

SPECTROPHOTOMETRIC STUDY OF THERMODYNAMICS OF SOME HEAVY METAL COMPLEXES OF 4-(2 - PYRIDYLAZO) RESORCINOL IN BINARY ACETONITRILE- DIMETHYLFORMAMIDE MIXTURES

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Abstract

The complexation reactions between 4-(2-pyridylazo)-resorcinol and Cd^{2+} , Hg^{2+} and Pb^{2+} ions have been investigated in acetonitrile-dimethylformamide mixtures at various temperatures using a spectrophotometric technique. The stoichiometry and the formation constants of the complexes formed in solution were calculated by computer refinement of absorbance-mole ratio data using nonlinear least-square program. The stoichiometries of resulting complexes are 1:1, 1:1-2:1 and 1:2 (metal-to-ligand ratio) for Pb^{2+} , Hg^{2+} and Cd^{2+} respectively. Linear relationship is observed between equilibrium constants and the mole fraction of acetonitrile in the solvent mixtures. The ΔH° and ΔS° of complex formation reactions were calculated from the temperature dependence of the stability constants. The effects of solvent composition on stability and thermodynamic parameters were discussed.

Introduction

Equilibrium data provide important means for speculation about the structural parameters influencing stability, linearity of free energy relations and solvent effects. Stability constants are very important both in the analysis of drugs, as well as, in the interpretation of their mechanism of action [1]. So up to the present, a large number of papers have been devoted to the study of

complexation reactions between metal ions and indicator ligands [2-4]. In spite of the large number of papers published, many gaps remain. A further significant defect is that some of the data are not reliable. Precise methods should be applied to obtain reliable data on the complexation reactions of indicators. Among the several physicochemical methods for studying the complex equilibria in solution, spectrophotometry (i.e. UV-Vis.) under broad experimental conditions and with subsequent computer treatment of experimental data is a very powerful method [5]. PAR, 4-(2-pyridylazo) resorcinol (Fig. 1- I), mono sodium salt has been used for many years as a suitable color complexing agent for a large number of metal ions over a wide range of experimental conditions [6]. In most cases, the ligand

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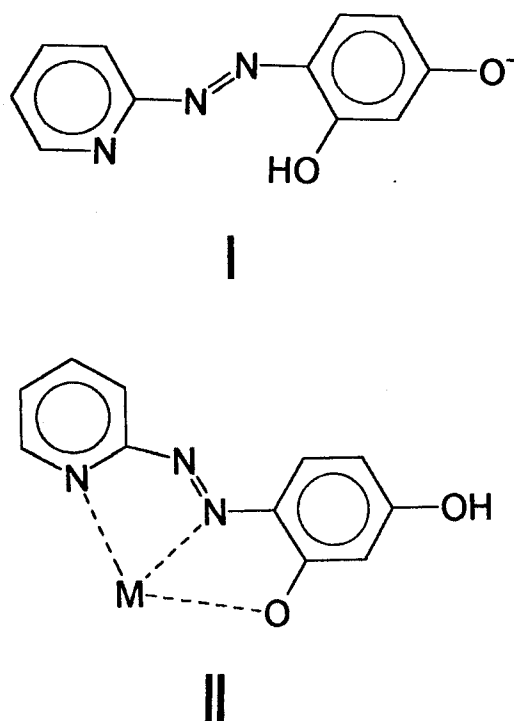


Figure 1. Structure of free (I) and 1:1 complexed (II) PAR from Ref. 11

forms 1:1 (Fig.1 - II), 1:2 and occasionally 1:3 (metal to ligand ration) complexes with di-, tri and tetravalent metal cations in aqueous and mixed solvents [7]. The complexation is accompanied by a relatively strong shift of the absorption band of PAR with $\lambda_{\max} = 413$ nm in aqueous solution towards longer wavelength.

Since the nature of solvent may strongly influence the stoichiometry and thermodynamics of metal complexes in solutions [8], we decided to study complexation between PAR and Cd^{2+} , Pb^{2+} and Hg^{2+} ions in binary acetonitrile dimethylformamide mixtures. To our knowledge, there aren't any reports on the complexation of these metal ions with PAR in non aqueous solvent mixtures. In this paper we report the first observation of the formation of both 1:1 and unusual 2:1 complexes of PAR with Hg^{2+} ion in solution, as well as, the thermodynamic parameters for corresponding complexation processes in different acetonitrile-dimethylformamide mixtures by a photometric titration method.

Experimental Section

Reagent grade mercury chloride, tetraethylammonium perchlorate (TEAP), nitrate salts of cadmium and lead and 4-(2-pyridylazo)resorcinol (all from Merck) were used without any further purification except for vacuum drying

over P_2O_5 for 72 hours. Spectroscopy grade acetonitrile (AN, Merck) and dimethylformamide (DMF, Merck) were purified and dried by previously described methods [9].

The spectra were recorded on a GBC Model 911 spectrophotometer and absorbance measurements at a fixed wavelength were made with a Metrohm 662 probe type photometer at various temperatures. In all measurements, the cell temperature was fixed at the desired temperature of ± 0.1 °C using a HAAKED1 thermostat.

In a typical experiment, 10ml of the PAR solutions in a given solvent mixture ($\sim 2 \times 10^{-5}$ M) was placed in the titration cell, thermostated at the desired temperature and the absorbance of the solution at λ_{\max} of complex 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 PAR mole ratio was achieved. In all experiments the ionic strength of the solutions was kept constant by TEAP at 0.1M.

For continuous variation method, in a series of 10ml volumetric flasks, the metal and ligand solutions of the same concentration ($\sim 2 \times 10^{-5}$ M) in a given solvent were mixed in such a way that volume and the moles of each reactants varied systematically. The absorbance of each solution was measured at λ_{\max} of the complex and corrected for ligand absorbance effect. The corrected absorbance was plotted against the volume or mole fraction of metal ($C_M / C_M + C_L$) where C_M and C_L are the metal and ligand concentration, respectively.

When one of the metal ions, M^{2+} reacts with a ligand L in the solution in the absence of proton equilibria, as it is usual for such a media, it may form 1:1 complex (model I), simultaneous 1:1 and 1:2 complexes (model II) and/or simultaneous 1:1 and 2:1 complexes (model III). The mass balance equations of the three possible models in the solution, shown in Table 1, can be solved in order to obtain equations for the free ligand (model I, II) or metal (model III) concentration (Table 2). The observed absorbance of solution is also given by

$$A_{\text{obs}} = \epsilon_L [L] + \sum_i \epsilon_{ML_i} [ML_i] + \sum_j \epsilon_{M_jL} [M_jL]$$

where ϵ values are the molar absorptivities of the species connoted. For evaluation of the formation constants from the absorbance $v_s C_M / C_L$ mole ratio data a non-linear, least-squares, curve fitting program written in this department on the basis of the Gauss-Newton algorithm [10]. The program is based on the iterative adjustment of the calculated values of absorbance to observed values

$$SS = \sum_i (A_{\text{obs},i} - A_{\text{calc},i})^2$$

where SS is the sum of squared difference in each iteration

step. Adjustable parameters are the stepwise formation constants of all species present and their molar absorptivities.

For models I, II and III, the free ligand or metal concentrations, [L] or [M], were calculated by means of a Newton-Raphson procedure. Once the value of [L] or [M] has been obtained, the concentrations of all other species involved are calculated from the corresponding mass-balance equations given in Table 1, using the current values of the formation constants at the current iteration step of the program. Adjustments of the parameters were continued until the SS differences between calculated and the observed value of the absorbance for all experimental points were minimized. The printout of the routine comprises the adjusted parameters, their standard derivation, and SS of the fitting process.

Results and Discussion

The visible spectra of PAR and its metal complexes in different AN-DMF mixtures were obtained. Samples of visible spectra for the titration of PAR with Cd²⁺, Pb²⁺ and Hg²⁺ ions in various mixtures of AN-DMF at 25°C are shown in Figures 2-4, respectively. As is usual for several complex formations, all of the resulting complexes are detected by a strong red shift (ca 130 nm) compared to the free ligand [11]. Generally, the electrostatic interaction of a bound metal ion would not be able to produce such

pronounced effects on the electronic structure of a dye molecule, and hence on its spectrum [12]. It thus seems reasonable to assume that a large change in the conjugation of the PAR molecule, brought about by metal ion complexation, is responsible for the spectral changes. The two six membered rings of the ligand that are quite twisted around the N-C bond in solution, would be fixed in the same plane as a result of complexation by metal ion. Consequently, a longer conjugated system result and complex PAR will absorb at lower energy, as compared to its free form. The stoichiometry of the complexes in different AN-DMF were examined by the method of continuous variations [14]. For each equilibrium model (I, II or III), a sample of the resulting plots are shown through Figure 5. Evidently, 1:1, 1:2 and 2:1 complexes are formed in solution for, Pb²⁺, Cd²⁺ and Hg²⁺, respectively. The formation of such species in AN-DMF mixtures was further supported by the mole ratio method, for example see Figure 6.

The stepwise formation constants of the resulting 1:1, 2:1 and 1:2 PAR-metal ion complexes in different AN-DMF solvent mixtures were obtained at various temperatures by absorbance measurements at of λ_{max} of complexes of solutions in which varying concentrations of metal ion were added to fixed amounts of PAR in the solutions. The resulting absorbance-mole ratio titration data were fitted to models I, II and III (Table 1 and 2); then,

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

Model	Reaction	Stability	Mass-Balance Eq.
I	$M + L = ML$	$K_1 = [ML]/[M][L]$	$C_M = [M] + [ML]$ $C_L = [ML] + [L]$
II	$M + L = ML$ $ML + L = ML_2$	$K_1 = [ML]/[M][L]$ $K_2 = [ML_2]/[ML][L]$	$C_M = [M] + [ML] + [ML_2]$ $C_L = [ML] + 2[ML_2] + [L]$
III	$M + L = ML$ $ML + M = M_2L$	$K_1 = [ML]/[M][L]$ $K_2 = [M_2L]/[ML][L]$	$C_M = [M] + [ML] + 2[M_2L]$ $C_L = [ML] + [M_2L] + [L]$

Table 2. Solution of the mass balance equations given in Table 1. In terms of the free ligand and metal concentration ([L] and [M])

Model	Solution
I	$K_1[L]^2 + (1 + K_1(C_M - C_L))[L] - C_L = 0$
II	$K_1K_2[L]^3 + (K_1(1 + K_2(2C_M - C_L)))[L]^2 + (1 + K_2(C_M - C_L))[L] - C_L = 0$
III	$K_1K_2[M]^3 + (K_1(1 + K_2(2C_L - C_M)))[M]^2 + (1 + K_1(C_L - C_M))[M] - C_M = 0$

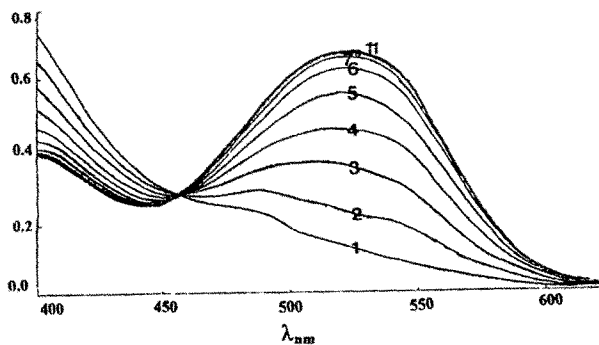


Figure 2. Visible spectra for titration of PAR (3.879×10^{-5} M) with Cd^{2+} in 40% AN 25°C. Respective concentration of the Cd^{2+} ion (M) in different solutions are: 1, 0; 2, 4.1×10^{-6} ; 3, 8.2×10^{-6} ; 4, 1.2×10^{-5} ; 5, 1.64×10^{-5} ; 6, 2.05×10^{-5} ; 7, 2.5×10^{-5} ; 8, 3.3×10^{-5} ; 9, 3.7×10^{-5} ; 10, 3.7×10^{-5} ; 11, 4.1×10^{-5} M

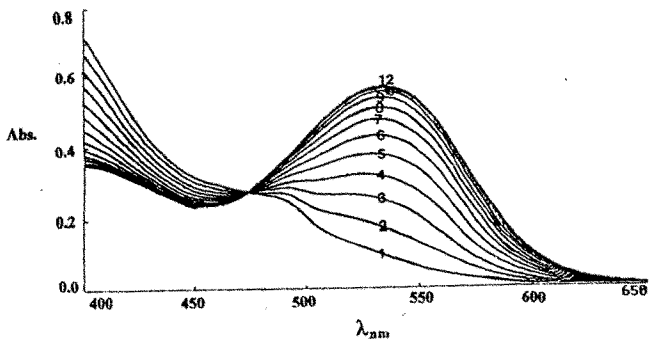


Figure 3. Visible spectra for titration of PAR (3.879×10^{-5} M) with Pb^{2+} ion in 0% AN at 25°C. Respective concentrations of the Pb^{2+} ion (M) in different solutions are: 1, 0; 2, 3.8×10^{-6} ; 3, 7.6×10^{-6} ; 4, 1.1×10^{-5} ; 5, 1.52×10^{-5} ; 6, 1.89×10^{-5} ; 7, 2.3×10^{-5} ; 8, 3.0×10^{-5} ; 9, 3.4×10^{-5} ; 10, 3.4×10^{-5} ; 11, 3.8×10^{-5} ; 12, 4.17×10^{-5} M

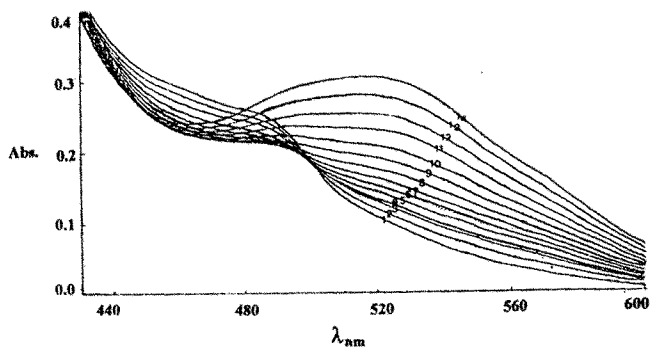


Figure 4. Visible spectra for titration of PAR (3.879×10^{-5} M) with Hg^{2+} ion in 0% AN 25°C. Respective concentration of the Hg^{2+} ion (M) in different solutions are: 1, 0; 2, 2.872×10^{-6} ; 3, 1.74×10^{-5} ; 4, 2.62×10^{-5} ; 5, 3.5×10^{-5} ; 6, 4.4×10^{-5} ; 7, 5.2×10^{-5} ; 8, 6.1×10^{-5} ; 9, 6.97×10^{-5} ; 10, 7.8×10^{-5} ; 11, 8.7×10^{-5} ; 12, 9.6×10^{-5} ; 13, 1.05×10^{-4} ; 14, 2.1×10^{-4} M

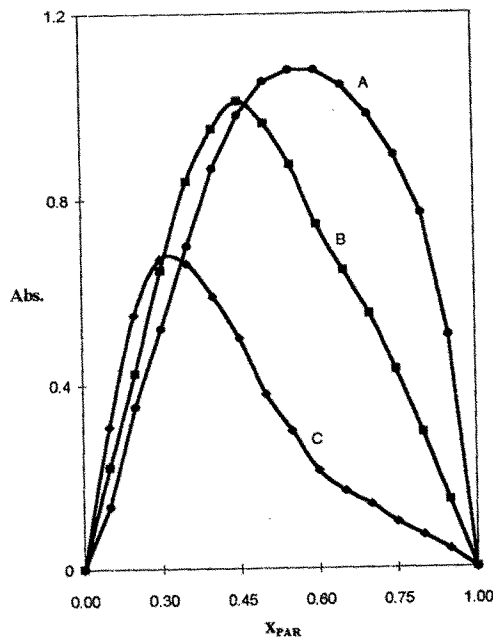


Figure 5. Continuous variation plot of Gd^{2+} - PAR in 40% AN (A), Pb^{2+} - PAR in 40% AN (B) and Hg^{2+} - PAR in 20% AN (C)

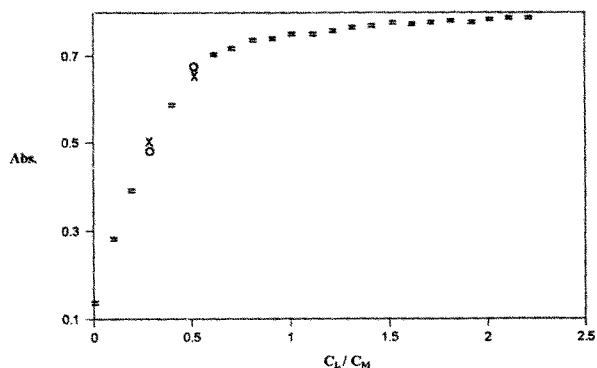


Figure 6. Sample Computer Fitting of absorbance-mole ratio data for a Cd^{2+} - PAR system in 40% AN: X is the observed point, O is the calculated point, = is the calculated and observed points when they are the same in the resolution of the plot

by considering the appearance of the computer fit, as shown in Figure 6, and the final sum of square of the fit SS, the best model for each series of the absorbance-mole ratio data was selected.

There are many reports on the complexation of PAR with different metal ions in aqueous solutions [3,11,13]. It is not surprising that the comparison of the present stability constant varies with those previously reported. This is due to the differences in various parameters such as medium, temperature, pH and several other factors that affect these constants.

Table 3. Formation constants, enthalpy and entropy values for different PAR-M²⁺ complexes in various AN-DMF mixture

Cation	Wt%AN in solvent mixture	Stoichiometry	log K ^{a)}				$\Delta H^{\circ a)}$ (KJ mol ⁻¹)	$\Delta S^{\circ a)}$ (J mol ⁻¹ ·K ⁻¹)
			25 °C	35 °C	45 °C	55 °C		
Pb ²⁺	0	1:1	6.12(0.07)	5.95(0.05)	5.73(0.06)	5.42(0.04)	-43.3(3.6)	-27(11)
	10	1:1	6.39(0.09)	6.17(0.04)	5.92(0.05)	5.60(0.06)	-48.9(3.0)	-41(9)
	20	1:1	6.65(0.07)	6.42(0.03)	6.11(0.04)	5.82(0.03)	-52.3(2.0)	-47(7)
	30	1:1	6.82(0.09)	6.51(0.09)	6.29(0.09)	5.94(0.05)	-54.3(1.2)	-51(4)
	40	1:1	> 7	> 7	> 7	> 7		
Cd ²⁺	0	2:1	9.69(0.04)	9.61(0.06)	9.52(0.04)	9.45(0.09)	-15.2(0.3)	134(1)
	10	2:1	9.85(0.07)	9.72(0.07)	9.61(0.08)	9.52(0.08)	-20.7(0.6)	119(2)
	20	2:1	10.22(0.10)	10.09(0.15)	9.85(0.10)	9.67(0.11)	-35.3(2.2)	77(7)
	30	2:1	10.51(0.10)	10.17(0.10)	9.92(0.14)	9.81(0.13)	-44.2(4.2)	51(3)
	40	2:1	11.01(0.17)	10.72(0.16)	10.41(0.17)	10.09(0.16)	-57.4(1.5)	18(5)
Hg ²⁺	0	1:1	4.40(0.01)	4.32(0.02)	4.23(0.02)	4.18(0.01)	-14.0(0.6)	37(2)
		2:1	3.88(0.01)	3.82(0.01)	3.78(0.01)	3.74(0.01)	-8.6(0.3)	45(1)
	10	1:1	4.67(0.02)	4.52(0.02)	4.43(0.03)	4.28(0.01)	-23.5(1.1)	10(4)
		2:1	3.97(0.01)	3.93(0.02)	3.90(0.02)	3.85(0.04)	-7.3(0.4)	51(1)
	20	1:1	4.95(0.04)	4.72(0.02)	4.54(0.04)	4.37(0.08)	-36.0(0.8)	-26(3)
		2:1	4.15(0.07)	4.08(0.03)	3.97(0.04)	3.88(0.06)	-17.2(0.8)	22(3)
	30	1:1	5.42(0.06)	5.20(0.06)	5.01(0.04)	4.80(0.04)	-38.4(0.6)	-25(2)
		2:1	4.43(0.07)	4.34(0.04)	4.27(0.05)	4.18(0.08)	-15.3(0.4)	33(2)
40	1:1	6.55(0.07)	6.35(0.06)	6.17(0.09)	5.87(0.08)	-41.4(2.9)	-13(9)	

^{a)} Values in parentheses indicate the standard deviations.

In order to have a better understanding of the thermodynamics of the complexation processes between PAR and metal ions in different AN-DMF 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, 2:1 and 1:2 complexes as a function of temperature. All the Log of stability constant values evaluated from the computer refinement of absorbance-mole ratio titration data are listed in Table 3. Van't Hoff plots of log K vs 1/T for different PAR complexes in various solvent mixtures were linear, Figure 7 and ΔH° and ΔS° values were determined in the usual manner from the slopes and intercepts of the plots, respectively. The results are also included in Table 3.

The data given in Table 3 show that the Hg²⁺- PAR system shows an unusual stoichiometry of metal-to-ligand 2:1, ratio. This behavior of Hg²⁺ is expected from a higher tendency of metal-metal interactions to form Hg²⁺ ... Hg²⁺ or tendency to form polynuclear complex via anion bridge [15]. This trend is also verified by the regular variation in titration of PAR with Hg²⁺. Figure 3 shows two distinct isobestic points in spectra that indicate the formation of 1:1 and 2:1 adducts in solution. For Pb²⁺-PAR system, formation of a 1:1 complex, but in the case of Cd²⁺-PAR 1:2 species are detected. This trend could be explained by the higher charge density of Cd²⁺ with respect to Pb²⁺ ion.

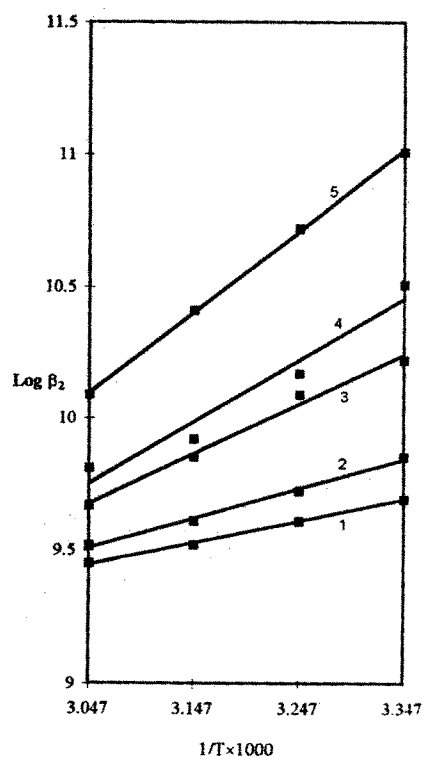


Figure 7. Van't Hoff's plots for Cd²⁺ - PAR systems in various mixtures: 1; 0% AN, 2; 10% AN, 3; 20% AN, 4; 30% AN, 5; 40% AN

It is also seen that in all solvent mixtures used, the stability of the PAR complexes decreases with increasing ionic radius of the cations. Thus, the order of stability of the complexes can be a consequence of stereochemical limitation of these metals.

It is obvious from the data in Table 3, that the solvent property has a fundamental role in the complex formation processes. In all cases, the stability of the resulting complexes increases with an increasing weight percentage of AN in the mixed solvent [16-18]. It is well known that the Gutmann Donicity of Solvent [19] plays an important role in different complexation equilibria. DMF is a solvent of high solvating ability (DN=26) which can effectively compete with PAR for the metal cation. Thus, the addition of AN as a relatively low donating solvent (DN=14.1) to DMF will increase the stability of PAR complexes.

It is seen that there is actually a linear relationship between Log K of the PAR complexes and mole fraction of AN, X_{AN} , (Figure 8), in the solvent mixtures. The same trend has already been reported for various complexes in different solvent mixtures [16,18]. It has been reasonably assumed that preferential solvation of the cations by DMF is mainly responsible for such a monotonic dependence of the overall stability of the PAR complexes on the solvent composition.

The data given in Table 3 indicate the dependence of the ΔH° and ΔS° values to the solvent composition, mainly due to variation in the solvation processes for different ionic species involved. The entropy changes in the Pb^{2+} - system are more negative than that of the Cd^{2+} and Hg^{2+} . This is probably due to the lower charge density and poorer solvation of Pb^{2+} . Subsequently, in the desolvation processes the number of the liberated solvent molecules is less than that of the other cations. Another factor that could explain the observed trend of the influence of solvent on the thermodynamic data is the nature of the cation used. This could be a consequence of the existence of different structural systems for the resulting PAR complexes of different metal ions used in solution.

As it is seen from Figure 7, there is a fashionable increase in the slope (ΔH°) of the curves when the weight percent of AN in solvent mixtures is increased. As mentioned previously, the addition of AN as a solvent with less solvating ability to the mixture lowered the solvation power of the medium. Thus, the lower the solvation power, the lower the competition of the solvent molecules in complexation reaction and the interaction between ligand and the metal ion and, consequently the enthalpy of complexation increase.

Despite the above mentioned variations in the solvent effect on the thermodynamics parameters of metal ion-PAR complexes, the $T\Delta S$ v.s. ΔH° plot of the

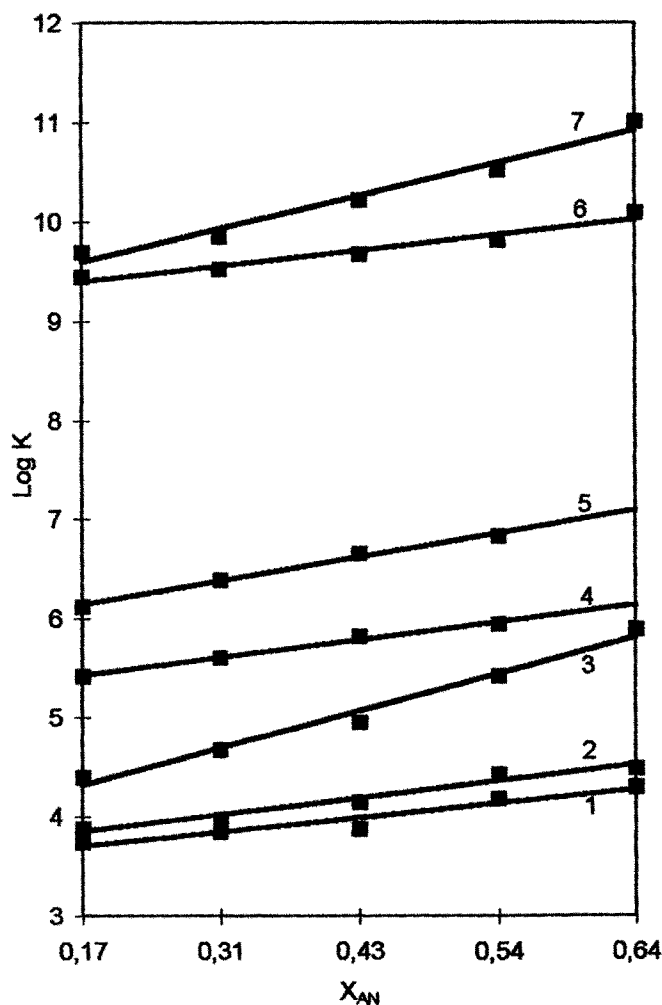


Figure 8. Variation of log K of different metal ion complexes of PAR with X_{AN} : 1; Hg^{2+} - PAR Log K_2 at 55 °C, 2; Hg^{2+} - PAR Log K_2 at 25 °C, 3; Hg^{2+} - PAR Log K_1 at 25 °C, 4; Pb^{2+} - PAR Log K_2 at 55 °C, 5; Pb^{2+} - PAR Log K at 25 °C, 6; Cd^{2+} - PAR Log β_2 at 55 °C

thermodynamic data obtained shows a fairly good linear correlation (Fig. 9) indicating the existence of enthalpy-entropy compensation in the complexation reactions. Such a compensation effect has been reported previously for different metal ion-ligand systems [16-21]. The linear correlation observed between $T\Delta S^\circ$ and ΔH° values can be expressed as $T\Delta S = T\Delta S^\circ - \alpha \Delta H^\circ$ with $T\Delta S^\circ = 18.82$ kJ mol⁻¹ and $\alpha = 0.64$.

The result suggests that the entropic effect consists of two components. The first component $T\Delta S^\circ$ is independent of enthalpy change and the second is proportional to it. The proportionality constant α might be considered a quantitative measure of the enthalpy-entropy compensation. For $\alpha=0.64$, only 36% of the increase in ΔH° contributed to complex stability. The positive intercept of $T\Delta S^\circ = 18.8$

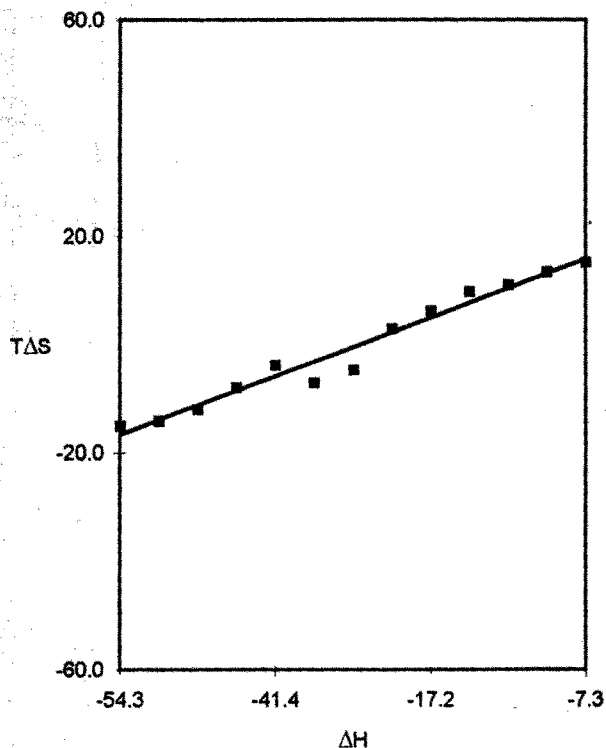


Figure 9. Plot of TAS v. s. ΔH° for complexation of different metal ions with PAR in various solvent mixtures

kJ mol⁻¹ reveals that complex formation is favored even in the absence of any enthalpic gain. These results show the fundamental role of solvent in the complexation process. Since both reactants involved in complexation are charged and thus more or less solvated by solvent molecules, complex formation may result in the release of significant number of solvent to the solution. Therefore, even when the cation-PAR bindings is weak, desolvation of cation and PAR may result in some positive entropic gain.

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