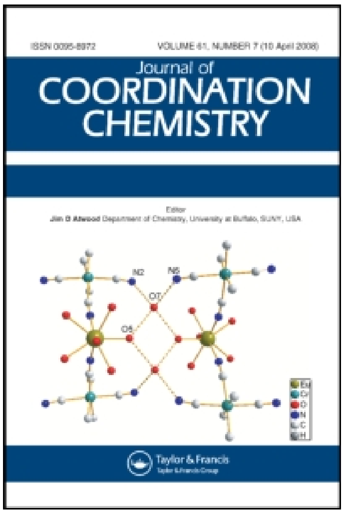

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SPECTROPHOTOMETRIC STUDY OF THE THERMODYNAMICS OF INTERACTION OF SOME METAL IONS WITH MUREXIDE IN BINARY ACETONITRILE-DIMETHYLSULFOXIDE MIXTURES

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To cite this Article Ghasemi, Jahanbakhsh and Shamsipur, Mojtaba(1995) 'SPECTROPHOTOMETRIC STUDY OF THE THERMODYNAMICS OF INTERACTION OF SOME METAL IONS WITH MUREXIDE IN BINARY ACETONITRILE-DIMETHYLSULFOXIDE MIXTURES', Journal of Coordination Chemistry, 36: 3, 183 — 194

To link to this Article: DOI: 10.1080/00958979508022560

URL: http://dx.doi.org/10.1080/00958979508022560

J. Coord. Chem., 1995, Vol 36, pp. 183–194
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SPECTROPHOTOMETRIC STUDY OF THE THERMODYNAMICS OF INTERACTION OF SOME METAL IONS WITH MUREXIDE IN BINARY ACETONITRILE-DIMETHYLSULFOXIDE MIXTURES

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(Received March 16, 1995; in final form May 11, 1995)

Complexation reactions between murexide and Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions have been studied in different acetonitrile-dimethylsulfoxide mixtures at various temperatures by a spectrophotometric technique. Formation constants of 1:1 and 2:1 (murexide to metal ion) complexes were determined from the absorbance-mole ratio data and found to vary in the order $Cu^{2+} > Cd^{2+} > Ni^{2+}$ $Co^{2+} > Zn^{2+} > Pb^{2+}$. A linear relationship is observed between log β_2 for different complexes and the mole fraction of acetonitrile in the solvent mixture. Enthalpy and entropy data for complexation were determined from the temperature dependence of stability constants. From the thermodynamic data obtained, the $T\Delta S°$ - $\Delta H°$ plot shows a fairly good linear correlation and indicates enthalpy-entropy compensation in the reactions.

KEYWORDS: murexide, complexes, formation constants, thermodynamics, spectrophotometry

INTRODUCTION

Murexide, the ammonium salt of purpuric acid (I) (5-[(hexahydroxy-2,4,6-trioxo-5-pyrimidinyl) imino]-2,4,6-(1H, 3H, 5H)-pyrimidinetrione, monoammonium salt) has been used for many years as a suitable complexing agent for a large number of metal ions over a wide range of experimental conditions.[1-4] In most cases, the ligand forms 1:1 complexes with mono-, di- and trivalent metal cations in aqueous,[3,5-8] nonaqueous[9-11] and mixed solvents.[12-14] The complexation is accompanied by a relatively strong shift of the absorption band of murexide, with $\lambda_{max} = 522$ nm in aqueous solution, towards shorter wavelengths;[3-15] the smaller the radius of the complexed cation, the larger is both the displacement and intensity of the band.[9,10] Since the metal ion-murexide equilibrium is very rapidly established

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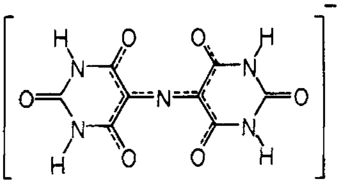

I

in aqueous[15] and methanol[16] solutions, the indicator has been used in the study of the thermodynamics[17–22] and kinetics[16,23,24] of a variety of metal complexes. Although evidence for the formation of 2:1 (ligand to metal) complexes between murexide and metal ions in solution has not been reported thus far, the formation and isolation of sandwich complexes of murexide with Ca^{2+}, Sr^{2+}, Cd^{2+}, Pb^{2+} and Fe^{2+} ions in crystalline form and corresponding structures have been reported by White and coworkers.[25–28]

Since the nature of solvent may strongly influence the stiochiometry and thermodynamics of metal complexes in solutions,[29,30] we decided to study complexation between murexide and Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions in binary acetonitrile-dimethylsulfoxide mixtures. In this paper we report the first observation of the formation of both 1:1 and 2:1 complexes of murexide with these cations in solution, as well as thermodynamic parameters for corresponding complexation processes in different acetonitrile-dimethysulfoxide mixtures by a spectrophotometric method.

EXPERIMENTAL

Reagent grade nitrate salts of cobalt, nickel, copper, zinc, cadmium, lead and murexide (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Reagent grade acetonitrile (AN, Merck) and dimethylsulfoxide (DMSO, Merck) were purified and dried by previously described methods.[31]

All spectra were recorded on a Philips PUB700 spectrophotometer and absorbance measurements were made with a Metrohm 662 probe type photometer at various temperatures. In all measurements, the cell was thermostated at the desired temperature ± 0.05 °C using a Lo-Temprol 154 Precision Scientific thermostat.

In a typical experiment, 10 cm^3 of the murexide solution in a given solvent mixture (3.0×10^{-5}–6.0×10^{-5} M) was placed in the titration cell, thermostated to the desired temperature and the absorbance of the solution at λ_{max} of murexide was measured. Then, a known amount of the metal solution in the same solvent mixture was added in a stepwise manner using a calibrated micropipette. The absorbance of the solution was measured after each addition. Addition of the metal ion solution was continued until the desired metal to murexide mole ratio was achieved.

When murexide, L^-, reacts with a metal ion, M^{2+}, in solution, it may form either a 1:1 complex (model I) or both 1:1 and 2:1 complexes (model II). The mass balance equations of the two possible models in solution, shown in Table 1, can be solved in order to obtain equations for the free ligand concentration [L] (Table 2). The observed absorbance of solution is also given by

Table 1 Mass-balance equations used in the computer program KINFIT for evaluation of spectrophotometric data.

Model	Reactions	Stability constants	Mass-balance equations
I	$M + L = ML$	$K_1 = [ML]/[M][L]$	$C_M = [M] + [ML]$ $C_L = [L] + [ML]$
II	$M + L = ML$ $ML + L = ML$	$K_1 = [ML]/[M][L]$ $K_2 = [ML_2]/[ML][L]$	$C_M = [M] + [ML] + [ML_2]$ $C_L = [L] + [ML] + 2[ML_2]$

$$A_{obs} = \varepsilon_L[L] + \varepsilon_{ML}[ML] + \varepsilon_{ML_2}[ML_2] \qquad (1)$$

where ε values are the molar absorptivities of the species denoted. For evaluation of the formation constants from the absorbance *vs* C_M/C_L mole ratio data, a non-linear, least-squares, curve fitting program KINFIT was used.[32] The program is based on the iterative adjustment of calculated values of absorbance to observed values by using either the Wentworth matrix technique[33] or the Powell procedure.[34] Adjustable parameters are the stepwise formation constants of all complexes present and the corresponding molar absorptivities (*i.e.*, 2 and 4 adjustable parameters for models I and II given in Table 1, respectively).

For models I and II, the free ligand concentrations, [L], were calculated by means of a Newton-Raphson procedure. Once the value of [L] had been obtained, the concentrations of all other species involved are calculated from the corresponding mass-balance equations given in Table 1, by using the estimated values of the formation constants at the current iteration step of the program. Refinement of the parameters was continued until the sum-of-squares of the residuals between calculated and observed values of the absorbance for all experimental points was minimized. The output of the program KINFIT comprises the refined parameters, the sum-of-squares and the standard deviation of the data.

RESULTS AND DISCUSSION

The absorption spectra of murexide and its complexes with Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions in various An-DMSO mixtures were obtained. Sample visible spectra for titration of murexide with Cu^{2+} ion in 40% AN at 25°C are shown in Figure 1. As it was pointed out before,[3,11,13,14] all the resulting complexes are distinguished by a strong and ion specific blue-shift (20-90 nm), the reasons for which are discussed elsewhere.[9,10,16] The stoichiometry of the complexes in different AN-DMSO mixtures was examined by the method of continuous variation.[35] A sample of the resulting plots is shown in Figure 2. It is evident that both 1:1 and 2:1 (murexide to metal ion) complexes are formed in solution. The

Table 2 Solution of the mass-balance equations given in Table 1 in terms of the free ligand concentration [L].

Model	Solution
I	$K_1[L]^2 + (1 + K_1(C_M\text{-}C_L)[L]\text{-}C_L = 0$
II	$K_1K_2[L]^3 + (K_1(1 + K_2(2\ C_M\text{-}C_L)))[L]^2 + (1 + K_1(C_M\text{-}C_L))[L]\text{-}C_L = 0$

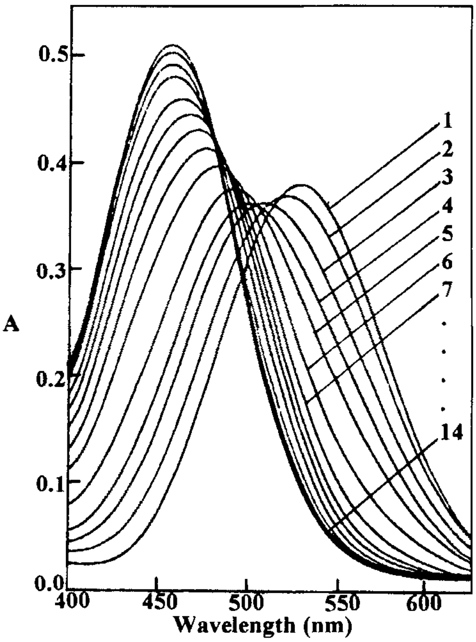

Figure 1 Visible spectra for titration of murexide (3.8×10^{-5} M) with Cu^{2+} ion in 40% AN at 25°C. Respective concentrations of the Cu^{2+} ion (M) in different solutions are: 1, 0; 2, 6.1×10^{-6}; 3, $1.3-10^{-5}$; 4, 1.9×10^{-5}; 5, 2.5×10^{-5}; 6, 3.1×10^{-5}; 7, 3.7×10^{-5}; 8, 4.3×10^{-5}; 9, 4.9×10^{-5}; 10, 5.5×10^{-5}; 11, 6.1×10^{-5}; 12, 6.8×10^{-5}; 13, 7.4×10^{-5}; 14, 8.0×10^{-5} M.

formation of such species in AN-DMSO mixtures was further supported by the mole ratio method (see Figure 3).

The stepwise formation constants of the resulting 1:1 and 2:1 murexide-metal ion complexes in different AN-DMSO solvent mixtures were obtained at various temperatures by absorbance measurements, at λ_{max} of murexide, of solutions in which varying concentrations of metal ions were added to fixed amounts of murexide in solution (see Figure 1). All the resulting absorbance-mole ratio data were best fitted to model II (Tables 1 and 2), which further supports the formation of both 1:1 and 2:1 complexes in solution. Sample computer fits of the absorbance-mole ratio data are shown in Figure 3. It is interesting to note that the existance of two inflection points at C_M/C_L values of about 0.5 and 1 in the mole ratio plots shown in Figures 3A and 3B clearly indicate the formation of 1:1 and 2:1 adducts in solution. Moreover, despite the absence of such clear inflection point at C_M/C_L of about 0.5 in Figure 3C, model I (*i.e.*, the formation of only a 1:1 complex) cannot be fitted to the observed data, while it is nicely fitted to model II by assuming the formation of the two complex species in solution.

In order to have a better understanding of the themodynamics of complexation between murexide and metal ions in different AN-DMSO mixtures, it is useful to consider the enthalpic and entropic contributions to these reactions. The enthalpy and entropy of the complexation reactions were determined by measuring the stepwise formation constants of the resulting 1:1 and 2:1 complexes as a function

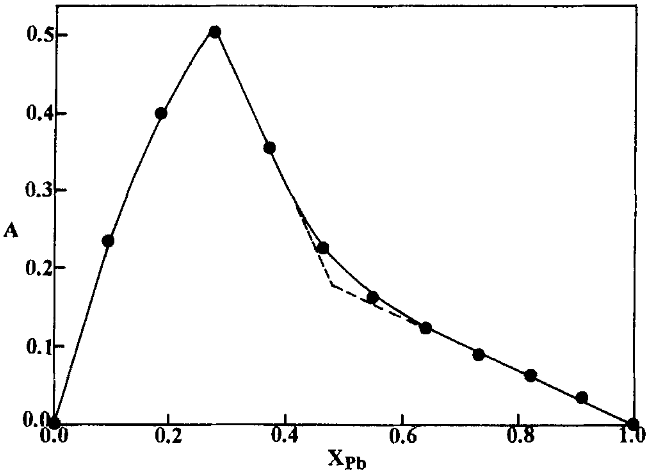

Figure 2 Continuous variation plot for Pb^{2+}-murexide in 40% AN. Conditions: total concentration, 7.7×10^{-4}; $\lambda = 510$ nm.

of temperature. All the log K_1 and log K_2 values evaluated from the computer fitting of the corresponding absorbance-mole ratio data are listed in Table 3. Van't Hoff plots of log K *vs* 1/T for different murexide complexes in various solvent mixtures were linear (see for example Figure 4). $\Delta H°$ and $\Delta S°$ values were determined in the usual manner from the slopes and intercepts of the plots, respectively, and the results are also included in Table 3.

The data given in Table 3 show that the sequence of the overall stability (log K_1 + log K_2) of the murexide complexes with the cations of the first transition series (*i.e.*, $Zn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$) follows the Irving-Williams order,[36] which generally holds for the equilibrium constants of transition metals.[11,13,20,37] On the other hand, the overall stability of the cadmium-murexide complex is about two orders of magnitude larger than that of lead-murexide. This is probably due to the size of the Cd^{2+} ion which could favour a suitable spatial fit with the flexible donating atoms of the ligand (bridging nitrogen atoms and neighbouring oxygens).[10] It should be noted that the Cd^{2+} ion has about the same size as Na^+ and Ca^{2+} ions,[3] which have been shown to form the most stable complexes among alkali and alkaline earth cations with murexide, respectively.[3,9,10]

From the data given in Table 3 it is obvious that solvent properties play a fundamental role in complex formation. In all cases, the stability of the resulting murexide complexes increases with increasing weight percent of AN in the mixed solvent. It is well known that the Gutmann donating ability of solvent[39] plays a key role in different complexation reactions.[9,10,17,18,21,38] DMSO is a solvent of high solvating ability (DN = 29.8) which can strongly compete with murexide for the metal ions. Thus, it is not surprising that addition of AN as a relatively low donor solvent (DN = 14.1) to DMSO will increase the stability of murexide complexes. It should be noted that the somewhat lower dielectric constant of AN (38.0) in comparison with that of DMSO (45.0) would cause the electrostatic contribution to the bond formation to increase with increasing amounts of AN in the solvent mixture.

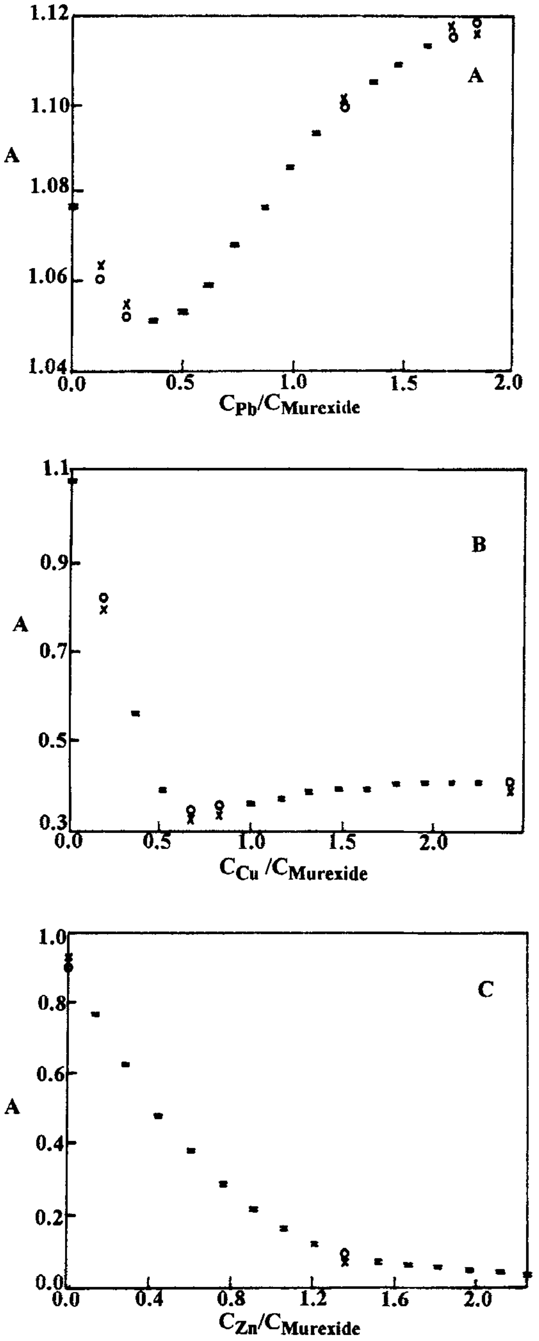

Figure 3 Computer fit of absorbance-mole ratio data obtained from the complexation of Pb^{2+} (A), Cu^{2+} (B) and Zn^{2+} (C) ions with murexide in 40% AN at 25°C: (X) experimental points; (O) calculated points; (=) experimental and calculated points are the same within the resolution of the plot.

Table 3 Formation constants and enthalpy and entropy values for different murexide-M^{2+} complexes in various AN-DMSO mixtures.

Cation	wt%AN in solvent mixture	Stoichio-metry	Log K^a				$\Delta H^{\circ a}$ (kJ mol^{-1})	$\Delta S^{\circ a}$ (J mol^{-1} K^{-1})	$\Delta H^\circ_1 + \Delta H^\circ_2$ (kJ mol^{-1})	$\Delta S^\circ_1 + \Delta S^\circ_2$ (J mol^{-1} K^{-1})
			25°C	35°C	45°C	55°C				
CO^{2+}	10	1:1	5.28(0.01)	5.30(0.01)	5.33(0.02)	5.35(0.03)	4.5(0.1)	116(1)	-21.0	115
		2:1	4.42(0.03)	4.26(0.04)	4.16(0.04)	4.00(0.09)	-25.5(1.0)	-1(4)		
	20	1:1	5.24(0.04)	5.29(0.02)	5.33(0.03)	5.37(0.01)	8.0(0.1)	127(1)	-11.7	147
		2:1	4.48(0.07)	4.39(0.08)	4.27(0.02)	4.17(0.04)	-19.7(0.6)	20(2)		
	30	1:1	5.20(0.01)	5.26(0.02)	5.32(0.03)	5.39(0.04)	11.7(0.3)	139(1)	-5.6	168
		2:1	4.54(0.01)	4.43(0.06)	4.35(0.06)	4.26(0.06)	-17.3(0.4)	29(1)		
	40	1:1	5.16(0.02)	5.24(0.02)	5.32(0.01)	5.41(0.01)	15.5(0.4)	151(1)	2.0	194
		2:1	4.62(0.02)	4.56(0.03)	4.47(0.03)	4.41(0.01)	-13.5(0.5)	43(2)		
Ni^{2+}	10	1:1	4.17(0.18)	4.80(0.09)	5.56(0.14)	6.00(0.02)	117.0(5.0)	473(16)	57.7	383
		2:1	5.68(0.2)	5.37(0.11)	5.00(0.09)	4.75(0.03)	-59.3(1.7)	-90(6)		
	20	1:1	4.72(0.09)	4.96(0.08)	5.20(0.06)	5.51(0.10)	48.7(2.2)	253(1)	6.1	218
		2:1	5.67(0.08)	5.40(0.21)	5.22(0.12)	4.97(0.09)	-42.8(1.4)	-35(5)		
	30	1:1	5.15(0.08)	5.12(0.05)	5.07(0.09)	5.05(0.04)	-6.6(0.4)	77(2)	-35.7	8
		2:1	5.64(0.09)	5.49(0.10)	5.32(0.11)	5.18(0.09)	-29.1(0.5)	11(2)		
	40	1:1	5.60(0.03)	5.31(0.08)	5.00(0.15)	4.72(0.26)	-55.3(0.7)	78(2)	-65.7	151
		2:1	5.64(0.04)	5.57(0.07)	5.53(0.1)	5.47(0.18)	-10.4(0.4)	73(1)		
Cu^{2+}	10	1:1	5.33(0.13)	5.78(0.10)	6.20(0.12)	6.63(0.10)	80.9(1.0)	373(3)	66.8	429
		2:1	5.37(0.10)	5.30(0.08)	5.21(0.06)	5.15(0.07)	-14.1(0.4)	56(2)		
	20	1:1	5.84(0.10)	6.05(0.09)	6.30(0.15)	6.53(0.09)	43.4(1.1)	257(4)	40.7	350
		2:1	5.32(0.08)	5.30(0.06)	5.28(0.10)	5.27(0.11)	-2.7(0.4)	93(1)		
	30	1:1	6.21(0.09)	6.30(0.21)	6.38(0.09)	6.47(0.15)	16.0(0.20)	173(1)	26.6	309
		2:1	5.27(0.10)	5.32(0.09)	5.38(0.07)	5.44(0.06)	10.6(0.3)	136(1)		
	40	1:1	6.64(0.08)	6.55(0.14)	6.48(0.07)	6.40(0.04)	-14.9(0.2)	77(1)	16.3	282
		2:1	5.23(0.04)	5.42(0.05)	5.56(0.04)	5.74(0.04)	31.2(0.8)	205(3)		

Table 3 Continued

Cation	wt%AN in solvent mixture	Stoichio-metry	Log K[a]				$\Delta H^{\circ a}$ (kJ mol^{-1})	$\Delta S^{\circ a}$ (J mol^{-1} K^{-1})	$\Delta H^{\circ}_1 + \Delta H^{\circ}_2$ (kJ mol^{-1})	$\Delta S^{\circ}_1 + \Delta S^{\circ}_2$ (J mol^{-1} K^{-1})
			25°C	35°C	45°C	55°C				
Zn^{2+}	10	1:1	5.00(0.02)	4.92(0.01)	4.77(0.04)	4.61(0.03)	-24.7(2.1)	-14(7)	-104.9	-209
		2:1	3.87(0.03)	3.39(0.06)	3.01(0.10)	2.57(0.25)	-80.2(1.5)	-195(5)		
	20	1:1	5.14(0.06)	5.07(0.06)	5.00(0.04)	4.93(0.05)	-13.2(0.1)	54(1)	-73.2	-73
		2:1	3.87(0.04)	3.53(0.04)	3.21(0.07)	2.91(0.08)	-60.0(0.1)	-127(1)		
	30	1:1	5.31(0.04)	5.28(0.03)	5.25(0.04)	5.22(0.06)	-5.7(0.01)	83(1)	-45.9	23
		2:1	3.89(0.06)	3.61(0.09)	3.40(0.10)	3.23(0.09)	-40.2(2.0)	-60(6)		
	40	1:1	5.48(0.06)	5.48(0.06)	5.50(0.07)	5.51(0.09)	1.8(0.1)	111(1)	2.5	188
		2:1	3.89(0.08)	3.89(0.8)	3.90(0.09)	3.90(0.08)	0.7(0.1)	77(1)		
Cd^{2+}	10	1:1	5.91(0.02)	5.82(0.03)	5.74(0.06)	5.66(0.02)	-15.6(0.4)	61(1)	-37.5	79
		2:1	4.65(0.02)	4.55(0.06)	4.44(0.06)	4.31(0.03)	-21.9(1.0)	18(3)		
	20	1:1	6.14(0.01)	5.99(0.10)	5.85(0.09)	5.71(0.06)	-26.8(0.1)	28(1)	-31.9	101
		2:1	4.70(0.01)	4.67(0.01)	4.64(0.03)	4.62(0.04)	-5.1(0.1)	73(1)		
	30	1:1	6.36(0.15)	6.17(0.16)	5.96(0.10)	5.79(0.08)	-36.0(0.5)	1(2)	-29.7	114
		2:1	4.77(0.05)	4.80(0.04)	4.84(0.01)	4.87(0.11)	6.3(0.2)	113(1)		
	40	1:1	6.51(0.15)	6.28(0.09)	6.07(0.1)	5.85(0.02)	-41.1(0.4)	124(2)	-30.7	238
		2:1	4.83(0.15)	4.88(0.06)	4.93(0.09)	5.00(0.02)	10.4(0.5)	114(1)		
Pb^{2+}	10	1:1	5.51(0.05)	5.40(0.04)	5.26(0.02)	5.15(0.02)	-22.9(0.6)	29(2)	-8.4	138
		2:1	3.15(0.1)	3.21(0.09)	3.30(0.07)	3.38(0.09)	14.5(0.7)	109(3)		
	20	1:1	5.48(0.04)	5.40(0.05)	5.31(0.06)	5.24(0.07)	-15.2(0.2)	54(1)	-0.8	167
		2:1	3.37(0.08)	3.44(0.10)	3.60(0.08)	3.60(0.08)	14.4(0.4)	113(1)		
	30	1:1	5.44(0.10)	5.41(0.09)	5.36(0.10)	5.32(0.09)	-7.7(0.4)	78(1)	2.9	185
		2:1	3.73(0.08)	3.78(0.09)	3.84(0.11)	3.90(0.13)	10.6(0.3)	107(1)		
	40	1:1	5.41(0.06)	5.43(0.09)	5.45(0.15)	5.46(0.10)	3.1(0.1)	114(1)	7.5	205
		2:1	3.96(0.15)	3.98(0.14)	3.99(15)	4.03(0.14)	4.4(0.2)	91(1)		

[a] Values in parentheses indicate standard deviations.

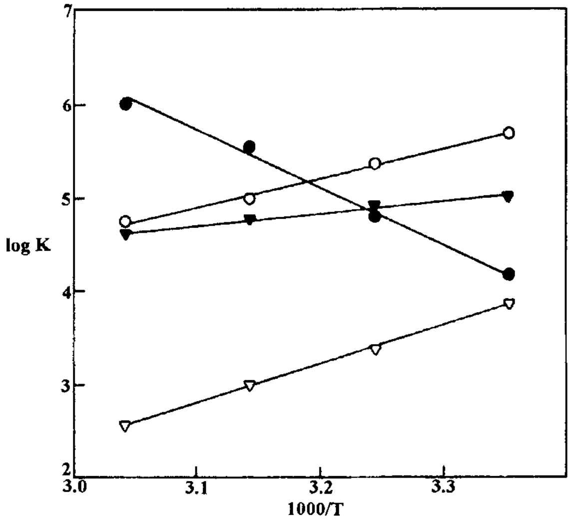

Figure 4 Van't Hoff plots for Ni^{2+}-murexide (O, K_1; ●, K_2) and Zn^{2+}-murexide (▽, K_1; ▼, K_2) systems in 10% AN.

It is interesting to note that there is a linear relationship between log β_2 (= log K_1 + log K_2) of the murexide complexes and the mole fraction of acetonitrile (X_{AN}) in the mixed solvent (Figure 5). The same trend has already been reported for various complexes in different solvent mixtures.[13,14,22,40-42] It has been reasonably assumed that the preferential solvation of the cations by DMSO is mainly responsible for such a monotonic dependence of the overall stability of the murexide complexes on the solvent composition.

The thermodynamic data given in Table 3 clearly indicate that the ΔH° and ΔS° values obtained for different metal ion-murexide complexes vary significantly with mixed solvent composition, mainly due to variation in the solvation-desolvation behaviour of the ionic species involved (*i.e.*, metal ion, murexide and their 1:1 complexes). It is interesting to note that the trend observed for the influence of solvent on the thermodynamic data varies with the nature of the cation used. This could be a result of the existence of different structural systems for the resulting murexide complexes of different metal ions used in solution. Such differences in the crystalline structure of some metal ion-murexide complexes (1:1 and 2:1 adducts) have already been reported in the literature.[25-27,43]

As it is obvious from Table 3, by increasing the weight percent of AN in the mixed solvent, both ΔH° and ΔS° values for the formation of both 1:1 and 2:1 adducts of murexide with Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions shift to more positive values, while those of Ni^{2+} and Cu^{2+}-murexide complexes show more negative enthalpy and entropy changes. However, it is well known that the tetrahedral complexes are the most common type for Co^{2+} and Cd^{2+} ions and are formed with a variety of O-donor and N-donor ligands.[44] On the other hand, the most common coordination structures for Ni^{2+} and Cu^{2+} are octahedral and square planar, being distorted in the case of copper complexes due to the Jahn-Teller effect.[44] Thus, due to the possible similarities in the coordination structure of the resulting complexes

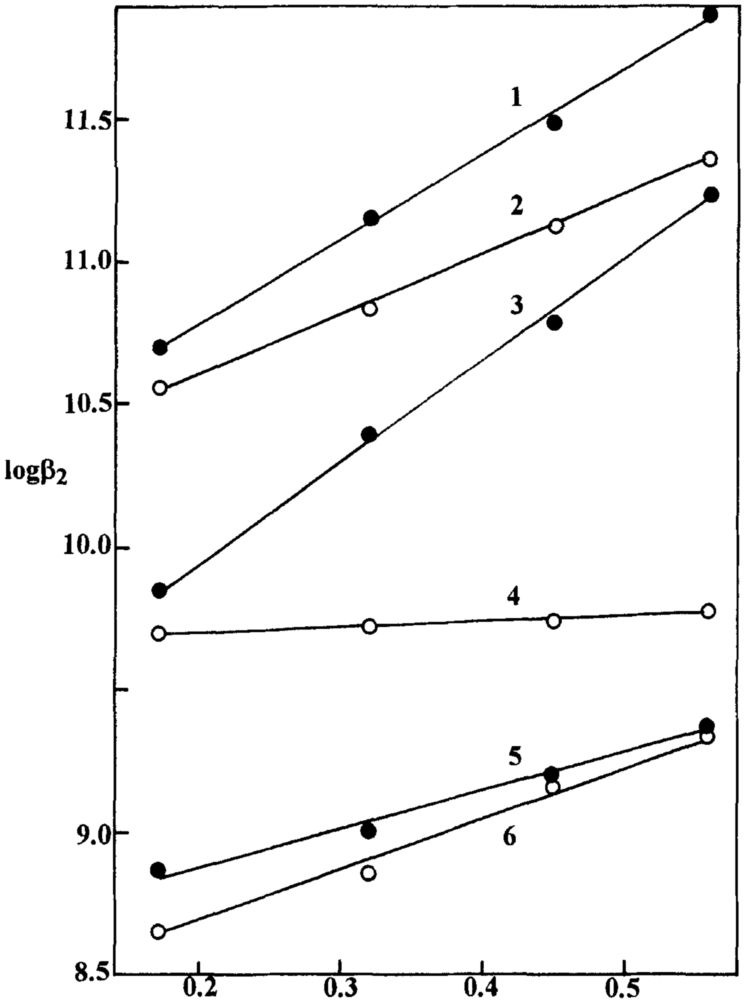

Figure 5 Variation of overall stabilities of different metal ion complexes of murexide with X_{AN}: 1, Cu^{2+}; 2, Cd^{2+}; 3, Ni^{2+}; 4, Co^{2+}; 5, Zn^{2+}; 6, Pb^{2+}.

between murexide and Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ions, on the one hand, and between those with Ni^{2+} and Cu^{2+}, on the other, it is not surprising to observe similar trends for the solvent effect on the thermodynamics of complexation for each series of complexes.

Despite the abovementioned variations in the solvent effect on the thermodynamic parameters of metal ion-murexide complexes, the $T\Delta S°$ - $\Delta H°$ plot of all thermodynamic data obtained shows a fairly good linear correlation (Figure 6), indicating the existence of enthalpy-entropy compensation in the complexation reactions. Such a compensation effect has been reported previously for different

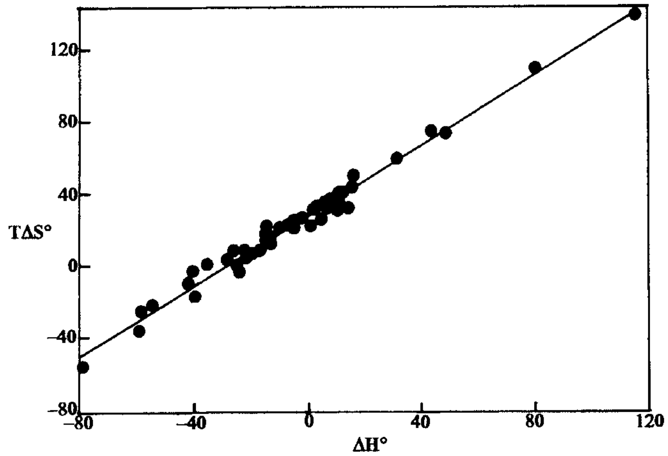

Figure 6 Plot of ΔH° vs TΔS° for 1:1 and 2:1 complexation of different metal ions with murexide in various solvent mixtures.

metal ion-ligand systems.[22,35,45] The linear correlation observed between TΔS° and ΔH° values can be expressed as

$$T\Delta S = T\Delta S_0^\circ + \alpha\Delta H^\circ \qquad (2)$$

with $T\Delta S_0^\circ = 28.7$ kJ mol^{-1} and $\alpha = 0.98$.

Equation (2) suggests that the entropic effect consists of two components. The first component ($T\Delta S_0^\circ$) is independent of enthalpy change and the second is proportional to it. The proportionality constant α might be considered as a quantitative measure of the enthalpy-entropy compensation. For $\alpha = 0.98$, only 2% of the increase in ΔH contributed to complex stability. The positive intercept of $T\Delta S_0^\circ = 28.7$ kJ mol^{-1} reveals that complex formation is favoured even in the absence of any enthalpic gain (*i.e.*, $\Delta H^\circ = 0$). These results show the fundamental role of solvent in the complexation process. Since both reactants involved in complexation (*i.e.*, metal ion and murexide) are charged and, thus, more or less solvated by solvent molecules, complex formation may result in the release of a significant number of solvent molecules to the solution. Therefore, even when cation-murexide binding is weak, desolvation of cation and murexide may result in some positive entropic gain.

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