Study of Complex Formation Between Dicyclohexano-18-Crown-6 (DCH18C6) with Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} Cations in Methanol–Water Binary Mixtures Using Conductometric Method

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Abstract

The complexation reactions between Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} metal cations with macrocyclic ligand, dicyclohexano-18-crown-6 (DCH18C6) were studied in methanol (MeOH)–water (H_2O) binary mixtures at different temperatures using conductometric method. In all cases, DCH18C6 forms 1:1 complexes with these metal cations. The values of stability constants of complexes which were obtained from conductometric data show that the stability of complexes is affected by the nature and composition of the mixed solvents. While the variation of stability constants of DCH18C6-Sr^{2+} and DCH18C6-Ba^{2+} versus the composition of MeOH–H_2O mixed solvents is monotonic, an anomalous behavior was observed for variations of stability constants of DCH18C6-Mg^{2+} and DCH18C6-Ca^{2+} versus the composition of the mixed solvents. The values of thermodynamic parameters (ΔH_c°, ΔS_c°) for complexation reactions were obtained from temperature dependence of formation constants of complexes using the van't Hoff plots. The results show that in most cases, the complexation reactions are enthalpy stabilized but entropy destabilized and the values of thermodynamic parameters are influenced by the nature and composition of the mixed solvents. The obtained results show that the order of selectivity of DCH18C6 ligand for metal cations in different concentrations of methanol in MeOH–H_2O binary system is: $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$.

Introduction

The first report of crown compounds was published in 1967 by Pedersen. He discovered the macrocyclic ligand, dibenzo-18-crown-6 (DB18C6) and observed that this compound and similar homologous form very strong complexes with alkali and alkaline earth metal cations [1]. After then, many researches have been carried out on complexation and applications of these compounds in different areas, such as chemical analysis [2], organic synthesis [3], in construction of ion-selective electrodes [4], separation of metal ions [5] and recognition of isomers [6].

Because of the vital role of alkali and alkaline earth metal cations in biological systems [7], an important part of the researches deals with the complexes of these metal cations with crown compounds. Macrocyclic crown ethers are similar to antibiotic ligands, both in structure and in their ability to form stable complexes and, therefore, these compounds can be used as models for investigation of ion transport through membrane in biological systems [8]. Studies of complexation reaction of crown ethers with metal ions in different solvents show that the thermodynamic and kinetic parameters are affected by the nature and composition of the solvent system [9, 10].

Different physico-chemical techniques such as polarography [11, 12], potentiometry [13, 14], spectrophotometry [15, 16], NMR spectrometry [17], calorimetry [18], conductometry [19, 20], fluorescence spectroscopy [21], electrospray ionization mass spectrometry [22] and capillary zone electrophoresis [23, 24] have been used to study the complex formation between macrocyclic ligands and different metal cations in solutions. Among these various methods, the conductometric technique is a sensitive and inexpensive method with a simple experimental arrangement for such investigations.

Since one of our main research interests is the influence of solvent properties on the thermodynamics of complexation reactions of macrocyclic ligands, we studied the complexing ability of dicyclohexano-18-crown-6 (DCH18C6) towards alkaline metal cations in MeOH–H_2O binary mixtures using conductometric method.

Materials and experimental procedures

DCH18C6 (a mixture of the *cis*-syn-*cis* and *cis*-anti-*cis* isomers) (Fluka), magnesium nitrate (BDH), calcium

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nitrate (Merck), strontium nitrate (SEARLE) and barium perchlorate (Merck) were used without further purification. Methanol (Merck) with the highest purity and triplet distilled water were used as solvents.

The experimental procedure to obtain the formation constants of complexes is as follows: a solution of metal salt (2×10^{-4}M) was placed in a titration cell and the conductance of the solution was measured , then a step-by-step increase in the crown ether concentration was performed by a rapid transfer from crown ether solution prepared in the same solvent (0.01 M) to the titration cell using a microburette and the conductance of the solution in the cell was measured after each transfer at the desired temperature.

The conductance measurements were performed on a digital AMEL conductivity apparatus, model 60, in a water-bath thermostated at a constant temperature maintained within ± 0.03 °C. The electrolytic conductance was measured using a cell consisting of two platinum electrodes to which an alternating potential was applied. A conductometric cell with a cell constant of 0.79 cm^{-1} was used throughout the studies.

Results

The variations of molar conductance Λ_m versus the ligand to the cation molar ratio ($[L]_t/[M]_t$) for complexation of DCH18C6 with Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} cations in MeOH–H$_2$O binary systems were studied at different temperatures. The variations of $\Lambda_{m\ versus\ ([L]_t}/[M]_t$) for DCH18C6-Ba^{2+} in MeOH–H$_2$O binary mixture and for DCH18C6-Sr^{2+} in pure MeOH are shown in Figures 1 and 2, respectively.
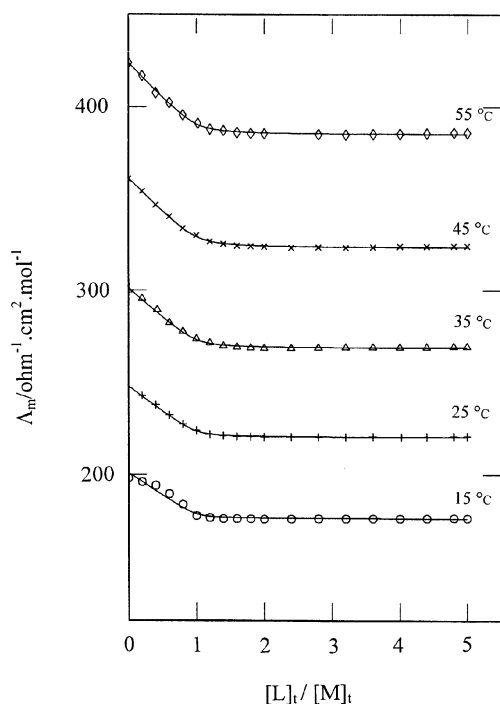

Figure 1. Molar conductance–mole ratio plots for DCH18C6-Ba^{2+} complex in MeOH–H$_2$O (mol% MeOH = 60) at different temperatures.
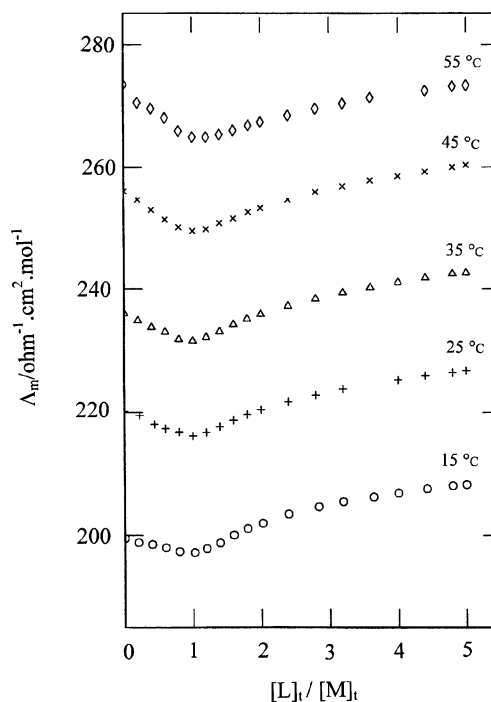

Figure 2. Molar conductance–mole ratio plots for DCH18C6-Sr^{2+} complex in neat MeOH at different temperatures.

The stability constants of DCH18C6 crown ether complexes at each temperature were calculated from variation of molar conductance as a function of [Ligand]/[M^{n+}] molar ratio using a GENPLOT computer program [25]. The details of calculation of the stability constants of complexes by conductometric method have been described in reference [20]. The stability constants (log K_f) for DCH18C6-M^{2+} (M^{2+} = Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) complexes in various solvent systems at various temperatures are listed in Table 1.

The changes in the standard enthalpy ($\Delta H_c°$) for complexation reactions were obtained from the slope of the van't Hoff plots assuming that ΔCp is equal to zero over the entire temperature range investigated. The changes in standard entropy ($\Delta S_c°$) were calculated from the relationship $\Delta G_c°,\ _{298.15} = \Delta H_c° - 298.15\ \Delta S_c°$. The results are summarized in Table 2.

The variation of log K_f versus the mole fraction of MeOH for DCH18C6-Sr^{2+} and DCH18C6-Mg^{2+} complexes in MeOH–H$_2$O binary system at different temperatures is shown in Figures 3 and 4, respectively, and the variation of stability constant (log K$_f$) of DCH18C6-M^{2+} (M^{2+} = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) complexes as a function of cationic radii in various MeOH–H$_2$O binary systems is shown in Figure 5.

Discussion

As is obvious from Figure 1, addition of DCH18C6 to barium ion solution at different temperatures shows a decrease in molar conductivity. This indicates that

Table 1. Log K_f values of DCH18C6-Mg^{2+}, DCH18C6-Ca^{2+}, DCH18C6-Sr^{2+} and DCH18C6-Ba^{2+} complexes in MeOH–H$_2$O binary mixtures at different temperatures

Medium	Log $K_f \pm$ SD[a]				
	15 °C	25 °C	35 °C	45 °C	55 °C
DCH18C6-Mg^{2+} [d]					
70%H$_2$O–30%MeOH[e]	3.51 ± 0.09	2.80 ± 0.09	b	2.7 ± 0.2	2.5 ± 0.1
40%H$_2$O–60%MeOH	2.62 ± 0.03	3.14 ± 0.03	b	2.9 ± 0.1	2.85 ± 0.09
20%H$_2$O–80%MeOH	2.76 ± 0.09	2.5 ± 0.1	2.1 ± 0.2	2.3 ± 0.1	2.28 ± 0.09
Pure MeOH	1.9 ± 0.3	2.1 ± 0.1	b	2.5 ± 0.1	2.57 ± 0.04
DCH18C6–Ca^{2+} [d]					
70%H$_2$O–30%MeOH[e]	2.8 ± 0.1	3.19 ± 0.05	2.81 ± 0.06	b	1.8 ± 0.1
40%H$_2$O–60%MeOH	3.42 ± 0.04	3.82 ± 0.09	3.72 ± 0.06	3.26 ± 0.03	3.02 ± 0.05
20%H$_2$O–80%MeOH	4.27 ± 0.06	3.97 ± 0.08	2.3 ± 0.2	3.41 ± 0.03	3.20 ± 0.07
Pure MeOH	1.02 ± 0.07	2.3 ± 0.1	3.25 ± 0.03	2.9 ± 0.2	3.43 ± 0.05
DCH18C6–Sr^{2+} [d]					
80%H$_2$O–20%MeOH[e]	3.55 ± 0.05	3.49 ± 0.02	3.42 ± 0.02	3.19 ± 0.07	3.16 ± 0.05
70%H$_2$O–30%MeOH	3.99 ± 0.03	3.85 ± 0.02	3.69 ± 0.01	3.57 ± 0.02	3.49 ± 0.03
60%H$_2$O–40%MeOH	4.3 ± 0.1	4.06 ± 0.05	3.99 ± 0.02	3.96 ± 0.03	3.71 ± 0.02
40%H$_2$O–60%MeOH	5.4 ± 0.3	4.66 ± 0.08	5.1 ± 0.2	4.50 ± 0.07	4.36 ± 0.06
20%H$_2$O–80%MeOH	>6	>6	>6	>6	>6
Pure MeOH	c	c	c	c	c
DCH18C6–Ba^{2+} [d]					
80%H$_2$O–20%MeOH[e]	4.43 ± 0.06	4.16 ± 0.04	4.09 ± 0.05	3.88 ± 0.04	3.82 ± 0.05
70%H$_2$O–30%MeOH	4.81 ± 0.03	4.48 ± 0.01	4.29 ± 0.03	4.15 ± 0.03	3.97 ± 0.01
60%H$_2$O–40%MeOH	5.1 ± 0.1	5.07 ± 0.09	4.6 ± 0.1	4.62 ± 0.06	4.34 ± 0.05
40%H$_2$O–60%MeOH	5.2 ± 0.4	5.09 ± 0.09	4.9 ± 0.1	4.82 ± 0.06	4.87 ± 0.07
20%H$_2$O–80%MeOH	>6	>6	>6	>6	>6
Pure MeOH	>6	>6	>6	>6	>6

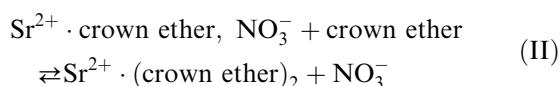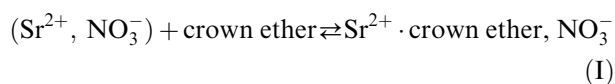[a] SD = Standard deviation.
[b] With high uncertainty.
[c] Fitting of data in equations [20] is impossible.
[d] The concentration of each metal cation was 2×10^{-4} M.
[e] The composition of binary mixtures is expressed in mol% for each solvent.

DCH18C6 forms a complex with Ba^{2+} cation and this complex is less mobile than free solvated Ba^{2+} ion. Similar behavior was observed for Sr^{2+} ion. The slope of the corresponding molar conductivity Λ_m versus [Ligand]/[Cation] ([L]$_t$/[M]$_t$) plots changes sharply at the point where the ligand to cation molar ratio is 1, which is an evidence for formation of a relatively stable 1:1 complex.

An anomalous behavior was observed in the case of complexation of Sr^{2+} ion with the ligand in pure methanol. As is obvious from Figure 2, addition of DCH18C6 to strontium ion in pure MeOH at different temperatures causes the molar conductivity to initially decrease until the mole ratio reaches 1:1 and then to increase. Such behavior may be described according to the following equilibria:

$$(Sr^{2+}, NO_3^-) + \text{crown ether} \rightleftarrows Sr^{2+} \cdot \text{crown ether}, NO_3^-$$
(I)

$$Sr^{2+} \cdot \text{crown ether}, NO_3^- + \text{crown ether}$$
$$\rightleftarrows Sr^{2+} \cdot (\text{crown ether})_2 + NO_3^-$$
(II)

It seems that addition of the ligand to strontium ion solution results in formation of a relatively stable 1:1 complex (I) which is present as an ion-pair, then addition of the second ligand to ion-pair complex, causes formation of a stable 1:2 complex with a sandwich structure (II) which decreases the interaction of NO$_3^-$ ion with strontium cation and results in dissociation of ion-pair. Similar behavior has been observed by Takeda and his coworkers [26] in their study of complex formation between 18C6 with K$^+$ and Rb$^+$ cations in propylenecarbonate, and also by Rounaghi *et al.* [27] for complexation of DCH18C6 with Tl$^+$ in MeOH-AN binary mixture.

The variation of stability constant (log K_f) of DCH18C6-Sr^{2+} complex as a function of solvent composition in MeOH–H$_2$O binary mixture is shown in Figure 3. There is a linear relationship between log K_f values and the mole fraction of methanol in mixed solvent system. It seems reasonable to assume that in this case, it is the preferential hydration of Sr^{2+} cation by water molecules that is responsible for this monotonic dependence of stability constant on the solvent composition. In water with a high Gutmann Donor

Table 2. Thermodynamic parameters for DCH18C6-Mg^{2+}, DCH18C6-Ca^{2+}, DCH18C6-Sr^{2+} and DCH18C6-Ba^{2+} complexes in MeOH–H$_2$O binary mixtures

Medium	Log K_f ± SD[a] (25 °C)	ΔG_c° ± SD[a] (kJ·mol^{-1})	ΔH_c° ± SD[a] (kJ·mol^{-1})	ΔS_c° ± SD[a] (J·mol^{-1}·K^{-1})
DCH18C6–Mg^{2+}[c]				
70%H$_2$O–30%MeOH[d]	2.80 ± 0.09	−15.9 ± 0.4	−41.8 ± 12.5	b
40%H$_2$O–60%MeOH	3.14 ± 0.03	−17.9 ± 0.2	12.5 ± 4.2	100 ± 21
20%H$_2$O-80%MeOH	2.5 ± 0.1	−13.8 ± 0.8	b	b
Pure MeOH	2.1 ± 0.1	−11.7 ± 0.4	33.4 ± 4.2	150 ± 17
DCH18C6-Ca^{2+}[c]				
70%H$_2$O–30%MeOH[d]	3.19 ± 0.05	−18.2 ± 0.3	b	b
40%H$_2$O–60%MeOH	3.82 ± 0.09	−21.7 ± 0.4	−54.3 ± 8.4	−104 ± 29
20%H$_2$O–80%MeOH	3.97 ± 0.08	−22.6 ± 0.4	−50.2 ± 4.2	−88 ± 21
Pure MeOH	2.3 ± 0.1	−12.9 ± 0.8	100 ± 29	b
DCH18C6-Sr^{2+}[c]				
80%H$_2$O–20%MeOH[d]	3.49 ± 0.02	−19.9 ± 0.1	−19.6 ± 2.9	b
70%H$_2$O–30%MeOH	3.85 ± 0.02	−21.9 ± 0.1	−23.4 ± 0.4	−5.4 ± 1.2
60%H$_2$O–40%MeOH	4.06 ± 0.05	−23.2 ± 0.3	−21.3 ± 0.8	7.1 ± 2.5
40%H$_2$O–60%MeOH	4.66 ± 0.08	−26.8 ± 0.4	−50.2 ± 8.4	b
DCH18C6-Ba^{2+}[c]				
80%H$_2$O–20%MeOH[d]	4.16 ± 0.04	−23.8 ± 0.2	−27.6 ± 0.2	−12.5 ± 4.2
70%H$_2$O-30%MeOH	4.48 ± 0.01	−25.6 ± 0.1	−36.4 ± 3.3	−37.6 ± 8.4
60%H$_2$O–40%MeOH	5.07 ± 0.09	−28.9 ± 0.4	−36.8 ± 3.3	−25.1 ± 8.4
40%H$_2$O–60%MeOH	5.09 ± 0.09	−28.9 ± 0.4	−18.4 ± 3.7	37.6 ± 12.5

[a]SD = Standard deviation.
[b]With high uncertainty.
[c]The concentration of each metal cation was 2×10^{-4} M.
[d]The composition of binary mixtures is expressed in mol % for each solvent.
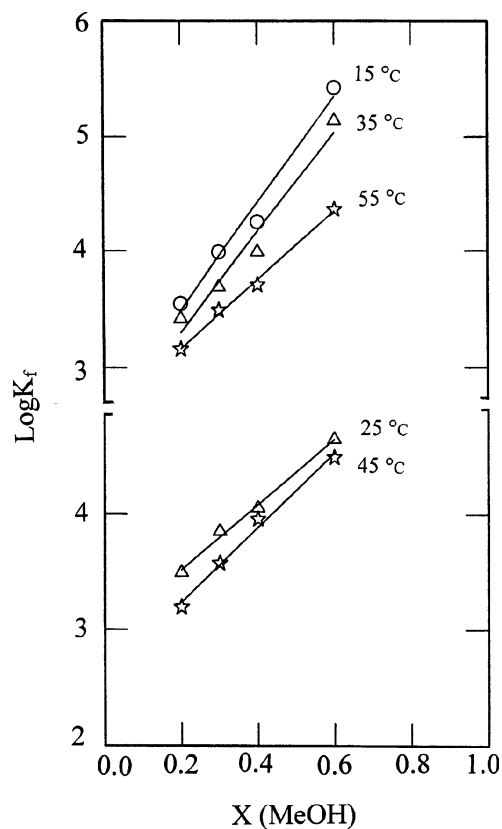

Figure 3. Variation of stability constant of DCH18C6-Sr^{2+} complex with the composition of the MeOH–H$_2$O binary system at different temperatures.
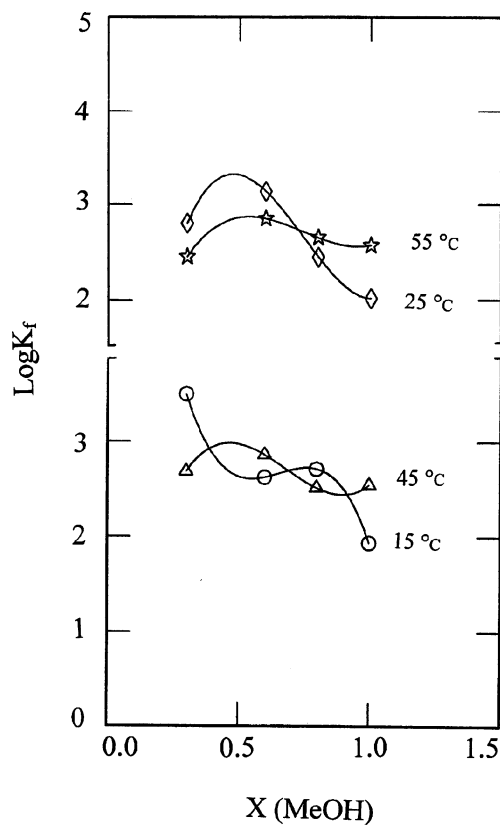

Figure 4. Variation of stability constant of DCH18C6-Mg^{2+} complex with the composition of the MeOH–H$_2$O binary system at different temperatures.
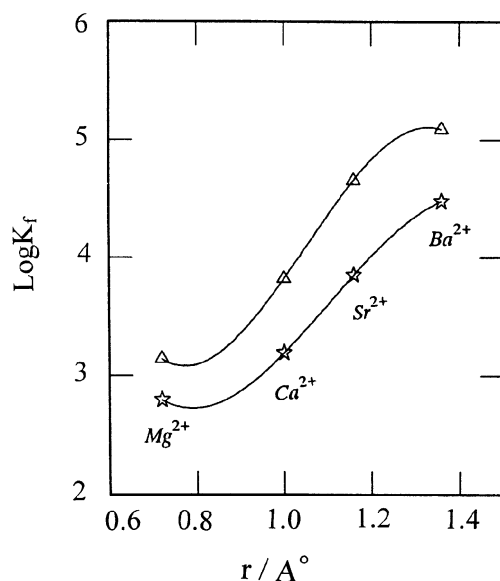
Figure 5. Variation of log K_f for DCH18C6-Mg^{2+}, DCH18C6-Ca^{2+}, DCH18C6-Sr^{2+} and DCH18C6-Ba^{2+} complexes versus cationic radii in MeOH–H$_2$O binary systems at 25 °C (☆:30% MeOH, Δ: 60% MeOH).

Number (DN = 33), the solvation of Sr^{2+} cation should be stronger than methanol of lower solvating ability (DN = 20), therefore, the stability of DCH18C6-Sr^{2+} complex increases as the concentration of water is lowered in MeOH–H$_2$O binary mixtures.

It is interesting to note that while the stability constant of DCH18C6-Sr^{2+} varies monotonically and linearly with the solvent composition in MeOH–H$_2$O binary mixtures, a very different behavior is observed for DCH18C6-Mg^{2+} complex (Figure 4). As is shown in Figure 4, the change in stability constant at various temperatures is not monotonic. Somewhat similar behavior is observed for DCH18C6-Ca^{2+} complex in the same binary systems. The anomalous behavior which is observed for variations of stability constants of DCH18C6-Mg^{2+} and DCH18C6-Ca^{2+} complexes versus the composition of MeOH–H$_2$O mixed solvents is due to some kinds of solvent–solvent interactions between these dipolar protic solvents and, therefore, changing the structure of solvent system when they are mixed with one another. It has been shown that the viscosity of the mixed solvents passes through a maximum which indicates the strong interaction between water and alcoholic solvents [28–30].

As illustrated in Table 2, the calculated thermodynamic parameters for DCH18C6-Mg^{2+}, DCH18C6-Ca^{2+}, DCH18C6-Sr^{2+} and DCH18C6-Ba^{2+} in MeOH–H$_2$O binary systems show that the ΔH_c° and ΔS_c° values are influenced by the solvent and vary with the solvent composition, but they do not vary monotonically with the solvent composition. Since there are many factors which contribute to changes in complexation enthalpies and entropies, we should not expect a regularity between these parameters and the solvent

composition of these binary mixture of associated solvents.

The variation of log K_f for formation of DCH18C6-Mg^{2+}, DCH18C6-Ca^{2+}, DCH18C6-Sr^{2+} and DCH18C6-Ba^{2+} complexes versus the ionic radii in two MeOH–H$_2$O binary mixtures (mol% MeOH = 30 and 60) is shown in Figure 5. As is evident in this Figure, the order of selectivity of these complexes at 25 °C is:

$$DCH18C6\text{-}Ba^{2+} > DCH18C6\text{-}Sr^{2+}$$
$$> DCH18C6\text{-}Ca^{2+} > DCH18C6\text{-}Mg^{2+}$$
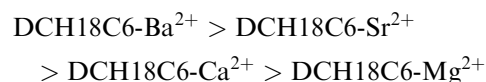
Similar selectivity order was observed in other compositions of the mixed solvent systems. The results in this investigation are similar to the results which have been obtained by Izatt and his coworkers [31] in studying of these complexes using calorimetry technique in aqueous solutions at 25 °C.

Acknowledgement

References

1. C.J. Pedersen: *J. Am. Chem. Soc.* **89**, 2495 (1967).
2. L. Alain and R. Robert: *Analyst* **2**, 218 (1973).
3. M. Hiraoka: *J.Am.Chem. Soc* . **33**, 782 (1975).
4. H.K. Frensdorff: *J.Am.Chem.Soc.* **93**, 600 (1971).
5. M. Hiraoka: *Shinzairyo Guide book* 75 (1975).
6. I. Zawisza, R. Bilewicz, E. Luboch and J.F. Biernat: *J. Electroanal. Chem.* **471** (2), 156 (1999).
7. J.D. Lamb, R.M. Izatt, J.J. Christensen and D.J. Eatough: in G.A. Melson, (ed.), *Coordination Chemistry of Macrocyclic Compounds*, Plenum Press, NewYork (1979) p. 145.
8. R.M. Izatt and D.P. Nelson: *Science* **164**, 443 (1969).
9. B.O. Strasser and A.I.Popov: *J. Am. Chem. Soc.* **107**, 789 (1985).
10. V.M. Loyola, R. Pizer and R.G. Wilkins: *J. Am. Chem. Soc*, **99** 7185 (1977).
11. G.H. Rounaghi, Z. Eshaghi and E. Ghiamati: *Talanta*, **43**, 1043 (1996).
12. A. Nezhadali, G.H. Rounaghi and M. Chamsaz: *Bull. Kor. Chem. Soc.* **21**, 685 (2000).
13. I.M. Kolthoff, W.J. Wang and M.K. Chantooni: *Anal. Chem.* **55**, 1202 (1983).
14. J. Massaux and J.F. Deseaz: *J .Am. Chem. Soc.* **104**, 2967 (1982).
15. R. Sinta, P.S. Rose and J. Smid: *J. Am. Chem. Soc.* **105**, 4337 (1983).
16. H.J. Buschmann, E.Cleve, S. Torkler and E. Schollmeyer: *Talanta* **51**, 145–149 (2004).
17. G.H. Rounaghi and A.I. Popov: *Polyhedron* **5**, 1329 (1986).
18. B.L. Hymore, J.D. Lamb, R.M. Izatt and J.J. Christensen: *Inorg. Chem.* **21**, 1598 (1982).
19. S. Katsuta, F. Tsuchiya and Y. Takeda: *Talanta* **51**, 637 (2000).
20. G.H. Rounaghi, Z. Eshaghi and E. Ghiamati: *Talanta* **44**, 275 (1997).
21. C. Erk and A. Gocmen: *Talanta* **53**, 137 (2000).

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22. E.C. Kempen and J.S. Brodbelt: *Anal. Chem.* **72**, (21) 5411 (2000).
23. T. Takayanagi, L.C. Manege and S. Motomizu: *J. Microcolumn Sep.* **12**, 113 (2000).
24. L.C. Manege, T. Takayanagi, M. Oshima and S. Motomizu: *Analyst* **125**, 699 (2000).
25. Genplot. Computer Graphic Service. U.S.A (1989).
26. Y. Takeda, H. Yano, M. Isuibashi and H. Isozumi: *Bull. Chem. Soc. Jpn.* **53**, 72 (1980).
27. G.H. Rounaghi, M. Samadi Kazemi and M. H. Soorgi: *Ind. J. Chem.* **40 A**, 345 (2001).
28. M. Mashima, T. Takase, S. Fukuda and N. Baba: *Bull. Chem. Soc. Jpn.* **49**, 2623 (1976).
29. M.S.K. Niazi: *Bull. Chem. Soc. Jpn.* **62**, 1253 (1989).
30. M.S.K.Niazi, S.S. Shah, J. Ali and M.I. Khan: *J. Solution Chem.* **19**, 623 (1990).
31. R.M. Izatt, D.P. Nelson, J.H. Rytting, B.I. Haymore and J.J. Christensen, *J. Am. Chem. Soc.* **93**, 1619 (1971).