

Conductance Study of the Thermodynamics of Some Transition and Heavy Metal Cryptates in Binary Acetonitrile – Dimethylsulfoxide Mixtures

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Abstract. A conductance study of the interaction between Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+} ions with cryptands C211, C221 and C222 in different acetonitrile–dimethylsulfoxide mixtures has been carried out at various temperatures. The formation constants of the resulting metal cryptates were determined from the molar conductance–mole ratio data. It was found that the stability of Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} cryptates vary in the order $\text{C211} > \text{C221} > \text{C222}$, while for Cd^{2+} cryptates the stability order is $\text{C221} > \text{C222} > \text{C211}$. A linear relationship is observed between $\log K_f$ of different metal cryptates and the mole fraction of acetonitrile in the solvent mixture. The enthalpy and entropy of cryptate formation reactions were determined from the temperature dependence of the formation constants. The enthalpy and entropy changes are quite sensitive to the solvent composition and the resulting $T\Delta S^\circ - \Delta H^\circ$ plot shows a fairly good linear correlation, indicating the existence of an entropy–enthalpy compensation in the cryptate formation reactions.

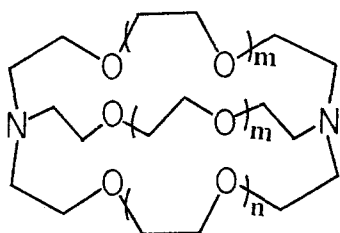
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Key words: Cryptates, transition and heavy metals, mixed solvent, conductance, complex stability, enthalpy–entropy compensation.

1. Introduction

The synthesis of macrobicyclic polyethers, or cryptands [1], and the discovery of their ability to form strong and selective 1 : 1 inclusion complexes, or cryptates, with a variety of metal ions have led to an extensive study of these ligands and their complexes [2–5]. The thermodynamics of complexation of cryptands C211, C221 and C222 (Figure 1) has been mainly studied with alkali and alkaline earth cations in water and in various nonaqueous solvents [4–11]. However, in comparison with numerous literature reports on alkali and alkaline earth cryptates, the systematic investigation of the thermodynamics of transition and heavy metal ion complexes

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$m = 0, n = 1$	C211
$m = 1, n = 0$	C221
$m = n = 1$	C222

Fig. 1. Structure of ligands.

with macrobicyclic ligands in various solvents has received much less attention [4, 5, 12–14].

It is well known that solvent properties play a fundamental role in the selectivity, thermodynamics and kinetics of macrocyclic complexes [4, 5]. There is currently an increasing interest in the study of physicochemical phenomena in binary mixed solvent systems and their interpretation in terms of the solutes' preferential solvation by one of the mixed solvent components [15–22]. In this paper we report a conductance study of Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} complexes with cryptands C211, C221 and C222 in various acetonitrile (AN)–dimethylsulfoxide (DMSO) mixtures at different temperatures, in order to investigate the influence of solvent properties, the nature of the metal ions and the structural characteristics of the macrobicyclic ligands on the thermodynamics of the resulting complexes. It should be noted that AN and DMSO have relatively close dielectric constants, ϵ , but quite different Gutmann donor numbers, DN , (i.e. for AN, $\epsilon = 38.0$ and $DN = 14.1$ and for DMSO, $\epsilon = 45.0$ and $DN = 29.8$) [23].

2. Experimental

Reagent grade nitrate salts of cobalt, nickel, copper, zinc cadmium and lead (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5 . Cryptand C222 (Fluka) was purified and dried as described previously [24]. Cryptands C221 and C211 (both from Merck) were used as received. Reagent grade DMSO and AN (both from Merck) were purified and dried by the previously described methods [25]. The conductivities of the solvent were less than $1.0 \times 10^{-7} \text{ S}^{-1} \text{ cm}^{-1}$.

Conductance measurements were carried out with a Metrohm 660 conductivity meter. A dip-type conductivity cell, made of platinum black, was used. The cell constant at the different temperatures used were determined by measuring the conductivity of a $0.0100 \text{ mol dm}^{-3}$ solution of analytical grade KCl (Merck) in triply distilled deionized water. The specific conductances of this solution at

various temperatures have been reported recently [26]. The corresponding cell constants at 25.0, 35.0, 45.0 and 55.0 °C are 0.8441, 0.8405, 0.8385 and 0.8360 cm^{-1} , respectively. In all measurements, the cell was thermostated at the desired temperature ± 0.03 °C using a Lo-Temprol 154 Precision Scientific thermostat.

In a typical experiment, 15–25 mL of the desired metal nitrate solution (1.0×10^{-4} – 3.0×10^{-4} mol dm^{-3}) was placed in the titration cell, thermostated to the desired temperature and the conductance of the solution was measured. Then, a known amount of the cryptand solution was added in a stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition. Addition of the ligand solution was continued until the desired ligand to cation mole ratio was achieved.

The formation constants, K_f , and limiting molar conductances, Λ_c , of the resulting 1 : 1 cryptates in different AN–DMSO mixtures, at various temperatures, were evaluated by fitting the observed molar conductances, Λ_{obs} , at various ligand-to-metal ion mole ratios to a previously derived equation [27], which expresses Λ_{obs} as a function of the free and complexed metal ion and the formation constant, by using a nonlinear least-squares program KINFIT [28]. The details are described elsewhere [27, 29–31].

3. Results and Discussion

The molar conductance of nitrate salts of Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} in different AN–DMSO solvent mixtures was monitored as a function of cryptand to metal ion mole ratio at various temperatures. The resulting molar conductance-mole ratio plots at 25 °C are shown in Figures 2–6. As can be seen, in all cases studied, addition of cryptand to the metal ion solutions causes a continuous decrease in the molar conductance of the solutions, indicating the lower mobility of the metal ion cryptates compared to the solvated cations. From Figures 2–6 it is immediately obvious that in some systems, such as Co^{2+} –C211/40% AN, Ni^{2+} –C211/40% AN, Ni^{2+} –C211/30% AN, Zn^{2+} –C211/40% AN, Cd^{2+} –C211/40% AN, Cd^{2+} –C211/30% AN, addition of the cryptands to the cation solutions results in a rather sharp decrease in the molar conductance which begins to level off at mole ratios greater than unity. The slope of the corresponding mole ratio plots changes sharply at the point where the ligand-to-cation mole ratio is equal to one, emphasizing the formation of a fairly stable 1 : 1 complex. However, in many other cases shown in Figures 2–6, the relatively large decrease in the molar conductance of metal nitrate solutions upon addition of the cryptands does not show any tendency of leveling off even at mole ratios of about 3, indicating the formation of weaker metal cryptates.

In order to achieve a better understanding of the thermodynamics of cryptate formation, it is useful to consider the enthalpic and entropic contributions to these reactions. These thermodynamic parameters were evaluated from the temperature dependence of the cryptate formation constants. A typical series of molar

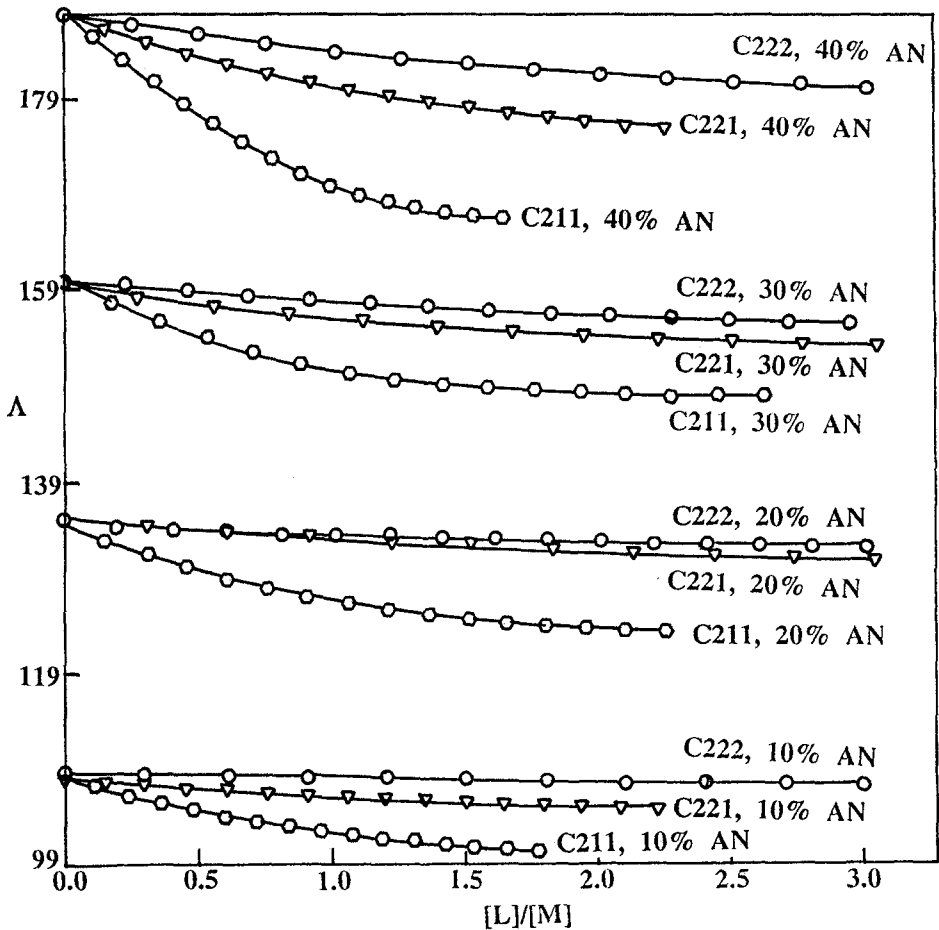


Fig. 2. Molar conductance vs. $C_L/C_{M^{2+}}$ curves for different cobalt cryptates in various AN-DMSO mixtures at 25 °C.

conductance-mole ratio plots at various temperatures is shown in Figure 7. The formation constants of all metal ion cryptates, studied in different AN-DMSO mixtures at various temperatures, were evaluated by computer fitting of the molar conductance-mole ratio data and the results are listed in Table I. Our assumption of 1 : 1 stoichiometry seems reasonable in the light of the fair agreement between the observed and calculated molar conductances.

It should be noticed that, in the procedure of calculation of formation constants, the association between M^{2+} ions and nitrate ion was considered negligible, under the highly dilute experimental conditions used [32]. It is interesting to note that the molar conductance of each metal nitrate solution in AN-DMSO mixtures increases considerably with increasing weight percent of AN in the solvent mixture (see Figures 1-6), mainly due to the relatively large difference between the viscosities

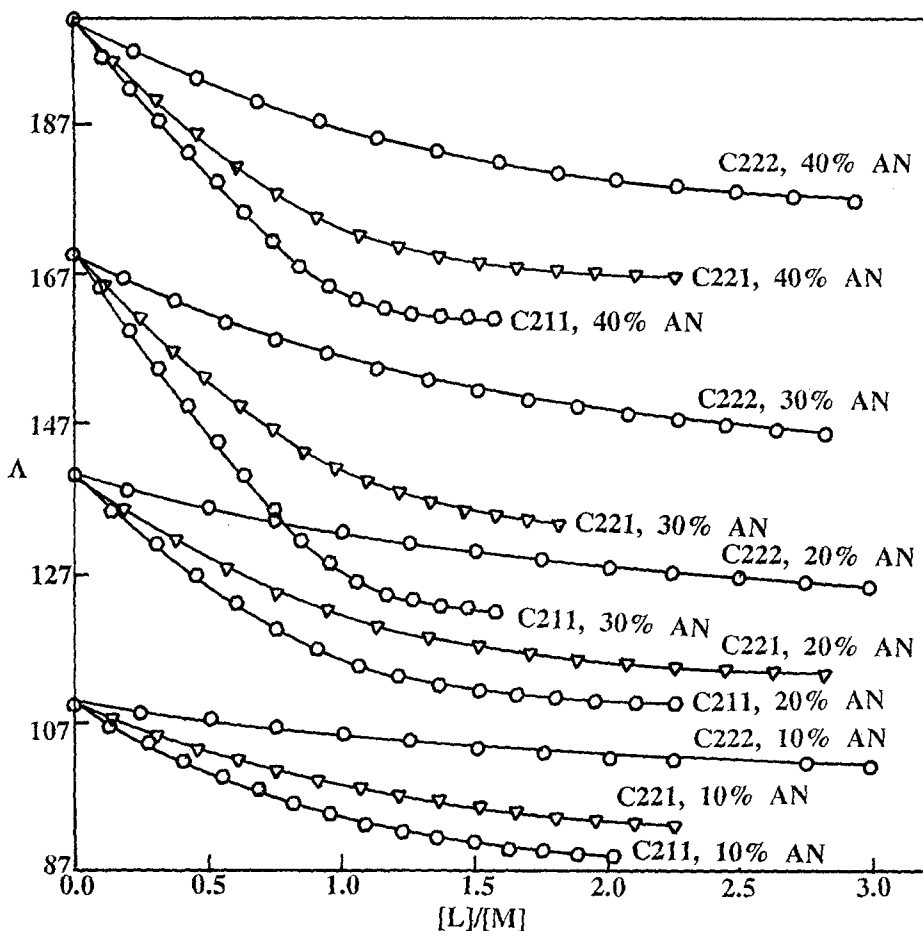


Fig. 3. Molar conductance vs. $C_L/C_{M^{2+}}$ curves for different nickel cryptates in various AN-DMSO mixtures at 25 °C.

of the two solvent components (i.e. 0.34 for AN and 1.96 for DMSO). Since the concentrations of cryptands were also kept below $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ during these experiments, corrections for the viscosity changes were also neglected.

Van't Hoff plots of $\log K_f$ vs $1/T$ for different metal cryptates were linear for all cases studied (see for example Figure 8). The enthalpies and entropies of cryptate formation were determined in the usual manner from the slopes and intercepts of these plots and the results are also included in Table I. It should be noted that the method used for the evaluation of the formation constant from the molar conductance-mole ratio data generally becomes unreliable for very stable complexes with $K_f > 10^6$ [31, 33, 34].

As can be seen from Table I, in all solvent mixtures used, the stability of Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} complexes with different cryptands vary in the order C211

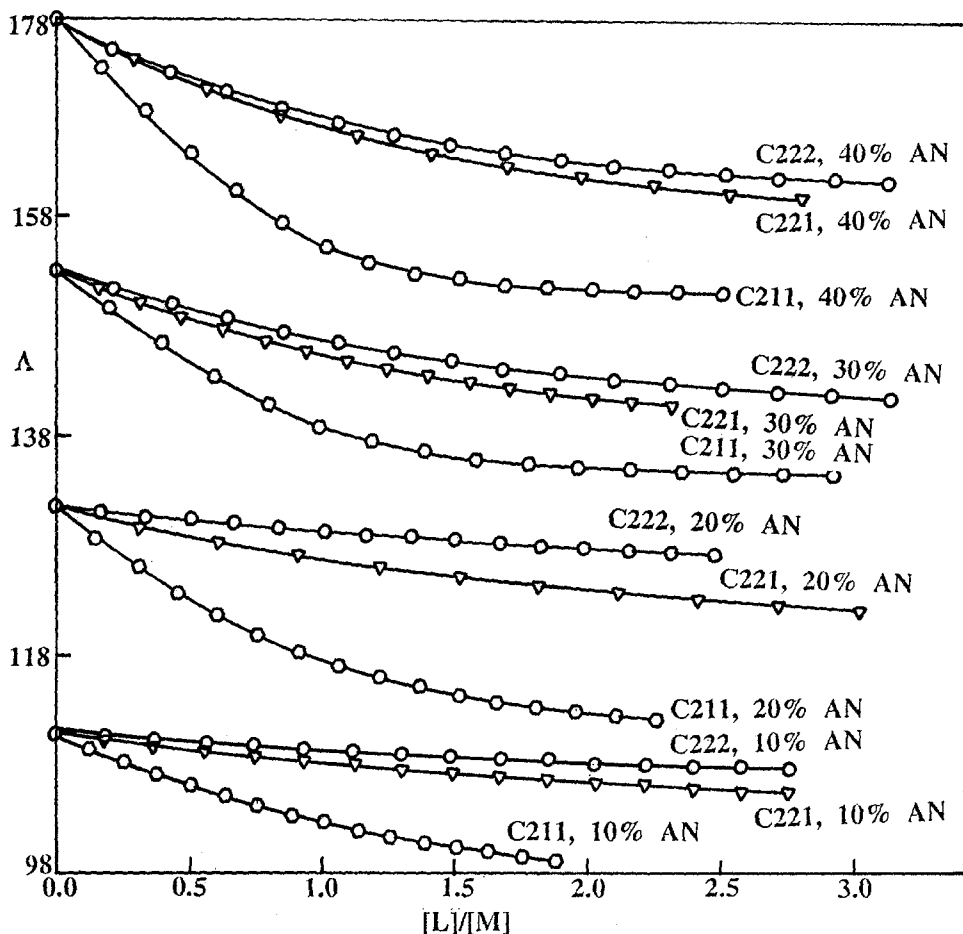


Fig. 4. Molar conductance vs. $C_L/C_{M^{2+}}$ curves for different zinc cryptates in various AN-DMSO mixtures at 25 °C.

> C221 > C222, most probably because of the convenient size of these cations [35, 36] for the cavity of C211 with a size of 1.6 Å [37]. On the other hand, the ionic size of these cations is too small for the larger cavities of C221 (2.2 Å) and, especially, C222 (2.8 Å) [37], resulting in the formation of weaker cryptates. However, the stability order for Cd^{2+} and Pb^{2+} ions, with larger ionic sizes than the first transition series cations, is quite different. The stability order for Cd^{2+} with an ionic size of 0.95 Å [36] is C221 > C222 > C211, in all solvent mixtures used. A similar stability order for cadmium cryptate has already been reported in the literature [4, 38].

The data given in Table I clearly illustrate the fundamental influence of the solvent properties on the cryptate formation reactions studied. In all cases, the stability of the resulting cryptates increases rapidly with increasing weight percent

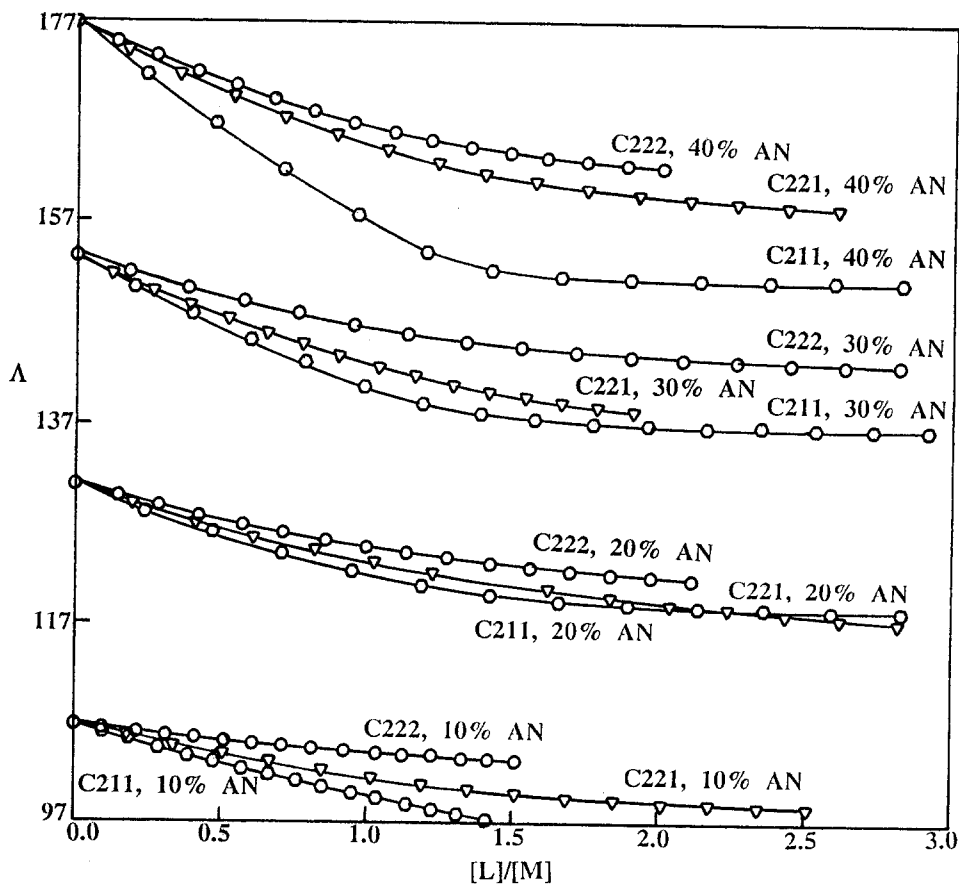


Fig. 5. Molar conductance vs. $C_L/C_{M^{2+}}$ curves for different cadmium cryptates in various AN-DMSO mixtures at 25 °C.

of AN in the mixed solvent. It is well known that the solvating ability of the solvent, as expressed by the Gutmann donor number [23], plays an important role in different complexation reactions [3, 8, 27, 29–31, 33, 34, 39, 40]. DMSO is a solvent of high solvating ability ($DN = 29.8$) which can strongly compete with cryptands for cations. Thus, it is not surprising that addition of AN as a relatively low donicity solvent ($DN = 14.1$) to DMSO will increase the stability of the cryptates

It is interesting to note that, with the exception of the Zn^{2+} —C222 cryptate, a linear relationship was found between $\log K_f$ of the cryptates and the mole fraction of acetonitrile (X_{AN}) in the mixed solvent. Some of the corresponding $\log K_f$ vs X_{AN} plots are shown in Figure 9. A similar trend has already been reported for several different metal complexes in various solvent mixtures [17, 18, 21, 22, 41–45]. It seems reasonable to assume that the preferential solvation of the cations

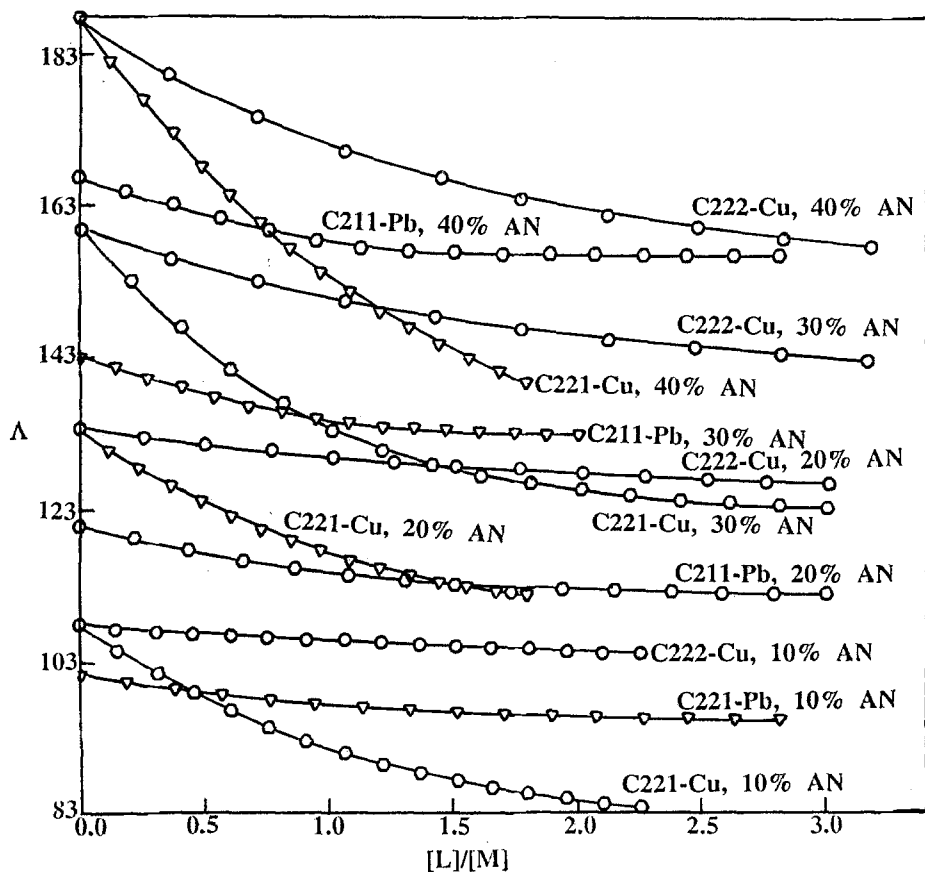


Fig. 6. Molar conductance vs. $C_L/C_{M^{2+}}$ curves for different copper and lead cryptates in various AN-DMSO mixtures at 25 °C.

by DMSO is mainly responsible for such a monotonic dependence of the formation constants of the cryptates on the solvent composition.

The thermodynamic data given in Table I clearly illustrate that the enthalpy and entropy changes obtained for different metal ion cryptates vary very significantly with the solvent mixture composition. As can be seen, in all cases studied the cryptates are enthalpy stabilized but, with the exception of a few cases, are entropy destabilized. It should be noted that similar thermodynamic behaviors were previously reported for most of the macrocyclic complexes studied in nonaqueous and mixed solvents [4, 5, 10–14]. The entropy change of the metal ion-cryptand system upon complexation has been related to some factors such as the change in conformational entropy of the ligand [34, 46], the cryptand's cavity size, the extent of cryptand-solvent interaction [47], and the difference in the solvation of the free and complexed cation.

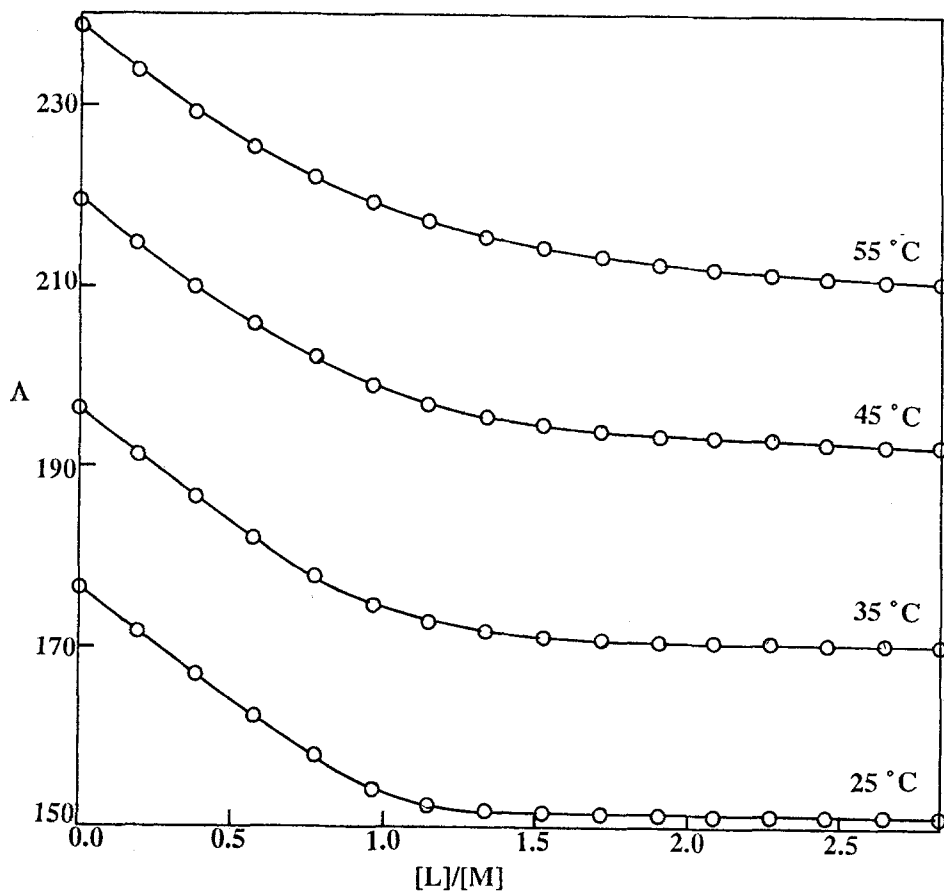


Fig. 7. Molar conductance vs. $[C221]/[Cd^{2+}]$ curves in 40% AN at various temperatures.

From the ΔH° and ΔS° values obtained for all metal ion cryptates (Table I) it is immediately obvious that, in most cases, the enthalpy changes shift to more negative values by increasing the amount of AN in the AN-DMSO mixture. This behavior is most probably due to the decreased competition of the solvent mixture with cryptand molecules for the cations. Meanwhile, the entropy change of the cryptate formation processes would also decrease significantly.

The decrease in ΔS° values, observed for different metal cryptates upon increasing the mole fraction of AN in the solvent mixture, could be due to the decreased solvation of the metal ion as well as the diminished degree of freedom of the resulting cryptate (compared with the free cryptand), mainly due to the increased rigidity of the cryptates formed. Consequently, the negative change in entropy may cancel some of the enthalpic gain resulting from stronger and tighter metal ion-cryptand binding.

TABLE I. Formation constants and enthalpy and entropy values for different metal cryptates in various AN-DMSO mixtures.^a

Cryptate	wt.% AN in solvent mixture	log K_f				$-\Delta H^\circ$ (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
		25 °C	35 °C	45 °C	55 °C		
Co ²⁺ —C222	10	2.78 ± 0.05	2.70 ± 0.06	2.61 ± 0.06	2.54 ± 0.07	15.2 ± 0.4	-2 ± 1
	20	3.00 ± 0.05	2.85 ± 0.04	2.65 ± 0.04	2.65 ± 0.04	22.0 ± 1.1	-16 ± 4
	30	3.27 ± 0.05	3.08 ± 0.05	2.86 ± 0.04	2.79 ± 0.04	31.2 ± 2.7	-42 ± 9
	40	3.45 ± 0.05	3.22 ± 0.05	3.00 ± 0.05	2.87 ± 0.05	37.9 ± 1.3	-61 ± 4
Co ²⁺ —C221	10	3.06 ± 0.05	2.95 ± 0.04	2.82 ± 0.03	2.74 ± 0.07	20.4 ± 0.7	-10 ± 3
	20	3.34 ± 0.05	3.17 ± 0.05	3.00 ± 0.05	2.87 ± 0.04	29.6 ± 0.6	-35 ± 2
	30	3.58 ± 0.05	3.40 ± 0.05	3.18 ± 0.05	2.97 ± 0.04	38.3 ± 1.3	-60 ± 4
	40	3.78 ± 0.06	3.51 ± 0.05	3.32 ± 0.05	3.06 ± 0.05	44.0 ± 1.4	-75 ± 5
Co ²⁺ —C211	10	4.10 ± 0.02	3.85 ± 0.07	3.71 ± 0.04	3.50 ± 0.06	36.4 ± 1.7	-44 ± 6
	20	4.40 ± 0.07	4.12 ± 0.06	3.85 ± 0.06	3.65 ± 0.05	47.3 ± 1.1	-74 ± 4
	30	4.64 ± 0.07	4.34 ± 0.07	4.15 ± 0.06	3.72 ± 0.04	49.6 ± 2.7	-77 ± 9
	40	4.85 ± 0.07	4.54 ± 0.07	4.28 ± 0.06	3.85 ± 0.06	60.9 ± 3.1	-111 ± 13
Ni ²⁺ —C222	10	3.21 ± 0.07	3.11 ± 0.04	3.01 ± 0.03	2.86 ± 0.03	21.5 ± 1.4	-10 ± 5
	20	3.49 ± 0.03	3.37 ± 0.04	3.22 ± 0.06	3.12 ± 0.07	23.6 ± 0.8	-12 ± 3
	30	3.75 ± 0.03	3.51 ± 0.07	3.40 ± 0.02	3.25 ± 0.01	30.2 ± 2.1	-30 ± 7
	40	3.92 ± 0.06	3.70 ± 0.07	3.52 ± 0.07	3.34 ± 0.07	36.0 ± 0.5	-46 ± 2
Ni ²⁺ —C221	10	4.00 ± 0.06	3.91 ± 0.03	3.84 ± 0.04	3.70 ± 0.05	18.1 ± 1.5	16 ± 5
	20	4.33 ± 0.08	4.15 ± 0.06	4.03 ± 0.07	3.91 ± 0.04	26.0 ± 1.0	-4 ± 3
	30	4.70 ± 0.04	4.44 ± 0.09	4.27 ± 0.08	4.15 ± 0.06	34.2 ± 2.5	-25 ± 8
	40	4.90 ± 0.10	4.63 ± 0.11	4.37 ± 0.09	4.30 ± 0.09	49.8 ± 0.7	-73 ± 3
Ni ²⁺ —C211	10	4.35 ± 0.04	4.21 ± 0.09	4.15 ± 0.04	3.96 ± 0.01	23.0 ± 2.4	6 ± 8
	20	4.79 ± 0.11	4.71 ± 0.10	4.42 ± 0.06	4.29 ± 0.09	30.0 ± 3.8	-29 ± 11
	30	5.30 ± 0.16	5.07 ± 0.09	4.83 ± 0.10	4.64 ± 0.11	41.6 ± 0.6	-38 ± 3
	40	5.60 ± 0.14	5.29 ± 0.10	5.00 ± 0.13	4.76 ± 0.11	52.7 ± 0.8	-70 ± 3

On the other hand, a weaker metal ion-cryptand binding is associated with an enthalpic loss which is partially compensated by a simultaneous entropic gain due to the greater degree of freedom of the resulting cryptate. The existence of such a compensating effect between the ΔH° and ΔS° values would cause the overall change in cryptate stability (ΔG°) to be smaller than might be expected from the change in either ΔH° or ΔS° independently.

There is actually a fairly good linear correlation between all the $T\Delta S^\circ$ and ΔH° values obtained in this study (Figure 10) with a regression equation

$$T\Delta S^\circ = T\Delta S_0^\circ + \alpha\Delta H^\circ \quad (1)$$

in which $T\Delta S_0^\circ = 15.1 \text{ kJ mol}^{-1}$, $\alpha = 0.78$ and $r = 0.9632$. Such a linear relationship between $T\Delta S^\circ$ and ΔH° was also reported by Inoue and Hakushi for

TABLE I. Continued.

Cryptate	wt.% AN in solvent mixture	log K_f				$-\Delta H^\circ$ (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
		25 °C	35 °C	45 °C	55 °C		
Cu ²⁺ —C222	10	3.10 ± 0.06	3.01 ± 0.07	2.96 ± 0.03	2.83 ± 0.01	16.0 ± 1.5	6 ± 5
	20	3.39 ± 0.04	3.23 ± 0.04	3.12 ± 0.06	3.02 ± 0.07	22.9 ± 1.0	-12 ± 3
	30	3.64 ± 0.06	3.45 ± 0.08	3.24 ± 0.08	3.07 ± 0.09	36.0 ± 0.6	-51 ± 2
	40	3.85 ± 0.04	3.61 ± 0.06	3.37 ± 0.07	3.09 ± 0.04	47.1 ± 1.5	-84 ± 5
Cu ²⁺ —C221	10	4.05 ± 0.06	3.91 ± 0.07	3.80 ± 0.06	3.71 ± 0.06	21.2 ± 0.7	6 ± 3
	20	4.27 ± 0.09	4.11 ± 0.07	3.93 ± 0.06	3.78 ± 0.06	30.9 ± 0.5	-22 ± 2
	30	4.50 ± 0.10	4.29 ± 0.04	4.16 ± 0.10	3.80 ± 0.04	33.3 ± 1.6	-26 ± 5
	40	4.73 ± 0.10	4.49 ± 0.10	4.21 ± 0.08	3.95 ± 0.08	59.3 ± 3.0	-108 ± 10
Zn ²⁺ —C222	10	2.90 ± 0.03	2.70 ± 0.03	2.64 ± 0.06	2.53 ± 0.01	22.0 ± 2.4	-18 ± 8
	20	3.10 ± 0.04	2.91 ± 0.05	2.75 ± 0.07	2.56 ± 0.01	33.3 ± 0.7	-52 ± 3
	30	3.71 ± 0.06	3.50 ± 0.06	3.20 ± 0.04	3.06 ± 0.03	42.2 ± 2.5	-71 ± 8
	40	3.92 ± 0.08	3.70 ± 0.08	3.40 ± 0.04	3.20 ± 0.02	46.1 ± 1.7	-79 ± 6
Zn ²⁺ —C221	10	3.16 ± 0.04	3.01 ± 0.06	2.81 ± 0.07	2.72 ± 0.02	28.5 ± 1.7	-35 ± 6
	20	3.43 ± 0.07	3.27 ± 0.04	3.04 ± 0.06	2.86 ± 0.01	36.3 ± 1.5	-56 ± 5
	30	3.81 ± 0.04	3.61 ± 0.04	3.30 ± 0.06	3.04 ± 0.07	49.0 ± 2.5	-91 ± 8
	40	4.10 ± 0.09	3.81 ± 0.08	3.57 ± 0.07	3.34 ± 0.06	42.7 ± 0.7	-80 ± 3
Zn ²⁺ —C211	10	3.93 ± 0.07	3.60 ± 0.04	3.47 ± 0.06	3.33 ± 0.05	36.4 ± 4.0	-47 ± 13
	20	4.33 ± 0.10	4.07 ± 0.09	3.92 ± 0.06	3.83 ± 0.04	31.1 ± 3.1	-21 ± 10
	30	4.69 ± 0.11	4.42 ± 0.09	4.24 ± 0.08	3.96 ± 0.06	44.4 ± 2.0	-59 ± 7
	40	5.05 ± 0.16	4.83 ± 0.10	4.65 ± 0.10	4.50 ± 0.10	34.4 ± 1.0	-19 ± 4
Cd ²⁺ —C222	10	3.79 ± 0.09	3.69 ± 0.06	3.53 ± 0.05	3.39 ± 0.05	25.4 ± 1.4	-13 ± 5
	20	4.12 ± 0.09	3.91 ± 0.06	3.70 ± 0.06	3.64 ± 0.06	31.1 ± 3.	-25 ± 10
	30	4.41 ± 0.12	4.28 ± 0.06	4.15 ± 0.04	4.01 ± 0.06	24.9 ± 0.6	1 ± 2
	40	4.65 ± 0.10	4.35 ± 0.08	3.90 ± 0.08	3.64 ± 0.06	65.2 ± 3.2	-130 ± 11
Cd ²⁺ —C221	10	4.21 ± 0.06	4.04 ± 0.05	3.80 ± 0.06	3.68 ± 0.06	34.3 ± 1.9	-34 ± 6
	20	4.78 ± 0.10	4.54 ± 0.06	4.33 ± 0.07	4.06 ± 0.08	44.3 ± 1.5	-57 ± 5
	30	5.30 ± 0.15	5.00 ± 0.09	4.69 ± 0.10	4.45 ± 0.09	53.6 ± 0.9	-78 ± 3
	40	5.70 ± 0.20	5.20 ± 0.09	4.75 ± 0.08	4.40 ± 0.09	81.9 ± 2.0	-165 ± 7
Cd ²⁺ —C211	10	3.32 ± 0.04	3.24 ± 0.03	3.16 ± 0.01	3.08 ± 0.01	15.0 ± 0.2	13 ± 1
	20	3.78 ± 0.04	3.65 ± 0.04	3.48 ± 0.06	3.39 ± 0.04	25.1 ± 1.2	-12 ± 4
	30	4.20 ± 0.06	4.01 ± 0.09	3.78 ± 0.09	3.62 ± 0.06	36.9 ± 1.0	-43 ± 4
	40	4.51 ± 0.09	4.20 ± 0.06	3.96 ± 0.06	3.66 ± 0.06	52.2 ± 1.3	-89 ± 5
Pb ²⁺ —C211	10	3.95 ± 0.04	3.83 ± 0.03	3.71 ± 0.03	3.60 ± 0.07	21.9 ± 0.1	2 ± 1
	20	4.35 ± 0.06	4.16 ± 0.07	3.96 ± 0.03	3.78 ± 0.04	35.8 ± 0.4	-37 ± 2
	30	4.85 ± 0.09	4.61 ± 0.09	4.30 ± 0.07	4.01 ± 0.09	70.4 ± 1.8	-143 ± 6
	40	5.15 ± 0.09	4.82 ± 0.10	4.42 ± 0.08	4.13 ± 0.07	64.5 ± 1.6	-118 ± 5

^aThe uncertainties associated with the thermodynamic parameters are reported as ± standard deviations.

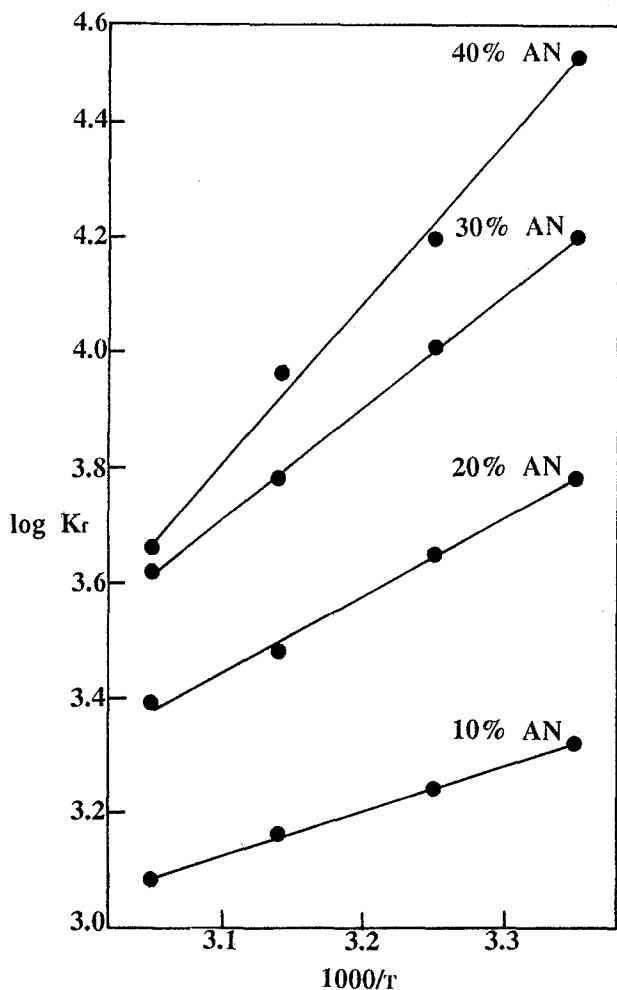


Fig. 8. Van't Hoff plots for Cd^{2+} —C221 in different AN—DMSO mixtures.

the complexation of metal ions with various types of ligands using the available thermodynamic parameters [48]. Equation (1) suggests that the entropic change consists of two components. The first component is independent of the enthalpy change ($T\Delta S_0^\circ$) and the second one is proportional to it ($\alpha\Delta H^\circ$). The proportionality factor, α , might be considered as a quantitative measure of the enthalpy–entropy compensation. The α value of 0.78 indicates that only 22% of the increase in ΔH° contributes to the increase in the cryptate stability.

The positive $T\Delta S_0^\circ$ value of 15.1 kJ mol^{-1} (the intrinsic entropic gain) emphasizes that the cryptate formation is favored even in the absence of any enthalpic gain (i.e. $\Delta H^\circ = 0$). This intrinsic entropic gain indicates the fundamental role of the solvent properties in the process of cryptate formation. Since, during the complexation of a cation by a cryptand, most of the coordinated solvent molecules

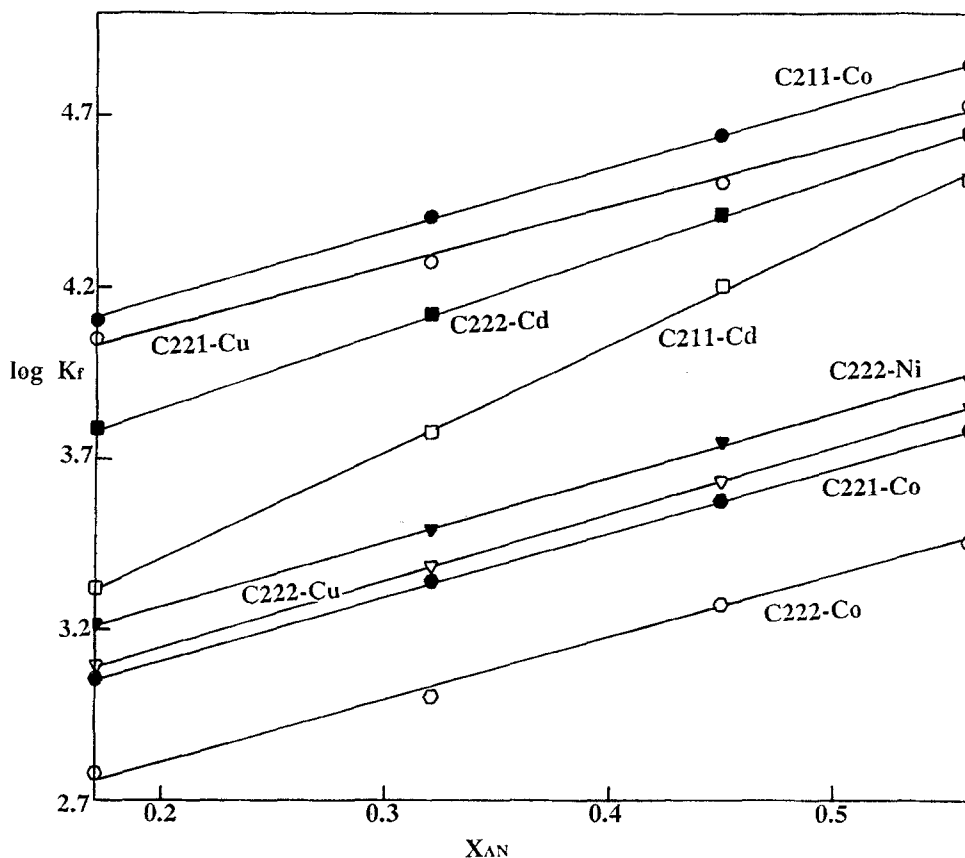


Fig. 9. Variation of $\log K_f$ of some metal cryptates at 25 °C with X_{AN} in the binary AN-DMSO mixtures.

are replaced by the donating atoms of the ligand, even when the cation-cryptand binding is weak, the increased degree of freedom due to the desolvation of cation may result in some positive entropic gain. In other words the $T\Delta S_0^\circ$ value indicates to what extent the solvation shell is replaced by the cryptand's donating groups. However, some contributions from the cryptate solvation as well as some possible interaction between solvent molecules and free cryptands [47] to the observed entropy changes cannot be neglected.

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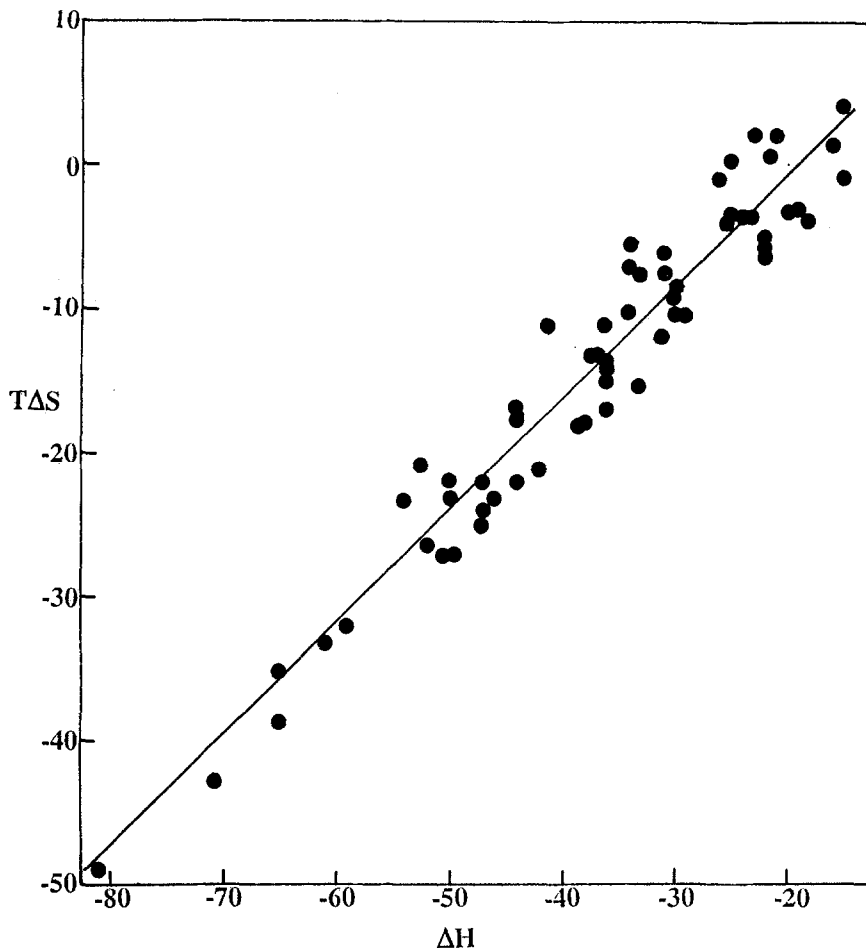


Fig. 10. Plot of $T\Delta S^\circ$ (kJ mol^{-1}) vs. ΔH° (kJ mol^{-1}) for different metal cryptates studied in various AN-DMSO mixtures.

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