

Studies of Extraction Exchange Equilibria. Pb(II)–Cd(II) Exchange in the CCl₄-Xanthate/Water System^{#,†}

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Summary. An extraction exchange equilibrium between cadmium xanthate in carbon tetrachloride and lead ions in water at *pH*s 5 and 7.5 was studied at $25 \pm 2^\circ\text{C}$. The exchange isotherm was used to calculate the separation factor $S_{\text{Pb}}/S_{\text{Cd}}$. The thermodynamic equilibrium constant and corresponding free-energy change per mole of exchange were calculated using the relevant analytical data and activity coefficients of the electrolyte ions in the aqueous phase and of the xanthate bound ions in the carbon tetrachloride phase. Non-ideal behaviour of the CCl₄-xanthate phase was also ascertained. From the present study it appears that the phenomenon may be treated similar to ion-exchange processes in synthetic organic ion exchangers.

Keywords. Extraction exchange; Equilibrium quotient; Exchange reaction constant; Separation factor; Activity coefficient; Thermodynamic equilibrium constant; Free energy change.

Untersuchungen über Extraktions – Austausch – Gleichgewichte. Der Pb(II)–Cd(II) Austausch im CCl₄-Xanthat/Wasser-System

Zusammenfassung. Das Extraktions – Austausch – Gleichgewicht zwischen Cadmiumxanthat in Tetrachlorkohlenstoff und Bleiionen in Wasser bei *pH* 5 bzw. 7.5 und $25 \pm 2^\circ\text{C}$ wurde untersucht. Die Austauschisotherme wurde dazu verwendet, den Trennfaktor $S_{\text{Pb}}/S_{\text{Cd}}$ zu berechnen. Die thermodynamische Gleichgewichtskonstante und die Differenz der freien Energie wurden aus den relevanten analytischen Daten und die Aktivitätskoeffizienten der Elektrolyten in der wässrigen Phase bzw. der durch Xanthat gebundenen Ionen in der Tetrachlormethanphase erhalten. Das nicht-ideale Verhalten der CCl₄-Xanthat-Phase wurde ebenfalls dokumentiert. Aus der vorliegenden Studie ergibt sich, daß das Phänomen analog zu Ionenaustauschprozessen in synthetischen organischen Ionenaustauschern behandelt werden kann.

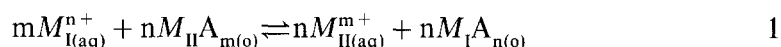
[#] Presented at the National Seminar on Recent Trends in Chemistry of Colloids, Surfaces and Electrolytes (SRTCCSE), April 1994, University of Calcutta, India.

[†] Dedicated to the late Professor *Wolfgang Pusch* (Max-Planck-Institut für Biophysik, Frankfurt, Germany)

Introduction

An extraction exchange reaction involves an interfacial interchange of a metal ion M_I^{n+} of an electrolyte in aqueous solution and a metal ion M_{II}^{n+} bound as a first order chelate $M_{II}A_m$ (ligand A^-) in a water-immiscible organic solvent. The two phases are mixed and both metals (M_I^{n+} and M_{II}^{n+}) form similar types of complexes with the ligand A^- which are soluble in the same organic solvent at a particular pH range of the aqueous solution. The extent of exchange depends upon the stabilities of the complexes in the organic phase, extraction constants, concentration of the counter-ion in the aqueous phase, pH , effectiveness of contact between the two phases, and temperature [1].

In analytical chemistry, an excess of M_I^{n+} ion in the aqueous solution at a constant pH and an inequality of extraction constants ($(K_{ex}^I)^m \gg (K_{ex}^{II})^n$) are recommended for a quantitative replacement of the metal M_{II}^{n+} in the non-aqueous phase via the ion-exchange reaction at a constant temperature.



In his studies on the extraction of some metal diethyldithiocarbamates in carbon tetrachloride, *Bode* has reported several cases of variation of the degree of replacement of a metal in the complex in the organic phase with different quantities of another metal in aqueous solution [2].

Apart from its analytical utility, the extraction exchange reaction (Eq. 1) deserves interest because of the physico chemical aspect of the metal-ion exchange equilibrium. The extraction exchange process resembles the exchange process associated with synthetic organic ion exchangers, particularly chelating exchangers [3, 4, 5]. The water-immiscible organic solvent containing all the chelate compound behaves as an ion exchanger. The metal ion acts as an exchangeable counter-ion; the rest resembles the hydrophobic moiety of an ion exchanger holding the fixed ion A^- , provided it does not undergo any change in composition during the course of the exchange reaction and thereafter. In both situations, the exchange reaction takes place at the interface and the extent of exchange depends primarily on the contact between the immiscible phases. And, as the position of a counter-ion in the empirical selectivity order associated under certain conditions with a particular ion-exchanger indicates its ability to take part in ion-exchange reaction with other ions, the capacity of a metal ion to enter into an extraction exchange reaction related to a particular ligand, solvent, and fixed other conditions like pH , temperature, etc. may be known from its position in the sequence of elements determined empirically from the extraction constants (K_{ex}) [1][§].

Thus, when a water-immiscible organic solvent holding a chelate compound $M_{II}A_m$ and an aqueous solution of an electrolyte containing an ion M_I^{n+} are mixed for a certain period at a definite temperature and at a pH range at which both

[§] A series representing the behaviour of metal ions extracted as diethyldithiocarbamates in $CHCl_3$ from aqueous solutions at pH 8.5–11 is $Hg^{2+} > Ag^+, Pd^{2+} > Cu^{2+} > Tl^{3+} > Bi^{3+} > Pb^{2+} > Fe^{3+} > Co^{2+}, Cd^{2+}, Tl^+ > Ni^{2+} > Zn^{2+} > In^{3+}, Sb^{3+} > Te^{4+} > Mn^{2+}$. A given element can be displaced from its chelate compound in $CHCl_3$ by elements to the left of it

$M_{II}A_m$ and $M_I A_n$ are completely extractable, an equilibrium between the exchanging metal ions will develop (Eq. 1). The thermodynamic equilibrium constant K following from the mass action law treatment of ion exchange is

$$K = \frac{a_{M_I A_n(o)}^m \cdot a_{M_{II}^{m+}}^n}{a_{M_I^{n+}}^m \cdot a_{M_{II} A_m(o)}^n} = \frac{[M_I A_n]_{(o)}^m [M_{II}^{m+}]^n}{[M_{II} A_m]_{(o)}^n [M_I^{n+}]^m} \cdot \frac{f_{M_I A_n(o)}^m \cdot \gamma_{M_{II}^{m+}}^n}{f_{M_{II} A_m(o)}^n \cdot \gamma_{M_I^{n+}}^m} \quad 2$$

This equilibrium constant is practically identical with the conventional exchange reaction constant K_e [1] defined as

$$\begin{aligned} K_e &= (K_{ex}^I)^m / (K_{ex}^{II})^n = (P_{M_I A_n}^m \cdot \beta_{M_I A_n}^m) / (P_{M_{II} A_m}^n \cdot \beta_{M_{II} A_m}^n) \\ &= (a_{M_I A_n(o)}^m / a_{M_I^{n+}}^m) \cdot (a_{M_{II}^{m+}}^n / a_{M_{II} A_m(o)}^n) \\ &= \frac{[M_I A_n]_{(o)}^m}{[M_I^{n+}]^m} \cdot \frac{[M_{II}^{m+}]^n}{[M_{II} A_m]_{(o)}^n} \cdot \frac{\alpha_{M_I A_n(o)}^m}{\alpha_{M_I}^m} \cdot \frac{\alpha_{M_{II}}^n}{\alpha_{M_{II} A_m(o)}^n} \end{aligned} \quad 3$$

The square bracketed terms with the subscript 'o' in Eqs. 2 and 3 represent mole fraction and amount concentration of the metal ions respectively bound in the complex in the organic phase. Without subscript 'o', they relate to the molar concentrations of the ions in the aqueous phase. The "side reaction coefficients" [6] are denoted by α ; for f and γ , see Glossary.

In order to determine the thermodynamic equilibrium constant of an extraction exchange reaction, it is necessary to evaluate the activity coefficients of the species in the aqueous and organic phases (in Eq. 2, the square bracketed terms are experimentally determinable). Thus, Eq. 2 can be expressed as

$$K = K'_a \cdot \frac{f_{M_I A_n(o)}^m \cdot \gamma_{M_{II}^{m+}}^n}{f_{M_{II} A_m(o)}^n \cdot \gamma_{M_I^{n+}}^m} = K_a \cdot \frac{f_{M_I A_n(o)}^m}{f_{M_{II} A_m(o)}^n} \quad 4$$

The ratio of the mean activity coefficients of the electrolytes ($\gamma_{\pm M_{II} Y_m}$ and $\gamma_{\pm M_I Y_n}$, Y^- being the common ion) of the corresponding ions M_{II}^{m+} and M_I^{n+} , rather than those of the free ions, in the aqueous solution of mixed electrolytes can be calculated by application of the interionic interaction principle of *Brönsted-Scatchard* and *Guggenheim* and determination of the relevant interaction coefficient terms B .

$$\log \gamma_i = Z_i^2 \cdot \log \gamma^{st} + \sum_j B_{ij} m_j \quad 5$$

The method of calculation for a mixture of binary electrolytes containing two different counter-ions and a common co-ion has been described by one of us earlier [7]. However, in the case of the presence of the buffer electrolyte as an additive in the aqueous solutions, though the ions therefrom do not take part in the exchange reaction, their entities are also to be taken into account in the calculation of B in order to determine the mean activity coefficient ratios of the electrolytes.

For the non-aqueous phase, one may refer the non-aqueous solvent solution of the complex of only one of the exchanging ions in equilibrium with an infinitely dilute aqueous solution of an electrolyte containing the same ion to a standard state, that is, when the mole fraction of the complexed metal ion in the organic phase is unity. Applying the *Gibbs-Duhem* equation for the binary mixture of the

complexed metal ions in the organic phase, it can be shown that

$$\ln f_{M_{I(o)}} = [(\bar{X}_{M_{I(o)}} - 1)/\{m + (n - m)\bar{X}_{M_{I(o)}}\}] \ln K_a + \int_{\bar{X}_{M_{I(o)}}}^{\bar{X}_{M_{I(o)}}=1} \ln K_a \cdot [n/\{m + (n - m)\bar{X}_{M_{I(o)}}\}^2] d\bar{X}_{M_{I(o)}}, \quad 6$$

$$\ln f_{M_{II(o)}} = [\bar{X}_{M_{I(o)}}/\{m + (n - m)\bar{X}_{M_{I(o)}}\}] \ln K_a - \int_{\bar{X}_{M_{I(o)}}=0}^{\bar{X}_{M_{I(o)}}} \ln K_a \cdot [m/\{m + (n - m)\bar{X}_{M_{I(o)}}\}^2] d\bar{X}_{M_{I(o)}}, \quad 7$$

and

$$\ln K = mn \int_{\bar{X}_{M_{I(o)}}=0}^{\bar{X}_{M_{I(o)}}=1} [1/\{m + (n - m)\bar{X}_{M_{I(o)}}\}^2] \ln K_a d\bar{X}_{M_{I(o)}} \quad 8$$

A concise derivation of these equations is given in the Appendix.

The activity coefficients $f_{M(o)}$ and the thermodynamic equilibrium constant K can be determined from Eqs. 6, 7, and 8 using the mole fractions of one of the ions $\bar{X}_{M(o)}$, corresponding $\log K_a$ values, and definite graphical integration values in a plot of $\log K_a$ against $d\bar{X}_{M(o)}$.

Apart from this rigorous but cumbersome approach, when the number of moles of the species in the Eq. 1 are the same and unity ($m = n = 1$), and the plot of $\log K_a$ vs. $d\bar{X}_{M(o)}$ is linear, a regular model equation along with the equation of the best fit straight line yields the organic phase activity coefficient terms and the thermodynamic equilibrium constant [8]. The constant a reflects the energy of interchange between $M_{I(o)}$ and $M_{II(o)}$. The standard free energy change per mole of exchange may be obtained by the relation $\Delta G^\theta = -RT \ln K$.

$$\bar{X}_{M_{I(o)}} \ln f_{M_{I(o)}} + (1 - \bar{X}_{M_{I(o)}}) \cdot \ln f_{M_{II(o)}} = a \bar{X}_{M_{I(o)}} \cdot (1 - \bar{X}_{M_{I(o)}}) \quad 9$$

$$\ln K_a = \ln K - a + 2a \cdot \bar{X}_{M_{I(o)}} \quad 10$$

In the present work, an attempt has been made to determine the thermodynamic equilibrium constant of an extraction exchange reaction involving chelate complexes of lead and cadmium as xanthates in carbon tetrachloride and cadmium and lead ions in aqueous solutions, treating the system in the regular model way.

Results and Discussions

Adhering to the conditions mentioned above, it was found that the CCl_4 extracts ($\text{CCl}_4\text{-XnCd}$ and $\text{CCl}_4\text{-XnPb}$) prepared from time to time for use in the exchange equilibrium experiments contained the same quantities of the metals. Both Cd and Pb xanthates (1:2) are stable in carbon tetrachloride [10]; an extended period of shaking with pure water, buffer solutions of $pH \sim 5$ and ~ 7.5 , or dilute alkali solution (KOH) do not decompose them to any perceptible quantity. Stoichiometry of exchange has been established in all equilibrium experiments within the experimental error. The concentrations of the ions before and after equilibrium in the appropriate phases and the corresponding K'_a values calculated therefrom are shown in Table 1.

The ratio of the mean activity coefficients of the electrolytes in the aqueous

Table 1. Equilibrium experiment data

Expt No	Pre-equil. distribn. (mmole $\times 10^3$)	Post-equil. distribn. (mmole $\times 10^3$)	Conc. of ions (Aq. soln.) (mol l ⁻¹ $\times 10^4$)		Mole frac Pb	log K' _a
	Org. extract as xanthate (25 ml) of	Aq. soln. as nitrate (25 ml) of	Organic phase (25 ml)			
			Pb ²⁺	Cd ²⁺	Org.	Aq.
					Pb ²⁺	Cd ²⁺
CdXn-Pb ²⁺ exchange						
	Cd	Pb ²⁺ pH ~ 7.5				
1	46.6	19.46	0.47	19.00	0.188	7.60
2	46.6	26.30	1.71	24.36	0.684	9.74
3	46.6	34.40	4.03	30.25	1.610	12.10
4	46.6	47.34	10.60	36.54	4.240	14.60
5	46.6	57.86	16.05	40.09	6.420	16.04
6	46.6	64.40	26.57	40.60	10.600	16.24
7	46.6	52.56	15.53	37.10	6.210	14.84
8	46.6	52.56	15.53	37.10	6.210	14.84
PbXn-Cd ²⁺ exchange						
	Pb	Cd ²⁺ pH ~ 5				
9	15.78	25.63	3.96	21.20	1.580	8.48
10	15.78	48.93	5.02	43.50	2.010	17.40
11	15.78	69.90	6.27	63.40	2.500	25.40
12	15.78	95.53	4.50	89.50	1.800	35.80
					0.696	0.157
					0.623	0.103
					0.580	0.090
					0.466	0.048

$$K'_a = \frac{[\text{Mole frac. Pb}]_o [\text{Molar conc. Cd}]_{aq}}{[\text{Mole frac. Cd}]_o [\text{Molar conc. Pb}]_{aq}}$$

phase containing acetate buffer as they appear in the calculation of $K_a = K'_a(\gamma_{\pm \text{Cd}(\text{NO}_3)_2}^3/\gamma_{\pm \text{Pb}(\text{NO}_3)_2}^3)$ are computed *via* consideration of the aforementioned interionic interaction principle. Considering the expression of $\log \gamma_i$ (Eq. 5) properly for each of the present ions and calculating therefrom the mean activity coefficient of the object electrolytes, the ratio may be expressed as

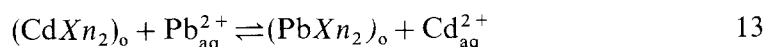
$$\begin{aligned} & \log[\gamma_{\pm \text{Cd}(\text{NO}_3)_2}^3/\gamma_{\pm \text{Pb}(\text{NO}_3)_2}^3] \\ & = 2(m_{\text{Cd}} + m_{\text{Pb}})(B_{\text{Cd},\text{NO}_3} - B_{\text{Pb},\text{NO}_3}) + m_{\text{Ac}}(B_{\text{Cd},\text{Ac}} - B_{\text{Pb},\text{Ac}}) \end{aligned} \quad 11$$

The values of the relevant parameters and expressions are shown in Table 2. Since the experimental values of the mean activity coefficients of pure $\text{Cd}(\text{Ac})_2$, $\text{Pb}(\text{Ac})_2$, $\text{Cd}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$ at an ionic strength 0.1 M ($m = 0.0333$) are not available in the literature, *Davies'* empirical equation taking into account the ion association factor [11] and *McInnes'* suitable ratio method [12] were utilized to obtain the primary mean activity coefficient values. The same ratio values without taking account of the interionic interactions, and also the ratios of only the counter-ion activity coefficients (single ion activity coefficients) calculated from *Kieland's* data [13] at the equilibrium ionic strengths are shown in the same table. It can be seen that in the low ionic strength range of the equilibrated aqueous solutions, although the single ion activity coefficient values may also be used in the calculation of the equilibrium constant K_a , the aqueous phase activity coefficient correction cannot improve the values of K'_a to any considerable extent, *i.e.* $K'_a \approx K_a$.

The extent of loading of one of the counter-ions (Pb^{2+}) as xanthate in the organic phase and the corresponding free ion concentration of the same ion in the aqueous phase, both expressed in mole fractions (\bar{X}_i and X_i) of the total of both metals is shown in the exchange isotherm diagram (Fig. 1). The negatively curved isotherm lying above the diagonal suggests that, as xanthate, lead is preferred to cadmium by the organic phase throughout. This exchange isotherm hints at the practical application of the extraction exchange method of separation of ions by use of the "separation factor" S_I/S_{II} , the quotient of the ratio of the mole fractions of the two counter-ions in the organic phase and in the aqueous phase

$$S_I/S_{II} = M_{I(o)}^{n+}/M_{II(o)}^{m+}/M_{I(aq)}^{n+}/M_{II(aq)}^{m+} \quad 12$$

The dimensionless numerical value of the separation factor can be determined from the ratio of the two rectangular areas (Fig. 1) which lie below and above the isotherm and touch the latter at the point which corresponds to the experimental condition. It may be noted that for equally charged counter-ions the separation factor becomes equal to the apparent equilibrium quotient K'_a (Eq. 4) or the apparent exchange reaction constant (Eq. 3) in which the ratio of the product of the activity coefficient terms or the product of the side reaction coefficient terms, respectively, are assumed to be unity.



In the present study, the separation factor $S_{\text{Pb}}/S_{\text{Cd}}$ calculated using the congruent points on the isotherm at different aqueous phase mole fractions of Pb^{2+} ($X_{\text{Pb}^{2+}}$) are found to be consistent with the corresponding K'_a ($\approx K_a$) values derived from the best fit curve from a $\log K_{\text{apb-cdXn}} \text{ vs. } \bar{X}_{\text{Pb}}$ plot shown in Fig. 2. For example, for the values $\bar{X}_{\text{Pb}} = 0.9, 0.8, 0.7, 0.6, 0.5, 0.4$, and 0.3, the corresponding values of

Table 2. Aqueous phase data (activity coefficients)

Expt. No.	Molarity of $\text{Pb}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2 \times 10^3$ buffer ion conc. (M)	Ionic str. of soln. including α -correction (M)	Activity coeff. of pure electrolytes (Davies equation with α -correction)	Net inter-ionic interaction action		$\gamma_{\pm}^{\text{obs}}$ $\text{Cd}(\text{NO}_3)_2$	$\gamma_{\pm}^3 \text{Cd}(\text{NO}_3)_2$	γ_{Cd}^{2+}	$\log K_a$
				coeff. terms					
				$\gamma_{\pm}^0 \text{Pb}(\text{NO}_3)_2$	$\gamma_{\pm}^0 \text{Cd}(\text{NO}_3)_2$				
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^a B_{MX_2} values are calculated from bunched ionic strength values, e.g. ionic strengths of the experiments 1, 2, 3, 9 are taken in a group of average ionic strength 0.103; similarly, expts. 4, 5, 6, 7, 8, 10, 11 of average ionic strength 0.107; ^b γ_{\pm}^0 values at individual ionic strengths have been considered

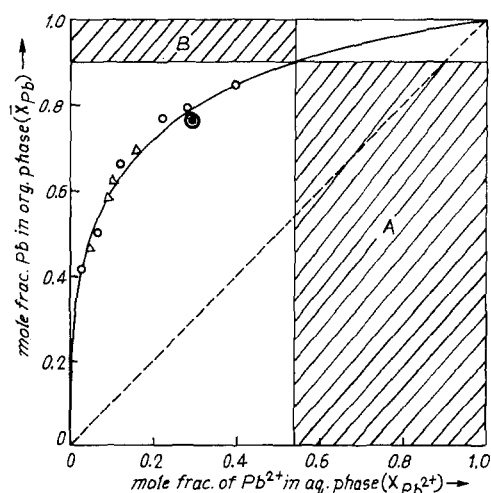


Fig. 1. Exchange isotherm ○: $\text{Cd}(\text{Xn})_2 - \text{Pb}^{2+}$, Δ : $\text{Pb}(\text{Xn})_2 - \text{Cd}^{2+}$; ⊙: preliminary result for equilibrium time (300 strokes for exchanges $\text{Cd}(\text{Xn})_2 - \text{Pb}^{2+}$ and $\text{Pb}(\text{Xn})_2 - \text{Cd}^{2+}$; separation factor $S_{\text{Pb}}/S_{\text{Cd}} = \text{area A}/\text{area B}$

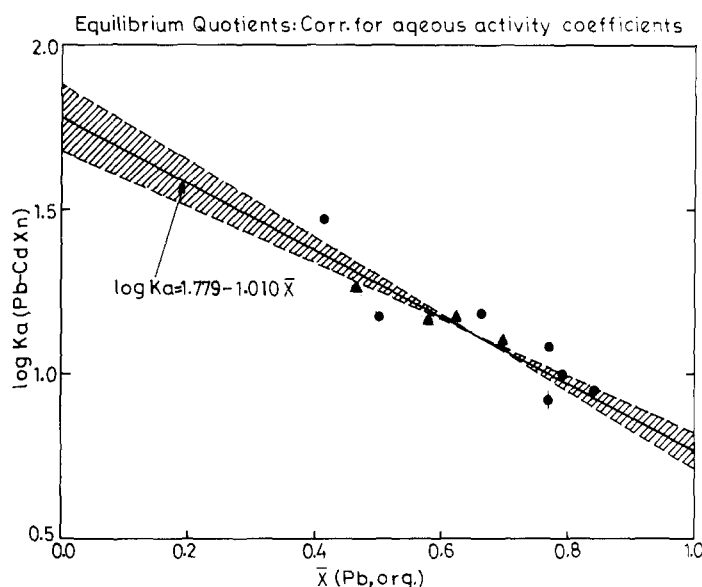


Fig. 2. Plot of equilibrium quotients with activity coefficient correction for the aqueous phase only; $\log K_{\text{aPb-CdXn}}$ vs. mole fraction of Pb as xanthate in CCl_4 phase (\bar{X}_{Pb}); ●: $\text{Cd}(\text{Xn})_2 - \text{Pb}^{2+}$, ▲: $\text{Pb}(\text{Xn})_2 - \text{Cd}^{2+}$; ⊙: P from equilibrium time experiment; solid line: the best fit curve using the equation $\log K_{\text{a}} = 1.779 - 1.010\bar{X}$ obtained by the least square method from the experimental points

$X_{\text{Pb}^{2+}}$ and $S_{\text{Pb}}/S_{\text{Cd}}$ are 0.54, 0.305, 0.175, 0.100, 0.050, 0.025, 0.011, and 7.5, 9.33, 10.99, 13.49, 18.62, 25.12, 35.30, respectively. The related K'_{a} ($\approx K_{\text{a}}$) values corresponding to these \bar{X}_{Pb} values are 7.41, 9.33, 11.80, 14.89, 18.79, 23.71, and 29.92. Again, $S_{\text{Pb}}/S_{\text{Cd}}$ values larger than unity indicates that Pb-xanthate is more stable than Cd-xanthate in the CCl_4 phase – an almost established fact for ligands in which sulfur is the donor atom. This is further supported from the stripping studies of these xanthates [9].

The functional relationship between the excess thermodynamic properties of the mixture (mixture of the complexes in the organic phase) and the composition is the origin of the activity coefficient of the complexed metal ions in the organic

phase.

$$\delta(n\Delta G^{\text{Ex}}/RT)/\delta_{n_i} = \ln f_i \quad 14$$

The non-ideal nature of the non-aqueous phase solution may be described in terms of the activity coefficients of the complexed ions. Following the aforementioned regular model (Eq. 9) for the present metal exchange reaction (Eq. 13), the activity coefficients of the metals in the organic phase may be determined by

$$\bar{X}_{\text{Pb(o)}} \ln f_{\text{Pb}} + (1 - \bar{X}_{\text{Pb(o)}}) \cdot \ln f_{\text{Cd}} = a \bar{X}_{\text{Pb}} (1 - \bar{X}_{\text{Pb}}) \quad 15$$

$$\ln K - \ln K_a = \ln f_{\text{Pb}} - \ln f_{\text{Cd}} \quad 16$$

and the straight line equation

$$\ln K_a = \ln K - a + 2a \bar{X}_{\text{Pb}} \quad 17$$

with $K = 18.8$ and $a = -1.163$ obtained by least square analysis of Eq. 17 and using the best fit linear equation $\log K_a = 1.779 - 1.010 \cdot \bar{X}$ through the experimental points (Fig. 2).

The activity coefficient values (f) of the complexed metal ions with their corresponding mole fractions in the organic phase are shown in Table 3.

The same values for the activity coefficients are obtained using Eqs. 6 and 7. In the calculation of the activity coefficients by these two methods, the necessary $\ln K_a$ values are taken from the points on the best fit line in Fig. 2. The thermodynamic equilibrium constant K determined by the graphical integration method (Eq. 8) has been found to be the same (18.8) as obtained by the regular model. The corresponding free energy change for the exchange reaction is $-7.27 \text{ kJ} \cdot \text{mol}^{-1}$. This quantity is comparable to the free energy change observed in many ion exchange processes with synthetic organic ion exchangers where actual chemical reactions do not take place. Only redistribution of ions by diffusion through interface occurs, and the driving force stems from the entropy of mixing (configuration entropy change etc.).

The non-ideal behaviour of the non-aqueous phase has been ascertained by its deviation from *Raoult's* law. The deviation is shown in Fig. 3 by the plot of the complexed metal activity a_M against the corresponding mole fraction \bar{X}_M as xanthate in the organic phase. For each \bar{X}_M value, the corresponding f values (determined from Eqs. 15 and 16) are used to calculate a_M ($a = \bar{X} \cdot f$). A negative deviation from *Raoult's* law is observed in both cases. This corroborates the empirical rule that a decreasing K_a vs. \bar{X} curve points to a negative deviation from *Raoult's* law [7, 14, 15] and indicates the existence of some interaction between carbon tetrachloride solutions of $\text{Pb}(\text{Xn})_2$ and $\text{Cd}(\text{Xn})_2$ in their binary mixtures.

Table 3. Organic phase data

$\bar{X}_{\text{Pb(o)}}$	0.05	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	0.95
f_{Pb}^a	0.350	0.390	0.475	0.566	0.658	0.748	0.830	0.900	0.955	0.988	0.997
f_{Cd}^a	0.997	0.988	0.955	0.990	0.830	0.748	0.658	0.566	0.475	0.389	0.350

^a Activity coefficients of metal xanthates (o)

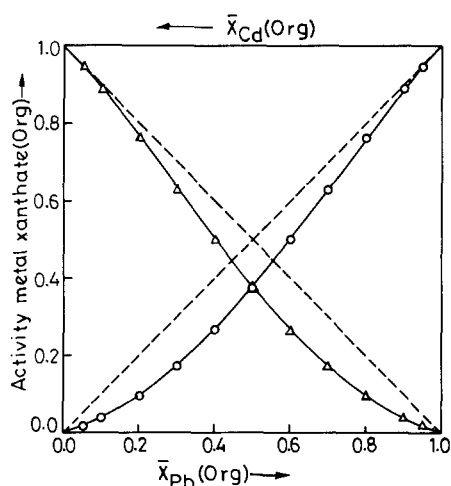


Fig. 3. Plot of the activities (a) and corresponding mole fractions of the metals as xanthate complex in the CCl_4 phase (\bar{x}); the related activity coefficient values (f) are calculated using Eqs. 15, 16, and $\log K_a = 1.779 - 1.010\bar{x}$; \circ : Pb-xanthate; Δ : Cd-xanthate

Experimental

Reagents

The following reagents with corresponding compositions were used throughout the study unless otherwise mentioned. Aqueous solutions: $Cd(NO_3)_2$ ($0.0466 \text{ mol}\cdot\text{l}^{-1}$), $Pb(NO_3)_2$ ($0.0526 \text{ mol}\cdot\text{l}^{-1}$), potassium ethylxanthate (1%), KOH ($0.005 \text{ mol}\cdot\text{l}^{-1}$), HNO_3 ($0.5 \text{ mol}\cdot\text{l}^{-1}$), HCl ($0.05 \text{ mol}\cdot\text{l}^{-1}$), $EDTA-Na_2$ ($0.01003 \text{ mol}\cdot\text{l}^{-1}$), xylitol orange (0.05%), 1,10-phenanthroline ($0.05 \text{ mol}\cdot\text{l}^{-1}$) in 1.5% HNO_3 ; buffer solutions: $pH \sim 5$ ($NaAc/HAc$), $pH \sim 7.5$ (NH_4Ac). Apart from these, carbon tetrachloride, pyridine and hexamine were used. Potassium ethylxanthate (99% pure) was purchased from Fluka. All other chemicals were CP or AR grade. The water used was demineralized and singly distilled (conductivity $5.8 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$).

General procedure

The extraction exchange equilibrium between Pb^{2+} and Cd^{2+} was studied by mixing a definite volume of a CCl_4 solution of the xanthate complex of one of the ions and the same volume of aqueous solution containing different quantities of the other ion. For the CCl_4 extract of the Cd-xanthate complex, CCl_4-XnCd (20 ml), the white $Cd(Xn)_2$ prepared in a 100 ml separatory funnel (by mixing aqueous solutions of 1 ml $Cd(NO_3)_2$, 5 ml buffer ($pH \sim 5$), 5 ml xanthate, and 4 ml water) was shaken with 15 ml of CCl_4 and 1 drop of pyridine (300 strokes, $2 \text{ strokes}\cdot\text{sec}^{-1}$). The CCl_4 layer was separated. The aqueous layer was extracted with further 5 ml CCl_4 . The combined CCl_4 extracts were shaken with 20 ml of KOH solution to remove any dissolved xanthic acid. In the same way the CCl_4 extract of Pb-xanthate, CCl_4-XnPb (20 ml), was prepared using 0.3 ml $Pb(NO_3)_2$ solution.

The equilibrium experiments were conducted from both sides at room temperature ($25 \pm 2^\circ\text{C}$) using the batch technique, starting with either one of the homoionic forms of freshly prepared CCl_4 extracts. For the $Cd_0-Pb_{aq}^{2+}$ exchange, several CCl_4-XnCd extracts, each 25 ml ($20 + 5 \text{ ml } CCl_4$), were shaken with the same volume of aqueous solutions of almost constant ionic strength containing different volumes of $Pb(NO_3)_2$ solutions (0.370, 0.500, 0.655 ml etc.), 5 ml buffer ($pH \sim 7.5$), and the necessary volume of water. In the case of $Pb_0-Cd_{aq}^{2+}$, different volumes of $Cd(NO_3)_2$ solution and a buffer of $pH \sim 5$ were used. Earlier studies indicate that both $Pb(Xn)_2$ and $Cd(Xn)_2$ chelates are completely extracted in CCl_4 in the pH range of 5 to 7.5 [9] (Fig. 4). Three hundred strokes ($2 \text{ strokes}\cdot\text{sec}^{-1}$) were found sufficient for attainment of equilibrium for either set of experiments;

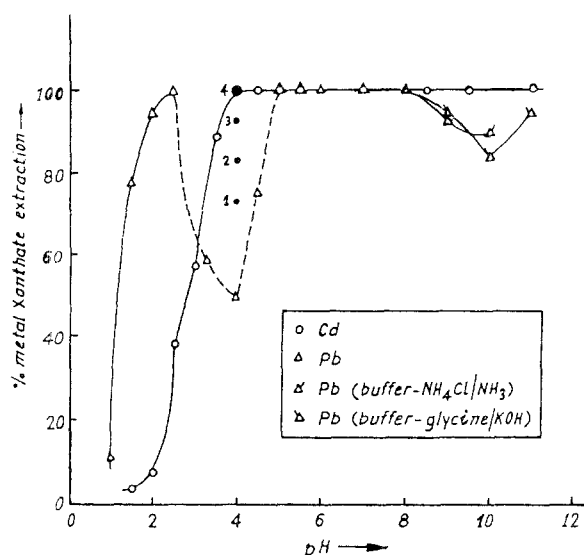


Fig. 4. Variation of extraction of $\text{Pb}(\text{Xn})_2$ and $\text{Cd}(\text{Xn})_2$ in carbon tetrachloride with pH of the aqueous solution; Δ , $\hat{\Delta}$, Δ : extraction time 3 min (2 strokes/sec); sequence of reagent addition: first buffer, then xanthate; 1 ●, 2 ●, 3 ●, 4 ●: extraction time for $\text{Pb}(\text{Xn})_2$ complex 15, 30, 45, and 60 min respectively

this equilibrium time was settled by experiments identical in condition with the equilibrium experiments.

The ionic concentrations of cadmium and lead in both aqueous and organic phases were determined by complexometric titrations (*EDTA*). Both metal ions present in the equilibrated organic phase were first stripped with nitric acid (0.5M) and then estimated. In an aliquot amount, Cd^{2+} and Pb^{2+} ions together were titrated with *EDTA* at pH 5–6 (hexamine) using xylenol orange as indicator. In order to determine the Cd^{2+} content, 1,10-phenanthroline solution was added and the *EDTA* liberated from the Cd-EDTA complex was then titrated with standard $\text{Pb}(\text{NO}_3)_2$ solution ($0.01015 \text{ mol} \cdot \text{l}^{-1}$). In some experiments, the concentration of the ions in the organic phase was determined by a method of successive stripping and then titrating them separately with *EDTA* [9].

Glossary

A^-	Ligand with charge 1 – which forms first order chelates with metal ions
B_{ij}	Coefficient characteristic of interaction between ions i and j
$a_{M_1 A_n(o)}$	Activity of the chelate in the organic phase
$a_{M_1^{n+}}$	Activity of the metal ion M_1^{n+} in the aqueous phase
a_q and a_o	Subscripts represent aqueous and organic (non-aqueous) phases
G^{Ex}	Excess <i>Gibbs</i> free energy
G^θ	Specific <i>Gibbs</i> free energy
K	Thermodynamic equilibrium constant
K_a	Equilibrium quotient without taking into account the activity coefficients of the species in the organic phase; subscript $M_1^{n+} - M_{II} A_m$: same meaning as in K'_a
K'_a	Equilibrium quotient; subscript $M_1^{n+} - M_{II} A_m$ indicates the reaction where an M_1^{n+} ion enters into the organic phase as a complex displacing M_{II}^{m+} therefrom
$\log \gamma^{\text{st}}$	<i>Debye-Hückel</i> expression for the ionic activity coefficient
K_e	Exchange reaction constant
m_i	Molar concentration of the ion i
m and n	Superscripts represent number of moles of the species involved in equilibrium equation
K_{ex}^1	Extraction constant of the metal I complex
f_i	Activity coefficient of the ion i present as complex in the organic phase

P_{MA_n}	Distribution constant of the complex ($a_{MA_n(aq)}/a_{MA_n}$, for $MA_n \rightleftharpoons MA_{n(o)}$)
R	Universal gas constant
Z_i	Charge of the ionic species
β_{MA_n}	Formation constant of the complex $M_1A_n(a_{M_1A_n}/a_{M_1^{n+}} \cdot a_{A^-}^n)$, for $M_1^{n+} + nA^- \rightleftharpoons M_1A_n$
γ_{\pm}	Mean activity coefficient of the electrolyte in aqueous solutions

Appendix

From Eq. 4,

$$\ln K = \ln K_a + m \ln f_{MA_n(o)} - n \ln f_{MA_m(o)}, \quad A1a$$

$f_{MA(o)}$ is the activity coefficient of metal in the CCl_4 -xanthate phase. Differentiating Eq. A1a (bearing in mind that K is constant), adding $(-m \cdot d \ln f_{MA_m(o)})$ at both sides and rearranging one gets

$$d \ln K_a + m(d \ln f_{MA_n(o)} - d \ln f_{MA_m(o)}) - (n - m) \cdot d \ln f_{MA_m(o)} = 0 \quad A1b$$

Writing $f_{MA_n(o)}$ and $f_{MA_m(o)}$ as f_{M_I} and $f_{M_{II}}$, and representing N , \bar{X} , and μ as number of moles, mole fraction, and chemical potential of a metal as xanthate in the organic phase, so that $\bar{X}_{M_I} = N_{M_I}/(N_{M_I} + N_{M_{II}})$, $\bar{X}_{M_I} + \bar{X}_{M_{II}} = 1$ and $\mu_M = RT \ln \bar{X}_M f_M$, then the *Gibbs-Duhem* relation yields

$$N_{M_I} d\mu_{M_I} + N_{M_{II}} d\mu_{M_{II}} = 0.$$

Multiplying both sides of the *Gibbs-Duhem* equation by the reciprocal of the total number of moles ($1/(N_{M_I} + N_{M_{II}})$) and substituting the result for $d\mu_M$, one gets $\bar{X}_{M_I} d \ln f_{M_I} + \bar{X}_{M_{II}} d \ln f_{M_{II}} = 0$ or $d \ln f_{M_{II}} + \bar{X}_{M_I} (d \ln f_{M_I} - d \ln f_{M_{II}}) = 0$. Using this relation in Eq. A1b and simplifying one gets

$$d \ln f_{M_{II}} = \bar{X}_{M_I} d \ln K_a / \{m + (n - m) \bar{X}_{M_I}\} \quad A2$$

and

$$d \ln f_{M_I} = -(1 - \bar{X}_{M_I}) d \ln K_a / \{m + (n - m) \bar{X}_{M_I}\} \quad A3$$

Applying partial integration to Eqs. A2 and A3 under restriction, *i.e.* from a state of pure homometallic entity in the organic phase (for which $\bar{X}_M = 1$, $f_M = 1$) to a state of heterometallic entity in the same phase (for which $\bar{X}_M = \bar{X}_M$ and $f_M = f_M$) and remembering that $\ln K_a$ is a function of \bar{X}_{M_I} , the activity coefficients at the equilibrium condition may be determined as was shown in the text in Eqs. 6 and 7. Substituting the results of $\ln f_{M_I}$ and $\ln f_{M_{II}}$ in Eq. A1a, one may get Eq. 8 (*cf.* text); m and n are the exponents of the activity coefficients. Representing the present extraction exchange reaction as shown at page 13 where $m = n = 1$,

$$K = K_a(f_{Pb(Xn)o}/f_{Cd(Xn)o})$$

and

$$\ln K = \int_{\bar{X}_{Pb}=0}^{\bar{X}_{Pb}=1} \ln K_a d\bar{X}_{Pb}.$$

Acknowledgements

One of the authors (A.K.C.) thankfully acknowledges the suggestion of the referee for modification of the paper. He is also grateful to *U.G.C. India* for the grant of a minor research project.

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Received December 19, 1994. Accepted (revised) April 11, 1995