grade solution (0·25%) in 0·25N H_2SO_4 was prepared in conductivity water and stored in an amber-coloured bottle. Solutions of sulphosalicylic acid (0·1%) and KCNS (1M) were prepared from analar grade reagents. All the other reagents used were of analar grade.

The potentiometric assembly used consists of Osaw Crompton potentiometer (Ambala, India), a saturated calomel reference electrode, a bright platinum rod (0·2 mm diameter) as indicator electrode and a salt bridge filled with sat. solutions of KCl to ensure the electrical contact between calomel reference electrode and the titration vessel.

Potentiometric titration method — To a portion (2-20 ml) of thioglycollic acid solution KCNS (1-2 ml) and osmic acid (0·3 ml) solutions were added. The mixture was diluted to 50 ml and titrated with standard solution of Fe(III). The potentials attained stable values immediately after the addition of each portion of the titrant except near the end-point where an interval of 2-3 min was needed.

Visual titration method — In this method the titration was carried out to the appearance of reddish-pink (in the case of sulphosalicylic acid) or pale-red (in the case of KCNS) colour giving an interval of 20-30 sec after the addition of each 0·04 ml portion of Fe(III) solution near the end-point.

Effect of varying [acid]— Best results were obtained in the *p*H range 1-3. At higher [acid], the reaction was slow as indicated by the slow attainment of stable potentials. At higher *p*H hydrolysis of Fe(III) rendered the titration difficult.

Effect of varying [thiocyanate] — The presence of 1-2 ml of 1M KCNS enhanced the speed of reaction near the equivalence point where the inflection was increased by about 30 mV.

Effect of varying [catalyst] — The presence of 0·2-0·5 ml of 0·25% solution of osmic acid increased the rate of reaction between Fe(III)-thiocyanate complex and thioglycollic acid so that the stable potentials are attained within a period of 2-3 min near the equivalence point.

The potential break at the equivalence point was about 170-180 mV per 0·04 ml of 0·1N Fe(III) solution. Thioglycollic acid in the range of 11-136 mg could be determined with Fe(III), with an average error of 0·12%. Similar experiments were carried out using 0·01N solutions of thioglycollic acid and Fe(III). In these titrations the optimum amount of osmic acid was found to be 0·1-0·3 ml of 0·1% solution per 50 ml of the titration mixture. Thioglycollic acid in the range of 1·5-10 mg could be determined in centinormal solution with an average error of 0·15%. Thioglycollic acid in the ranges of 11-102 and 17-170 mg could also be determined visually with average errors of 0·27 and 0·13% using thiocyanate and sulphosalicylic acid as indicators, respectively.

The pale yellow colour of osmium-thioglycollic acid complex interferes in the visual detection of the end-point if a higher concentration of catalyst than prescribed is present.

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Solvent Extraction & Ion-exchange Studies on Cadmium & Thallium Complexes with Glycollic & Lactic Acids

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Complexes of cadmium and thallium with glycollic and lactic acids have been studied by the method of solvent extraction using potassium dinonylnaphthalene sulphonate as the auxiliary ligand. An ion-exchange study of cadmium lactate, glycollate and fluoride complexes has been also carried out. The stability constants were calculated for all the systems.

Solvent extraction has been widely used for the study of non-extractable complexes by the method of competitive reactions[1,2]. Ion-exchange has also been employed for such studies. In continuation of our earlier work on indium complexes[3], the results of our studies on cadmium and thallium complexes with glycollic and lactic acids are reported in this note.

Cadmium as Cd^{115m} and thallium as Tl^{204} were obtained from the Isotope Division, BARC, and were assayed using GM detectors. Dinonylnaphthalene sulphonic acid (R. T. Vanderbilt & Co.) was estimated by titration with sodium hydroxide[4]. Its potassium salt was prepared by repeated equilibration with 1·0M potassium nitrate. Benzene (BDH, AK) was used as the diluent. Stock solutions of glycollic (Riedel De Haen) and lactic (Baker analysed) acids were standardized by titration with sodium hydroxide. The ionic strength was maintained at 0·5M by the addition of requisite amounts of potassium nitrate.

Extraction studies were carried out as described earlier[3] at 30°±1°. Experiments with cation exchanger were performed using Dowex 50W-X8 (Baker analysed, 50-100 mesh) in potassium form by batch equilibration method.

Solvent extraction studies — The extraction of cadmium by the potassium salt of dinonylnaphthalene sulphonic acid (HDNNS) was studied in the presence and absence of glycollic and lactic acids at different *p*H. The concentration of potassium ions was kept constant at $0{\cdot}50 \pm 0{\cdot}01M$ so that the distribution ratio, D_0, for cadmium would be constant.

The concentrations of the glycollate and lactate ions were calculated from the *p*H of the solutions and the *p*K value of glycollic acid determined from a separate series of experiments by the *p*H-titration technique[5]. The *pK* values were found to be $3{\cdot}38 \pm 0{\cdot}02$ for glycollic acid and $3{\cdot}52 \pm 0{\cdot}02$ for lactic acid at 30° at an ionic strength of $0{\cdot}5M$ (potassium nitrate).

The extraction mechanism can be written as shown in Eq. (1),

$$Cd^{2+} + [(KDNNS)_x]_0 \rightleftharpoons [CdDNNS]_0 + 2K^+ \qquad \dots(1)$$

so that the extraction depends inversely on the second power of the concentration of potassium ions. The distribution ratio, D_0, of cadmium by KDNNS can be written as shown in Eq. (2).

$$D_0 = \frac{[CdDNNS]_0}{[Cd] + \sum_1^N [Cd(NO_3)_n]} \qquad \dots(2)$$

In the presence of glycollate ion, X, the distribution ratio, D, is given by

$$D = \frac{[CdDNNS]_0}{[Cd] + \sum_1^N [Cd(NO_3)_n] + \sum_1^N [CdX_n]} \qquad \dots(3)$$

It can be shown from the above equations that

$$C\left(\frac{D_0}{D} - 1\right) = \beta_1'[X] + \beta_2'[X]^2 + \dots \qquad \dots(4)$$

where $C = 1 + \beta_1''[NO_3] + \beta_2''[NO_3]^2 \qquad \dots(5)$

β_n' and β_n'' represent the stability constants of cadmium glycollate and nitrate complexes respectively.

The values of D, D_0 and D_0D^{-1} (or F_0) are presented in Table 1. The plot of log F_0 versus *p*X is a curve (Fig. 1) indicating the presence of two or more species. The data were analysed for the stability constants taking into account the reported[6] values for the nitrate complex of cadmium ($\beta_1'' = 0{\cdot}62$ and $\beta_2'' = 0{\cdot}10$). The values of log F_0 were obtained at different concentrations of glycollate and lactate ions from the smooth curve. The correction factor, C, was calculated at these values from the known concentrations of potassium nitrate. Eq. (4) was solved for the individual stability constants by the method of weighted least-squares using BESM-6 computer, the values obtained being $\beta_1' = 37{\cdot}4 \pm 1{\cdot}6$ and $\beta_2' = 560 \pm 28$ for Cd-glycollate complex and $\beta_1' = 17{\cdot}8 \pm 1{\cdot}8$ and $\beta_2' = 114 \pm 17$ for Cd-lactate complex.

TABLE 1 — SOLVENT EXTRACTION DATA FOR CADMIUM-GLYCOLLATE COMPLEXES

($[K^+] = 0{\cdot}50M$; $D_o = 1{\cdot}40$)

[Glycollic acid] ×10*M*	*p*H	*pX*	−log *D*	log F_o
0·05	3·39	2·60	−0·12	−1·23
0·10	3·41	2·28	−0·07	−0·74
0·15	3·43	2·10	−0·05	−0·59
0·20	3·42	1·98	−0·00	−0·41
0·30	3·44	1·80	0·07	−0·20
0·50	3·44	1·57	0·16	0·02
0·75	3·45	1·39	0·30	0·26
1·00	3·46	1·27	0·41	0·42
1·50	3·47	1·08	0·63	0·69
2·00	3·49	0·95	0·75	0·84
4·75	2·94	0·90	1·22	1·35
2·50	3·46	0·87	0·97	1·08
4·75	3·51	0·56	1·55	1·69

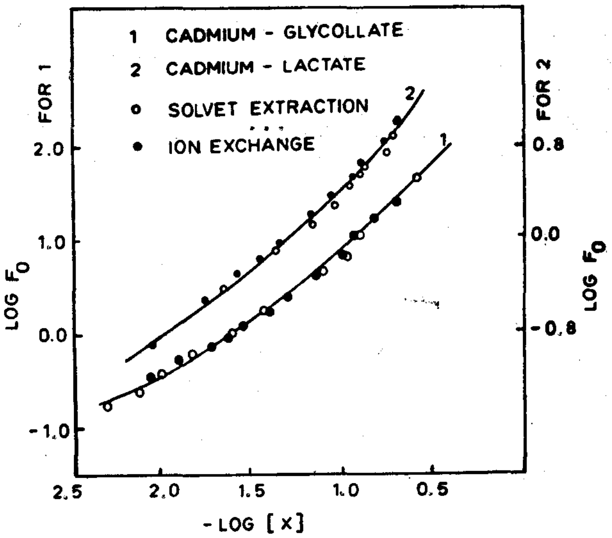

Fig. 1 — Plots of log F_0 versus log $[X]$ for cadmium glycollate (curve 1) and cadmium lactate (curve 2) complexes

Ion-exchange studies — HDNNS being a cation exchanger, it was thought worthwhile to study the behaviour of an analogous solid cation exchanger to compare the advantages of the two methods. Experiments were carried out using Dowex 50W-X8 by batch equilibration method, 0·25 g of the resin being used for each experiment. The results are shown in Fig. 1. The function, F_0, plotted as a function of pX was calculated from Eq. (6).

$$F_0 = D_0D^{-1} - 1 = \beta_1'[X] + \beta_2'[X]^2 + \dots \qquad \dots(6)$$

where D_0 (77·7 ml g^{-1}) and D represent the distribution ratios of cadmium in the absence and presence of the ligand respectively. D_0 or D is defined as

$$D = \frac{[M]_{resin}}{[M]_{solution}} \frac{[\text{ml of solution}]}{[\text{g of resin}]} \qquad \dots(7)$$

It can be seen from Fig. 1 that the data can be superimposed on those obtained by solvent extraction and hence no further analysis of the data for calculating the stability constants is necessary.

Cadmium fluoride complexes — Complexes of cadmium with fluoride ion were studied by ion-exchange using Dowex 50W-X8 in sodium form. Experiments were carried out in sodium perchlorate medium. The *p*H of the solutions was kept in the range 4-6 where the dissociation of hydrogen fluoride was complete. The decrease in the distribution ratio was quite small but the variation of D_0D^{-1} as a function of [fluoride] indicated the formation of weak fluoride complexes. From the plot of log F_0 against $[X]$, function F_1 can be written as shown in Eq. (8).

$$F_1 = F_0/[X] = \beta_1' + \beta_2'[X] + \dots \qquad \dots(8)$$

The stability constants were calculated from a plot of F_1 against $[X]$ and had the values, $\beta_1' = 3{\cdot}1$ and $\beta_2' = 2{\cdot}0$. The values reported here can be regarded as only approximate values since several other factors are likely to affect the systems in the case of such weak complexes.

Thallium complexes — Complexes of thallium(I) with glycollic and lactic acids were studied by solvent extraction using KDNNS as the auxiliary ligand. The extraction of thallium was practically independent of *p*H at a concentration of 0·5*M* (potassium ions). Experiments were carried out at varying concentrations of lactate or glycollate ions, keeping the concentration of HDNNS in potassium form at 0·015*M*. The formation of weak complexes makes it necessary to employ high concentrations of the complexing agent and hence the concentration of potassium nitrate decreases steadily. The stability of thallium nitrate complexes as well as thallium and potassium glycollate complexes will have to be taken into account in these cases so that reliable and exact values of the stability constants cannot be calculated. These studies only indicate qualitatively the formation of weak complexes of thallium.

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