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Determination of the Thermodynamic Parameters, Stoichiometry, and Stability Constants for Complex Formation of Dicyclohexyl-18-crown-6 and 15-Crown-5 with Y^{3+}, La^{3+}, and Hg^{2+} Cations in Binary Solutions[1]

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Abstract—The complexation of Y^{3+}, La^{3+}, and nd Hg^{2+} cations with macrocyclic ligands, dicyclohexyl-18-crown-6 (DCH18C6) and 15-crown-5 (15C5) have been studied in acetonitrile (AN)–*N*,*N*-dimethylformamide (DMF) binary solutions at different temperatures using conductometric method. The conductance data revealed 1 : 1 [ML] stoichiometry for most complexes in pure DMF and AN–DMF binary solutions, except for the (DCH18C6–Y^{3+}) complex in pure AN (1 : 2, [ML_2]). The stability constants of DCH18C6–La^{3+} and 15C5–La^{3+} in pure AN were higher than in pure DMF at all temperatures. Nonlinear behavior was observed for the stability constants of complexes against the composition of AN–DMF binary solutions at all temperatures. The minimum log K_f value for the 15C5–La^{3+} complex in AN–DMF binary solutions was obtained at $\chi_{AN} = 0.5$, which may be due to negative excess viscosities η^E of AN–DMF mixtures over the whole composition range with a minimum value of $\chi_{AN} = 0.5$. Moreover, the selectivity order of DCH18C6 and 15C5 for Y^{3+}, La^{3+}, and Hg^{2+} cations 25°C depended on the AN–DMF ratio. The thermodynamic parameters (ΔH^0_C) for complex formation were obtained from the temperature dependences of the stability constants of the complexes using the van't Hoff plots, and the standard entropy (ΔS^0_C) was calculated from the relationship: $\Delta G^0_{C,\,298.15} = \Delta H^0_C - 298.15\Delta S^0_C$.

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INTRODUCTION

It is well known that crown ethers react with various metal cations to form stable stoichiometric complexes [1]. The complexation of a solvated metal cation with crown ether may be treated as substitution of solvent molecules in the first solvation sphere by the ligand molecules. Therefore, the metal cation–solvent interaction competes with the metal cation–ligand interaction, and the stability of crown ether complexes in solution is expected to be affected mainly by the solvent nature in combination with the relative size of the cation and crown ether cavity.

Widespread use of non-aqueous solvents, especially dipolar aprotic ones, in various fields of pure and applied chemistry has contributed greatly to advances in chemical science and technologies. Taking into account that the solvation capacities of crown ether molecules and cations change with variation of a mixed solvent composition and that the species are solvated competitively by the constituent solvents, the effect of mixed solvent properties on the formation of crown ether–metal cation complexes is interesting.

Solvent effects on transition metal complexes were reviewed [2], and much attention was paid to binary solvent mixtures [3, 4]. It was shown that many properties change when solvents are mixed together; in particular such solvent characteristics as excess adiabatic compressibility (β^E), excess intermolecular free length (L^E_f), excess volume (V^E), excess viscosity (η^E), and excess acoustic impedance (Z^E) are of considerable interest in understanding the nature of intermolecular interactions in binary liquid mixtures [5–8].

In this work, we studied the effect of the composition of acetonitrile (AN)–*N*,*N*-dimethylformamide (DMF) binary solutions on the thermodynamic param-

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

Table 1. Complex formation constants log K_f of DCH18C6–Y^{3+}, DCH18C6–La^{3+}, and DCH18C6–Hg^{2+} in AN–DMF binary mixture at different temperatures

Solvent (molar ratio)	25°C	35°C	45°C	55°C
		DCH18C6–Y^{3+}		
DMF	2.74±0.03	2.74±0.02	2.65±0.02	2.67±0.03
AN–DMF (25 : 75)	2.85±0.05	2.69±0.03	2.70±0.01	2.61±0.07
AN–DMF (50 : 50)	2.96±0.07	3.02±0.06	2.62±0.08	2.94±0.04
AN–DMF (75 : 25)	2.91±0.02	[a]	[b]	2.87±0.08
AN	[c]	[c]	[c]	[c]
		DCH18C6–La^{3+}		
DMF	2.84±0.07	2.79±0.03	2.68±0.07	2.76±0.04
AN–DMF (25 : 75)	2.75±0.05	2.69±0.03	2.70±0.01	2.61±0.07
AN–DMF (50 : 50)	2.78±0.07	2.77±0.08	2.94±0.04	2.84±0.03
AN–DMF (75 : 25)	2.95±0.06	3.01±0.04	2.91±0.03	3.01±0.04
AN	>6	>6	>6	>6
		DCH18C6–Hg^{2+}		
DMF	[b]	[b]	[b]	[b]
AN–DMF (25 : 75)	[b]	[b]	[b]	[b]
AN–DMF (50 : 50)	>6	>6	>6	>6
AN–DMF (75 : 25)	[b]	[b]	[b]	[b]
AN	[b]	[b]	[b]	[b]

[a] Weak complex.
[b] Too large standard deviation.
[c] The data cannot be fitted in equation.

eters and the stability constant of complex formation of dicyclohexyl-18-crown-6 and 15-crown-5 with Y^{3+}, La^{3+}, and Hg^{2+} cations at different temperatures using the conductometric method.

EXPERIMENTAL

Dicyclohexyl-18-crown-6 (DCH18C6) (a mixture of *cis* and *trans* isomers; Merck), 15-crown-5 (15C5; Sigma–Aldrich), lanthanum chloride ($LaCl_3 \cdot 6H_2O$; Analar), Yttrium nitrate [$Y(NO_3)_3 \cdot H_2O$; Merck], and mercury(II) nitrate [$Hg(NO_3)_2$; Merck] were used without additional purification. Acetonitrile (AN) and *N*,*N*-dimethylformamide (DMF) (all from Merck) of highest purity were used.

The complex formation constants were determined according to the following procedure. A solution of metal salt (5×10^{-4} M) was placed in a titration cell, and the conductance of the solution was measured. A required amount of a solution of crown ether (2×10^{-3} M) was then quickly added to the titration cell so that to increase step-by-step the crown ether concentration, and the conductance of the resulting solution was measured after each addition step at a desired temperature. The conductance measurements were performed using an Elmetron CC-411 digital conductivity apparatus in a water-bath thermostat (Fanavaran Sahand Azar, model 4500) 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 0.94 cm^{-1} was used throughout the study.

RESULTS AND DISCUSSION

The changes of molar conductivity (Λ_m) versus the ligand to cation molar ratio for the complexation of DCH18C6 and 15C5 with Y^{3+}, La^{3+}, and Hg^{2+} cations

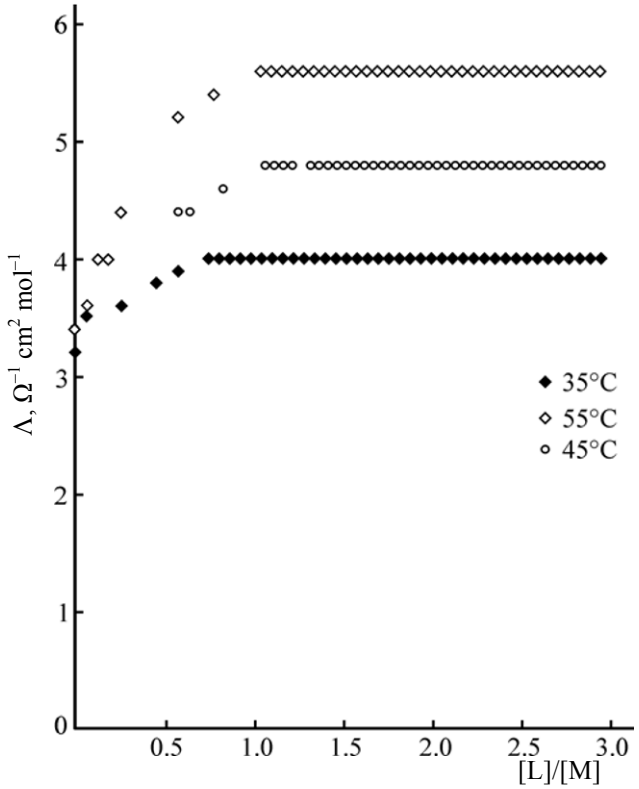

Fig. 1. Plots of the molar conductance versus the ligand-to-metal cation molar ratio for the complexation of 15C5 with Hg^{2+} in pure DMF.

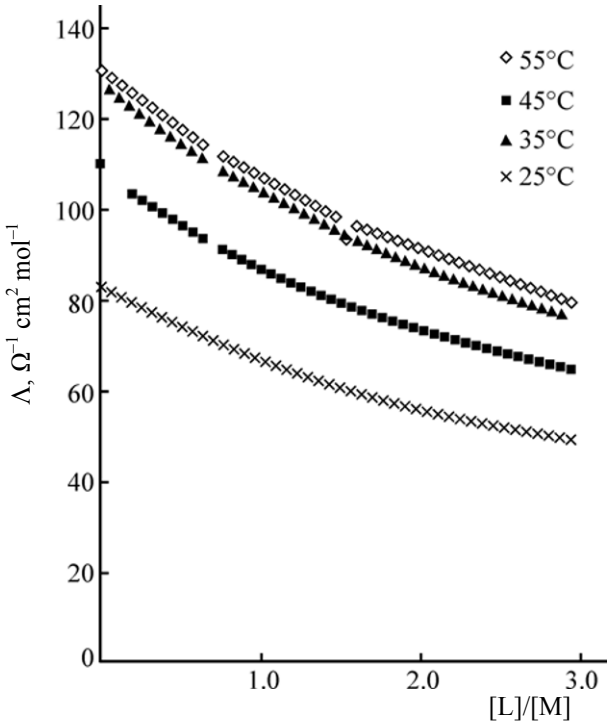

Fig. 2. Plots of the molar conductance versus the ligand-to-metal cation molar ratio for the complexation of 15C5 with La^{3+} in an AN–DMF binary mixture (AN/DMF molar ratio 75 : 25).

in AN–DMF binary solutions were studied at different temperatures. Figures 1–3 show three typical examples of molar conductance–molar ratio dependences. The stability constants (log K_f) for [DCH18C6–M^{n+}] and [15C5–M^{n+}] (M^{n+} = Y^{3+}, La^{3+}, Hg^{2+}) in AN–DMF mixtures are listed in Tables 1 and 2, respectively. The details of the calculation of stability constant of complexes were described previously [9].

The changes in the standard enthalpies (ΔH^0_C) for the complexation reactions were determined in the usual manner from the slopes of the van't Hoff plots, and the changes in the standard entropies (ΔS^0_C) were calculated from the relationship $\Delta G^0_{C,\,298.15} = \Delta H^0_C - 298.15\Delta S^0_C$. The results are summarized in Tables 3 and 4. A typical of example of the van't Hoff plot is shown in Fig. 4.

As is obvious from Fig. 1, addition of 15C5 to Hg^{2+} in pure DMF at different temperatures results in increase in the molar conductivity, which indicates that the 15C5–Hg^{2+} complex in DMF is more mobile than free solvated Hg^{2+} cation. However, the molar conductivity of 15C5–La^{3+} in AN–DMF (75 : 25 mol %) decreases with addition of 15C5; this means that the mobility of free solvated La^{3+} cation is higher than the mobility of the 15C5–La^{3+} complex (Fig. 2). These results show that the nature and composition of binary solution affect solvation of the cation, ligand, and obtained complex. On the other hand, in most cases the slope of the molar conductivity versus ligand-to-cation molar ratio plot sharply changes at the point where the ligand-to-cation molar ratio is about unity, indicating the formation of a relatively stable 1 : 1 [LM]. An exception was the DCH18C6–Y^{3+} complex in pure AN where the corresponding ligand-to-metal cation ratio was 2 : 1 [L_2M] (Fig. 3).

The 1 : 1 complexation reaction of a metal cation M^{n+} with crown ether is represented by the following equilibrium:

$$M^{n+} + L \leftrightarrow ML^{n+}$$

The corresponding equilibrium constant K_f is given by

$$K_f = \frac{[ML^{n+}]f^{n+}_{ML}}{[M^{n+}][L]f^{n+}_{M}f_L},$$

Table 2. Complex formation constants log K_f of 15C5–Y^{3+}, 15C5–La^{3+}, and 15C5–Hg^{2+} in AN–DMF binary mixtures at different temperatures

Solvent (molar ratio)	25°C	35°C	45°C	55°C
		15C5–Y^{3+}		
DMF	2.91±0.02	2.80±0.02	2.65±0.05	2.77±0.02
AN–DMF (25 : 75)	2.92±0.04	2.90 ±0.03	2.93±0.04	[a]
AN–DMF (50 : 50)	[b]	3.02±0.06	2.62±0.08	2.94±0.04
AN–DMF (75 : 25)	2.91±0.02	[a]	[b]	2.87±0.08
AN	[c]	[c]	[c]	[c]
		15C5–La^{3+}		
DMF	2.83±0.02	2.88±0.02	2.93±0.02	2.86±0.02
AN–DMF (25 : 75)	2.87±0.06	2.85±0.04	2.94±0.04	2.95±0.02
AN–DMF (50 : 50)	2.68±0.07	2.77±0.08	2.90±0.04	2.78±0.08
AN–DMF (75 : 25)	2.90±0.06	3.01±0.04	2.91±0.03	3.01±0.04
AN	[a]	>6	>6	>6
		15C5–Hg^{2+}		
DMF	[b]	>6	>6	>6
AN–DMF (25 : 75)	[b]	[b]	[b]	[b]
AN–DMF (50 : 50)	[b]	[b]	[b]	>6
AN	[b]	[b]	[b]	[b]

[a] Too large standard deviation.
[b] Weak complex.
[c] The data cannot be fitted in equation.

where $[ML^{n+}]$, $[M^{n+}]$, and [L] denote the molar concentrations of the complex, metal cation, and crown ether, respectively, and f stands for the activity coefficient of the above species. Under high dilution conditions employed in our experiments, the ratio $f_{ML}^{n+}/f_{M}^{n+} f_L$ approaches unity; therefore, the obtained equilibrium constants may be regarded as thermodynamic equilibrium constants.

As is seen from Tables 1 and 2, the stability constants log K_f of the DCH18C6–La^{3+} and 15C5–La^{3+} complexes at all temperatures in pure AN are higher than in pure DMF. The Gutmann donor number of acetonitrile is smaller than that of DMF (14.1 and 26.6, respectively) [10]; therefore, the solvation of metal cations by acetonitrile must be weaker than by the other solvent since the log K_f values of the corresponding complexes in AN are higher than in pure DMF.

Moreover, the stability of the complexes formed by metal cations with 15C5 in AN–DMF (25 : 75, 75 : 25) at 25°C decreases in the order: $Y^{3+} > La^{3+} > Hg^{2+}$ (Table 2), i.e., the most stable complex is that obtained from Y^{3+} and 15C5. This result is expected since the

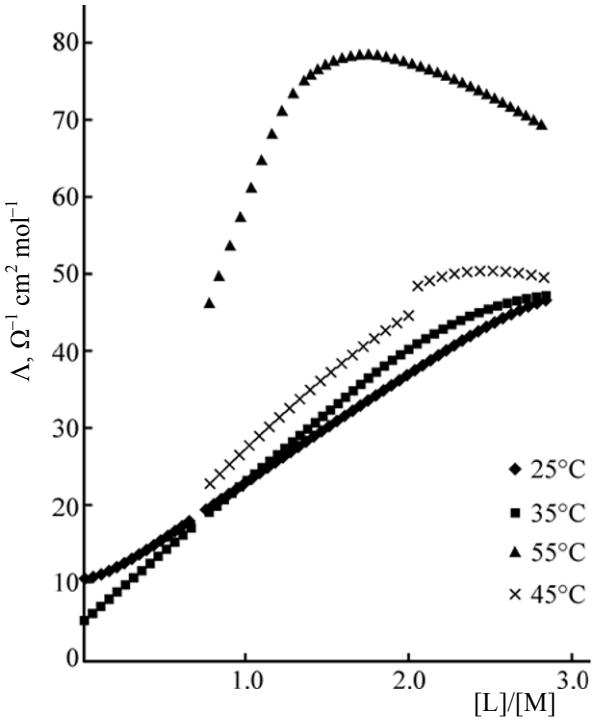

Fig. 3. Plots of the molar conductance versus the ligand-to-metal cation molar ratio for the complexation of DCH18C6 with Y^{3+} in pure acetonitrile.

Table 3. Selectivity orders of DCH16C6 and 15C5 for Y^{3+}, La^{3+}, and Hg^{2+} cations in various media at 25°C

Solvent (molar ratio)	DCH18C6	15C5
DMF	$La^{3+} > Y^{3+} > Hg^{2+}$	$La^{3+} > Y^{3+} > Hg^{2+}$
AN–DMF (25 : 75)	$La^{3+} > Y^{3+} > Hg^{2+}$	$Y^{3+} > La^{3+} > Hg^{2+}$
AN–DMF (50 : 50)	$Hg^{2+} > Y^{3+} > La^{3+}$	–
AN–DMF (75 : 25)	$La^{3+} > Y^{3+} > Hg^{2+}$	$Y^{3+} > La^{3+} > Hg^{2+}$

ion size of Y^{3+} (0.93 Å) [11] is very close to the size of the 15C5 cavity (0.86–1.1 Å). On the other hand, the ion size of La^{3+} (1.18 Å) [11] is close to the size of Hg^{2+} (1.16 Å) [11], but the former gives a more stable complex with 15C5. This may be rationalized by the higher charge density on La^{3+} as compared to Hg^{2+}, which ensures stronger interaction with the 15-crown-5 ligand.

As it can be figured out from Table 1, the stability constant of DCH18C6–Hg^{2+} is less than those of DCH18C6–La^{3+} and DCH18C6–Y^{3+} in pure DMF and AN–DMF binary solutions (25 and 75 mol % of AN). A probable reason is that the interaction between Hg^{2+} as a soft acid with the oxygen atoms of DCH18C6 as hard base is weaker than the interactions involving the other examined metal cations.

Comparison of the data in Tables 1 and 2 shows that the selectivity order for Y^{3+}, La^{3+}, and Hg^{2+} cations at 25°C changes with the composition of AN–DMF binary solutions. The selectivity orders of the DCH18C6 and 15C5 ligands for these cations are given in Table 3.

Figure 5 shows variation of log K_f versus the mole fraction of AN for the 15C5–La^{3+} complex in AN–DMF at different temperatures. The observed plots are nonlinear, and analogous patterns were revealed for 15C5–Y^{3+}, DCH18C6–Y^{3+}, and DCH18C6–La^{3+}, which may be associated with interaction between acetonitrile and *N*,*N*-dimethylformamide molecules. Dipolar AN molecules are oriented somewhat antiparallel to each other, while DMF dipoles are randomly oriented [12]. Ali et al. [13] showed that the values of excess adiabatic compressibility (β^E), excess intermolecular free length (L_f^E), excess volume (V^E), and excess viscosity (η^E) are negative for AN–DMF binary mixtures. The authors suggested that negative deviations from rectilinear dependence indicate the extent of dissociation or association between unlike molecules. The minimum log K_f value for the 15C5–La^{3+} complex corresponds to χ_{AN} = 0.5. It was also shown previously that the minimum excess viscosity η^E of AN–DMF binary mixtures is observed at χ_{AN} = 0.5, i.e., the viscosities of associates formed by unlike molecules (AN andDMF) are lower than those of the pure components.

The thermodynamic parameters (ΔH_C^0, ΔS_C^0 and ΔG_C^0) for the complexation between crown ethers and metal cations are summarized in Table 4. In most cases, the complexes are enthalpy destabilized but entropy stabilized; the changes of the thermodynamic parameters for the complexation in AN–DMF are determined by the solvent composition. The interaction

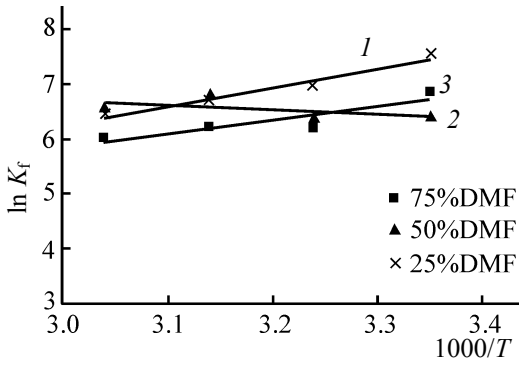

Fig. 4. Van't Hoff plots for the DCH18C6–La^{3+} complex in AN–DMF binary mixtures containing (*1*) 25, (*2*) 50, and (*3*) 75 mol % of acetonitrile.

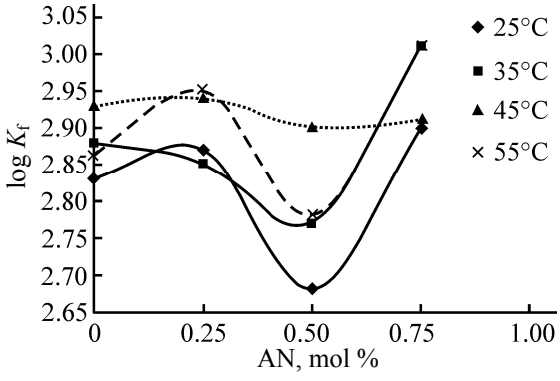

Fig. 5. Variation of the stability constants (logK_f) of the 15C5–La^{3+} complex with the mole fraction of acetonitrile (χ_{AN}) in AN–DMF binary mixtures at different temperatures.

Table 4. Thermodynamic parameters for the formation of the DCH18C6–Y^{3+}, DCH18C6–La^{3+}, 15C5–Y^{3+}, and 15C5–La^{3+} complexes in AN–DMF binary mixtures at 25°C

Solvent (molar ratio)	ΔH_C^0, kJ/mol	ΔS_C^0, J mol^{-1} K^{-1}	ΔG_C^0, kJ/mol
	DCH18C6–Y^{3+}		
DMF	–7.77±0.01	52.43±0.09	–15.64±0.13
AN–DMF (25 : 75)	–13.92±0.01	54.56±0.10	–16.28±0.17
	DCH18C6–La^{3+}		
DMF	[a]	[a]	–15.64±0.31
AN–DMF (25 : 75)	5.74±0.01	55.16±0.06	–16.41±0.09
AN–DMF (50 : 50)	24.02±0.04	51.36±0.01	–15.29±0.13
AN–DMF (75 : 25)	4.57±0.05	55.49±0.02	–16.55±0.11
	15C5–Y^{3+}		
DMF	–19.78±0.01	55.54±0.01	–16.58±0.06
AN–DMF (25 : 75)	1.05±0.01	55.87±0.02	–16.66±0.12
AN–DMF (75 : 25)	2.85±0.04	[a]	–16.58±0.06
	15C5–La^{3+}		
DMF	3.84±0.04	–56.10±0.01	–16.72±0.05
AN–DMF (25 : 75)	4.86±0.01	55.06±0.01	–16.41±0.20
AN–DMF (50 : 50)	[a]	[a]	–15.29±0.36
AN–DMF (75 : 25)	[a]	[a]	–16.56±0.19

[a] Too large standard deviation.

between unlike solvent molecules plays an important supplementary role. This leads to large deviations from the ideal behavior expected from Raoult's law for vapor pressure depression of binary systems. Sharma et al. [14] suggested that molecular association between AN and DMF may be attributed to the interaction either between a fractional negative charge on the nitrogen atom of AN and fractional positive charge on the hydrogen atom of DMF or between a fractional positive charge on the nitrogen atom of DMF and π-electron cloud of the triple bond of the AN molecule.

CONCLUSIONS

The stability, selectivity, and thermodynamic parameters of the formation of crown ether complexes with metal cations depend on several factors such as the cavity size of the ligand, the character of heteroatoms in the polyether ring, and the diameter and nature of the cation. The results obtained in this work show that the solvent nature and composition of binary solution are also important, since the stability and the order of selectivity of DCH18C6 and 15C5 for Y^{3+}, La^{3+}, and Hg^{2+} cations change in AN–DMF binary mixtures. Conductometric measurements revealed the 1 : 1 [LM] stoichiometry for most complexes, except for the 2 : 1 complex [L_2M] obtained from DCH18C6 and Y^{3+} in pure acetonitrile.

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REFERENCES

1. Izatt, R.M., Pawlak, K., Bradshow, J.S., and Bruening, R.L, *Chem. Rev*., 1991, vol. 91, p. 1721.
2. Hush, N.S. and Reimers, J.R., *Chem. Rev*., 2000, vol. 100, p. 775.
3. Gholami, M.R. and Yangieh, A.H., *Anal. Sci*., 2005, vol. 21, p. 945.
4. Reichardt, C., *Solvents and Solvent Effects in Organic Chemistry*, New York, VCH, 1990, 2nd ed.
5. Dewan, R.K., Mehta, S.K., Parashar, L., and Bala, K., *J. Chem. Soc., Faraday Trans*., 1991, vol. 87, p. 1561.
6. Ali, A. and Nain, A.K., *Acoustics Lett*., 1996, vol. 19, p. 181.
7. Ali, A., Nain, A.K., and Kamil, M., *Thermochim Acta*, 1996, vol. 274, p. 209.
8. Mehra, R., *Phys. Chem*., 2005, vol. 219, p. 425.
9. Rounaghi, G.H., Gerry, G.N., and Kazemi, M.S., *J. Inclusion Phenom. Macrocyclic Chem*., 2006, vol. 55, p. 167.
10. Izutsu, K., *Electrochemistry in Nonaqueous Solutions*, Weinheim: Wiley, 2002.
11. Kalidas, C., Hefter, G., and Marcus, Y., *Chem. Rev*., 2000, vol. 100, p. 819.
12. Piekarski, H. and Piekarski, A., *Phys. Chem*., 2004, vol. 218, p. 679.
13. Ali, A., Hyder, S., and Nain, A.K., *J. Mol. Liq*., 1999, vol. 79, p. 89.
14. Sharma, A.K., Sharma, D.R., and Gill, D.S., *J. Phys. D: Appl. Phys*., 1985, vol. 18, p. 1119.