STUDIES ON COMPLEXATION IN SOLUTION WITH A PAPER ELECTROPHORETIC TECHNIQUE [THE SYSTEM MERCURY(II)/NICKEL(II)/ LEAD(II) – SARCOSINE]

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ABSTRACT

Complexation reactions of sarcosine with mercury(II), nickel(II) and lead(II) have been studied in the solution phase using a paper ionophoretic technique. This method is based on movement of a spot of metal ion in an electric field at various pHs of background electrolyte. A graph of pH versus mobility was used to obtain information on the metal complexes and to calculate stability constants. The stability constants of the ML^+ and ML_2 complexes of mercury(II), nickel(II) and lead(II) – sarcosine have been found to be (7.95 ± 0.02; 6.79 ± 0.06), (6.69 ± 0.01; 5.29 ± 0.04) and (4.34 ± 0.02; 2.69 ± 0.07) (logarithm stability constant values), respectively at a temperature of 35 ° C and ionic strength of 0.1 M.

Keywords: Paper electrophoretic technique; mercury(II) complexes; nickel(II) complexes; lead(II) complexes; sarcosine; stability constant.

INTRODUCTION

Quantitative indication of the process of forming a complex comes from the evaluation of the stability constants which characterize the equilibria corresponding to the successive addition of ligands. That is, we can consider the steps

$$M + L \leftrightarrows ML$$

$$ML + L \leftrightarrows ML_2$$

$$\vdots \qquad\qquad \vdots$$

$$ML_{n-1} + L \leftrightarrows ML_n$$

These are characterized by equilibrium constants K_1, K_2 ….., K_n such that

$$K_1 = [ML] / [M][L]$$
$$K_2 = [ML_2] / [ML][L] \text{ and}$$
$$K_n = [ML_n] / [ML_{n-1}][L]$$

These constants K, are termed as stepwise formation constants. An alternative formulation is to consider the overall formulation reaction

$$M + nL \leftrightarrows ML_n$$

Characterized by the n^{th} over all formation constant βn

$$\beta_n = [ML_n] / [M][L]^n = K_1 .. K_2 \ldots\ldots K_n.$$

Chemical literature[1,2] confirms that anionic species of amino acids are the sole ligating species for metal ions. Nickel is integral component of the enzymes ureases may be involved in the action of hydrogenase. Mercury is extremely harmful, even a concentration of 0.03 ppm in drinking water is not permissible. Mercury deactivates sulphur containing enzymes with active – SH groups, affects brain cells and the central nervous system[3]. Lead destroys sulfur containing proteins and enzymes, causes damage to DNA, RNA, brain and central nervous system functions. Lead also inhibit several step in the formation of hemoglobin and conversion of ATP to ADP. Mercury(II), nickel(II) and lead(II) are well known for its biomedical applications and toxicity[4-27]. Sarcosine is a N-methyl derivative of glycine. It is a natural amino acid found in muscles and other body tissues. It is normally not detected in human blood or urine. Sarcosine has several applications in biological systems[28-39].

The usual drawbacks of paper electrophoretic technique like variation in the temperature during the electrophoresis, capillary flow on paper, electroosmosis and adsorption affecting the mobility of charged moieties, are quite well known[40]. The technique described here is 98% free from these vitiating factors. The technique is very convenient in use and gives results in fair agreement with the accepted literature values.

Publications[41-43] from our laboratory described a new method for the study of binary complexes by using paper ionophoretic technique, and reports an observation on the determination of the stability constant values of binary complexes of mercury(II) / nickel(II) / lead(II) – sarcosine .

EXPERIMENTAL SECTION

Instruments

Electrophoresis equipment from Systronic (Naroda, India), model 604, was used. The equipment has a built in power supply (a.c. – d.c.) that is fed directly to the electrophoresis tank. The potential in each experiment was kept at 200 V and electrophoresis was carried out for 60 minutes.

An Elico (Hyderabad, India), Model L_{1-10}, with glass and calomel electrodes assembly and working on 220 V/50 Hz established a.c. mains, was used for the pH measurements. The electrophoresis cell showing sandwiched paper strips and water supply is shown in Figure 1.

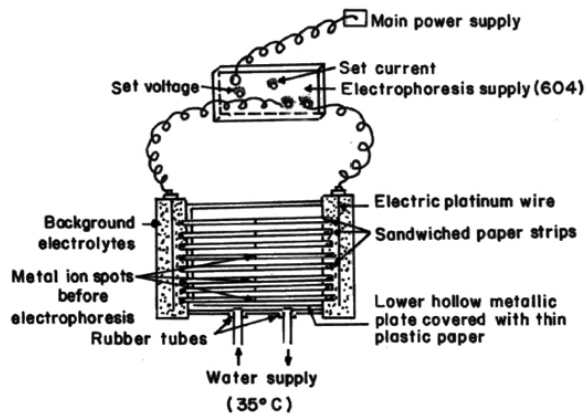

Fig. 1: Electrophoresis cell showing sandwiched paper strips.

Chemicals

Mercury(II), nickel(II) and lead(II) perchlorate solutions were prepared by preliminary precipitation of metal carbonates from a 0.1 M solution of sodium carbonate (AnalaR grade, BDH, Poole, UK). The precipitates were thoroughly washed with boiling water and treated with calculated amounts of 1 % perchloric acid. The resulting mixture was heated to boiling on a water bath and then filtered. The metal content of the filtrates were determined and final concentration was kept at 0.005 M[44, 45]. The position of the Ni^{2+} spots on the paper at the end of the experiment was detected using ammonical dimethylglyoxime (DMG), that of Pb^{2+} detected by 0.1% solution of 1-(2-pyridylazo) – 2- naphthol (PAN) (Merck, Darmstadt, Germany) in ethanol, that of Hg^{2+} detected using hydrogen sulphide in water. The 0.005 M glucose (BDH, AnalaR) solution was prepared in water and used as an indicator for the correction due to electroosmosis. A saturated aqueous solution (0.9 mL) of silver nitrate was diluted with acetone to 20 mL. Glucose was detected by

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spraying with this silver nitrate solution and then with 2% ethanolic solution of sodium hydroxide, when a black spot was formed. Paper strips showing position of metal ion spots after electrophoresis is shown in Figure 2.

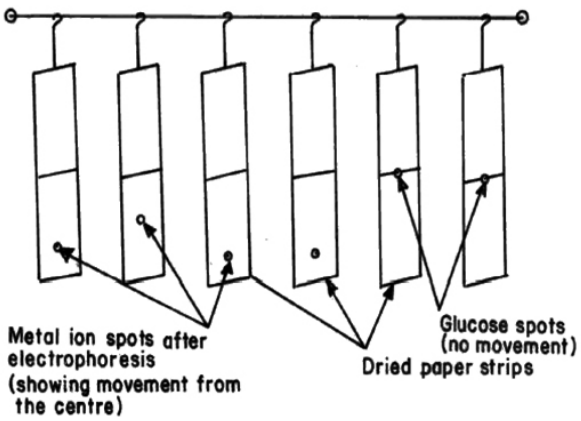


Fig. 2: Paper strips showing position of metal ion spots after electrophoresis.

Background electrolyte

Stock solution of 5.0 M perchloric acid was prepared from its 70% solution (SDS, AnalaR grade). 2.0 M sodium hydroxide and 0.5 M sarcosine (BDH, Poole, UK) solutions were prepared. The background electrolyte used in the study of binary complexes were 0.1 M perchloric acid and 0.1 M sarcosine. The system was maintained at various pH by the addition of sodium hydroxide.

Procedure

Whatman No. 1 filter paper for chromatography was used for the purpose of electrophoresis. For recording observation of particular metal ion, two paper strips were spotted with the metal ion solution along with additional two spotted with glucose using 1.0 mL pipette and then mounted on the insulated plate. Each of the two electrolyte vessels was filled with 150 mL of background electrolyte containing 0.1 M perchloric acid and 0.01 M sarcosine. The paper become moistened with the background electrolyte solutions due to diffusion. The second insulated plate was placed on paper strips and then thermostated water (35° C) was circulated in the plates to keep the temperature constant. The lid was then placed on the instrument to make it air tight. It was left for 15 minutes to insure wetting of strips. Subsequently a direct 200 V potential was applied between electrodes. Electrophoresis was carried for 60 minutes after which the paper strips were removed from the tank and dried.

The metal ion and glucose spots were detected by specific reagents. The leading and tailing edges were measured from marked center point and the mean taken. The distance moved by glucose was subtracted (in case of migration toward anode) to obtain correct path length. Migration towards anode and cathode were designated by negative and positive signs respectively. The scheme for paper electrophoresis set-up is shown in Figure 3. Electrophoretic observations on metal ions were recorded at various pH values of the background electrolyte, the ionic strength being maintained at 0.1 M. The observed mobility of migrant was calculated by using the formula.

$$U = \frac{d}{X \cdot t}$$

After applying the correction factor the observed mobility is given as

$$U = \frac{d \pm d_G}{X \cdot t}$$

where U = mobility of metal ion / complex ion; d = mean of duplicate distance travelled by metal ion / complex ion; d_G = mean of duplicate distance travelled by glucose spot; x = field strength (7.5 V/cm); t = time for electrophoresis. The speed of the metal ions/complex ions are reported with pH values. A plot of mobility against pH is shown in Figure 4.

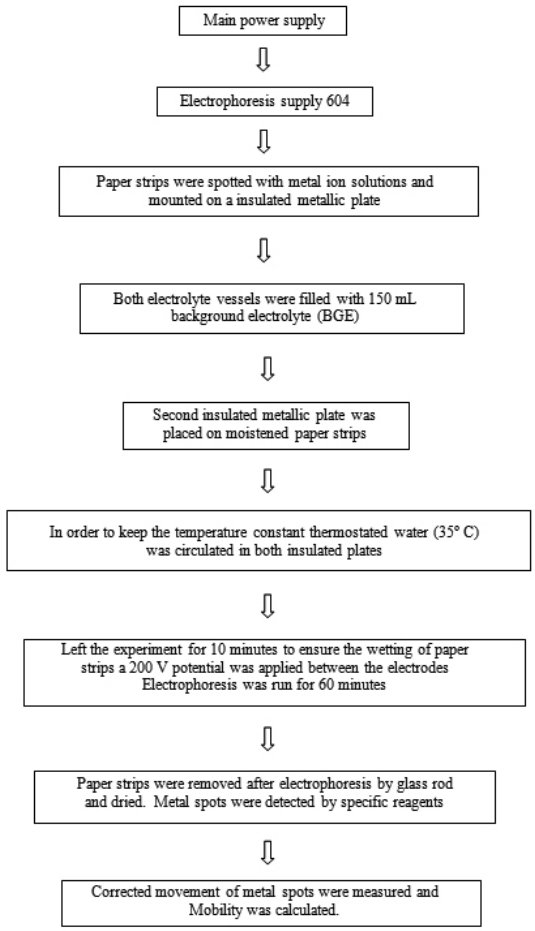


Fig. 3: The scheme for paper electrophoresis set-up

RESULTS

The ionophoretic mobility of the metal spot against pH gives a curve with a number of plateaus as is shown in Figure 4. A constant speed over a range of pH is possible only when a particular complex species is overwhelmingly formed. Thus, every plateau is indicative of formation of a certain complex species. The first one in the beginning corresponds to a region in which metal ions are uncomplexed. In the region of low pH, concentration of [CH_3 (NH_2^+) CH_2 COOH] species of sarcosine is maximum and this species is non-complexing, beyond this range, metal ion spots have progressively decreasing mobility, complexation of metal ions should be taking place with anionic species of sarcosine whose concentration increases progressively with increase of pH. Figure 4 reveals that mercury(II), nickel(II) and lead(II) ions form their first complex movements toward negative electrode. Hence, one sarcosine anionic species [CH_3 (NH) CH_2 COO^-] must have combined with Hg(II), Ni(II) and Pb(II) to give 1:1 [Hg {CH_3 (NH) CH_2 COO}]$^+$, [Ni {CH_3 (NH) CH_2 COO}]$^+$ and [Pb {CH_3 (NH) CH_2 COO}]$^+$ complex cations, respectively. The third plateau in each case is in zero region showing neutral nature of metal ligand complex. Hence, two anionic species of sarcosine [CH_3 (NH) CH_2 COO^-] must have combined with metal ion to give 1:2 [Hg {CH_3 (NH) CH_2 $COO\}_2$], [Ni {CH_3 (NH) CH_2 $COO\}_2$] and [Pb {CH_3 (NH) CH_2 $COO\}_2$] neutral complexes, respectively. Further increase of pH has no effect on the mobility of metal ions, which indicates no further interaction between metal ions and ligands. In general, the complexation of metal ions with sarcosine anion may be represented as:

$$M^{2+} + L^- \overset{K_1}{\leftrightarrows} ML^+ \quad (1)$$

$$ML^+ + L^- \overset{K_2}{\leftrightarrows} ML_2 \quad (2)$$

where M^{2+} is Hg^{2+} Ni^{2+} and Pb^{2+} metal ions; $[L^-]$ is the sarcosine anion; K_1 and K_2 are the first and second stability constants, respectively. The metal spot on the paper is thus a combination of uncomplexed metal ions; 1:1 and 1:2 complexes. The spot is moving under the influence of electric field and the overall mobility is given by equation of Jokl [46].

$$U = \frac{\Sigma u_{xp} \cdot \beta_{xp} [HpL]^x}{\Sigma \beta_{xp} [HpL]^x} \qquad (3)$$

where $[HpL]^x$ is the concentration of general complex species; β_{xp} is the overall mobility constant of the complex and $u_{x\text{-}p}$ is the speed of the general complex $[M(HpL)^x]$ present in the combination. On taking into consideration different equilibria, the above equation is transformed into following form:

$$U = \frac{u_0 + u_1 K_1 [L^-] + u_2 K_1 K_2 [L^-]^2}{1 + K_1 [L^-] + K_1 K_2 [L^-]^2} \qquad (4)$$

where u_0, u_1 and u_2 are mobilities of uncomplexed metal ion, 1:1 and 1:2 metal complexes, respectively. For the calculation of the first stability constant K_1, the region between the first and second plateau is pertinent. The overall mobility U is equal to the arithmetic mean of mobility of uncomplexed metal ion, u_0, and that of first complex, u_1, at pH where $K_1 = 1/[CH_3(NH)CH_2COO^-]$. With the help of dissociation constants of pure sarcosine (electrophoretically obtained value, ($K_{a1} = 10^{-2.20}$; $K_{a2} = 10^{-9.99}$) the concentration of sarcosine anion $[L^-]$ is determined for the pH, from which, K_1 can be calculated. The concentration of complexing sarcosine anion $[L^-]$ is calculated with the help of equation (5).

$$[L^-] = \frac{[L_T]}{1 + [H] / K_{a2} + [H]^2 / K_{a1} \bullet K_{a2}} \qquad (5)$$

where $[L_T]$ is total concentration of ligand sarcosine (0.01 M); K_{a1} and K_{a2} are first and second dissociation constant of pure sarcosine, respectively.

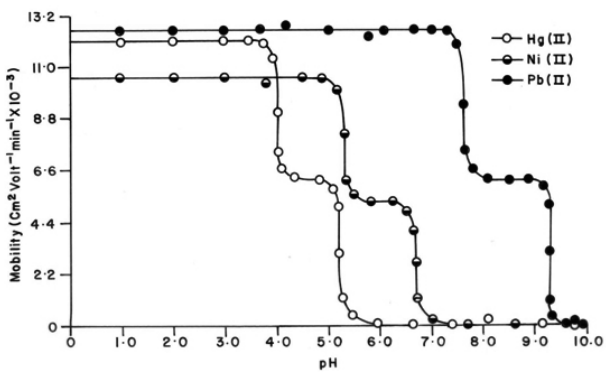


Fig. 4: Mobility curves for the metal(II) – sarcosine system. —○— = Hg(II) – sarcosine —◐— = nickel(II) – sarcosine —●— = Pb(II) – sarcosine. pHs were maintained by addition of sodium hydroxide. Ionic strength = 0.1 M; temperature = 35° C. The paper strips were spotted with 0.1 mL of sample solution and glucose (for making osmotic corrections).

The stability constant, K_2, of second complex can be calculated by taking into consideration the region between second and third plateau of mobility curve. The calculated values of K_1 and K_2 are given in Table 1.

Table 1. Stability constants of binary complexes of mercury(II), nickel(II) and lead(II) with sarcosine.

Metal ions	Complexes	Stability constant	Logarithm stability constant values *
Mercury(II)	ML^+ ML_2	K_1 K_2	7.95 ± 0.02 6.79 ± 0.06
Nickel(II)	ML^+	K_1	6.69 ± 0.01 [(5.24) [48]] [(5.50) [49]]
	ML_2	K_2	5.29 ± 0.04 [(4.30) [48]] [(4.38) [49]]
Lead(II)	ML^+ ML_2	K_1 K_2	4.34 ± 0.02 2.69 ± 0.07

Note: Ionic strength = 0.1 M; temperature = 35º C; M = metal cations (Hg^{2+}, Ni^{2+}, Pb^{2+}); L = ligand (sarcosine); sarcosine anion = $[CH_3(NH)CH_2COO^-]$.

DISCUSSION

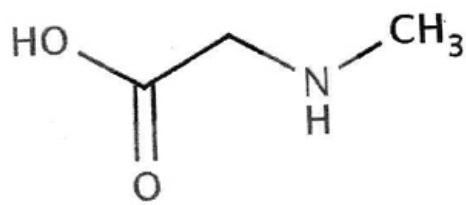
Comparison of logarithm stability constant values of metal ions complexes follow the order:

$$\log K_1 > \log K_2$$

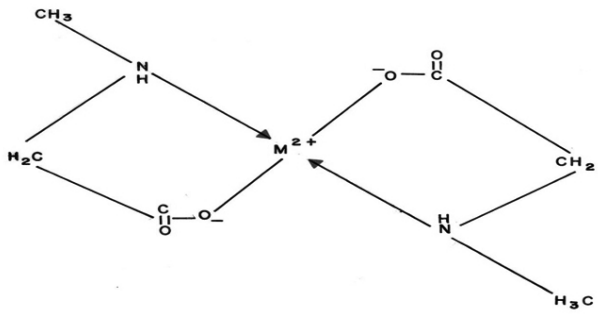
The values of second stability constant in each complex found to be lower in comparison to first stability constant values. It is therefore inferred that the coordinating tendency of a ligand decreases with higher state of aggregation[47]. It is observed from the Table 1 the first and second stability constant follow the order.

$$\text{mercury(II)} > \text{nickel(II)} > \text{lead(II)}$$

High stability constant values of mercury(II) – sarcosine complexes indicate strong bonding between mercury(II) cation and sarcosine anion while low stability constant value between lead(II) and sarcosine complexes indicate weak bonding between lead(II) cation and sarcosine anion. The higher stabilities of mercury(II) – sarcosine complexes may be ascribed to be its greater affinity for the oxygen donor ligands. The molecular structure of sarcosine ($C_3H_7NO_2$) is given below:



It is also observed from Table 1 that the stability constant values are approximately similar to literature values. The slight deviation in the values obtained from different sources is mainly due to the difference in temperature, ionic strength and experimental conditions used by different workers. The stability constants of metal complexes, can be very easily calculated by this technique; therefore the present method is advantageous over other methods (viz. polarography, potentiometry, solubility, etc.) reported in chemical literature. The present technique is limited to charged species, and the precision of the method is not high as other physicochemical methods. However, uncertainity in the results is ± 2%. It is not felt that it can replace the most reliable methods, although it is new approach worth developing. The proposed structure of the ML_2 complex is given as follows:



CONCLUSIONS

The following conclusions can be drawn from the present study:

1. Mercury(II) – sarcosine and lead(II) – sarcosine complexes are found to have maximum and minimum logarithmetic stability constant values, respectively.
2. The logarithmetic stability constant values of ML^+ complexes are found to be higher in comparison to ML_2 complexes in each system.
3. The present advanced electrophoretic technique has thus been proved to be helpful in deciding whether a binary complex system is formed or not, and if it is formed its stability constant can also be determined.

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