ΔG_{tr} values are highest in the case of Na_2SO_4 followed by NaCl and KCl and they are all positive. Those for sodium salts are higher than those for potassium salts. In the case of argon all transfer quantities are found to be positive. Argon, being an inert molecule, forms a water clathrate structure with ease; hence, it has a larger positive ΔS_{tr}. Butanol and ethyl acetate and the polar solutes show the same trend as the phenols studied in the present case.

Figure 3 shows a plot of ΔH_{tr} vs. ΔS_{tr} for the phenolics from water to salt solutions (Na_2SO_4, NaCl, $NaClO_4$, KSCN). Lumry (*4*) has discussed such plots for reactions involving small molecules and proteins and has attributed a linear behavior to properties of water as a solvent, especially water structure.

The plots are approximately parallel straight lines with slopes in the range 200-230 K. The "isoequilibrium" temperature thus tallies with those (285-340 K) for several ionization and H-bonding reactions in water. Such linear compensations of ΔH-ΔS in the absence of any other known strong reaction involving the solute is strong evidence that hydrophobic interaction is the driving force for the transfer phenomenon. In the transfer from organic liquids to water, however, no such correlation is expected nor is it obtained, indicating water structure does not have any special significance here.

Acknowledgment

We are grateful to Dr. S. P. Bhattacharyya of IACS, Calcutta, for helpful suggestions and discussions.

Registry No. NaF, 7681-49-4; Na_2SO_4, 7757-82-6; $(NH_4)_2SO_4$, 7783-20-2; NaCl, 7647-14-5; $NaNO_3$, 7631-99-4; KCl, 7447-40-7; KNO_3, 7757-79-1; $NaClO_4$, 7601-89-0; KSCN, 333-20-0; *p*-chlorophenol, 106-48-9; *p*-bromophenol, 106-41-2; *p*-nitrophenol, 100-02-7; benzene, 71-43-2.

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Received for review November 4, 1982. Accepted June 27, 1983.

Electrophoretic Studies of Cobalt(II)-, Zinc(II)-, Beryllium(II)-, Uranyl(II)-, Chromium(III)-, and Thorium(IV)-Oxalate-Nitrilotriacetate Complexes in Solution

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A new method involving the use of paper electrophoresis (PE) is described for the study of equilibria in mixed-ligand complex systems in solution. This technique is based on the movement of a spot of a metal ion under a potential field, with the complexants added in the background electrolyte (0.1 M sodium perchlorate), at pH 10.0. The concentration of one of the complexants, L, is kept constant, while that of the second, L^1, is varied. A graph of − log [L] against mobility is used to obtain information on the formation of the mixed-ligand complex and to calculate the stability constant. With this technique, the values of the overall stability constants of the complex metal-oxalate-nitrilotriacetate have been found to be $10^{7.49}$, $10^{6.58}$, $10^{7.42}$, $10^{8.98}$, $10^{9.89}$, and $10^{9.74}$ for Co^{II}, Zn^{II}, Be^{II}, $U^{II}O_2$, Cr^{III}, and Th^{IV} complexes, respectively, at μ = 0.1 and temperature = 40 °C.

Introduction

Paper electrophoresis (PE) has been applied to the study of metal complexes in solution, and attempts have been made to determine the stability constant of the complex species (*1-3*). In recent work (*4*) of this laboratory, a new method was developed for the study of the stepwise formation of complexes formed between various metal ions and tartaric acid. Although the use of PE for the study of metal complex systems with a single ligand seems to be well established, there is not systematic study of the formation of mixed-ligand complexes using this technique. However, Czakis-Sulikowska (*6*) made some observations on the formation of mixed-halide complexes of mercury(II) using the PE technique, but the studies were only qualitative and did not throw light either on the nature of the species or on their stabilities.

Theoretical Section

A metal ion M is assumed to complex with ligand anions L to give complex ions as follows, the charges of the ions being ignored:

$$M + pL \rightleftharpoons ML_p \tag{1}$$

The gross stability constant is given by the expression

$$\beta_{ML_p} = [ML_p]/([M][L]^p) \tag{2}$$

Addition of another ligand, L^1, to the system may lead to its partial substitution in the complex species, forming a mixed complex unit.

$$ML_p + L^1 \rightleftharpoons ML_{p-1}L^1 + L \tag{3}$$

The equilibrium constant for the above equilibrium is given by

$$K_{ML_{p-1}L^1} = [ML_{p-1}L^1][L]/([ML_p][L^1]) \tag{4}$$

Substituting the value of $[ML_p]$ by $\beta_{ML_p}[M][L]^p$ from eq 2 into eq 4, one obtains the gross stability constant of the mixed-ligand complex.

$$\beta_{ML_p}K_{ML_{p-1}L^1} = [ML_{p-1}L^1]/([M][L]^{p-1}[L^1]) = \beta_{ML_{p-1}L^1} \tag{5}$$

0021-9568/84/1729-0141$01.50/0

Table I. Type of Metal-Oxalic Acid-NTA Complexes at μ = 0.1 and Temperature = 40 °C

metal	Co^{II}	Zn^{II}	Be^{II}	$U^{II}O_2$	Cr^{III}	Th^{IV}
type of complex	$Co(OX)_2^{2-}$	$Zn(OX)_2^{2-}$	$Be(OX)_2^{2-}$	$UO_2(OX)_2^{2-}$	$Cr(OX)_3^{3-}$	$Th(OX)_3^{2-}$
type of mixed complex	$Co(OX)NTA^{3-}$	$Zn(OX)NTA^{3-}$	$Be(OX)NTA^{3-}$	$UO_2(OX)NTA^{3-}$	$Cr(OX)_2NTA^{4-}$	$Th(OX)_2NTA^{3-}$

Table II. Equilibrium Constants (log $K_{ML_{p-1}L^1}$ and log $\beta_{ML_{p-1}L^1}$) of Metal-Oxalic Acid-NTA Complexes at μ = 0.1 and Temp = 40 °C

− log [NTA]	log $K_{ML_{p-1}L^1}$	log $\beta_{ML_{p-1}L^1}$	log β_{ML_p}
	Co^{II}-Oxalic Acid-NTA System		
2.98	1.87	7.00	5.13
2.96	2.47	7.60	
2.94	2.74	7.87	
		av = 7.49	
	Zn^{II}-Oxalic Acid-NTA System		
2.88	1.29	6.40	5.11
2.84	0.93	6.04	
2.80	2.21	7.32	
		av = 6.58	
	Be^{II}-Oxalic Acid-NTA System		
2.92	1.33	6.76	5.43
2.86	2.03	7.46	
2.82	2.61	8.04	
		av = 7.42	
	$U^{II}O_2$-Oxalic Acid-NTA System		
3.02	2.13	8.60	6.47
3.00	2.60	9.07	
2.98	2.80	9.27	
		av = 8.98	
	Cr^{III}-Oxalic Acid-NTA System		
3.00	1.80	9.37	7.57
2.98	2.11	9.68	
2.96	2.45	10.02	
		av = 9.69	
	Th^{IV}-Oxalic Acid-NTA System		
3.04	1.61	9.28	7.67
3.02	2.13	9.80	
3.00	2.49	10.16	
		av = 9.74	

Further addition of L^1 to system 3 may lead to further substitution in $ML_{p-1}L^1$ by L^1, but in the present study there is no evidence for it.

In the electrophoretic study reported here, the concentration of L is fixed and L^1 is varying; hence, the overall mobility U of any given spot is given by

$$U = U_1 f_{ML_p} + U_2 f_{ML_{p-1}L^1} \qquad (6)$$

where U_1, U_2 and f_{ML_p}, $f_{ML_{p-1}L^1}$ are the mobilities and the mole fractions of the ML_p and $ML_{p-1}L^1$ species, respectively. Substituting the values of mole fraction from eq 4 and simplifying, we obtain

$$U = \frac{U_1 + U_2 K_{ML_{p-1}L^1}[L^1][L]^{-1}}{1 + K_{ML_{p-1}L^1}[L^1][L]^{-1}} \qquad (7)$$

From eq 7 the value of $K_{ML_{p-1}L^1}$ can be obtained at different mobilities and, when theis value is multiplied by β_{ML_p}, the stability constant $\beta_{ML_{p-1}L^1}$ works out. (The charges of the complexes have been omitted for simplicity.)

Experimental Section

An electrophoretic apparatus (Systronics, type 604, India) was used, together with the various accessories supplied with the instrument. The apparatus was of the cassette type, and chromatograms could be run simultaneously on eight paper strips. The power unit was capable of yielding a maximum of 300 V dc. In each case, electrophoresis was carried out for 60 min at 240 V and at 40 °C. Whatman No. 1 paper strips were used with an applied voltage gradient of 9 V cm^{-1}.

pH measurements were made with a Leeds and Northrup pH meter using a glass-calomel electrode assembly.

Chemicals. Cobalt(II), zinc(II), beryllium(II), uranyl(II), chromium(III), and thorium(IV) perchlorates were prepared by suitable methods and standardized as usual. The final concentrations were kept at 5.0 × 10^{-3} M.

1-(2-pyridylazo)-2-naphthol (PAN), 0.1% (w/v) in ethanol, was used for detecting all the metal ions except beryllium. Aqueous aluminum and ammonium acetate solutions were sprayed on paper to detect beryllium metal spots. A saturated aqueous solution (0.9 mL) of silver nitrate was diluted with acetone to 20 mL. Glucose was detected by spraying with this solution, and then with 2% ethanolic sodium hydroxide, forming a black spot.

Background Electrolyte. Stock solutions of 2.0 M perchloric acid, 2.0 M sodium hydroxide, and 0.5 M oxalic acid were prepared from AnalaR samples (BDH, Poole, Great Britain); 0.01 M nitrilotriacetic acid (NTA) was prepared from a sample obtained from E. Merck (Dermstadt, GFR). Each solution was standardized as usual. The background electrolyte consisted of a mixture containing 0.1 M sodium perchlorate (obtained by neutralizing perchloric acid with sodium hydroxide solution), 5.0 × 10^{-3} M oxalic acid, and varying amounts of 0.01 M NTA; it was maintained at pH 10.0 by addition of sodium hydroxide solution. At each step the concentrations of the various ingredients of the background electrolyte were so adjusted to keep the ionic strength as well as the oxalic acid concentration fixed.

Procedure. The midpoint of each paper strip was marked and moistened with the background electrolyte. Excess electrolyte was allowed to drain off and the papers were mounted on the cassette. A spot of the metal solution was then applied at the marked point by use of a 1.0-μL micropipet. In each set, seven strips were mounted, including strips which were spotted with glucose. Each of the two electrode vessels was filled with 175 cm^3 of the background electrolyte. The cassette was closed and placed on the electrode vessels. The electrophoretic migration of the metal spot on the paper was observed for various compositions of the background electrolyte. After electrophoresis, the spots of various metal ions were detected by spraying with appropriate reagents. The distances of the leading and tailing edges from the marked center were measured; the metal ions moved toward the anode in each case (and the distances are therefore negative) whereas glucose moved sometimes to the cathode and sometimes to the anode. The mean of the two distances was noted and the distance traveled by glucose under identical conditions was added or subtracted (as the case may be) to obtain the corrected path length. The mobilities were then calculated and expressed in 10^3 cm^2 V^{-1} min^{-1}. Each experiment was performed twice and averages have been taken.

Results and Discussion

In separate experiments with the metal-oxalate system and the metal-NTA system, it has been found that around pH 10.00 almost all the oxalic acid (5.0 × 10^{-3} M) used in the systems

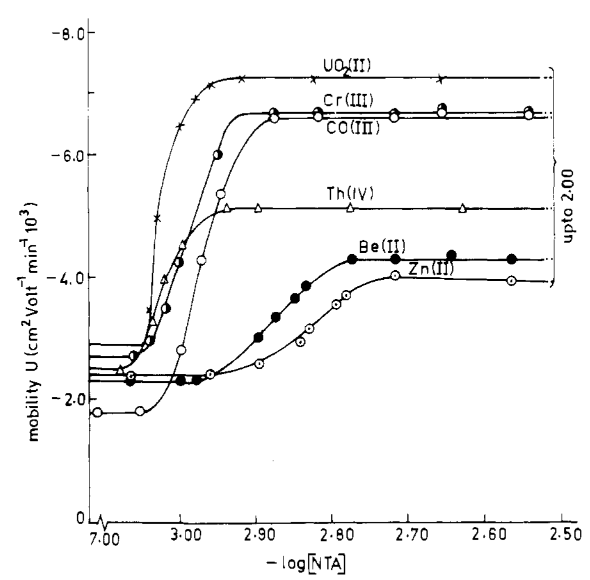

Figure 1. Metal-oxalic acid-NTA system: - log [NTA] vs. mobility.

exists as $C_2O_4^{2-}$ and the unprotonated ions, e.g., $C_2O_4^{2-}$, form complexes with the metal ions.[4] It has been found previously (*4*) that, around pH 10.00, NTA^{3-} is the principal complexing species with the above-mentioned metal ions; therefore, it will take part in the formation of mixed-ligand complexes. Hence, the present study carried out at pH 10.00 is actually the study of interconversion of pure complexes wherein mixed complex is formed in an intermediate stage.

The mobilities were plotted against the logarithms of the concentration of NTA (Figure 1). The graphs for various metal ions had two plateaus. The first plateau corresponds to the formation of $[M(C_2O_4)_p{}^{(2p-n)-}]$ and the second plateau to the formation of the formation of the mixed-ligand species $[M(C_2O_4)_{p-1}NTA^{(2p+1-n)-}]$. Further reaction between the last-mentioned complex species and NTA^{3-} is not possible, as evidenced by two (and not three) plateaus in the mobility graphs (Figure 1). The second plateau gave mobilities of -6.60×10^3, -3.95×10^3, -4.30×10^3, -7.30×10^3, -6.60×10^3, and -5.20×10^3 cm^2 V^{-1} min^{-1} for Co^{II}, Zn^{II}, Be^{II}, U^{II}O$_2$, Cr^{III}, and Th^{IV}, respectively. In the presence of only NTA^{3-} the mobilities of the above-mentioned ions in the form of complex with NTA^{3-} are -3.60×10^3, -5.00×10^3, -1.20×10^3, -3.60×10^3, -0.60×10^3, and -3.80×10^3 cm^2 V^{-1} min^{-1}, respectively (*5*). As the latter mobilities are different from the former, formation of mixed-ligand complexes is inferred in each case.

Various types of complexes formed with metal-oxalic acid and mixed complexes have been reported (*5*) in Table I. The values of log $K_{ML_{p-1}L^1}$ and log $\beta_{ML_{p-1}L^1}$ have been obtained at different - log [NTA] by employing eq 7 and they have been reported in Table II.

Acknowledgment

I thank Dr. K. L. Yadava, Chemistry Department, Allahabad University, Allahabad, India, for supplying the electrophoresis apparatus and for encouragement.

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Received for review February 22, 1983. Accepted August 26, 1983.

Temperature Influence on the Ternary System 1-Butanol-Butanone-Water

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Solubility and liquid-liquid phase equilibrium data have been measured for the ternary system 1-butanol-butanone-water at temperatures ranging from 15 to 20 °C. Data for the binodal curves have been determined by the cloud-point method. Data for the tie lines have been determined by gas-chromatographic analysis. Experimental results show the extreme phase sensitivity of this system to temperature. At 17 °C the ternary system has two separate biphasic regions, while at 18 °C the system has only one region of immiscibility. This rapid and unusual temperature dependence is not very common for ternary liquid systems.

Introduction

Mutual solubility of liquids usually increases with temperature (*1*). Although this behavior is the most common, there are cases where an increase in temperature causes a solubility decrease. Francis (*2*) has compiled some examples of this behavior in binary systems. However, the number of published studies relating to ternary systems with this temperature dependence is very small.

Galán (*3*) reported some binodal curves for the system 1-butanol-butanone-water, showing that at 15 °C this ternary system had two separate biphasic regions, while at 20 °C the system had only one biphasic region. In our paper, extensive data for this system have been determined. Binodal curves at 15, 16, 17, 18, 19, and 20 °C are reported in order to mark the temperature of overlapping of the two biphasic regions. Moreover, several tie lines have been determined for each temperature. The coordinates of the plait points are also reported.

Experimental Section

Materials. The contents of volatile impurities in 1-butanol and butanone (analytical reagent grade; Merck) were determined by

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0021-9568/84/1729-0143$01.50/0