

# Thermodynamics of Cesium Cation Complexation with Dibenzo-24-Crown-8 in Mixed Nonaqueous Solvents

JACQUELINE E. STEFFENS and SADEGH KHAZAEI\*

*Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026, USA.*

(Received: 21 November 1994; in final form: 17 May 1995)

**Abstract.** Thermodynamics of complexation of cesium cation by dibenzo-24-crown-8 was studied in three binary solvent mixtures: acetonitrile–nitromethane (AN/NM), *N,N*-dimethylformamide–nitromethane (DMF/NM) and acetonitrile–propylene carbonate (AN/PC) using the  $^{133}\text{Cs}$ -NMR technique. In all cases the variation of the formation constant,  $K_f$ , with the solvent composition was monotonic:  $K_f$  increased as the mole-% of the solvent of low donicity was increased. The temperature dependence of  $K_f$  indicated that the complexes are generally enthalpy stabilized, but entropy destabilized. The enthalpy and entropy of complexation reactions are quite sensitive to the solvent composition. However, their variation with solvent composition was not monotonic but showed maxima or minima at the isosolvation points of the cation or the complexed cation. In all cases an enthalpy–entropy compensating effect was observed.

**Key words:** Crown ether,  $^{133}\text{Cs}$ -NMR, enthalpy–entropy compensation, mixed-solvents.

## 1. Introduction

Thermodynamics of macrocyclic complexes of alkali and alkaline earth cations have been investigated mainly in water, water–methanol and neat nonaqueous solvents [1–6]. It has been shown that the selectivity of complexation not only depends on the ratio of the cation diameter and the diameter of the crown ether cavity, but also on the solvating ability of the solvent with respect to both the cation and the complex [8–14]. Therefore, studies of the complexation reactions as a function of the solvent composition in binary solvent mixtures might be used to investigate the factors which contribute to the changes in complexation enthalpies and entropies and hence the selectivity of the crown ethers towards cations.

Izatt and Wu reported the thermodynamic parameters of complexation of alkali metal cations by crown ethers in dioxane–water mixtures [15]. Popov and coworkers [16] studied the complexation of  $\text{Cs}^+$  ion with dibenzo-21-crown-7(DB21C7) and dibenzo-24-crown-8(DB24C8) in five binary solvent mixtures at ambient temperature. The temperature dependence of the formation constant of  $\text{Cs}^+$  cation complexes with these ligands was also studied in DMF–AN binary solvent mixture [17]. These studies showed that a decrease in the concentration of DMF, the solvent

\* Author for correspondence.

with higher Gutmann donor number [18], resulted in a more negative  $\Delta H_c$  and a less negative  $\Delta S_c$ .

In this paper we extend the thermodynamic studies of complexation of DB24C8 with the  $\text{Cs}^+$  cation to three more binary solvent systems: AN/NM, DMF/NM, and AN/PC. Only 1:1 complexes were formed in all of the solvent mixtures used. Complex formation constants,  $K_f$ , were obtained from the variation of the  $^{133}\text{Cs}$  chemical shift as a function of  $C_{\text{ligand}}/C_{\text{salt}}$  molar ratio at constant  $C_{\text{salt}}$ . Enthalpy and entropy of complexation reactions were obtained from the temperature dependence of the  $K_f$  values.

## 2. Experimental

### 2.1. CHEMICALS

The ligand 1,13-dibenzo-24-crown-8 (DB24C8, Aldrich) was recrystallized from *n*-heptane and was dried under vacuum over Drierite for several days [17].

Sodium tetraphenylborate (Fischer) was dried under vacuum for several days. Cesium tetraphenylborate ( $\text{CsBPh}_4$ ) was prepared by dissolving equimolar amounts of cesium chloride (Alpha Inorganics) and sodium tetraphenylborate in tetrahydrofuran (Fischer), and adding water to precipitate out  $\text{CsBPh}_4$  [19]. The solution was cooled in an ice bath, vacuum filtered and washed with copious amounts of deionized water.  $\text{CsBPh}_4$  was dried under reduced pressure over Drierite for two days. Atomic absorption analysis showed less than 0.0005% sodium contamination.

Nitromethane (NM, Mallinkrodt) and acetonitrile (AN, Aldrich) were refluxed over calcium hydride for at least two days, then fractionally distilled onto freshly activated 3 Å molecular sieves [20]. *N,N*-dimethylformamide (DMF, Aldrich) and propylene carbonate (PC, Aldrich) were refluxed under reduced pressure over calcium hydride, then vacuum distilled onto 3 Å molecular sieves. Only the middle 70% of the distilled solvents were collected. All purified solvents were stored in a dry box under nitrogen atmosphere. The water content of the purified solvents was measured by Karl Fischer titration and found to be less than 100 ppm while never exceeding 250 ppm when measured at the end of the experiment.

Stock solutions of  $\text{CsBPh}_4$  (0.0050M) were prepared in proper solvent mixtures by direct weighing of salts. Samples for NMR measurement were prepared by placing weighed amounts of the ligand in 2 mL volumetric flasks and diluting with the salt stock solution and then transferring to the 10 mm o.d. NMR tubes (Wilmad). Sample preparation was performed in the dry box.

### 2.2. MEASUREMENTS

Cesium-133 chemical shift measurements were performed on a JEOL-FX-90Q pulsed Fourier transform spectrometer operating at a field strength of 2.114 Tesla and equipped with a  $^2\text{D}$  external lock and a variable temperature probe. On this

spectrometer  $^{133}\text{Cs}$  resonates at 11.70 MHz. The spectra were obtained with a sweep width of 1300 Hz and 8 K points.

Cs-133 chemical shifts were initially referred to a 0.7 M CsBr solution in  $\text{D}_2\text{O}$  which was sealed in a 5 mm o.d. NMR tube and coaxially mounted in a 10 mm o.d. NMR tube. The space between the tubes was evacuated to maintain the temperature of the reference sample at ambient temperature [21]. The chemical shift of the reference sample was set to zero between each sample run, by placing the reference sample in the probe for the short period required for one pulse. The chemical shift of the reference stayed the same within 0.05 ppm. All chemical shifts were corrected for the difference in the bulk diamagnetic susceptibility [22] of the solvent and the aqueous solution and then were referred to infinitely dilute  $\text{Cs}_{(\text{aq})}^+$  solution. Downfield (paramagnetic) shift is positive.

Variable temperature measurements were made by using the JEOL NM-5471 temperature controller. The probe temperature was monitored by a Beckman Dovie 410 A temperature indicator equipped with a copper–constantan thermocouple. The thermocouple was immersed in methanol or DMF in a 10 mm o.d. NMR tube and was placed in the probe to measure the sample temperature indirectly. Sample temperatures are accurate within  $\pm 1^\circ\text{C}$ .

Atomic absorption measurements were made on a Varian SpectrAA-10 instrument. The water content of the solvents was measured with a model 684 KF Metrohm coulometer.

### 2.3. METHOD

In all cases the exchange of the cation between the free solvated and complexed sites was fast on the NMR time scale and only one population-averaged signal was observed. Also, only 1 : 1 (ligand : metal cation) complexes were formed according to the following equation.



The polynomial in terms of the free ligand concentration,  $[L]$ , was derived from the equilibrium constant expression and the mass balance equation:

$$K_f[L]^2 - \{K_f(C_L - C_M) - 1\}[L] - C_L = 0 \quad (2)$$

where  $C_L$  and  $C_M$  are the analytical concentrations of the ligand and the salt, respectively. The observed chemical shift,  $\delta_{\text{obs}}$ , is expressed by the following equation [23]:

$$\delta_{\text{obs}} = (\delta_0 + \delta_1[L]K_f)/(1 + K_f[L]) \quad (3)$$

where  $\delta_0$  and  $\delta_1$  are the chemical shifts of the free solvated cesium cation and the complexed cation, respectively. The adjustable parameters,  $K_f$  and  $\delta_1$ , were

TABLE I. Solvent properties and formation constants of the  $\text{Cs}^+$ -DB24C8 complexes in neat solvents at ambient temperature.

Solvent	$D^a$	$\epsilon^b$	$\text{Log } K_f$
NM	2.7	35.9	$4.14 \pm 0.11$
AN	14.1	37.5	$3.60 \pm 0.04$
PC	15.1	65.0	$2.99 \pm 0.04$
DMF	26.6	36.7	$2.21 \pm 0.03$

<sup>a</sup>Gutmann donor number [18].

<sup>b</sup>Dielectric constant.

obtained by fitting Equations (2) and (3) to the  $^{133}\text{Cs}$  chemical shift data using the weighted nonlinear least squares program KINFIT4 [24]. Stability constants are not corrected for the effect of ion pair formation. Formation constants were obtained at various temperatures and used with the Van 't Hoff equation to obtain enthalpy and entropy changes of complexation:

$$\ln K_f = -(\Delta H_c/RT) + (\Delta S_c/R) \quad (4)$$

### 3. Results and Discussion

Thermodynamics of complexation of DB24C8 with  $\text{Cs}^+$  cation in three binary solvent mixtures AN/NM, DMF/NM and AN/PC were studied using the  $^{133}\text{Cs}$ -NMR technique. The DMF-AN system has been studied previously [17]. The solvents were chosen so that they represent a range of Gutmann donor number ( $D$ ) and dielectric constant ( $\epsilon$ ) as shown in Table I. Since AN, NM and DMF have similar dielectric constants, then in AN/NM, DMF/NM and DMF/AN solvent mixtures we should expect similar ion association of the cationic species. AN and PC have similar donor numbers but different dielectric constants. Therefore, the effect of ion association on the complexation reaction might be studied in AN/PC solvent system.

Variation of  $^{133}\text{Cs}$  chemical shift as a function of DB24C8/ $\text{Cs}^+$  mole ratio, ( $C_L/C_M$ ), was obtained at various solvent compositions of the binary solvent mixtures and at various temperatures. This variation at ambient temperature for the three binary solvent systems is shown in Figures 1-3. Similar plots were obtained at various temperatures. The formation constants at various solvent compositions and temperatures were calculated using Equations 1-3 and are reported in Table II. Figures 4-6 show the Van 't Hoff plot for each system.  $\Delta H_c$  and  $\Delta S_c$  values which were obtained from the slopes and the intercepts of such plots are given in Table III.

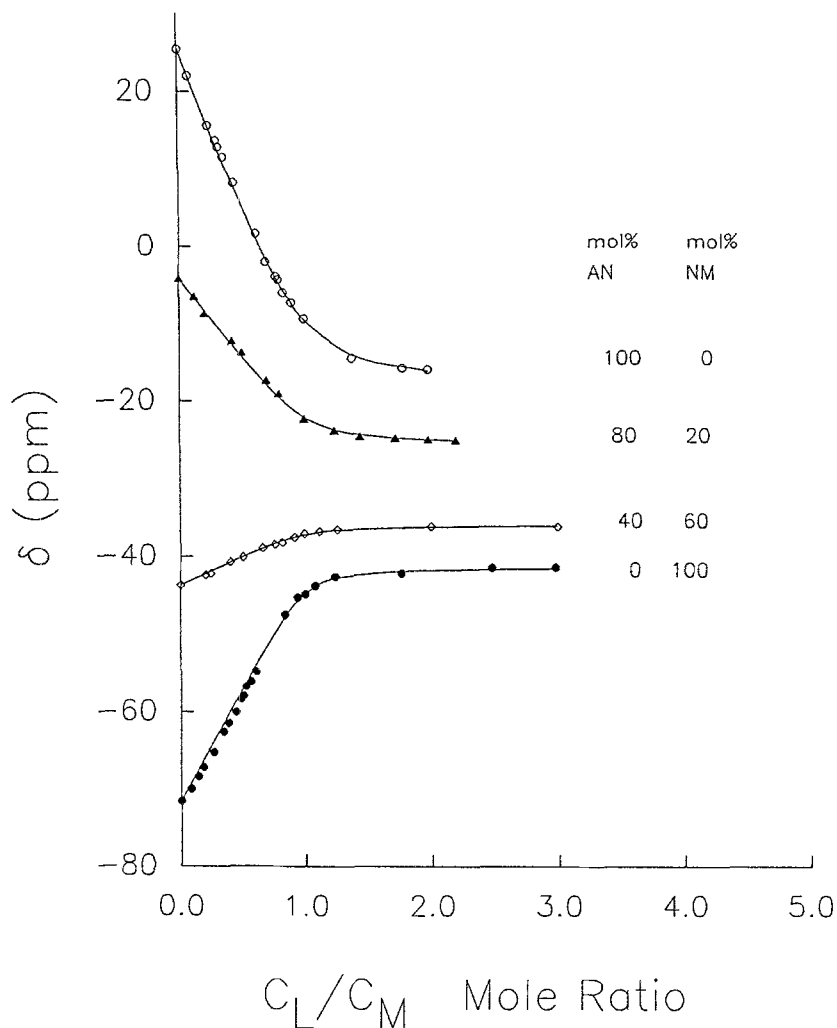


Fig. 1. Cesium-133 chemical shift as a function of (DB24C8)/(Cs<sup>+</sup>) mole ratio in AN/NM solvent mixture at various compositions and at the ambient temperature. Solid lines are calculated curves.

Figures 1–3 depict the variation of the <sup>133</sup>Cs chemical shift as a function of  $C_L/C_M$  molar ratio at various compositions of the solvent and at the ambient temperature. The plots show that the stability of the complex is sensitive to the solvent composition. For example, Figure 1 shows that as the concentration of the low donicity solvent, NM, increases, a more rapid leveling of the chemical shift occurs above mole ratio one, which is indicative of stronger complex formation. Complex formation constants,  $K_f$ , are given in Table II.

In most cases, the log  $K_f$  values reported in Table II show trends with respect to solvent composition and temperature. The trend disappears where large errors

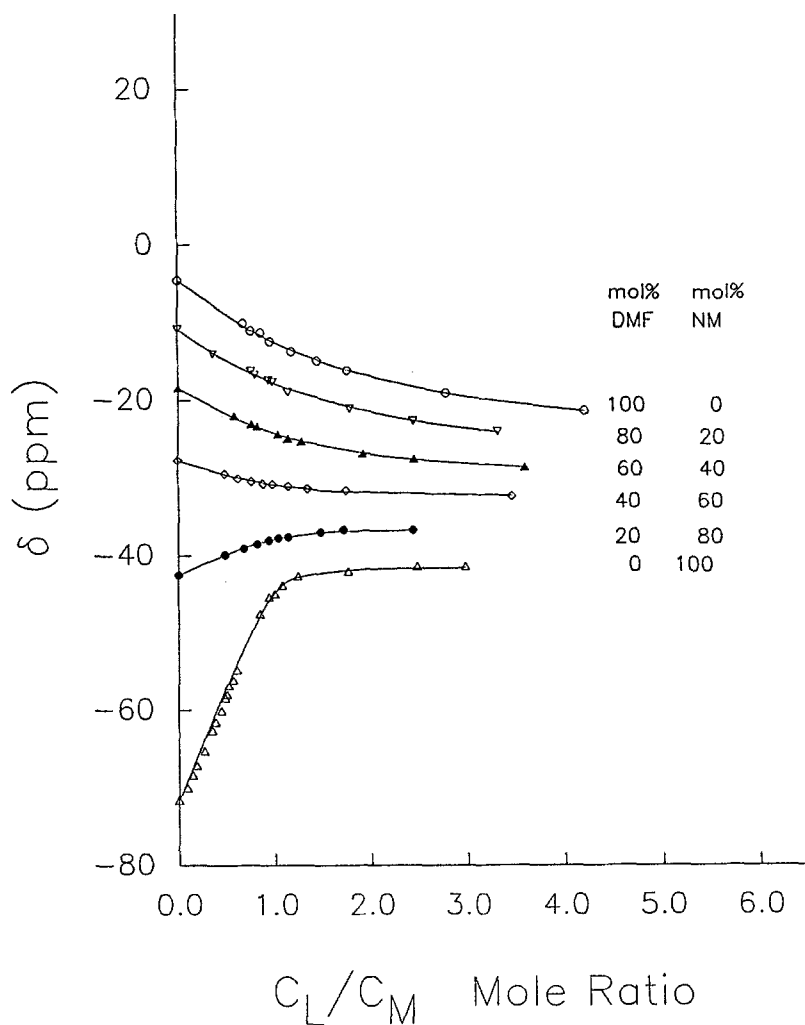


Fig. 2. Cesium-133 chemical shift as a function of (DB24C8)/(Cs<sup>+</sup>) mole ratio in DMF/NM solvent mixture at various compositions and at the ambient temperature. Solid lines are calculated curves.

are associated with the  $K_f$  values. These errors arise from two basic sources: the small chemical shift range as a function of  $C_L/C_M$  mole ratio or temperature; and the broad NMR signals obtained in some cases. These effects limit the temperature range over which the formation constants can be measured accurately.

Table III contains the free energy, enthalpy and entropy changes upon complexation. Figures 7–9 show the variations of  $\Delta H_c$  and  $T\Delta S_c$  as a function of solvent composition for each binary solvent system. For the system AN/NM both  $\Delta H_c$  and  $\Delta S_c$  increase as the concentration of the solvent of higher donicity is increased. In the DMF/NM solvent system both enthalpy and entropy increase initially as

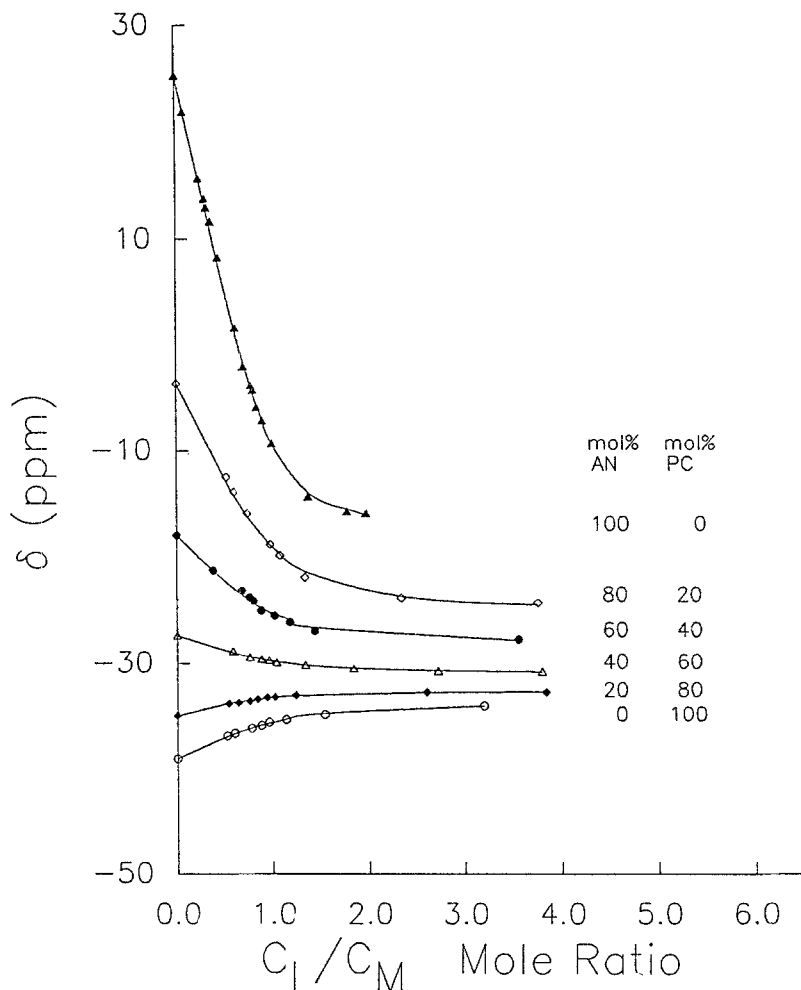


Fig. 3. Cesium-133 chemical shift as a function of (DB24C8)/(Cs<sup>+</sup>) mole ratio in PC/AN solvent mixture at various compositions and at the ambient temperature. Solid lines are calculated curves.

the mole-% of DMF is increased, pass through maxima, and then decrease to the values of  $\Delta H_c = -33.5$  kJ/mole and  $\Delta S = -69.6$  J/K mole in pure DMF. For the PC/AN binary solvent system the enthalpy and entropy of complexation are rather insensitive to the solvent composition from 0% AN to 80% AN, but  $\Delta H_c$  and  $\Delta S_c$  increase on going from 80% AN to pure AN. These data indicate that other factors besides solvent donating ability are responsible for enthalpy and entropy changes upon complexation.

Frankel *et al.* [25, 26] defined the isosolvation point of a binary solvent mixture as the composition at which both solvents participate equally in the inner solvation shell of the cation. Popov and coworkers used <sup>23</sup>Na chemical shift as a measure of the solvating ability of the solvent and obtained the isosolvation point from the

TABLE II. Formation constants of complexation of cesium cation and DB24C8 in binary solvent mixtures at different temperatures.

Medium	Temp. (°C)	Log $K_f$	Medium	Temp. (°C)	Log $K_f$
Pure AN	77	$2.84 \pm 0.07$	60%DMF+	61	$2.09 \pm 0.05$
	48	$3.41 \pm 0.03$	40%NM	46	$2.34 \pm 0.03$
	27	$3.60 \pm 0.04$		27	$2.52 \pm 0.04$
	11	$3.86 \pm 0.09$		-5	$3.15 \pm 0.03$
	-5	$4.03 \pm 0.10$		-27	$3.61 \pm 0.03$
80%AN+	59	$3.28 \pm 0.05$	20%DMF+	78	$2.79 \pm 0.07$
20%NM	47	$3.57 \pm 0.06$	80%NM	52	$2.98 \pm 0.05$
	27	$3.78 \pm 0.09$		43	$3.06 \pm 0.16$
	2	$4.20 \pm 0.12$		27	$3.28 \pm 0.10$
40%AN+	56	$3.50 \pm 0.08$	Pure PC	64	$2.46 \pm 0.05$
60%NM	41	$3.75 \pm 0.07$		41	$2.86 \pm 0.07$
	27	$3.84 \pm 0.11$		27	$2.99 \pm 0.04$
	6	$4.37 \pm 0.61$		-7	$3.52 \pm 0.20$
Pure NM	77	$3.12 \pm 0.07$	80%PC+	64	$2.61 \pm 0.06$
	65	$3.38 \pm 0.16$	20%AN	51	$2.74 \pm 0.04$
	41	$3.87 \pm 0.05$		27	$3.17 \pm 0.10$
	27	$4.14 \pm 0.11$		-3	$3.67 \pm 0.17$
	8	$4.43 \pm 0.23$			
Pure DMF	66	$1.46 \pm 0.05$	40%PC+	63	$2.60 \pm 0.06$
	43	$1.97 \pm 0.04$	60%AN	42	$3.05 \pm 0.07$
	27	$2.21 \pm 0.03$		24	$3.25 \pm 0.11$
	3	$2.66 \pm 0.05$		3	$3.72 \pm 0.16$
80%DMF+	51	$1.89 \pm 0.06$	20%PC+	78	$2.71 \pm 0.04$
20%NM	27	$2.31 \pm 0.06$	80%AN	42	$3.04 \pm 0.07$
	5	$2.74 \pm 0.06$		26	$3.24 \pm 0.06$
	-9	$2.91 \pm 0.07$		3	$3.64 \pm 0.07$

solvent composition corresponding to the mid-point of the chemical shift in two pure solvents [27, 28]. Table IV summarizes the isosolvation points of  $\text{Cs}^+$  and  $\text{Cs}^+ \cdot \text{DB24C8}$  cationic species as obtained from our  $^{133}\text{Cs}$  chemical shift results. In the AN/NM solvent system, the isosolvation points of the cesium cation and the complexed cation are both around 50 mole-%. This means that the number of the solvent molecules in the first coordination sphere of the cationic species is simply proportional to the mole% of the solvent. Then the changes in enthalpy and entropy of complexation should be proportional to the donor ability of the solvent and show a trend with the solvent composition. Our data clearly follow this trend as is shown in Figure 7.

On the other hand, the isosolvation points for cesium cation and the complexed cation in DMF/NM are  $\sim 25$  mole% and  $\sim 30$  mole-% DMF, respectively. At com-



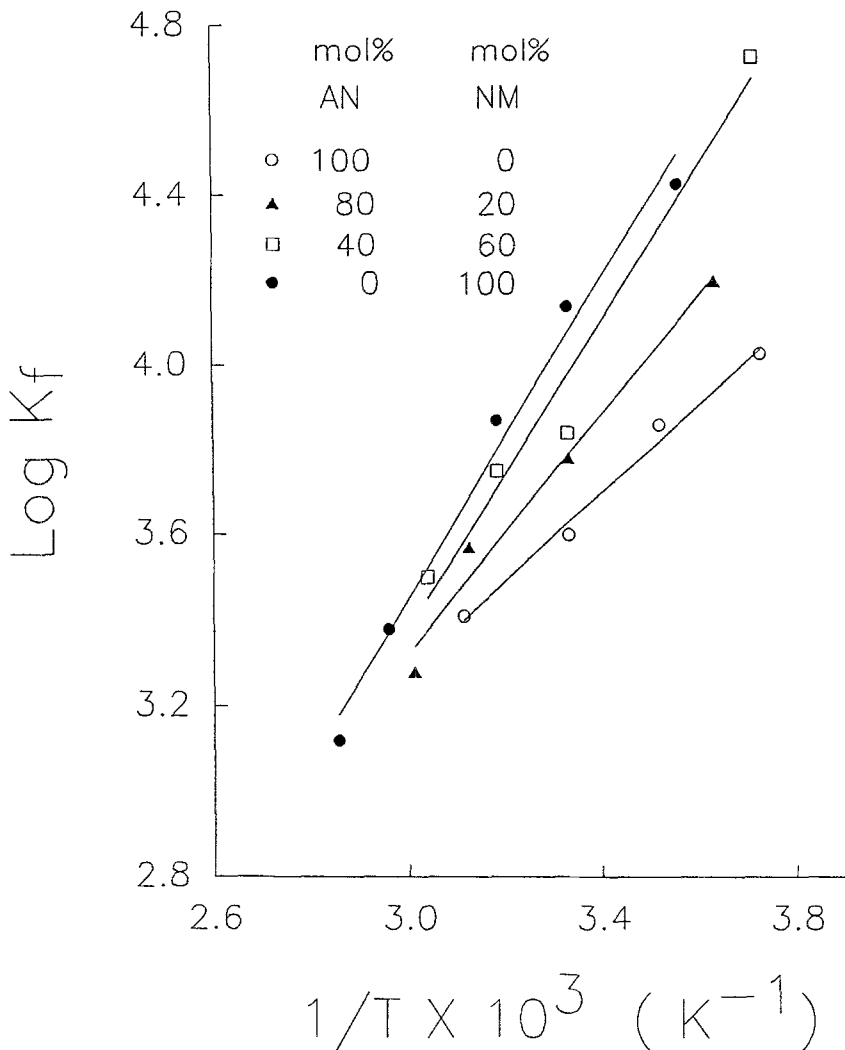


Fig. 4. Van't Hoff plots for complexation of  $\text{Cs}^+$  ion by DB24C8 in AN/NM solvent mixture at various compositions.

positions containing less than 25 mole-% DMF, this solvent competes with NM and since DMF is a solvent of higher donicity than NM, the enthalpy of complexation increases at these solvent compositions. In a strongly solvating medium, such as in DMF, the solvation of the cation (and possibly of the ligand) should be stronger than in a solvent of lower solvating ability such as NM. Therefore less energy should be necessary for the desolvation of the cation in the case of NM than for DMF. As a result, it should be expected that the  $\Delta H_c$  value will be less negative as the nitromethane composition of the DMF/NM mixture is increased. The increase in the  $\Delta S_c$  value is probably due to the additional solvent molecules

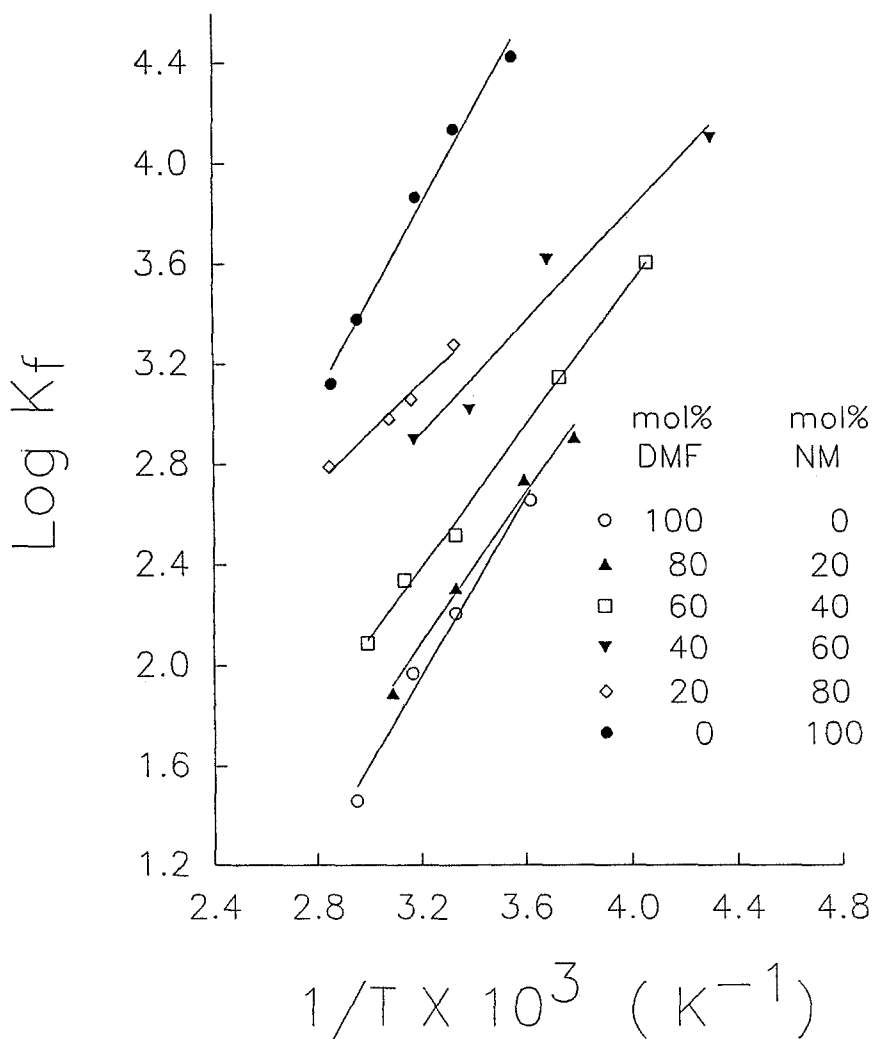


Fig. 5. Van 't Hoff plots for complexation of  $\text{Cs}^+$  ion by DB24C8 in DMF/NM solvent mixture at various compositions.

which may be released in the complexation. Similar results have been obtained for the complexation of  $\text{Cs}^+$  cation with DB24C8 in DMF/AN solvent mixtures [17]. At compositions containing more than 30 mole-% DMF, the solvation shell is almost entirely DMF and the decrease in  $\Delta H_c$  might be due to the difference in the solvation of cesium cation and the complexed cation by DMF. Since the cation is more solvated than the complex, the positive contribution from desolvation of  $\text{Cs}^+$  ion exceeds the negative contribution from complex cation solvation.

The isosolvation point of cesium cation and the complexed cation in AN/PC solvent system are  $\sim 25$  mole-% and 20 mole-% PC, respectively, even though the

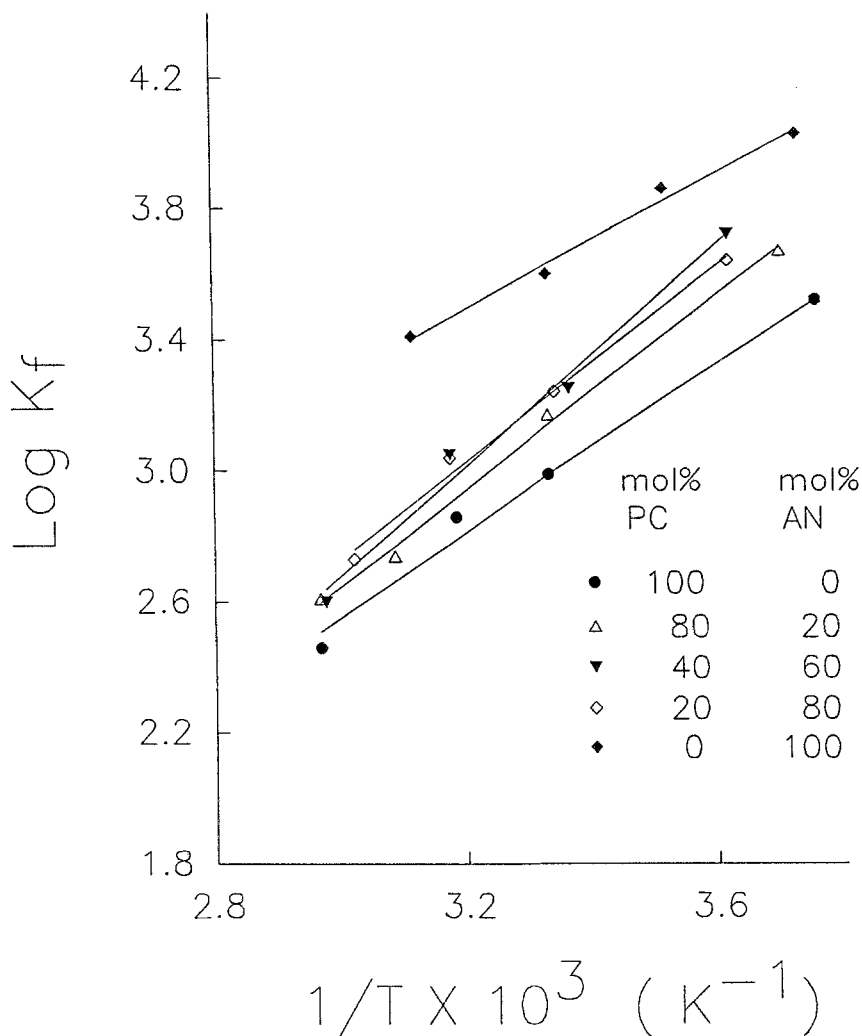


Fig. 6. Van't Hoff plots for complexation of  $\text{Cs}^+$  ion by DB24C8 in PC/AN solvent mixture at various compositions.

donor numbers of these solvents are similar. The enthalpy and entropy changes might be attributed to the extent of ion pairing of the cations in these solvents. As the mole-% of acetonitrile decreases, the extent of ion pairing decreases and since  $\Delta H_{ip} > 0$  [21], then the enthalpy decreases. At compositions below  $\sim 60$  mole-% AN, again the enthalpy change might be due to the difference in the solvation of the cation and the complexed cation.

Popov and coworkers [17] obtained the thermodynamic parameters of complexation of DB24C8 with cesium thiocyanate in DMF/AN solvent mixtures. The value of  $\Delta G_c$  at 25 °C in pure DMF agrees with the results obtained with  $\text{BPh}_4^-$  while

TABLE III. Thermodynamic parameters of complexation of cesium cation and DB24C8 in binary solvent systems.

Medium	Mole-%	$\Delta G_c^0$ (25 °C) (kJ mol <sup>-1</sup> )	$\Delta H_c^0$ (kJ mol <sup>-1</sup> )	$\Delta S_c^0$ (JK <sup>-1</sup> mol <sup>-1</sup> )
AN/NM	100%AN	-20.85 ± 0.23	-19.9 ± 1.4	+3.2 ± 4.9
	80%	-21.82 ± 0.51	-26.8 ± 2.7	-16.7 ± 8.9
	40%	-22.92 ± 0.63	-34.6 ± 4.4	-39.2 ± 14
	0%	-23.52 ± 0.63	-36.1 ± 2.6	-42.2 ± 8.4
DMF/NM	100%DMF	-12.76 ± 0.76	-33.5 ± 2.9	-69.6 ± 9.4
	80%	-13.26 ± 0.34	-28.4 ± 2.9	-50.8 ± 7.9
	60%	-14.84 ± 0.23	-27.0 ± 0.9	-40.8 ± 3.1
	20%	-18.68 ± 0.57	-19.1 ± 1.8	-1.4 ± 5.5
	0%	-23.52 ± 0.63	-36.1 ± 2.6	-42.2 ± 8.4
PC/AN	100%PC	-17.21 ± 0.23	-24.9 ± 2.0	-25.8 ± 6.7
	80%	-18.06 ± 0.27	-28.1 ± 1.2	-33.7 ± 3.9
	40%	-18.68 ± 0.63	-32.0 ± 2.8	-44.7 ± 9.1
	20%	-18.60 ± 0.34	-28.2 ± 1.8	-32.2 ± 6.1
	0%	-20.85 ± 0.23	-19.9 ± 1.4	+3.2 ± 4.9
DMF/AN <sup>a</sup>	100%DMF	-12.47 ± 0.17	-25.6 ± 0.5	-43.0 ± 1.8
	61.5%	-14.14 ± 0.17	-26.8 ± 1.3	-41.8 ± 4.6
	22.7%	-17.57 ± 0.04	-30.1 ± 0.9	-41.6 ± 3.0
	0%	-22.89 ± 0.42	-34.0 ± 0.7	-36.2 ± 2.9

<sup>a</sup>Data from Ref. [17], 0.005 M CsSCN was used.

TABLE IV. Isosolvation point of Cs<sup>+</sup> cation and Cs<sup>+</sup>·DB24C8 complex in various solvent systems.

Medium	Isosolvation point	
	Cs <sup>+</sup>	Cs <sup>+</sup> ·DB24C8
AN/NM	~60% AN	~55% AN
DMF/NM	~25% DMF	~30% DMF
PC/AN	~25% PC	~20% PC

the values of  $\Delta H_c$  and  $\Delta S_c$  are very different from our results (Table III). The difference in enthalpy and entropy values for the thiocyanate and tetraphenylborate may well be due to the differences in the interionic attractions. In the former case, we may have stronger ion pair formation [21]. The reduction in entropy resulting from the formation of the ion pair is more than balanced by the increase in entropy due to the release of solvent molecules from the separated solvated ions. Likewise, the negative contribution from the Coulombic attraction of the cation and the anion is balanced by the energy need to break ion-solvent bonds in the solvated ions.

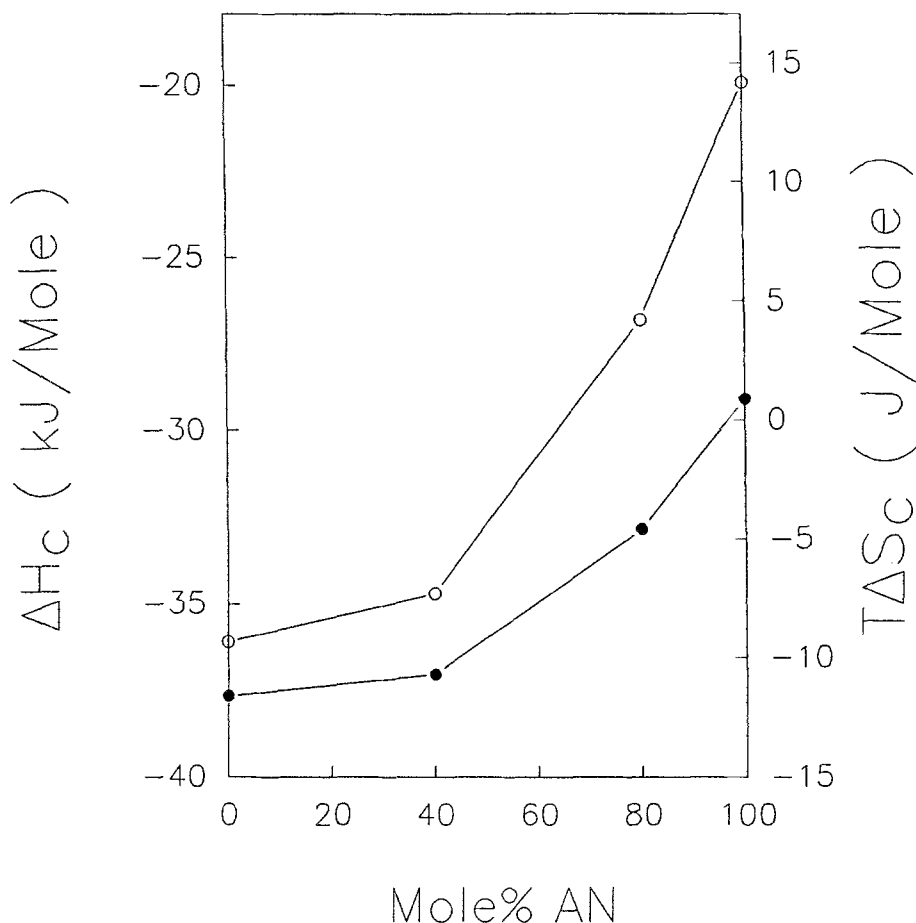


Fig. 7. Plots of  $\Delta H_c$ ,  $\circ$ , and  $T\Delta S_c$ ,  $\bullet$ , vs. mole-% AN for complexation of  $\text{Cs}^+$  ion by DB24C8 in AN/NM solvent mixtures.

It is obvious from Figures 7–9 that  $\Delta H_c$  and  $\Delta S_c$  compensate each other in all cases, with  $\Delta H_c$  being the dominant factor responsible for the stability of the complex. Although the origin of this compensating effect is not fully known, this effect can be discussed in terms of cation–ligand binding. As the binding between the cation and the ligand becomes stronger, the degree of freedom of the complex is reduced due to the decreased flexibility of the ligand. It is obvious that the above explanation is rather simplistic. Other factors, such as solvation of the cation and the complex, as well as the conformational changes of the ligand upon complexation, might also influence the degree of this compensatory effect.

Inoue and Hakushi [29] have discussed this compensation effect and found a linear relationship between  $\Delta H_c$  and  $T\Delta S_c$  for the complexation of metal cations with various types of ligands using the available thermodynamic parameters:

$$T\Delta S_c = \alpha\Delta H_c + \beta$$

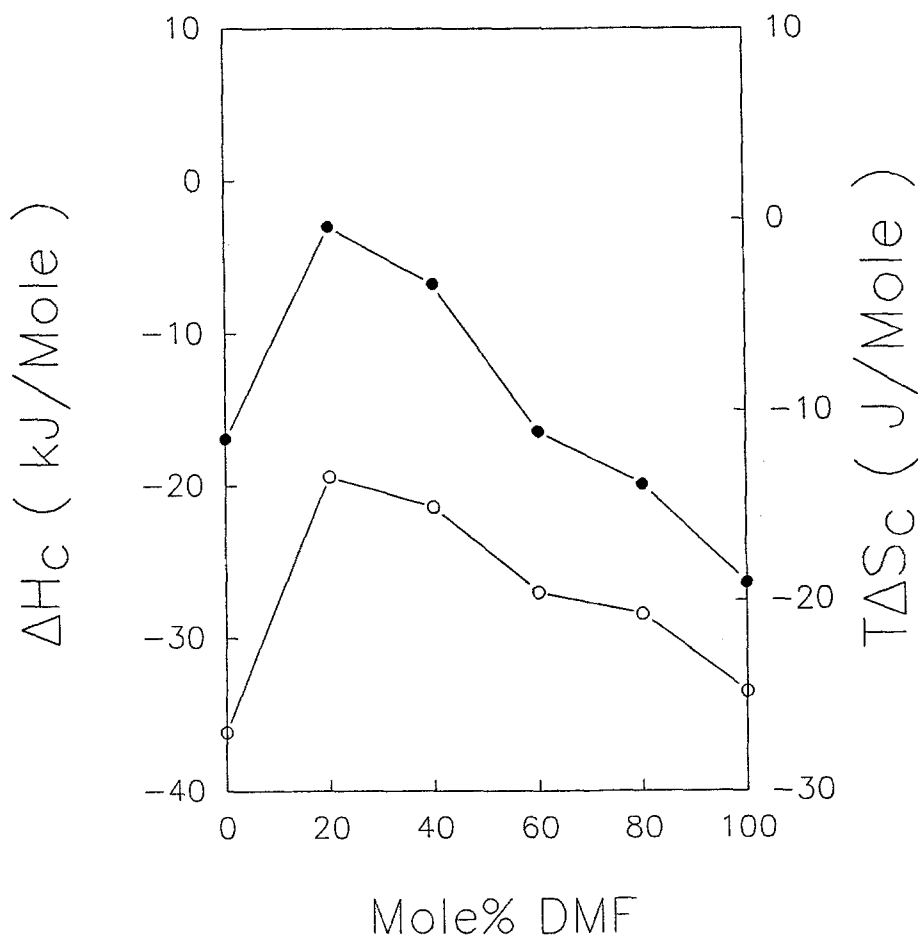


Fig. 8. Plots of  $\Delta H_c$ ,  $\circ$ , and  $T\Delta S_c$ ,  $\bullet$ , vs. mole-% DMF for complexation of  $\text{Cs}^+$  ion by DB24C8 in DMF/NM solvent mixtures.

They concluded that the slope,  $\alpha$ , and the intercept,  $\beta$ , of the plots of  $\Delta H_c$  and  $\Delta S_c$  are characteristic of the type of the ligand. For crown ethers, a slope of  $\sim 0.75$  and an intercept of  $\sim 10$  kJ/mole were obtained ( $r = 0.87$ ,  $n = 207$ ). Our data for all systems at different solvent compositions give  $\alpha = 0.82$  and  $\beta = 13.6$  kJ/mole ( $r = 0.77$ ,  $n = 18$ ) which is consistent with the above results. The above discussion suggests that the entropic effect consists of two components: one which is proportional to the enthalpic change; and the other independent of it. The  $\alpha$  value might be considered as a quantitative measure of the entropic compensating effect. For  $\alpha = 0.82$ , only about 18% of the increase in  $\Delta H_c$  contributes to increases in the complex stability. The positive intercept means that complex formation can occur even in the absence of enthalpic gain. This is due to the solvent effect which increases the entropy due to the increase in the degree of freedom as a result of desolvation of the cation.

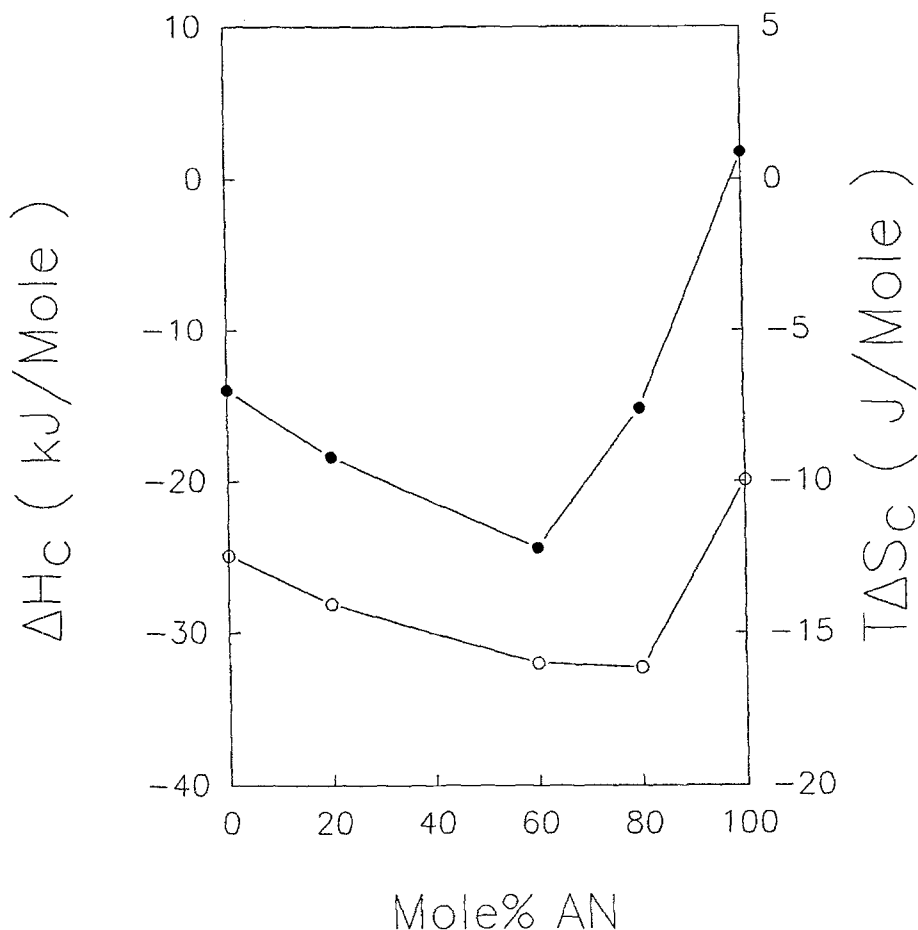


Fig. 9. Plots of  $\Delta H_c$ ,  $\circ$ , and  $T\Delta S_c$ ,  $\bullet$ , vs. mole-% AN for complexation of  $\text{Cs}^+$  ion by DB24C8 in PC/AN solvent mixtures.

This entropy gain indicates the extent by which the cation solvation is replaced by the ligand. Enthalpy-entropy compensation effects have also been observed in drug-receptor binding [30] and other host-guest complexation processes [31].

Even though many factors contribute to changes in enthalpy and entropy of complexation reactions, it seems that solvent properties such as donor number, dielectric constant and the isosolvation point can be used to explain the unusual changes of enthalpy and entropy as a function of solvent composition. It is interesting to report that we have observed similar behavior in thermodynamic parameters for complexation of cesium ions with dibenzo-30-crown-10 in binary solvent mixtures.

## Acknowledgements

We gratefully acknowledge the support of this study by the Graduate School and the Department of Chemistry, Southern Illinois University, at Edwardsville.

## References

1. R. M. Izatt, K. Pawlak, J. S. Bradshaw and R. L. Bruening: *Chem. Rev.* **91**, 1721 (1991) and references therein.
2. K. Ozutsumi, K. Ohtsu and T. Kawashima: *J. Chem. Soc. Faraday Trans.* **90**, 127 (1994).
3. Y. Inoue, Y. Liu, L. H. Tong, M. Ouchi and T. Hakushi: *J. Chem. Soc. Perkin Trans. 2* **10**, 1947 (1993).
4. K. Ozutsumi and S. Ishiguro: *Bull. Chem. Soc. Jpn.* **65**, 1173 (1992).
5. A. Jabbari and M. Shamsipur: *Spectros. Lett.* **26**, 1715 (1993).
6. R. T. Streeper and S. Khazaeli: *Polyhedron* **10**, 221 (1991).
7. L. Soong, G. E. Leroi, A. I. Popov: *Inorg. Chem.* **29**, 1366 (1990).
8. K. M. Tawarah, S. A. Mizyed: *J. Solution Chem.* **18**, 387 (1989).
9. M. K. Jr. Chantooni, G. Ronald and I. M. Kolthoff: *J. Solution Chem.* **17**, 175 (1988).
10. H.-J. Buschman: *J. Solution Chem.* **17**, 277 (1988).
11. R. D. Boss and A. I. Popov: *Inorg. Chem.* **25**, 1747 (1986).
12. Y. Takeda, Y. Kudo and S. Fujiwara: *Bull. Chem. Soc. Jpn.* **58**, 1315 (1985).
13. Y. Takeda, Y. Ohyagi and S. Akabori: *Bull. Chem. Soc. Jpn.* **57**, 3381 (1984).
14. G. Rounaghi and A. I. Popov: *J. Inorg. Nucl. Chem.* **43**, 911 (1981).
15. R. M. Izatt, G. Wu: *Thermochim. Acta* **154**, 161 (1989).
16. G. Rounaghi and A. I. Popov: *Polyhedron* **5**, 1329 (1986).
17. G. Rounaghi and A. I. Popov: *Inorg. Chim. Acta* **114**, 145 (1986).
18. V. Gutmann: *Coordination Chemistry in Nonaqueous Solutions*, Springer, New York (1968).
19. W. J. DeWitte, L. Liu, E. Mei, J. L. Dye and A. I. Popov: *J. Solution Chem.* **6**, 337 (1977).
20. D. M. Bowers, R. H. Erlich, S. Policec and A. I. Popov: *J. Inorg. Nucl. Chem.* **33**, 81 (1971).
21. S. Khazaeli, A. I. Popov and J. L. Dye: *J. Phys. Chem.* **86**, 4238 (1986).
22. D. H. Live and S. I. Chan: *Anal. Chem.* **42**, 791 (1970).
23. E. T. Roach, P. R. Handy and A. I. Popov: *Inorg. Nucl. Chem. Lett.* **9**, 359 (1973).
24. J. L. Dye and V. A. Nicely: *J. Chem. Educ.* **48**, 433 (1971).
25. L. S. Frankel, T. R. Stengle and C. H. Langford: *Chem. Commun.* 393 (1965).
26. L. S. Frankel, C. H. Langford and T. R. Stengle: *J. Phys. Chem.* **74**, 1376 (1970).
27. R. H. Erlich and A. I. Popov: *J. Am. Chem. Soc.* **93**, 5620 (1971).
28. R. H. Erlich, M. S. Greenberg and A. I. Popov: *Spectrochim. Acta* **29A**, 543 (1973).
29. Y. Inoue and T. Hakushi: *J. Chem. Soc. Perkin Trans. 2* 935 (1985).
30. P. Gilli, V. Ferretti, G. Gilli and P. A. Borea: *J. Phys. Chem.* **98**, 1515 (1994).
31. Y. Inoue, Y. Liu, L. Tong, B. Shen and D. Jin: *J. Am. Chem. Soc.* **115**, 10637 (1993).