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Ionophoretic Studies in Copper(II)-, Nickel(II)-, Cobalt(II)-, Uranyl(II)-, and Thorium(IV)-Tartaric Acid Systems

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Stability constants of copper(II), nickel(II), cobalt(II), uranyl(II), and thorium(IV) tartrates (tart) have been determined by paper electrophoresis at $I = 0.1$ and 40 °C. Tartaric acid (5.0×10^{-3} M) was added to the background electrolyte (1.0×10^{-1} M) perchloric acid. The relative concentrations of the liganding species were varied by changing the pH of the electrolyte. The gross stability-constant values of $Cu(tart)^0$, $Ni(tart)_2^{2-}$, $Co(tart)_2^{2-}$, and $Th(tart)_3^{2-}$ and the equilibrium stability-constant values of $[Cu_2(tart)_2^0]/([Cu^{2+}]^2[tart^{2-}]^2)$, $[UO_2(tart)^-][H^+]/[UO_2(tart)^0]$, $[(UO_2)_2(tart)_2^{2-}][H^+]^2/[UO_2(tart)_2^-]^2$, and $[(UO_2)_2(tart)_2^{2-}][H^+]^2/([UO_2^{2+}]^2[tart^{2-}]^2)$ have been determined.

Introduction

Tartrate complexes of copper, cobalt, uranyl, and thorium have been studied by various techniques, and stability constants reported (*1*). The use of paper ionophoresis in the determination of stability constants is very limited. Jokl (*2*) used the method to investigate equilibria in a number of systems involving Cu(II), Co(II), and Zn(II) with amino acids and aminopoly(carboxylic acids). A theoretical treatment similar to that of Jokl was given by Biernat (*3*) for the study of successive complexes in solution, while Soni and Bartusek (*4*) investigated molybdato complexes with *o*-diphenols. In the present work the approach of Jokl with some modifications has been employed to follow the metal-ligand equilibria in copper, nickel, cobalt, uranyl, and thorium tartrates.

Theoretical Section

In an aqueous solution of tartaric acid, the species $(CHOH)_2(COOH)_2$, $(CHOH)_2C_2O_4H^-$, and $(CHOH)_2C_2O_4^{2-}$ exist, the relative proportions depending upon the pH. The dissociation constants K_1 and K_2 are 1.10×10^{-3} and 6.90×10^{-5}, respectively. These values have been used to calculate the various species in solution at various pHs. Generally, tartaric acid chelates with a metal ion through its two carboxylic acid groups, but under certain conditions the oxygen atoms of the hydroxyl groups present in the acid also act as donor atoms (*1*).

When an n-valent metal ion complexes with an aqueous solution of tartaric acid, the nature of the complex ion depends upon the ligand species. The equilibria may be represented as follows:

$$M^{n+} + xH_2L^- \rightleftharpoons M(H_2L)_x^{(x-n)-} \tag{1}$$

$$M^{n+} + x'H_2L^{2-} \rightleftharpoons M(H_2L)_x^{(2x-n)-} \tag{2}$$

where n, x, and $x' = 0, 1, 2, 3, \ldots$ and $H_2L^- = (CHOH)_2C_2O_4H^-$ or $tart^-$, $H_2L^{2-} = (CHOH)_2C_2O_4^{2-}$ or $tart^{2-}$. The equilibrium constants are given by the following expressions:

$$\beta_x = [M(H_2L)_x^{(x-n)-}]/([M^{n+}][H_2L^-]^x) \tag{3}$$

$$\beta_{x'} = [M(H_2L)_{x'}^{(2x'-n)-}]/([M^{n+}][H_2L^{2-}]^{x'}) \tag{4}$$

When the migration of a spot containing metal ions in the presence of excess tartaric acid as background electrolyte is subjected to paper ionophoresis, the overall mobility of the spot U is given by (*2*)

$$U = U_0f_0 + U_1f_1 + U_2f_2 + U_3f_3 + \ldots \tag{5}$$

where U and f represent the specific velocities and mole fractions, respectively, of the constituent ions.

Jokl (*2*) determined the stability constants of metal complex formed by the progressive interaction of increasing amounts of a ligand with a metal ion, leading to stepwise formation of complexes in solution. His experiment consists in spotting the paper with a solution of the metal ion and studying the migration of the spot using a buffer solution of known pH containing increasing amounts of the ligand.

In the present work the background electrolyte is 5.0×10^{-3} M tartaric acid and 1.0×10^{-1} M perchloric acid solution, the pH of which is varied by the addition of sodium hydroxide solution. By substituting in eq 5, $U_{x'}$ the respective mole fractions by $\beta_x[H_2L]^x$, where β_x represents the xth formation constant, $[H_2L]$ the ligand concentration, and x the stoichiometry of the reaction, when the complex species are $M(H_2L)_x^{(x-n)-}$ and $M(H_2L)_{x'}^{(2x'-n)-}$, one may rewrite the equation in the following form:

$$U = \frac{U_0 + \sum_{x=1}^{x} U_x\beta_x[H_2L^-]^x + \sum_{x'=1}^{x'} U_{x'}\beta_{x'}'[H_2L^{2-}]^{x'}}{1 + \sum_{x=1}^{x} \beta_x[H_2L^-]^x + \sum_{x'=1}^{x'} \beta_{x'}'[H_2L^{2-}]^{x'}} \tag{6}$$

Here U_0, U_x, and $U_{x'}$ are the mobilities of M^{n+}, $M(H_2L)_x^{(x-n)-}$, and $M(H_2L)_{x'}^{(2x'-n)-}$, respectively.

A plot of pH against the overall mobility of the metal spot gives a curve with several plateaus, and the number of these indicates the number of species in the system. From eq 6 the stability constant β_x has been calculated by taking the average velocity at the point corresponding to $\beta_x[H_2L]^x = 1$ (*2*) on considering the transition range between first and second plateaus.

For calculating $\beta_{x'}$ the transition range between the second and third plateaus has been taken into consideration. When the values of U, $[H_2L^-]^x$, $[H_2L^{2-}]^{x'}$ β_x, and mobilities of ions are substituted into eq 6, $\beta_{x'}$ works out.

The above-mentioned theory is valid only for the mononuclear complexes. In our studied system the formation of binuclear and even hydroxo complexes has been observed (*1*). It has been assumed that simple mononuclear complexes undergo intermolecular reactions to form binuclear complexes which in turn lose protons from the hydroxyl groups of the ligands to form binuclear hydroxo complexes. The case may be reversed also, i.e., the simple mononuclear complex, e.g., in the UO_2^{2+}-tartaric acid system.

For hydroxo complex formation it has been assumed that a proton is liberated from the complex itself, i.e.

$$ML \rightleftharpoons MH_{-1}L^- + H^+ \tag{7}$$

Hence, at the average mobility point between the respective plateaus, the mole fractions of each of the species, i.e., ML and $MH_{-1}L^-$, will be one-half. Therefore

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$$\tfrac{1}{2} = [MH_{-1}L^-]/([ML] + [MH_{-1}L^-]) \qquad (8)$$

or

$$\tfrac{1}{2} = \frac{K[ML]/[H^+]}{[ML] + K[ML]/[H^+]} \qquad (9)$$

or

$$K = [H^+]$$

where K is the equilibrium constant of eq 7.

Again the formation of the polynuclear complex can result from the intermolecular reaction among the mononuclear complexes, i.e.

$$nML \rightleftharpoons M_nL_n \qquad (10)$$

At the average mobility point between the plateaus of the mononuclear and polynuclear complexes, the mole fraction of the polynuclear species will be one-half, i.e.

$$\tfrac{1}{2} = K_{\mathrm{Poly}}[ML]^{n-1}/(1 + K_{\mathrm{Poly}}[ML]^{n-1}) \qquad (11)$$

where K_{Poly} is the equilibrium constant of eq 10. As

$$[ML] = K[M][L] \qquad (12)$$

therefore, substituting the value of [ML] into eq 11, we get the following equation:

$$K_{\mathrm{Poly}} = 1/(K^{n-1}\{[M][L]\}^{n-1}) \qquad (13)$$

Initially the concentration of ML is maximum or one, and finally it becomes zero. Now, as the value of K is constant, hence, the actual change will be in the value of [M] and [L]. Therefore, the conclusion is made that the value of the product [M][L] becomes just one-half at the average mobility point, i.e., initially

$$K[M][L] = 1$$

$$[M][L] = 1/K \qquad (14)$$

Therefore, at the average mobility point [M][L] will be just half of the value of $1/K$.

Experimental Section

Instruments. Paper ionophoresis equipment of type No. 604 (Systorniks, India) was used. The potential in each experiment was kept at 240 V and ionophoresis was carried out for 60 min (temperature, 40 °C).

Whatman No. 1 paper strips (28 × 1.5 cm) with an applied voltage gradient (9 V/(cm s)) were used.

pH measurements were made with a Leeds and Northrup pH meter using glass calomel electrodes.

Chemicals. Metal perchlorates were prepared by an appropiate method using analytical-grade reagents, and 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 of the metal ion spots. A saturated solution of silver nitrate in acetone was sprayed onto the paper and subsequently fumed with NH_3 to detect glucose in the spot.

Background Electrolyte. Stock solutions of 1.0 M perchloric acid, 1.0 M sodium hydroxide, and 5.0 × 10^{-1} M tartaric acid were prepared from BDH AnalaR samples and standardized as usual.

Procedure

The spot was applied with a 0.1-μL pipet. The midpoint of each strip was marked, and the metal ion spots were applied on them. Strips were then mounted on the apparatus so that they became moistened with the background electrolyte after some time. Each of the electrode vessels was filled with 175 mL of background electrolyte. The apparatus was then converted with a transparent, triangular-shaped PVC lid, and a direct current at 240 V was applied for 60 min. The strips were then removed from the cassette and dried. The metal ions and glucose spots were detected after removing the strips from the cassette and spraying them with appropriate reagents after drying. The leading and tailing edges of the metal spots were measured from the marked point, and the distance moved by glucose was subtracted (in the case of migration toward the cathode) or added (in the case of migration toward the anode) to obtain the corrected path length. Migrations toward the anode and the cathode are indicated by − and + signs, respectively. Each experiment was performed twice, and the mobility of one experiment was within a variation range of ±2% with respect to the other. The average of these two mobilities has been plotted against pH in Figure 1.

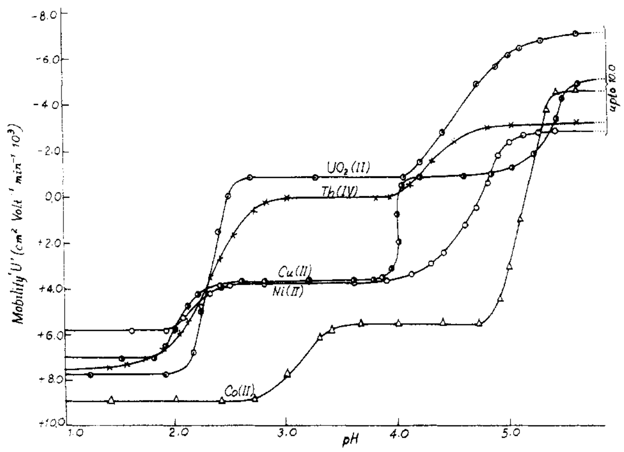

Figure 1. Metal–tartaric acid system: mobility vs. pH.

Table I. Stability-Constant (log β_x) Values of Metal Tartrates at $I = 0.1$ and 40 °C

	Cu(II)	Ni(II)	Co(II)	UO_2-(II)	Th(IV)
pH	2.05	2.15	3.10	2.38	2.28
liganding species	$tart^{1-}$	$tart^{1-}$	$tart^{1-}$	$tart^{2-}$	$tart^{1-}$
no. of liganding species	1	1	1	1	4
log β_x	3.25	3.16	2.55	4.91	12.23
lit. value	3.1 ± 0.1 ($I = 0.1$, 20 °C)		2.80 ± 0.1 ($I = 0.1$, 20 °C)		

Results and Discussion

In Figure 1 the mobilities of copper(II), nickel(II), cobalt(II), uranyl(II), and thorium(IV) tartrates are plotted against pH, and each curve except that of Cu(II) shows three plateaus. For all of the curves the log β_x values (Table I) have been calculated by taking the average velocity point of the lowermost and middle plateaus, for there, obviously, $\beta_x[\text{ligand}]^n$ will be 1. From the corresponding pH value, the relative concentration of the liganding species has been calculated and the stability determined. For calculating $\beta_x{}'$ values, we have arbitrarily chose three points between the upper and middle plateaus. At all of the points the relative concentrations of $tart^-$ and $tart^{2-}$ have been determined, and the stabilities calculated, although the former method can also be applied. Both methods would yield the same result.

For calculation of the stability constants of binuclear and hydroxo complex species, the method outlined in the Theoretical Section has been adopted.

Table II. Stability-Constant (log $\beta_{x'}$) Values of Metal Tartrates at $I = 0.1$ and 40 °C

pH	$10^3 U$, $cm^2 V^{-1} min^{-1}$	$10^3 \cdot$ [$tart^{1-}$], M	$10^3 \cdot$ [$tart^{2-}$], M	x'	log $\beta_{x'}$ this study	log $\beta_{x'}$ lit.
		Copper(II) Tartrate				
4.00	+1.00	2.80	1.93	1	3.40	
4.00	+0.50	2.80	1.93	1	3.41	
4.00	0	2.80	1.93	1	3.42	
					av = 3.41	
		Nickel(II) Tartrate				
4.26	+3.00	2.14	2.74	2	5.08	
4.75	0.00	0.98	4.03	2	5.57	
5.00	−2.80	0.63	4.36	2	6.32	
					av = 5.65	
		Cobalt(II) Tartrate				
5.00	+2.90	0.63	4.36	2	4.67	
5.15	0.00	0.44	4.53	2	4.99	
5.26	−2.30	0.35	4.64	2	4.88	
					av = 4.84	4.20[a]
		Thorium(IV) Tartrate				
4.20	−1.00	2.32	2.54	3	9.23	
4.40	−2.00	1.78	3.15	3	9.15	
4.60	−2.65	1.32	3.64	3	9.05	
					av = 9.14	

[a] At $I = 0.0$ and 25 °C.

Table III. Stability Constants of Copper(II) and Uranyl(II) Tartrates (Those of Binuclear and Hydroxo Complexes) at $I = 0.1$ and 40 °C

equilibrium considered	stability constant this study	stability constant lit.[a]
Copper(II) Tartrate		
$[Cu_2(tart)_2{}^0]/([Cu^{2+}]^2[tart^{2-}]^2)$	$10^{6.89}$	$10^{8.20}$
Uranyl(II) Tartrate		
$[UO_2(tart)^-][H^+]/[UO_2(tart)^0]$	$10^{-4.6}$	$10^{-5.60}$
$[(UO_2)_2(tart)_2{}^{2-}][H^+]^2/[UO_2(tart)^-]^2$	$10^{-9.4}$	
$[(UO_2)_2(tart)_2{}^{2-}][H^+]^2/([UO_2{}^{2+}]^2[tart^{2-}]^2)$	$10^{-8.8}$	$10^{-8.2}$

[a] $I = 1.0$ and temp = 25 °C.

The first plateaus in all cases indicate individual mobilities of hydrated metal ions. In the case of copper the second plateau represents the protonated complex species and the third plateau represents a binuclear complex species. In the case of nickel and cobalt the second plateau represents a protonated or cationic complex species.

In the case of thorium the middle plateau is due to the formation of $Th(tart)_4{}^0$ neutral species as its mobility is near the zero mobility point. The uppermost plateau is due to the formation of an anionic complex species for all of the metal ions. In the case of uranyl the second plateau is due to the formation of $UO_2(tart)_1{}^0$ neutral species. This is due to the fact that this species finally forms a binuclear complex (*1*) which the final plateau represents.

It has been assumed that the neutral $UO_2(tart)^0$ first loses a proton from one of the hydroxyl groups of the ligand which subsequently forms a binuclear species, i.e.

$$UO_2{}^{2+} + tart^{2-} \rightleftharpoons UO_2(tart)^0$$

$$UO_2(tart)^0 \rightleftharpoons UO_2(tart)^- + H^+$$

$$2UO_2(tart)^- \rightleftharpoons (UO_2)_2(tart)_2{}^{2-}$$

All of these stability-constant values (log $\beta_{x'}$) have been given in Table II. Table III deals with the stability-constant values of binuclear and hydroxo complexes.

In the literature no mention is made of most of the complexes. For those having literature values, comparisons are too difficult because the literature values of I and temperature are quite different from the calculated values, although differences are very small wherever they are available. The precision of the method is comparable to that of paper chromatography. With future refinements in instrumentation, this new technique will be worth developing for it will enrich knowledge of the nature of charges and mobilities of complexes.

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Limiting Activity Coefficients from Differential Ebulliometry

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Infinite-dilution activity coefficients were measured for 147 systems using an improved differential ebulliometric technique. The results compare well with the limited literature data available. The observed temperature dependence of the data was also found to be reasonable.

Introduction

While the many advantages of limiting activity coefficients (γ^∞) in characterizing miscible solution behavior are well documented (*1–3*), their use has been primarily limited by the paucity of accurate data available. To help overcome this limitation, an improved differential ebulliometric technique was used to measure γ^∞'s for many industrially important systems.

The technique traces back to Swietoslawski in 1925, who, using the principle of the Cottrell pump, designed ebulliometers capable of measuring boiling points with extreme accuracy. Since 1925 the ebulliometer has been used very successfully (*4*) in the determination of boiling points, molecular weights, mutual solubilities, and sample purities and, most recently, in obtaining infinite-dilution activity coefficients (γ^∞'s). Eckert et al. (*1*) solved the major problems confronting previous researchers, namely, those of pressure fluctuations and loss of

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