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PHYSICAL CHEMISTRY OF SOLUTIONS

Complexation Study of Cryptand 222 with Lanthanum(III) Cation in Binary Mixed Non-aqueous Solvents[1]

S. Dolatshahi, G. H. Rounaghi, and S. Tarahomi

Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran

e-mail: ghrounaghi@yahoo.com, ronaghi0970@mshdiau.ac.ir, tarahomis@yahoo.com

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Abstract—Conductometric titrations have been performed in some binary solvent solutions of acetonitrile (AN), 1,2–dichloroethane (DCE), ethylacetate (EtOAc) and methylacetate (MeOAc) with methanol (MeOH), at 288, 298, 308, and 318 K to give the complex stability constant and the thermodynamic parameters for the complexation of lanthanum(III) cation with 4,7,13,16,21,24–hexaoxa–1,10–diazabicyclo[8.8.8]–hexacosane (cryptand 222). The stability constant of the resulting 1:1 complex at each temperature was determined from computer fitting of the conductance-mole ratio data. The results revealed that, the stoichiometry and the stability order of (cryptand 222 · La)$^{3+}$ complex changes with the nature and also the composition of the solvent system. A non-linear relationship was observed between the stability constant ($\log K_f$) of (cryptand 222 · La)$^{3+}$ complex versus the composition of the binary mixed solvents. Thermodynamically, the complexation of lanthanum(III) cation with the cryptand 222, is mainly entropy governed and the values of these parameters are influenced by the nature and composition of the binary mixed solvent solutions.

Keywords: cryptand 222, La^{3+}, mixed non-aqueous solvents, conductometry.

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INTRODUCTION

Cryptands are macrobicyclic amines with polyether linkages connecting the bridgehead nitrogen atoms. They are usually spherical and capable of encapsulating metal ions in their cage-like cavities to form stable complexes. Since their discovery by Lehn and co-workers, a considerable amount of work has been published on the interactions of these molecules with metal cations in aqueous and non-aqueous media [1, 2]. These investigations have pointed out that various factors may contribute to the stability of the inclusion compounds (cryptates) formed by the cryptands; among these, of particular importance are the relative sizes of the cation and the ligand cavity, the number of co-ordination sites of the ligand, the charge density of the cation, the solvent properties, and the nature of the metal–ligand interactions.

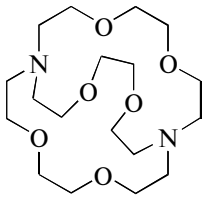
Experimental investigations on the complex-formation reactions of alkali– and alkaline–earth–metal ions with cryptands in aqueous solution can easily be carried out, while the same measurements with lanthanide(III) ions have proved to be rather difficult for two reasons: the very slow kinetics of formation and the metal-ion hydrolysis, which can compete with the cryptate formation [3]. In order to overcome these difficulties and to study the solvent effect, a number of investigations have been carried out in mixed (water–solvent) or anhydrous solvents [4–6].

The combination of pure solvents as mixed solvents substantially increases the diversity of reaction media. Investigation of solvent effects on thermodynamic and kinetic functions is interesting both experimentally and theoretically in chemical and biochemical analysis. The study of solvent effects on chemical and physical processes in binary mixtures is more complicated than in pure solvents, because the solute–solvent and solvent–solvent interactions can create new solvent properties leading to preferential solvation.

The study of complexation reactions of cryptands with metal cations in non-aqueous matrices could be used as an efficient strategy to design the analytical systems such as, potentiometric sensors, bulk liquid membrane transport, optical sensors, solid phase extraction and biochemistry fields. Thus, thermodynamic studies of macrocyclic complexation reactions with metal cations not only provide relevant information on the binding process, but also lead to a better understanding of the selective behavior of these ligands toward different metal cations.

In continuation of our previous works [7–9], here, we report the results of a conductometric study for determination of the stoichiometry, stability and thermodynamic parameters of cryptand 222:

[1] The article is published in the original.



complex with La^{3+} cation in acetonitrile–methanol (AN–MeOH), 1,2 dichloroethane–methanol (DCE–MeOH), ethylacetate–methanol (EtOAc–MeOH), and methylacetate–methanol (MeOAc–MeOH) binary solvent solutions.

EXPERIMENTAL

Reagents and Apparatus

The analytical-grade $LaCl_3$ (Merck, 99.9%) and cryptand 222 (Kryptofix Merck, 98%) were used without further purification except vacuum drying. The organic solvents (all from Merck, >99% purity) were used without further purification. The conductivity of each solvent was less than 3.0×10^{-7} S^{-1} cm^{-1} at 25°C. All conductance titrations were performed using a digital Metrohm conductometer (model 712). All solutions were thermostated at a constant temperature that was maintained within ±0.01 K by circulation of thermostated water through the outer jacket of the cell. The solutions were stirred with a magnetic stirrer, and the electrolytic conductance was measured using a double-walled glass conductivity cell consisting of two platinum electrodes to which an alternating potential was applied. The calibration of conductometric cell was made with the use of an aqueous KCl (0.1 mol L^{-1}) solution and the cell constant was determined to be 0.89 cm^{-1}.

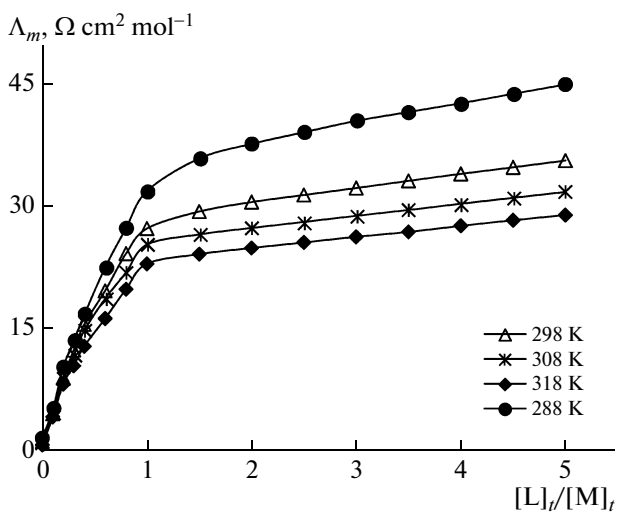


Fig. 1. Molar conductance–mole ratio plots for the (cryptand 222 · La)$^{3+}$ complex in MeOAc–MeOH ([MeOAc] = 90%) binary solution at different temperatures.

Procedure

The experimental procedure to obtain the stability constant of the (cryptand 222 · La)$^{3+}$ complex by conductometric procedure was as follows: A solution of metal salt (1.0×10^{-4} mol L^{-1}, 20 mL) was placed in a titration cell, thermostated at a given temperature, and the conductance of the solution was measured. Then the solution of the ligand (2×10^{-3} mol L^{-1}) was transferred step-by-step to the titration cell using a precalibrated microburette and the conductance of the solution was measured after each transfer at the desired temperature. Addition of the ligand solution was continued until the total concentration of the ligand was approximately five times higher than that of metal ion. The conductance of the solution was measured after each addition and the data were used for the calculation of the stability constant of the complex.

RESULTS AND DISCUSSION

Conductance Studies

The complex formation between cryptand 222 and the La^{3+} cation in AN–MeOH, DCE–MeOH, EtOAc–MeOH, and MeOAc–MeOH binary mixtures was investigated by molar conductance changes upon addition of the ligand to the La^{3+} cation solution at 288, 298, 308, and 318 K. Some of the resulting molar conductance (Λ_m) versus cryptand 222 to La^{3+} molar ratio ($[L]_t/[M]_t$) plots are shown in Fig. 1. As is evident from this figure, addition of cryptand 222 to the solution of the La^{3+} in MeOAc–MeOH ([MeOAc] = 90%) binary solution at different temperatures results in an increase in molar conductivity with an increase in the ligand concentration which indicates that the (cryptand 222 · La)$^{3+}$ complex is more mobile than the free solvated La^{3+} cation. A similar behavior was observed in most of the binary mixed nonaqueous solvents.

The slope of the corresponding molar conductivity versus ligand/cation mole ratio plots changes at the point where the ligand–to–cation mole ratio is about 1, which is evidence for the formation of a relatively stable 1 : 1 complex between cryptand 222 and La^{3+} cation. The ML program selected gave the best statistical fit with the titration data which emphasizes the formation of a ML complex.

It is interesting to note that the complexation of La^{3+} cation with cryptand 222 in DCE–MeOH binary solutions are totally different from those of the other solutions. As can be seen from Fig. 2, addition of cryptand 222 to La^{3+} solution in DCE–MeOH ([DCE] = 50%) system causes the molar conductivity to decrease until the mole ratio reaches 1 : 1, and then to increase. This may be explained in terms of following equilibria:

$$(La^{3+}, 3Cl^-) + \text{cryptand} \longleftrightarrow (La^{3+} \cdot \text{cryptand} \cdot 3Cl^-),$$

$$(La^{3+} \cdot \text{cryptand} \cdot 3Cl^-) + \text{cryptand} \longleftrightarrow [La^{3+}(\text{cryptand})_2] + 3Cl^-.$$

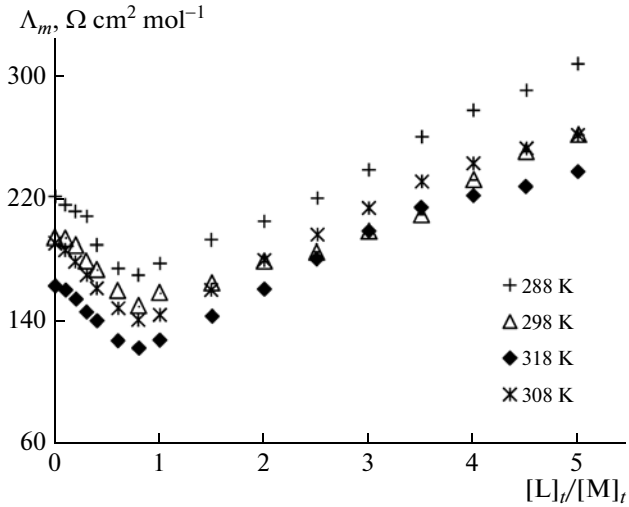


Fig. 2. Molar conductance–mole ratio plots for the (cryptand 222 · La)$^{3+}$ complex in DCE–MeOH ([DCE] = 50%) binary solution at different temperatures.

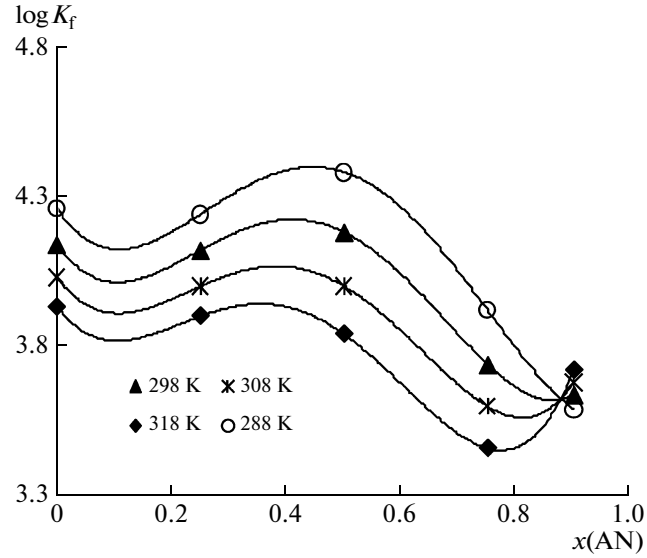


Fig. 3. Changes of the stability constant (log K_f) of the (cryptand 222 · La)$^{3+}$ complex with the mole fraction of AN in AN–MeOH binary solution at different temperatures.

It seems that addition of cryptand 222 to La^{3+} results in the formation of a stable 1 : 1 (ML) complex which is present as an ion-pair. Further addition of cryptand 222 to the ion-pair complex causes formation of a 1 : 2 (ML_2) complex with a sandwich structure which decreases the space for diffusion and interaction of Cl^- with La^{3+} resulting in dissociation of the ion-pair and, therefore, the molar conductivity increases.

Calculation of Complex Formation Constant

The 1 : 1 binding of metal cation with macrocylic ligand can be expressed by the following equilibrium:

$$M^{n+} + L \longrightarrow ML^{n+}. \quad (1)$$

The corresponding equilibrium constant, K_f, is given by:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} \times \frac{f_{(ML^{n+})}}{f_{(M^{n+})} f_{(L)}}, \quad (2)$$

where $[ML^{n+}]$, $[M^{n+}]$, [L], and f, represent the equilibrium molar concentrations of the complex, free cation, ligand and the activity coefficient of the indicated species, respectively. In this paper, L = cryptand 222 and $M^{n+} = La^{3+}$. Under the dilute experimental conditions that we used, the activity coefficient of the uncharged ligand, $f_{(L)}$, can reasonably be assumed to be unity [10]. The use of Debye Huckel limiting law of 1 : 1 electrolytes leads to the conclusion that, $f_{(M^{n+})} \sim f_{(ML^{n+})}$, therefore, the activity coefficient in Eq. (2) is cancelled out.

The mass balance equation of ML type equations

$$c_M = [M^{n+}] + [ML^{n+}], \quad (3)$$

$$c_L = [L] + [ML^{n+}] \quad (4)$$

used in computer program GENPLOT should be solved in order to obtain for the free ligand concentration [L], equation

$$K_f[L]^2 + (1 + K_f(c_M - c_L))[L] - c_L = 0. \quad (5)$$

The complex formation constant in terms of the molar conductivity can be expressed as [10, 11]

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]}, \quad (6)$$

where

$$[L] = c_L - c_M(\Lambda_M - \Lambda_{obs})/(\Lambda_M - \Lambda_{ML}), \quad (7)$$

c_L is the total concentration of the ligand, [L] is the free concentration of the ligand, c_M is the total concentration of the cation; Λ_M represents the molar conductance of the cation solution before addition of the ligand, Λ_{obs} corresponds to the molar conductivity of the solution during titration and Λ_{ML} is the molar conductance of the complexed ion.

The complex stability constant (K_f) was calculated by computer fitting of Eqs. (6) and (7) to the molar conductance-mole ratio data by using a nonlinear least-squares program. The calculations were obtained from approximately 16 experimental points in each titration using the computer program GENPLOT [12]. Under the highly dilute experimental conditions used, association as ion-pairs has been considered negligible. Since the concentration of cryptand 222 was kept below 2.0×10^{-3} mol L^{-1} during the experiments, corrections for the viscosity changes were also neglected. The complex stability constants (log K_f) obtained are listed in Table 1.

Table 1. Stability constant ($\log K_f \pm$ SD) values for the (cryptand 222 · La)$^{3+}$ complex in binary mixed nonaqueous solvents at different temperatures

MeOH, mol %	288 K	298 K	308 K	318 K
AN–MeOH				
0	b	b	b	b
10	3.59 ± 0.03	3.64 ± 0.05	3.68 ± 0.04	3.72 ± 0.03
25	3.92 ± 0.03	3.74 ± 0.06	3.60 ± 0.10	3.46 ± 0.11
50	4.38 ± 0.09	4.18 ± 0.05	4.00 ± 0.05	3.84 ± 0.06
75	4.24 ± 0.20	4.12 ± 0.10	4.00 ± 0.07	3.90 ± 0.06
100	3.78 ± 0.10	4.14 ± 0.10	4.02 ± 0.08	3.93 ± 0.06
DCE–MeOH				
0	b	b	b	b
10	c	c	c	c
25	c	c	c	c
50	c	c	c	c
75	c	c	c	c
100	c	c	c	c
EtOAc–MeOH				
0	b	b	b	b
10	4.89 ± 0.13	5.06 ± 0.18	5.24 ± 0.25	5.40 ± 0.28
25	4.17 ± 0.04	4.38 ± 0.04	4.57 ± 0.05	4.76 ± 0.06
50	3.70 ± 0.04	3.80 ± 0.04	3.91 ± 0.03	3.98 ± 0.05
75	3.91 ± 0.08	3.59 ± 0.08	3.40 ± 0.08	3.15 ± 0.07
100	3.78 ± 0.10	4.14 ± 0.10	4.02 ± 0.08	3.93 ± 0.06
MeOAc–MeOH				
0	b	b	b	b
10	4.78 ± 0.08	5.03 ± 0.15	5.24 ± 0.21	5.47 ± 0.18
25	4.14 ± 0.05	4.43 ± 0.06	4.64 ± 0.09	4.86 ± 0.09
50	3.53 ± 0.05	3.51 ± 0.04	3.49 ± 0.03	3.47 ± 0.09
75	3.58 ± 0.07	3.46 ± 0.15	3.36 ± 0.08	3.25 ± 0.11
100	3.78 ± 0.10	4.14 ± 0.10	4.02 ± 0.08	3.93 ± 0.06

Note: SD is standard deviation. (b) The salt is not dissolved. (c) The data can not be fitted to equations.

Effect of Solvent Composition

Comparison of the data given in Table 1 reveals that the stability constant of the (cryptand 222 · La)$^{3+}$ complex in the binary mixed solvent solutions with 10 and 25 mol % of MeOH, varies in the order: MeOAc–MeOH ≥ EtOAc–MeOH > AN–MeOH. This can be attributed to the higher dielectric constant of AN (ε = 36) compared with EtOAc (ε = 6.02) and MeOAc (ε = 6.7) which results in a decrease in electrostatic interaction between cryptand 222 and La^{3+} cation in solution. But as is evident in this table, the stability order of the complex in the binary mixed solvent systems with 50 and 75 mol % of MeOH, changes to: AN–MeOH > EtOAc–MeOH ≥ MeOAc–MeOH. The results obtained in this study, reveal that the stability constant of the complex is dependent on the solvent composition.

On the other hand, stability of the resulting complex decreases with increasing the concentration of MeOH in EtOAc–MeOH and MeOAc–MeOH binary solutions. There is actually an inverse relationship between the stabilities of the complexes and the solvating abilities of the solvents. Since methanol has a higher donicity (DN = 20.0) than EtOAc (DN = 17.1), and MeOAc (DN = 16.5), therefore, it shows more competition than EtOAc and MeOAc molecules for La^{3+} cation. In addition, the ligand may be more solvated by MeOH molecules via hydrogen bonding with respect to the two other organic solvents. Furthermore, when the concentration of MeOH increases, the formation of the (cryptand 222 · La)$^{3+}$ complex is weakened. This result may indicate that the solvating ability of the solvent is more important in the recognition of ions by macrocyclic compounds.

The change in stability constant ($\log K_f$) of (cryptand 222 · La)$^{3+}$ complex versus the composition of the binary mixed solvents shows a nonlinear profile at all systems, this profile for AN–MeOH binary solution is plotted in Fig. 3. This behavior can be explained on the basis of the solvent-solvent interactions between the two constituent solvent molecules which result in changing the structure of the solvent systems with their composition and, therefore, changing the solvation numbers of the La^{3+}, cryptand 222 and even the (cryptand 222 · La)$^{3+}$ complex in solutions. In addition, it may be due to the formation of mixed solvates in the binary mixed solvent solutions. In addition, this non-monotonic behavior, probably reflects a balance between the solvation properties, donicity, dielectric constant, hydrogen bonding ability, etc. of the solvent systems.

Thermodynamic Calculations

To have a better understanding of the thermodynamics of the complexation reaction, the enthalpic and entropic contributions of the reaction were evaluated from the slope and intercept of the van't Hoff plots, respectively.

$$2.303R\log K_f = -\Delta H/T + \Delta S.$$

Plots of $\log K_f$ versus $1/T$ in all cases were linear, a typical example of these plots is shown in Fig. 4. The values of the corresponding standard thermodynamic quantities are given in Table 2. It is immediately obvious from these data, that in most of cases, the enthalpy values of (cryptand 222 · La)$^{3+}$ complex are positive

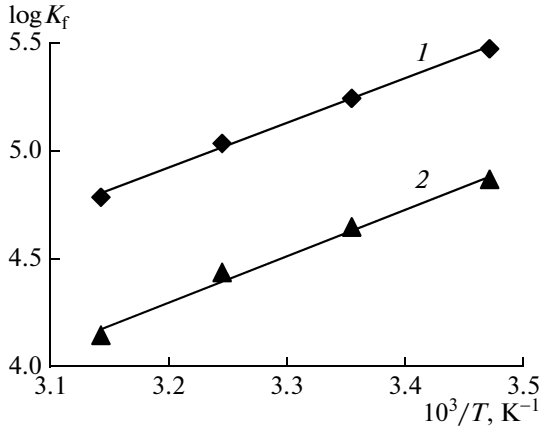


Fig. 4. van't Hoff plots for the (cryptand 222 · La)$^{3+}$ complex in MeOAc–MeOH([MeOAc] = 10% (*1*) and 25% (*2*)) binary solutions.

with positive entropic changes. This means that the complexation process between La^{3+} cation and cryptand 222 is chiefly entropy driven. This is reasonably accounted that the positive entropy changes are related to the extensive desolvation of the cation and the ligand upon complexation [13, 14].

Table 2. Thermodynamic parameters (±SD) for the (cryptand 222 · La)$^{3+}$ complex in binary mixed nonaqueous solvents at different temperatures

MeOH, mol %	$-\Delta G_c^\circ$ (25°C), kJ/mol	ΔH_c°, kJ/mol	ΔS_c°, J/(mol K)
AN–MeOH			
10	20.74 ± 0.20	7.5 ± 0.1	95.0 ± 0.4
25	21.43 ± 0.80	−26.5 ± 0.6	−17.0 ± 2
50	23.91 ± 0.30	−31.3 ± 0.2	−25.0 ± 0.7
75	23.52 ± 0.30	−19.8 ± 0.2	−12.0 ± 0.8
100	23.64 ± 0.20	b	b
EtOAc–MeOH			
10	28.88 ± 0.90	29.7 ± 0.7	197.0 ± 2.3
25	24.94 ± 0.70	34.1 ± 0.5	198.0 ± 1.6
50	21.68 ± 3.40	16.5 ± 2.4	128.0 ± 8.0
75	20.75 ± 3.40	43.0 ± 2.4	75.0 ± 8.0
100	23.64 ± 0.02	b	b
MeOAc–MeOH			
10	28.61 ± 1.30	39.65 ± 0.90	229.0 ± 3.1
25	25.09 ± 1.90	41.3 ± 1.3	223.0 ± 4.4
50	20.02 ± 0.20	b	56.0 ± 0.4
75	19.77 ± 0.60	18.9 ± 0.4	3.0 ± 1.5
100	23.64 ± 0.02	b	b

Note: (b) With high uncertainty.

As is evident from Table 2, the standard thermodynamic parameters do not vary monotonically with the solvent composition. This is due to the variation in the extent of the contribution of such important parameters as solvation-desolvation of the species involved in the complexation reaction i.e., La^{3+}, cryptand 222 and (cryptand 222 · La)$^{3+}$ complex and also the conformational changes of the ligand in the solutions. Similar behaviors have previously been reported for various complexes in several binary mixed solvents [7–9, 15].

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REFERENCES

1. R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, and J. J. Christensen, Chem. Rev. **85**, 271 (1985).
2. M. Shamsipur and J. Ghasemi, J. Incl. Phenom. Macrocycl. Chem. **20**, 117 (1994).
3. A. Cassol, P. di Bernardo, G. Pilloni, M. Tolazzib, and P. L. Zanonato, J. Chem. Soc. Dalton Trans., p. 2689 (1995).
4. G. Anderegg, Helv. Chim. Acta **64**, 1790 (1981).
5. R. Pizer and R. Selzer, Inorg. Chem. **22**, 1359 (1983).
6. H.-J. Bushmann, G. Wenz, E. Schollmeyr, and L. Mutihac, Inorg. Chem. Commun. **4**, 211 (2001).
7. G. H. Rounaghi, E. Nazari, and A. Ghaemi, J. Coord. Chem. **63**, 2349 (2010).
8. G. H. Rounaghi, R. Rahmanian, M. Mohajeri, and S. Tarahomi, J. Solution Chem. **40**, 377 (2010).
9. G. H. Rounaghi and S. Heydari, Russ. J. Coord. Chem. **34**, 836 (2008).
10. M. R. Ganjali, A. Rohollahi, A. Moghimi, and M. Shamsipur, Pol. J. Chem. **70**, 1172 (1996).
11. G. R. Khayatian, M. Shamsipur, and S. Shariati, J. Incl. Phenom. Macrocycl. Chem. **45**, 117 (2003).
12. *Genplot, A Data Analysis and Graphical Plotting Program for Scientist and Engineers*, Computer Graphic Service (Ltd, Ithaca, New York, 1989).
13. C. Möller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).
14. M. Shamsipur and H. R. Pouretedal, J. Solution Chem. **28**, 1187 (1999).
15. M. Jozwiak, Thermochim. Acta **417**, 31 (2004).