Equilibria in the System Cobalt/Di-2-ethylhexylphosphoric Acid/Water

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The distribution of cobalt between various concentrations of di-2-ethylhexylphosphoric acid (DEHPA) and an aqueous phase has been studied. The concentrations of DEHPA (≡ H.R.) range from 5 to 20% v/v. The temperature was 25 ± 1 °C. A thermodynamic analysis of the equilibria is reported. The average log K value is −3.96 ± 0.13. Activity coefficients are reported, and an improved method for the calculation of $\gamma_{H_2R_2}{}^2/\gamma_{Co}$ in the organic phase is given.

Introduction

Since 1970 the methods of calculation of the activity coefficients of the aqueous electrolytes in high ionic strength media involving the multicomponent system have been much improved due to the work done by Pitzer (*1–7*).

The application of thermodynamics to equilibria in practical hydrometallurgical operations involving the aqueous phase is now possible. For the modelling of a practical liquid–liquid extraction equilibrium where a metal is distributed between an aqueous and organic phase it is also necessary to know the activity of species in the organic phase; such data are generally not available.

Only a few papers on the thermodynamic modelling of the equilibrium distribution of metals with DEHPA have been published. Baes et al. (*6*) reported on the extraction of UO_2^{2+} from the acidic perchlorate solution to *n*-hexane containing DEHPA. Information concerning the activity coefficients of the extractant was given.

Brisk (*7*) studied the distribution of metals ($Me^{2+} = Co^{2+}$, Ni^{2+}, Cu^{2+}) bewteen aqueous sulfate solution and a kerosene solution of DEHPA. The method of calculation of activity coefficients of the metals in the aqueous phase was based on the Guntelberg's modified Debye–Hückel equation. Therefore only the total ionic strength of the aqueous phase was considered in the calculation. The slope of the plot of (pH + log $a_{Me^{2+}(aq)}$) against the log D was found to be <2, and this was attributed to the hydrolysis of metal in the aqueous phase. In fact, the stability constant of the ion pair formed between Me^{2+} (Co^{2+}) and SO_4^{2-} is several orders of magnitude higher than the stability constant of the metal–hydroxide complex (*8*). Also these workers assumed that the activity coefficient of the metal–organic complex at the tracer concentration in the organic phase was unity. This last assumption is questionable because of the strong interaction between the extractant and the metal–organic complex.

The present paper presents a new thorough approach to the thermodynamic model for the distribution of cobalt in the important commercial system where DEHPA is the extractant and the cobalt is present in the aqueous phase of medium ionic strength.

Experimental Section

Materials. The cobalt sulfate solutions were made from Analytical Reagent grade salts dissolved in distilled water.

Extractant solutions were prepared by dissolved DEHPA in *n*-heptane. The *n*-heptane used for dilution was BDH Laboratory Reagent grade.

DEHPA was a BDH product. Part of the DEHPA was purified by using the Cu-precipitation method. However, when the results from the purified samples were compared with those from DEHPA without purification no difference was found in the UV spectra and in the pH titration curves. Eventually, a simple vacuum distillation method was used for purification. The temperature for distillation was 90 °C (vacuum ca. 1–2 mm Hg). After such a distillation the acid content increased from 96% to 97–98%.

Procedure. Glass conical flasks (100 mL) were charged with the aqueous sulfate solution and the DEHPA solutions; initially the aqueous phase was about 5 mL less than the organic phase. Then sodium hydroxide solution was added dropwise to the solutions which were vigorously stirred. Finally water was added after the alkali addition so as to keep the total volume of aqueous phase constant and in a ratio of 1:1 to the organic. The mixtures were then shaken for at least 6 h at 25 ± 1 °C. The concentrations of NaOH used for adjustment of pH were not higher than 0.5 M, e.g., 0.1, 0.2, 0.5 M depending on the concentration of Co in the aqueous phase and the concentration of DEHPA in the organic phase. Thus care was taken to avoid hydrolysis of Co^{2+} in the aqueous phase.

Special attention was paid to pH measurements. Before measuring the samples, standard pH buffers, namely 3, 4, 5 or 2, 3, 4, were used for calibration and a linear dependence was established between these three pH standards. The Orion Research Model 701 was used. The errors in pH measurement were estimated ±0.03 pH units. The H^+ activity is calculated from pH values. The molalities of species in the aqueous or organic phase, m_i, were used. Molalities for the organic phase were calculated by using the density data of the organic phase determined in our laboratory, the molalities of the aqueous phase were assumed to be equal to the molarities due to the low concentrations used in the experiments.

Activity coefficients of species, γ_i, refer to infinite dilute standard states. In the case of DEHPA the activity coefficients refer to the dimer since it is the most stable state in the organic phase under the experimental conditions of this study.

Results and Calculations

The results of experiments are listed in Tables I–V.

Activity Coefficients of Co^{2+} in the Aqueous Phase. The calculation of activity coefficients of Co^{2+} was based mainly on Pitzer's theory (*1–5*) but with a slight improvement.

There are two approaches in the calculation of activity coefficients. One is the so-called "stoichiometric activity

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Table I. Distribution of Co between the Organic and the Aqueous Phases[a]

		equilibrium, mol/dm^{-3}					
		aqueous phase			organic phase		
no.	init aq $m_{Co^{2+}} \times 10^2$ (aq)	pH	$m_{Co^{2+}} \times 10^2$	$m_{Na^+} \times 10^3$ (added)	$C_{H_2R_2}$	$C_{Co(or)} \times 10^3$	D[b]
1-1	0.6855	3.11	0.508	2.0	0.0693	1.827	0.47
1-2		3.26	0.429	4.0	0.0679	2.549	0.63
1-3		3.54	0.239	8.0	0.0641	4.444	1.86
1-4		4.27	0.01	10.0	0.0627	5.127	51.22
2-1	1.155	2.91	1.04	0.0	0.0707	1.169	0.11
2-2		3.03	0.909	2.0	0.0691	1.950	0.20
2-3		3.17	0.877	4.0	0.0674	2.786	0.32
2-4		3.37	0.690	8.0	0.0636	4.680	0.68
3-1	1.450	2.89	1.313	0.0	0.0705	1.247	0.10
3-2		3.02	1.236	2.0	0.0688	2.101	0.17
3-3		3.14	1.137	4.0	0.0667	3.154	0.28
3-4		3.30	0.985	8.0	0.0638	4.602	0.65
4-1	1.752	2.87	1.620	0.0	0.0704	1.303	0.08
4-2		3.00	1.531	2.0	0.0690	1.995	0.13
4-3		3.10	1.445	4.0	0.0669	3.075	0.21
4-4		3.20	1.373	6.0	0.0651	3.943	0.29

[a] Initial concentration of the extractant DEHPA: 5% v/v. [b] Distribution coefficient.

Table II. Distribution of Co between the Organic and the Aqueous Phases[a]

		equilibrium, mol dm^{-3}					
		aqueous phase			organic phase		
no.	init aq $m_{Co^{2+}} \times 10^2$	pH	$m_{Co^{2+}} \times 10^2$	$m_{Na^+} \times 10^2$ (added)	$C_{H_2R_2}$	$C_{Co(or)} \times 10^3$	D[b]
1-1	1.102	2.80	0.907	0.0	0.1128	1.577	0.18
1-2		3.24	0.499	1.0	0.1041	5.934	1.19
1-3		3.85	0.065	2.0	0.0956	10.30	15.74
2-1	1.658	2.77	1.435	0.0	0.1125	1.852	0.13
2-2		3.16	1.05	1.0	0.1039	6.146	0.58
2-3		3.53	0.529	2.1	0.0937	12.22	2.12
2-4		3.93	0.134	3.0	0.0843	15.93	11.43
3-1	1.386	2.77	1.378	0.0	0.1127	1.746	0.13
3-2		3.18	0.789	1.0	0.1042	5.793	0.76
3-3		3.57	0.318	2.0	0.0950	10.62	3.34
3-4		3.88	0.102	2.5	0.0905	12.83	12.64
4-1	2.192	2.74	2.002	0.0	0.1122	1.984	0.10
4-2		3.11	1.581	1.0	0.1037	6.238	0.40
4-3		3.36	1.115	2.0	0.0945	10.87	0.97
4-4		3.49	0.888	2.5	0.0898	13.18	1.48

[a] Initial concentration of the extractant DEHPA: 8% v/v. [b] Distribution coefficient.

Table III. Distribution of Co between the Organic and the Aqueous Phases[a]

		equilibrium, mol dm^{-3}					
		aqueous phase			organic phase		
no.	init aq $m_{Co^{2+}} \times 10^2$ (aq)	pH	$m_{Co^{2+}} \times 10^2$	$m_{Na^+} \times 10^2$ (added)	$C_{H_2R_2}$	$C_{Co(or)} \times 10^3$	D[b]
1-1	1.447	3.00	0.921	0.80	0.1359	5.425	0.59
1-2		3.36	0.392	1.89	0.1257	10.51	2.68
1-3		3.57	0.207	2.4	0.1221	12.30	5.9
1-4		4.49	0.117	3.20	0.1182	14.24	121.56
2-1	1.741	2.97	1.19	0.80	0.1355	5.588	0.47
2-2		3.20	0.807	1.60	0.1282	9.232	1.14
2-3		3.79	0.149	3.20	0.1149	15.89	10.67
3-1	2.902	2.65	2.630	0.0	0.1413	2.70	0.10
3-2		2.88	2.322	0.80	0.1350	5.829	0.25
3-3		3.26	1.591	2.4	0.1208	12.97	0.82
3-4		3.57	0.873	4.0	0.1062	20.27	2.32
4-1	4.254	2.66	3.226	0.0	0.1409	2.888	0.09
4-2		2.87	2.893	0.80	0.1348	5.958	0.21
4-3		3.05	2.537	1.6	0.1276	9.542	0.38
4-4		3.31	1.795	3.2	0.1134	16.64	0.93

[a] Initial concentration of the extractant DEHPA: 10% v/v. [b] Distribution coefficient.

coefficients" in which the ion-pair formation is neglected. An example of this method is given in the original reference in the calculation of the $\gamma_{Me^{2+}}$ for the bivalent sulfates including Co^{2+} (*4*). A second method is called "the free activity coefficient method" as applied to the example of sulfuric acid. In this case Pitzer suggested that all species be considered so that for sulfuric acid both free H^- and SO^{2-} together with the HSO_4^- are considered. We note that the stability constants of HSO_4^- and $CoSO_4$ at zero ionic strength are similar (for $CoSO_4$, log k = 2.14, for HSO_4^-, log k = 1.96) (*8*). We have tried both methods for the calculation of $\gamma_{Co^{2+}}$ in the aqueous phase: that is, the method involving "stoichiometric activity coefficients" and the method which considers the ion-pair formation of $CoSO_4$, i.e., "the free activity coefficients". The latter gives more consistent results.

Thus, for the single electrolyte $CoSO_4$, we have mean stoi-

Table IV. Distribution of Co between the Organic and the Aqueous Phases[a]

		equilibrium, mol dm^{-3}					
		aqueous phase			organic phase		
no.	init aq $m_{Co^{2+}} \times 10^2$ (aq)	pH	$m_{Co^{2+}} \times 10^2$	$m_{Na^+} \times 10^2$ (added)	$C_{H_2R_2}$	$C_{Co(or)} \times 10^2$	D[b]
1-1	3.665	2.79	2.748	1.333	0.1867	0.917	0.33
1-2		3.01	2.111	2.670	0.1739	1.554	0.74
1-3		3.21	1.514	4.00	0.1620	2.151	1.42
1-4		3.43	0.835	5.330	0.1492	2.799	3.35
2-1	4.863	2.59	4.255	0.667	0.1921	0.643	0.15
2-2		2.90	3.395	2.670	0.1749	1.503	0.44
2-3		3.17	2.425	4.667	0.1543	2.534	1.05
2-4		3.35	1.743	6.000	0.1419	3.155	1.81
3-1	6.046	2.43	5.641	0.0	0.1969	0.405	0.07
3-2		2.88	4.491	2.67	0.1743	1.533	0.34
3-3		3.12	3.556	4.67	0.1550	2.501	0.70
3-4		3.33	2.483	6.67	0.1344	3.533	1.42
4-1	7.821	2.42	7.379	0.0	0.1962	0.441	0.06
4-2		2.75	6.577	2.0	0.1801	1.244	0.19
4-3		2.98	5.615	4.0	0.1609	2.206	0.39
4-4		3.21	4.270	6.67	0.1335	2.574	0.84

[a] Initial concentration of the extractant DEHPA: 14% v/v. [b] Distribution coefficient.

Table V. Distribution of Co between the Organic and the Aqueous Phases

		equilibrium, mol dm^{-3}					
		aqueous phase			organic phase		
no.	init aq $m_{Co^{2+}} \times 10^2$ (aq)	pH	$m_{Co^{2+}} \times 10^2$	$m_{Na^+} \times 10^2$ (added)	$C_{H_2R_2}$	$C_{Co(or)} \times 10^2$	D[b]
1-1	5.052	2.38	4.514	0.0	0.2867	0.5379	0.12
1-2		2.60	3.877	1.667	0.2740	1.174	0.30
1-3		2.87	3.105	3.333	0.2586	1.946	0.63
1-4		3.02	2.328	5.00	0.2430	2.724	1.17
2-1	7.832	2.31	7.205	0.0	0.2850	0.6271	0.09
2-2		3.01	4.856	6.667	0.2380	2.977	0.61
2-3		3.36	2.718	10.00	0.1952	5.115	1.88
2-4		3.643	1.426	13.30	0.1694	6.406	4.49

[a] Initial concentration of the extractant DEHPa: 20% v/v. [b] Distribution coefficient.

chiometric activity coefficients $\gamma_{\pm}$, and mean free activity coefficients $\gamma_{\pm(1)}$, and

$$m_{Co(aq)total} m_{SO_4 total} \gamma_{\pm}^2 = m_{Co(aq)free} m_{SO_4 free} \gamma_{\pm(l)}^2 \qquad (i)$$

The additional conditions are

$$m_{Co(aq)total} = m_{Co(aq)free} + m_{CoSO_4} \qquad (ii)$$

$$m_{SO_4 total} = m_{SO_4 free} + m_{CoSO_4} \qquad (iii)$$

$$(m_{Co(aq)free} m_{SO_4 free}) \gamma_{\pm(1)}^2 / m_{CoSO_4} = 1/K_2' \qquad (iv)$$

Here m_{CoSO_4} = molality of ion pair of $CoSO_4$, and $m_{Co(aq)total}$, $m_{Co(aq)free}$, $m_{SO_4 total}$, and $m_{SO_4 free}$ are the total and free molalities of Co^{2+} and SO_4^{2-} respectively; K_2' is the stability constant of the ion-pair $CoSO_4 = 204$.

Note that for this system, $m_{Co(aq)total} = m_{SO_4 total}$ and $m_{Co(aq)free} = m_{SO_4 free}$; then (i) becomes

$$m_{Co(aq)total} \gamma_{\pm} = m_{Co(aq)free} \gamma_{\pm(1)} \qquad (1)$$

The additional conditions

$$m_{Co(aq)total} = m_{Co(aq)free} + m_{CoSO_4} \qquad (2)$$

$$(m_{Co(aq)free} \gamma_{\pm(1)})^2 / m_{CoSO_4} = 1/K_2' \qquad (3)$$

From eq 1–3 the values of $\gamma_{\pm(1)}$ and $m_{Co(aq)free}$ can now be calculated, since the values of $\gamma_{\pm}$ for different $m_{Co(aq)total}$ are available from literature. The results are listed in Table VI.

Table VI. Stoichiometric and Free Activity Coefficients of Cobalt

$m_{Co^{2+}}$(aq) (total)	$\gamma_{\pm}$	m_{Co}(aq) (free) $\times 10^3$	$\gamma_{\pm(1)}$
0.0001	0.9030	0.10	0.9183
0.001	0.7170	0.90	0.8010
0.005	0.5060	3.69	0.6849
0.01	0.4090	6.59	0.6209
0.02	0.3200	11.64	0.5496
0.05	0.2180	25.76	0.4231
0.1	0.1570	49.72	0.3156

The Parameter Estimation for the Free Activity Coefficients of the Single Electrolyte $CoSO_4$. According to Pitzer (*5*) the equations for calculation of single 2–2 valent electrolytes are

$$\ln \gamma_{\pm(1)} = 4f^r + m_{Co(aq)free} B^r_{MX} + M^2_{Co(aq)free} C^r_{MX} \qquad (4)$$

$$f^r = -A_f(I^{1/2}/(1 + bI^{1/2}) + (2/b) \ln (1 + bI^{1/2})) \qquad (5)$$

$$B^r_{MX} = 2B^{(0)}_{MX} + (2B^{(1)}_{MX}/\alpha_1^2 I)(1 - (1 + \alpha_1 I^{1/2} - \tfrac{1}{2} I \alpha_1^2) \exp(-\alpha_1 I^{1/2})) + (2B^{(2)}_{MX}/\alpha_2^2 I)(1 - (1 + \alpha_2 I^{1/2} - \tfrac{1}{2} I \alpha_2^2) \exp(-\alpha_2 I^{1/2})) \qquad (6)$$

$$C^r_{MX} = \tfrac{3}{2} C^{\phi}_{MX} \qquad (7)$$

where I is ionic strength; $I = 4m_{Co(aq)free}$.

The values of the parameters are those given by Pitzer: $A_f = 0.391$, $b = 1.2$, $\alpha_1 = 1.4$, and $\alpha_2 = 12$. Parameters $B^{(0)}_{MX}$, $B^{(1)}_{MX}$, $B^{(2)}_{MX}$, C^{ϕ}_{MX} were estimated by using a simple linear regression program. Two sets of parameters, $B^{(0)}_{MX}$, $B^{(1)}_{MX}$, $B^{(2)}_{MX}$, C^{ϕ}_{MX}, were obtained. Both sets of parameters were used in the calculation of the free activity coeficients; results showed a difference of less than 1%.

Set one: $B_{MX}^{(0)} = -2.3923$, $B_{MX}^{(1)} = 7.2688$, $B_{MX}^{(2)} = 55.5858$, and $C_{MX}^{\phi} = 4.8667$.

Set two: $B_{MX}^{(0)} = -6.01$, $B_{MX}^{(1)} = 14.54$, $B_{MX}^{(2)} = 40.54$, $C_{MX} = 0$.

The Calculation of Activity Coefficients of Free Co^{2+} in a Multicomponent Aqueous Phase. The extraction process involving DEHPA is, in fact, an ion-exchange process and so instead of the mean activity coefficients the single ion Co^{2+} ionic activity coefficients were used. $(H_2SO_4)_{total} = m$, $(CoSO_4)_{total} = m_3$, $(Na_2SO_4) = m_4$, $(Na^+) = 2m_4$, $(Co^{2+})_{free} = m_5$, $(H^+) = m_0$, $(HSO_4^-) = m_1$, $(SO_4^{2-}) = m_0 + m_5 + m_4 - m$, $(CoSO_4)_{ion\ pair} = m_3 - m_5$, and we use the simplifed equations of Pitzer

$$\ln \gamma_{M^+} = Z_{M^+}{}^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + |Z_M| \sum_c \sum_a m_c m_a C_{ca} \quad (8)$$

$$\ln \gamma_{X^-} = Z_X{}^2 F + \sum_c m_c (2B_{cX} + ZC_{cX}) + |Z_X| \sum_c \sum_a m_c m_a C_{ca} \quad (9)$$

where

$$F = -A_f (I^{1/2}/(1 + bI^{1/2}) + (2/b) \ln (1 + bI^{1/2})) + \sum_c \sum_a m_c m_a B_{ca}{}' \quad (10)$$

and $A_f = 0.391$, $b = 1.2$.

For 1–1 and 1–2 electrolytes:

$$B_{MX} = B_{MX}^{(0)} + 2B_{MX}^{(1)} (1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2}))/(\alpha I^{1/2}) \quad (11)$$

and $\alpha = 2.0$.

$$B_{MX}{}' = -2B_{MX}^{(1)} (1 - (1 + \alpha I^{1/2} + \tfrac{1}{2}\alpha^2 I) \exp(-\alpha I^{1/2}))/(\alpha I^{1/2})^2 \quad (12)$$

For 2–2 electrolytes:

$$B_{MX} = B_{MX}^{(0)} + 2B_{MX}^{(1)} (1 - (1 + \alpha_1 I^{1/2}) \times \exp(-\alpha_1 I^{1/2}))/(\alpha_1 I^{1/2})^2 + 2B_{MX}^{(2)} (1 - (1 + \alpha_2 I^{1/2}) \exp(-\alpha_2 I^{1/2}))/(\alpha_2 I^{1/2})^2 \quad (13)$$

$$B_{MX}{}' = -2B_{MX}^{(1)} (1 - (1 + \alpha_1 I^{1/2} + \tfrac{1}{2}\alpha_1{}^2 I) \exp(-\alpha_1 I^{1/2}))/(\alpha_1 I^{1/2})^2 - 2B_{MX}^{(2)} (1 - (1 + \alpha_2 I^{1/2} + \tfrac{1}{2}\alpha_2{}^2 I) \exp(-\alpha_2 I^{1/2}))/(\alpha_2 I^{1/2})^2 \quad (14)$$

$$C_{MX} = C_M^{\phi}/(2[Z_M Z_X)^{1/2}) \quad (15)$$

$$I = (1/2) \sum_i m_i z_i{}^2 = 3m_4 + 4m_5 + 2m_0 - m \quad (16)$$

$$Z = \sum_i m_i [z_i] = 2 \sum m_c z_c = 2(2m_4 + 4m_5 + 3m_0) \quad (17)$$

Then

$$\ln \gamma_{Co^{2+}} = 4F + m_1(2B_{Co-1} + ZC_{Co-1}) + m_2(2B_{Co-2} + ZC_{Co-2}) + 2(m_5 m_2 C_{Co-2} + m_5 m_1 C_{Co-1} + 2m_4 m_1 C_{Na-1} + 2m_4 m_2 C_{Na-2} + m_0 m_1 C_{H-1} + m_0 m_2 C_{H-2}) \quad (18)$$

$$\ln \gamma_{SO_4^{2-}} = 4F + m_5(2B_{Co-2} + ZC_{Co-2}) + 2m_4(2B_{Na-2} + ZC_{Na-2}) + m_0(2B_{H-2} + ZC_{H-2}) + 2(m_5 m_2 C_{Co-2} + m_5 m_1 C_{Co-1} + 2m_4 m_1 C_{Na-1} + 2m_4 m_2 C_{Na-2} + m_0 m_1 C_{H-1} + m_0 m_2 C_{H-2}) \quad (19)$$

Thus

$$\ln \gamma_{CoSO_4} = (1/2)(\ln \gamma_{Co} + \ln \gamma_{SO_4}) = 4F + (m_2 + m_5)B_{Co-2} + [(1/2)Z(m_2 + m_5) + 2m_5 m_2]C_{Co-2} + m_1 B_{Co-1} + [(1/2)Zm_1 + 2m_5 m_1]C_{Co-1} + 2(m_4 m_1 C_{Na-1} + m_0 m_1 C_{H-1}) + 2m_4 B_{Na-2} + m_0 B_{H-2} + (1/2)[Zm_0 + 2m_0 m_2]C_{H-2} + [(1/2)Zm_4 + 2m_4 m_2]C_{Na-2} \quad (20)$$

$$F = -A_f(I^{1/2}/(1 + bI^{1/2}) + (2/b) \ln (1 + bI^{1/2})) + m_5 m_1 B_{Co-1}{}' + m_5 m_2 B_{Co-2}{}' + 2m_4 m_1 B_{Na-1}{}' + 2m_4 m_2 B_{Na-2}{}' + m_0 m_2 B_{H-2}{}' + m_0 m_1 B_{H-1}{}' \quad (21)$$

Similarly we can calculate the value of γ_{H^+}, $\gamma_{SO_4^{2-}}$, and $\gamma_{HSO_4^-}$ and $\gamma_{H^+}\gamma_{SO_4^{2-}}/\gamma_{HSO_4^-}$.

$$\ln (\gamma_{H^+}\gamma_{SO_4^{2-}}/\gamma_{HSO_4^-}) = 4F + 2B_{H-1}(m_1 - m_0) + 2B_{H-2}(m_2 + m_0) + 2m_5(B_{Co-2} - B_{Co-1}) + 4m_4(B_{Na-2} - B_{Na-1}) \quad (22)$$

$$F = -A_f(I^{1/2}/(1 + bI^{1/2}) + (2/b) \ln (1 + bI^{1/2})) + m_5 m_1 B_{Co-1}{}' + m_5 m_2 B_{Co-2}{}' + m_0 m_1 B_{H-1}{}' + m_0 m_2 B_{H-2}{}' + 2m_4 m_1 B_{Na-1}{}' + 2m_4 m_2 B_{Na-2}{}' \quad (23)$$

In this calculation the parameter C_{MX} was omitted because of the low concentrations of m_0, m_1, and m_2 and because the value of $\gamma_{H^+}\gamma_{SO_4^{2-}}/\gamma_{HSO_4^-}$ does not participate in the general eq 1.

The subscripts 1 and 2 here represent HSO_4^- and SO_4^{2-}, respectively; i.e. $B_{H-2} = B_{H-SO_4}$, $B_{H-2}{}' = B_{H-SO4}{}'$, $B_{Co-1} = B_{Co-HSO_4}$, $B_{Co-1}{}' = B_{Co-HSO_4}{}'$, etc.

Since the parameters for HSO_4^- are not available in literature, the values for ClO_4^- were used, as it was done in ref *3*.

The following equations apply:

$$a_{H^+} = m_0 \gamma_{H^+} \quad (24)$$

$$1/K_1{}' = (m_0 m_2 \gamma_{H^+}\gamma_{SO_4^{2-}})/(m_1 \gamma_{HSO_4^-}) \quad (25)$$

$$1/K_2{}' = (m_5 m_2 \gamma_{\pm CoSO_4}{}^2)/(m_3 - m_5) \quad (26)$$

$$m_2 = m + m_5 + m_4 - m_1 \quad (27)$$

Here $1/K_1{}'$ and $1/K_2{}'$ are the dissociation constants for the ion pairs HSO_4 and $CoSO_4$, e.g. $K_1{}' = 95.24$, $K_2{}' = 204$. These values are slightly different from the values of dissociation constants of these complexes (*8*).

From eq 24–27 four unknown variables, namely, m_5, m_2, m_1, m_0, and the activity coefficient of Co_{free} can be calculated by using a simple iteration procedure. The iteration procedure was accomplished with the aid of a HP-85 computer. The results of the calculation are listed in Tables VII–XI.

The correctness of the calculation is checked as follows. For each initial concentration of extractant four different aqueous feeds corresponding to different pH values were adopted. Then several equilibrium organic Co^{2+} concentrations were selected for each series of aqueous feeds by interpolation of experimental data. In this way, sets of values of pH, aqueous cobalt, sodium sulfate and sulfuric acid concentrations, which were in equilibrium with a constant concentration of cobalt in the organic phase, were obtained. Then the value of

$$K_1 = (a_{H^+})^2/a_{Co^{2+}} = Ka_{H_2R_2}{}^2/a_{Co(or)} \quad (28)$$

would be constant, since both the $m_{Co(0)}$ and the $m_{H_2R_2(0)}$ are constant (and assuming that the composition of the organic phase is not changed due to changes in the aqueous phase). It was also proved that the sodium is not extracted and water is extracted but only in an insignificant amount. Therefore K_1 takes a fixed value. The results are listed in Tables XII–XIV. K in eq 28 is the extraction constant.

From the data in Tables XII–XIV fairly constant values of K_1 were observed for constant Co concentrations in the organic phase with the fixed initial extractant concentrations (H_2R_2). Although a slight scatter is evident throughout, it can be attributed to the errors in pH measurements, because ±0.03 units of error can cause about ±10% error in the value of K_1.

The calculated values of cobalt activity coefficients can be compared with values taken from the literature (stoichiometric activity coefficients) and confirms the correctness of our calculation method. In those experiments, where the SO_4^{2-}

Table VII. Results of Calculation of Aqueous Activity Coefficients of Co^{2+}(free)[a]

pH	$m_{\mathrm{Co(total)}} \times 10^2$	$m_{\mathrm{Na_2SO_4}} \times 10^3$	$m_{\mathrm{H_2SO_4}} \times 10^3$	$m_{\mathrm{Co(free)}} \times 10^2$	$\gamma_{\mathrm{Co(free)}}$	$K_1 \times 10^4$
3.11	0.508	1.0	8.27	0.347	0.696	2.50
3.26	0.429	2.0	5.49	0.293	0.705	1.43
3.54	0.239	4.0	4.44	0.157	0.731	0.736
2.91	1.040	0.0	11.69	0.668	0.626	3.68
3.03	0.909	1.0	9.50	0.574	0.642	2.34
3.17	0.877	2.0	7.86	0.543	0.644	1.24
3.37	0.690	4.0	6.80	0.417	0.663	0.664
3.02	1.236	1.0	10.1	0.754	0.608	2.015
3.14	1.137	2.0	11.54	0.677	0.620	1.284
3.30	0.985	4.0	6.03	0.577	0.629	0.710
2.87	1.620	0.0	13.01	0.978	0.573	3.296
3.00	1.531	1.0	9.95	0.912	0.581	1.875
3.10	1.445	2.0	10.75	0.842	0.590	1.265

[a] The initial concentration of DEHPA in the organic phase is 5% v/v.

Table VIII. Results of Calculations of Aqueous Activity Coefficients of Co^{2+}(free)[a]

pH	$m_{\mathrm{Co(total)}} \times 10^2$	$m_{\mathrm{Na_2SO_4}} \times 10^2$	$m_{\mathrm{H_2SO_4}} \times 10^3$	$m_{\mathrm{Co(free)}} \times 10^2$	$\gamma_{\mathrm{Co(free)}}$	$K_1 \times 10^4$
2.80	0.907	0.0	1.677	0.589	0.641	6.77
3.24	0.499	0.5	0.934	0.303	0.683	1.58
3.85	0.065	1.0	0.300	0.367	0.722	0.75
2.77	1.473	0.0	1.851	0.896	0.585	5.48
3.16	1.054	0.5	1.46	0.596	0.621	5.96
3.53	0.529	1.05	0.72	0.284	0.658	0.47
3.93	0.093	1.5	0.93	0.067	0.682	3.06
2.77	1.371	0.0	1.746	0.843	0.594	5.51
3.18	0.789	0.5	0.973	0.460	0.648	1.50
3.57	0.318	1.0	0.622	0.175	0.685	0.61
3.88	0.102	1.25	0.40	0.053	0.700	0.48
2.75	2.002	0.0	1.984	1.154	0.548	4.91
3.11	1.581	0.5	1.238	0.861	0.577	4.91
3.36	1.115	1.0	0.874	0.583	0.603	0.547
3.49	0.888	1.25	0.680	0.457	0.614	0.365

[a] The initial concentration of DEHPA in the organic phase is 8% v/v.

Table IX. Results of Calculations of Aqueous Activity Coefficients of Co^{2+}(free)[a]

pH	$m_{\mathrm{Co(total)}} \times 10^2$	$m_{\mathrm{Na_2SO_4}} \times 10^2$	$m_{\mathrm{H_2SO_4}} \times 10^3$	$m_{\mathrm{Co(free)}} \times 10^2$	$\gamma_{\mathrm{Co(free)}} \times 10$	$K_1 \times 10^4$
3.00	0.921	0.4	1.425	0.536	0.635	2.95
3.36	0.392	0.945	1.060	0.215	0.670	1.30
3.57	0.207	1.20	0.40	0.101	0.707	1.07
2.97	1.185	0.4	1.588	0.672	0.610	2.76
3.20	0.807	0.8	1.232	0.441	0.637	1.42
3.79	0.149	1.57	0.190	0.075	0.673	0.53
2.65	2.630	0.0	2.703	1.460	0.511	6.83
2.88	2.322	0.40	1.829	1.253	0.527	2.60
3.26	1.591	1.20	0.970	0.802	0.562	0.67
3.57	0.873	2.00	0.270	0.416	0.588	0.29
2.66	3.226	0.0	2.888	1.745	0.483	5.77
2.87	2.893	0.4	1.956	1.529	0.493	2.36
3.05	2.537	0.8	1.543	1.285	0.514	1.19
3.31	1.795	1.60	0.64	0.872	0.540	0.51

[a] The initial concentration of DEHPA in the organic phase: 10% v/v.

Table X. Results of Calculation of Aqueous Activity Coefficients of Co^{2+}(free)[a]

pH	$m_{\mathrm{Co(total)}} \times 10^2$	$m_{\mathrm{Na_2SO_4}} \times 10^2$	$nL_{\mathrm{H_2SO_4}} \times 10^3$	$m_{\mathrm{Co(free)}} \times 10^2$	$\gamma_{\mathrm{Co(free)}}$	$K_1 \times 10^4$
2.79	2.748	0.667	2.57	1.403	0.503	3.81
3.01	2.111	1.334	2.20	1.031	0.529	1.77
3.21	1.514	2.0	1.51	0.712	0.547	0.97
3.42	0.835	2.67	1.32	0.372	0.568	0.66
2.59	4.225	0.333	3.09	2.208	0.438	6.71
2.90	3.395	1.333	1.69	1.647	0.466	2.06
3.17	2.425	2.333	2.01	1.111	0.495	0.83
3.35	1.743	3.00	1.55	0.771	0.510	0.52
2.43	5.641	0.0	4.05	2.951	0.395	11.81
2.88	4.491	1.333	2.20	2.156	0.429	1.87
3.12	3.559	2.333	1.68	1.639	0.449	0.78
3.33	2.483	3.333	0.99	1.098	0.470	0.42
2.41	7.379	0.0	4.41	3.820	0.355	10.60
2.75	6.577	1.0	2.44	3.210	0.373	2.69
2.98	5.615	2.0	2.06	2.624	0.392	1.09
3.21	4.270	3.33	2.41	1.910	0.414	0.41

[a] The initial concentration of DEHPA in the organic phase: 14% v/v.

Table XI. Results of Calculation of Aqueous Activity Coefficients of Co^{2+}(free)[a]

pH	$m_{Co(total)} \times 10^2$	$m_{Na_2SO_4} \times 10^2$	$nL_{H_2SO_4} \times 10^3$	$m_{Co(free)} \times 10^2$	$\gamma_{Co(free)}$	$K_1 \times 10^4$
2.38	4.514	0.0	5.38	2.390	0.429	16.91
2.60	3.877	0.833	3.41	1.960	0.448	7.10
2.87	3.105	1.66	2.795	1.470	0.475	2.61
3.02	2.379	2.50	2.24	1.067	0.493	1.71
2.31	7.205	0.0	6.27	3.721	0.358	18.40
3.01	4.855	3.33	3.56	2.186	0.398	10.83
3.36	2.718	5.00	1.15	1.149	0.432	3.79
3.64	1.426	6.40	0.002	0.578	0.442	2.03

[a] The initial concentration of DEHPA in the organic phase: 20% v/v.

Table XII. Check on the Correctness of Calculated Activity Coefficients of Co^{2+}(free)[a]

organic phase			aqueous phase						
$m_{H_2R_2}$ (init)	$m_{H_2R_2}$ (free)	$m_{Co} \times 10^3$	pH	m_{Co} (total) $\times 10^3$	$m_{Na_2SO_4} \times 10^3$	$m_{H_2SO_4} \times 10^4$	m_{Co} (free) $\times 10^3$	γ_{Co} (free)	$K_1 \times 10^5$
0.113	0.107	3.00	3.20	4.94	1.163	7.75	3.365	0.699	1.680
			3.04	9.45	0.95	9.45	5.937	0.638	2.235
			2.99	12.5	0.766	10.06	7.685	0.605	2.247
			2.98	15.51	0.794	11.10	9.244	0.580	2.089
	0.1049	4.00	3.27	4.28	2.048	5.380	2.917	0.704	1.394
			3.14	8.84	1.681	8.180	5.511	0.644	1.517
			3.09	11.86	1.528	11.60	7.070	0.615	1.532
			3.62	14.92	1.507	10.19	8.794	0.585	1.458
	0.1029	5.00	3.38	3.620	2.826	4.070	2.435	0.713	0.981
			3.22	8.236	2.412	0.728	5.089	0.650	1.100
			3.17	11.23	2.290	1.054	6.645	0.620	1.138
			3.13	14.33	2.220	0.973	8.255	0.592	1.119
	0.1009	6.00	3.48	2.96	3.500	3.800	1.966	0.722	0.789
			3.30	7.628	3.143	6.800	4.667	0.656	0.849
			3.23	10.60	3.052	8.840	6.240	0.624	0.900
			3.19	13.74	2.933	9.750	7.852	0.597	0.910

[a] The initial concentration of DEHPA in the organic phase: 5% v/v.

Table XIII. Check on the Correctness of Calculated Activity Coefficients of Co^{2+}(free)[a]

organic phase			aqueous phase						
$m_{H_2R_2}$ (init)	$m_{H_2R_2}$ (free)	$m_{Co} \times 10^3$	pH	m_{Co} (total) $\times 10^3$	$m_{Na_2SO_4} \times 10^3$	$m_{H_2SO_4} \times 10^3$	m_{Co} (free) $\times 10^3$	γ_{Co} (free)	$K_1 \times 10^4$
0.1851	0.1791	3.0	2.84	8.899	0.261	1.640	5.740	0.644	5.700
			2.78	14.46	0.245	1.845	8.789	0.588	5.260
			2.79	13.21	0.249	1.699	8.120	0.598	5.423
			2.74	20.13	0.120	1.600	11.68	0.545	5.286
	0.1731	6.0	3.03	7.06	2.44	1.305	4.381	0.665	2.941
			2.93	12.63	2.157	1.509	7.441	0.604	3.029
			2.93	11.06	2.358	1.369	6.548	0.619	3.145
			2.90	18.26	2.082	1.581	5.591	0.559	2.701
	0.1651	10.0	3.29	4.612	5.439	0.893	2.775	0.687	1.395
			3.14	10.18	4.910	1.109	5.790	0.624	1.468
			3.18	8.20	5.170	0.995	4.745	0.644	1.463
			3.10	15.76	4.874	1.189	8.605	0.577	1.299
	0.1531	16.0	3.82	0.943	9.710	0.347	0.528	0.719	0.611
			3.46	6.506	8.314	0.689	3.620	0.655	0.520
			3.55	3.910	9.380	0.579	2.162	0.679	0.543
			3.33	12.01	9.610	0.751	6.312	0.596	0.571

[a] The initial concentration of DEHPA in the organic phase: 8% v/v.

concentrations are low, the difference between $m_5\gamma_{Co(free)}$ and $m_3\gamma_{Co(total)}$ is small. When the concentrations of SO_4^{2-} are high, these differences are increased but all differences are within a reasonable range.

Calculation of the Thermodynamic Constant, K, of the Extractant Equilibrium. Petkovic and Rurarac's method (*9*, *10*) has been used to calculate K. From eq 28 we obtain

$$\log (a_{H^+}^2/a_{Co(aq)}) = \log K + \log (a_{H_2R_2}^2/a_{Co(or)}) \quad (29)$$

It is obvious that when $a_{H_2R_2}^2 = a_{Co}$ then

$$\log (a_{H^+}^2/a_{Co}) = \log K$$

If $\log (a_{H^+}^2/a_{Co(or)})$ is plotted against $a_{H_2R_2}$ or $m_{H_2R_2}$ for a fixed initial concentration of the extractant, then the coordinate at the inflection point, which corresponds to a zero value of the second derivative of this function (eq 29), gives the log K value.

In order to extend the validity of this method Rurarac suggested that the "chemical equivalent" instead of the molalities be used to express extraction equilibria; eq 29 becomes

$$\log (a_{H^+}^E/a_{Co(aq)}^E) = \tfrac{1}{2} \log K + \log (a_{H_2R_2}^E/a_{Co(or)}^E) \quad (30)$$

Here superscript E implies the equivalent scale, i.e., $a_{Co}^E = (a_{Co})^{1/2}$, $a_{H^+}^E = a_{H^+}$, and $a_{H_2R_2}^E = a_{H_2R_2}$. It is also obvious that eq 30 will be reduced at the inflection point to $\log (a_{H^+}^E/a_{Co(aq)}^E) = {}^1/_2 \log K$ when $a_{Co(or)}^E = a_{H_2R_2}^E$. We now plot the value of $\log (a_{H^+}^E/a_{Co(aq)}^E) \equiv {}^1/_2 \log (a_{H^+}^2/a_{Co(aq)})$ against $m_{H_2R_2}$ for five sets of experiments with different initial extractant concentrations in the organic phase; this plot is shown in Figure 1. A nearly constant inflection point at $\log (a_{H^+}^E/a_{a\,Co(aq)}^E) = -2$ was observed (see Table XV and Figure 1. (Note: A mathematical approach was

Table XIV. Check on the Correctness of Calculated Activity Coefficients of Co^{2+}(free)[a]

organic phase			aqueous phase						
$m_{H_2R_2}$ (init)	$m_{H_2R_2}$ (free)	$m_{Co} \times 10^3$	pH	m_{Co} (total) $\times 10^3$	$m_{Na_2SO_4} \times 10^3$	$m_{H_2SO_4} \times 10^3$	m_{Co} (free) $\times 10^3$	γ_{Co} (free)	$K_1 \times 10^4$
0.2389	0.223	8.0	2.99	9.739	3.453	1.450	5.703	0.637	2.970
			2.94	12.48	3.175	1.640	7.172	0.605	3.028
			2.83	24.09	2.748	2.038	13.13	0.523	3.227
			2.80	30.12	2.563	2.194	16.11	0.492	3.187
	0.2189	10.0	3.03	8.465	4.765	1.380	4.931	0.641	2.714
			3.01	11.25	4.573	1.549	6.353	0.6148	2.495
			2.89	22.86	4.136	1.761	12.19	0.530	2.615
			2.88	28.84	3.981	1.924	15.20	0.498	2.350
	0.2069	16.0	3.30	4.643	8.701	1.16	2.570	0.674	1.429
			3.25	7.550	8.767	1.173	4.075	0.641	1.230
			3.11	19.17	8.300	1.223	9.914	0.548	1.132
			3.07	25.03	8.235	1.526	12.69	0.515	1.095
	0.1949	22.0	3.77	0.821	12.64	−0.00	0.444	0.699	0.9385
			3.56	3.854	12.96	0.645	1.985	0.662	0.575
			3.30	15.48	12.46	0.938	7.823	0.563	0.579
			3.22	21.21	12.49	1.257	10.48	0.530	0.649

[a] The initial concentration of DEHPA in the organic phase: 10% v/v.

Table XV. Determination of the Inflection Point and the Equilibrium Constant

initial DEHPA, % v/v	$m_{H_2R_2}$[a]	log $(a^E_{H^+}/a_{Co}(aq))$[a]	log K
5	0.102	-2.002	-4.005
8	0.104	-1.935	-3.869
10	0.209	-1.917	-3.834
14	0.275	-1.997	-3.994
20	0.391	-2.047	-4.094

[a] At the inflection point.

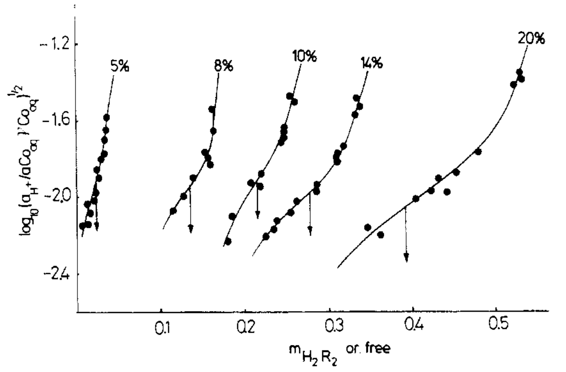

Figure 1. Determination of the inflection point and the equilibrium constant.

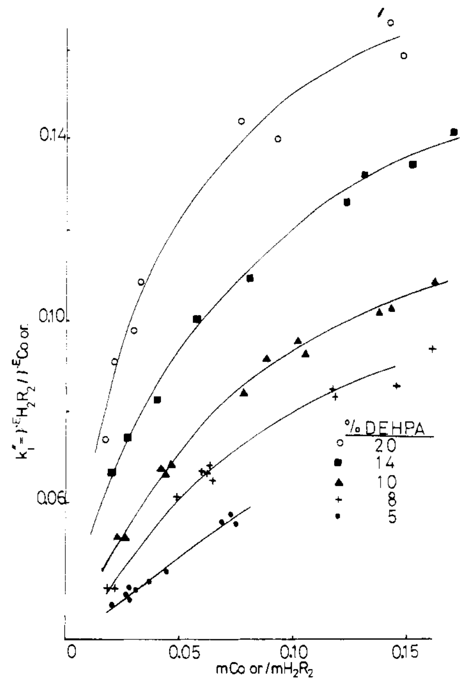

Figure 2. Dependence of K_1^{11} on $m_{Co(or)}/m_{H_2R_2}$ at different initial concentrations of the extractant.

used to obtain the inflection points since all the curves in Figure 1 can be fitted by third-order polynomial equations.)

The Calculation of the Organic Phase Activity Coefficient. The chemistry of the DEHPA–metal system in the organic phase is complex. There are interactions between extractant and solvate, aggregation of the extractant and the organic metal complex, and interaction between the extractant and diluent, etc. Thus it is difficult to describe the equilibria in the organic phase in terms of detailed activity coefficients. A more realistic approach is to neglect individual equilibria and attribute the overall effects to activity coefficients of the most important species. From eq 28 we obtain

$$K^1 = \gamma_{H_2R_2}{}^2/\gamma_{Co(or)} = \left(\frac{1}{K}\right)(a_{H^+}{}^2/a_{Co(aq)})(m_{Co(or)}/m_{H_2R_2}{}^2) = (K^1/K)(m_{Co(or)}/m_{H_2R_2}{}^2) \quad (31)$$

At a constant concentration of extractant, K^1 should be a function of either $m_{Co(or)}$ or $m_{H_2R_2}$, or the ratio $m_{Co(or)}/m_{H_2R_2}{}^2$, but it was found that these functions were very complicated. This difficulty is due not only to the complexity of the chemistry in the organic phase but also because the numerator and denominator in the ratio (eq 31) are raised to different powers. In order to reduce the problem, the chemical equivalent scale was used to describe the organic activity. Högfeldt (*11*) has used this approach to describe solid/liquid ion-exchange equilibria. The extraction equilibrium can thus be expressed in the form:

$$2(\tfrac{1}{2}Co^{2+})_{aq} + 2H_2R_2 = 2(\tfrac{1}{2}CoR_2\tfrac{1}{2}H_2R_2)_{or} + 2H^+ \quad (32)$$

The equilibria constant K is given by

$$K = (a^E_{Co(or)}\,a^E_{H^+}/a^E_{Co(aq)}\,a^E_{H_2R_2})^2 \quad (33)$$

$$K_1{}^{11} = \gamma^E_{H_2R_2}/\gamma^E_{Co(or)} = K^{-1/2}(m_{Co(or)}/m_{H_2R_2})(a_{H^+}{}^2/a_{Co(aq)})^{1/2} \quad (34)$$

In Figure 2, $K_1{}^{11}$ is plotted against the ratio $(m_{Co(or)}/m_{H_2R_2})$ for each initial extractant concentration. The function of $K_1{}^{11}$ vs. $(m_{Co(or)}/m_{H_2R_2})$ can be expressed in terms of a second-order polynomial.

$$K_1{}^{11} = a + b(m_{Co(or)}/m_{H_2R_2}) + c(m_{Co(or)}/m_{H_2R_2})^2 \quad (35)$$

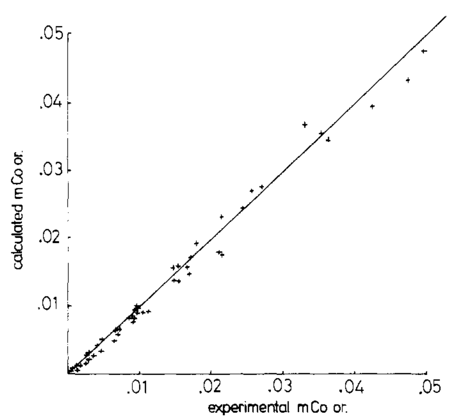

Figure 3. Comparison between calculated and observed values of $m_{\mathrm{Co(or)}}$.

in which $m_{\mathrm{H_2R_2}} = m_{\mathrm{H_2R_2(init)}} - 2m_{\mathrm{Co(or)}}$; subscript (init) refers to the initial concentration.

Inspection of Figure 2 shows that the K_1^{11} is a function of $(m_{\mathrm{Co(or)}}/m_{\mathrm{H_2R_2}})$ and the initial concentration of extractant only.

It is convenient to express the initial concentration in terms of mole fraction, $X_{\mathrm{H_2R_2(init)}}$. Thus we have

$$K_1^{11} = a + bX_{\mathrm{H_2R_2(init)}} + c(X_{\mathrm{H_2R_2(init)}})^2 + d(m_{\mathrm{Co(or)}}/m_{\mathrm{H_2R_2}}) + e(m_{\mathrm{Co(or)}}/m_{\mathrm{H_2R_2}})^2 + fX_{\mathrm{H_2R_2(init)}}(m_{\mathrm{Co(or)}}/m_{\mathrm{H_2R_2}}) + gX_{\mathrm{H_2R_2(init)}}(m_{\mathrm{Co(or)}}/m_{\mathrm{H_2R_2}})^2 \quad (36)$$

The best fit parameters were $a = 0.00488$, $b = 2.4089$, $c = -23.4329$, $d = 0.3090$, $e = 0.5607$, $f = 9.2910$, and $g = -17.4210$. The concentration of Co in the organic phase can then be calculated from the following second-order equation.

$$(m_{\mathrm{Co(or)}}/m_{\mathrm{H_2R_2}})^2\,(e + gX_{\mathrm{H_2R_2(init)}}) + (m_{\mathrm{Co(or)}}/m_{\mathrm{H_2R_2}})(d + fX_{\mathrm{H_2R_2(init)}} - K^{-1/2}\,(a_{\mathrm{H^+}}{}^2/a_{\mathrm{Co(aq)}})^{1/2}) + a + bX_{\mathrm{H_2R_2(init)}} + cX^2_{\mathrm{H_2R_2(init)}} = 0 \quad (37)$$

The comparison between calculated and observed values of $m_{\mathrm{Co(or)}}$ is made in Figure 3. The standard deviation is 8.642 × 10^{-3} which suggests a reasonable fit (although considerable scatter for some points is evident). In Figure 3 a few points, for which the $m_{\mathrm{Co(or)}} > 0.05$, were not plotted since the scale of the plot would be too extended.

Conclusion

(1) The activity coefficient of Co^{2+} in the multicomponent aqueous phase was calculated by using Pitzer's equation with the consideration of ion-pair $CoSO_4$. The correctness of this calculation was checked by our experiments.

(2) Thermodynamic extraction constant K was estimated by using Petkovic's method. From five sets of initial extraction concentrations a reasonable constant value of K was obtained.

(3) The activity coefficients of the organic phase were calculated, and the equivalent concentration scale was used to describe the extraction equilibria. It was shown that with the use of the equivalent scale the functions become much simpler than if the molality were used to express thermodynamic concentration.

Registry No. HDEHP, 298-07-7; Co, 7440-48-4.

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Synergic Extraction of Mixed Adducts of Cobalt(II) 8-Quinolinates[†]

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Cobalt(II) forms the strongest adduct with 5-nitro-8-quinolinol. Among all other oxines, the 5-NO_2 analogue was the least basic and its 2-methyl analogue was the most basic ligand investigated. An adduct of cobalt 2-methyl-8-quinolinate chelate as an acceptor and 5-nitro-8-quinolinol as a donor forms the strongest adduct, whereas that of cobalt 5-nitro-8-quinolinate as an acceptor and 2-methyl-8-quinolinol as a donor forms the weakest adduct. Synergic enhancement was observed in the extraction of Co(II) on the addition of small amounts of 5-nitro-8-quinolinol due to the formation of the most stable adduct, $Co(2\text{-}Me\text{-}8\text{-}Q)_2\cdot(5\text{-}NO_2\text{-}8\text{-}HQ)$. Relatively less stable adducts were observed when 5-NO_2-8-HQ was used as a chelating agent and other oxines as adducting ligands. Synergy coefficients of Co(II) adducts of the mixed ligands were evaluated.

Introduction

In the solvent extraction studies of nickel (*1*) and cobalt(II) (*2*) with 8-quinolinol and its substituted analogues, it was observed that the adduct formation constants increase with the decrease in the basicity of the ligands. Similar trend was observed in the extraction of pyridine adducts of nickel (*3*) and cobalt 8-quinolinates (*4*). The value of the adduct formation constant was found to be maximum with 5-nitro-8-quinolinol whose p*K* value was the least, i.e., 8.79, among the oxines studied. This was attributed to the dual function of the reagents which act both as an acceptor-chelating agent and as a donor base. As a result the increase in the donor basicity was compensated, to a certain extent, by the ability to form with a weaker acceptor a more stable metal adduct.

Among the oxines studied, the 5-nitro-8-quinolinol ligand was the least basic and its 2-methyl analogue was the most basic ligand investigated. An adduct of cobalt 2-methyl-8-quinolinate chelate as an acceptor and 5-nitro-8-quinolinol as a donor would be the strongest adduct or an adduct of cobalt-5-nitro-8-

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