [31]. [b] This work.

The changes of $\log K_f$ of $(Co\text{-}15C5)^{2+}$ complex versus the composition of AN-NB binary system at various temperatures is not linear (Fig. 3). A non-linear relationship was also observed in the most of the other binary solvent solutions. But in the case of AN-MeOH binary mixed solvent, a monotonic behavior is observed between the $\log K_f$ of the complex with the composition of this solvent system. The non-linear behavior is possibly related to the interactions between solvent molecules in their binary mixtures which result in changing the structure of the mixed solvents and, therefore, changing the solvation of the cation, ligand and the resulting complex in solutions. The interactions between some binary mixed solvents have been investigated. As an example, there is an interaction between AN and MeOH molecules (K_{ass} = 1.23) via hydrogen bonding in their binary mixtures [28]. The solvating properties of the components in mixtures can even be significantly modified by solvent–solvent interactions when the energy of the latter is comparable with the energy difference of solvent-ion interactions for both components. In addition, this non-monotonic behavior may be due to the preferential

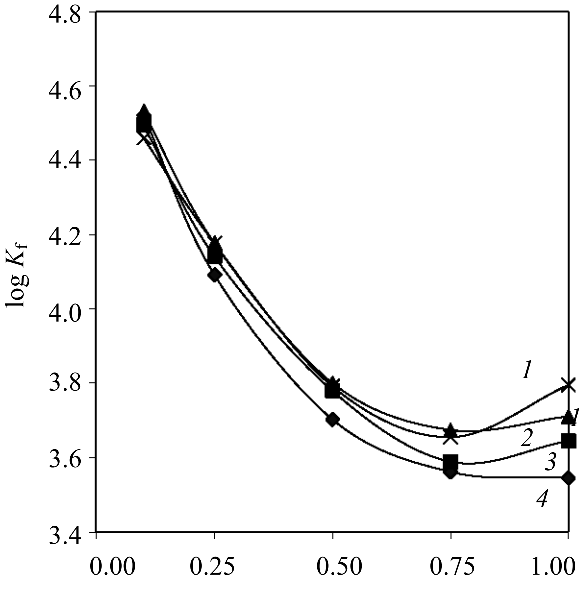

Fig. 3. Changes of stability constant of $(Co\text{-}15C5)^{2+}$ complex with the composition of the AN-NB binary mixture at different temperatures, °C: (*1*) 15, (*2*) 25, (*3*) 35, and (*4*) 45.

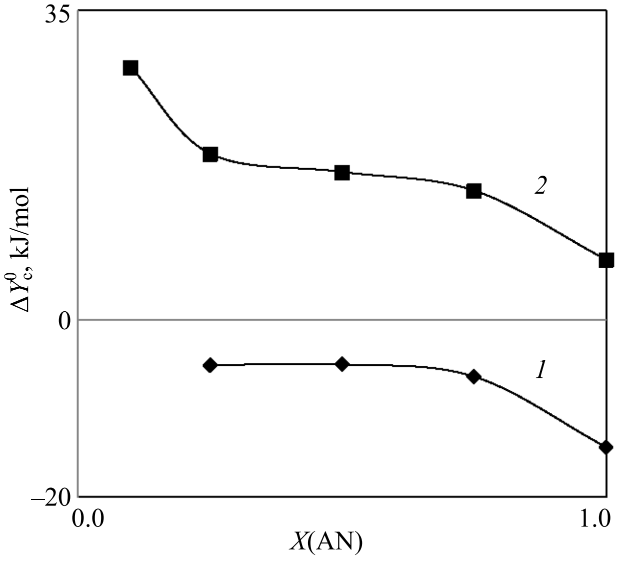

Fig. 4. Effect of composition of AN-NB binary mixed solvent on the enthalpy and entropy of formation of $(Co\text{-}15C5)^{2+}$ complex. (*1*) (ΔH_c^0) and (*2*) ($T\Delta S_c^0$).

solvation of the metal cation. The cobalt(II) ion is a convenient subject for studying of preferential solvation as in donor solvents it forms a solvation sphere of definite stoichiometry and geometry that is predicted by the ligand field theory: six solvent molecules arranged in pseudo octahedral symmetry. In binary mixtures, the formula of the solvated ion is $[CoX_nY_{6-n}]^{2+}$, where X and Y denote to the molecules of the solvent components. The very latest confirmation of this formula arises from FT-IR studies of the solvent molecules in Co(II)–DMF–MeOH solution systems, from which the number of MeOH and DMF molecules in the solvation sphere of this metal cation has been determined for different mixed solvent compositions [29].

Thermodynamic calculations. As it is demonstrated in Table 1, in some of the solvent systems, the formation constant of $(Co\text{-}15C5)^{2+}$ complex decreases by increasing the temperature which indicates that the complexation reaction between 15C5 and Co^{2+} cation in these solvent systems is exothermic.

In order to have a clear picture of the thermodynamics of the complexation of Co^{2+} cation with 15C5, it is useful to investigate the enthalpy and entropy contributions to the complexation reaction. The ΔH_c^0 and ΔS_c^0 values can be obtained experimentally through van't Hoff plots. As can be seen in Table 2, the change in the standard entropy during the formation of $(Co\text{-}15C5)^{2+}$ complex in most solvent systems is positive, but the change in the standard enthalpy is negative in some of the studied solvents. As is obvious from Table 2, in the case of some solvent systems, the stability constant of $(Co\text{-}15C5)^{2+}$ complex does not change significantly with the temperature, hence, the values of ΔH_c^0 is negligible and the complexation reaction in these systems seems to be athermic.

Complexation enthalpy changes are mainly related to: (1) cation-crown interactions, (2) solvation of the metal ion, the crown ether, and the metal ion complexes formed in solution, (3) repulsion between neighboring donor atoms, and (4) steric deformation of the crown ether molecule. Entropy changes are linked to: (1) change in the number of particles involved in the complexation process, and (2) conformational changes of the crown ether accompanying the complexation [30]. As is evident in Table 2, the standard thermodynamic parameters (ΔH_c^0 and ΔS_c^0) change non-monotonically with the nature and composition of the mixed solvents. Since there are many parameters which contribute to the changes of enthalpy and entropy of the complexation reaction, we should not expect to observe a monotonic behavior between these thermodynamic quantities and the solvent composition of these binary solvent solutions (Fig. 4).

ACKNOWLEDGMENTS

The authors acknowledge the support of this work by Islamic Azad University, Mashhad Branch, Mashhad, Iran.

REFERENCES

1. Ekmekci, G., Uzun, D., Somer, G., and Kalayci, S., *J. Membr. Sci*., 2007, vol. 288, p. 36.
2. Mohapatra, P.K., Lakshmi, D.S., Bhattacharyya, A., and Manchanda, V.K. *J. Hazard. Mater*., 2009, vol. 169, p. 472.
3. Mohapatra, P.K. and Manchanda, V.K., *Talanta*, 1998, vol. 47, p. 1271.
4. Buschmann, H.J. and Mutihac, L., *Anal. Chim. Acta*, 2002, vol. 466, p. 101.
5. Oshima, T., Suetsugu, A., and Baba, Y., *Anal. Chim. Acta*, 2010, vol. 674, p. 211.
6. Brandt, K., Kruszynski, R., Bartczak, T.J., and Porwolik-Czomperlik, I., *Inorg. Chim. Acta*, 2001, vol. 322, p. 138.
7. Kuz'mina, I.A. and Sharnin, V.A., *Russ. J. Gen. Chem*., 2011, vol. 81, p. 2316.
8. Izatt, R.M., Pawlak, K., Bradshaw, J.S., and Bruening, R.L., *Chem, Rev*., 1995, vol. 95, p. 2529.
9. Solov'ev, V.P., Strakhova, N.N., Raevsky, O.A., Rudiger, V., and Schneider, H.J., *J. Org. Chem*., 1991, vol. 61, p. 5221.
10. Izatt, R.M., Bradshaw, J.S., Nielsen, S.A., Lamb, J.D., and Christensen, J.J., *Chem. Rev*., 1985, vol. 85, p 271.
11. Izatt, R.M., Pawlak, K., and Bradshaw, J.S., *Chem. Rev*., 1991, vol. 91, p. 1721.
12. Al-Mustafa, J., Hamzah, S., and Marji, D., *J. Sol. Chem*., 2004, vol. 30, p. 681.
13. Rofouei, M., Ahmadalinezhad, A., and Taghdiri, M., *J. Incl. Phenom. Macrocycl. Chem*., 2007, vol. 58, p. 377.
14. Ossowski, T., Trokowski, R., Rogowska, D., and Kira, J., *Polish J. Chem.,* 2001, vol. 75, p. 345.
15. Rounaghi, G.H., Mohajeri, M., Soruri, F., and Mohamadzadeh Kakhki, R., *J. Chem. Eng. Data*, 2011, vol. 56, p. 2836.
16. Razghandi, F., Rounaghi, G.H., and Eshaghi, Z., *J. Incl. Phenom. Macrocycl. Chem*., 2012, vol. 73, p. 87.
17. Kinisinger, J.B., Tannahill, M.M., Greenberg, M.S., and Popov, A.I., *J. Phys. Chem*., 1973, vol. 77, p. 2444.

18. Burger, K., *Ionic Solvation and Complex Formation Reactions in Non-Aqueous Solvents*, Budapest: Akademia Kiado, 1983.
19. Marcus, Y., *Ionic Solvation*, Chichester: Wiley, 1985.
20. Takeda, Y., *Bull. Chem. Soc. Jpn.*, 1983, vol. 56, p. 3600.
21. Debye, P. and Huckel, H., *Phys. Z.*, 1928, vol. 24, p. 305.
22. Khayatian, G.R., Shamsipur, M., and Shariati, S., *J. Incl. Phenom. Macrocycl. Chem.*, 2003, vol. 45, p. 117.
23. Genplot, A., *Data Analysis and Graphical Plotting Program for Scientist and Engineers. Computer Graphic Service*, New York: Ithaca Ltd., 1989.
24. Shamsipur, M. and Saeidi, M., *J. Sol. Chem.*, 2000, vol. 29, p. 1187.
25. Gutmann, V., *The Donor–Acceptor Approach to Molecular Interactions*, New York: Plenum Press, 1978.
26. Rounaghi, G.H. and Popov, A.I., *Polyhedron* 1986, vol. 5, p. 1935.
27. Antina, E.V., Barannikov, V.P., Berezin, M.B., and V’yugin, A.I., *Physical Chemistry of Solutions of Macroheterocyclic Compounds*; in *Problems of the Chemistry of Solutions and Technology of Liquid-Phase Materials*, Ivanovo, 2001, p. 217.
28. Krestov, G.A., Novosyolov, N.P., and Perelygin, I.S., *Ionic Solvation*, New York: Ellis Horwood, 1994.
29. Szymбnska-Cybulska, J. and Kamiйnska-Piotrowicz, E., *J. Sol. Chem.*, 2006, vol. 35, p. 1631.
30. Christy, F.A. and Shrivastav, P.S., *J. Anal. Chem.*, 2001, vol. 41, p. 236.
31. Takeda, Y., Katsuta, K., Inoue, Y., and Hakushi, T., *Bull. Chem. Soc. Jpn*, 1988, vol. 61, p. 627.