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Extraction Equilibria of Zinc with Bis(2-ethylhexyl)phosphoric Acid

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Equilibria of aqueous solutions of $ZnSO_4 + H_2SO_4$ with bis(2-ethylhexyl)phosphoric acid in isododecane (pentamethylheptane), a system which is proposed as an EFCE (European Federation of Chemical Engineering) test system for reactive extraction, and of aqueous solutions of $ZnCl_2 + HCl$ with bis(2-ethylhexyl)phosphoric acid in isododecane were investigated. Equilibrium concentrations and physical properties (density, viscosity, interfacial tension) are given at 298 K. The experimental data could be described well with a model that assumes the formation of one organic complex and regards the hydrogen sulfate equilibrium in the aqueous phase. The Pitzer equation was used for the aqueous phase, and the theory of Hildebrand and Scott was used to describe nonidealities in the organic phase. For quick estimations, shortcut formula for physical properties and the activities are given.

Introduction

For many years, test systems for liquid−liquid extraction have been used to characterize and discriminate between different types of extraction apparatuses. The physical extraction test systems published by Misek et al. (1978, 1985) are classified according to their interfacial tensions. For high interfacial tension, water + acetone + toluene is proposed, for medium interfacial tension, water + acetone + butyl acetate is proposed, and for low interfacial tension, water + succinic acid + butanol is recommended.

Since the 80s, a test system for reactive extraction has been discussed (Bart et al., 1987; Bart et al., 1994; Koncar et al., 1988; Koncar, 1990; Wachter et al., 1993). The extraction of zinc sulfate with bis(2-ethylhexyl)phosphoric acid (D2EHPA) was proposed, but further investigation is necessary concerning two questions. For constant ionic strength in the aqueous phase, inert salts, for example, sodium sulfate, are necessary. Also the kinds of solvent used to dilute the ion exchanger and the newly formed organic zinc complex are still under discussion. Svendsen carried out experiments with the aromatic solvent cumene (Svendsen et al., 1990), but for extraction processes, aliphatic solvents are preferred because of their lower toxicity. Koncar (1990) suggested the use of *n*-dodecane. This solvent met all requirements but was too expensive for use in reactive extraction. Other investigations, which used heptane as solvent, were carried out by Slater, Bradford, Hancil, Prague (Hancil et al., 1990; Wachter, 1996), and Klocker et al. (1997). Because of the flammability of the solvent heptane, explosion-proof apparatuses are required. For this reason, Schröter suggested isododecane as a solvent which meets all technical requirements (Schröter, 1994).

In the present work, physical properties and equilibrium data are presented for the system zinc sulfate with D2EHPA in the organic solvent isododecane. An equilibrium model based on chemical potential theory is presented and used to describe the data. In addition, equilibrium data for the system zinc chloride with D2EHPA in isododecane are given and described with the same model.

Experimental Section

Reagents. The aqueous components in the sulfate system have been zinc sulfate (Merck p.a., purity > 99.5%) in the concentration range 5×10^{-5} to 5×10^{-2} mol/L and sulfuric acid (Riedel de Häen Fixanal) between 0 and 0.01 mol/L. In the chloride system, zinc chloride (Merck p.a., purity > 98%) was used in the concentration range 5×10^{-5} to 5×10^{-2} mol/L, and hydrochloric acid (Riedel de Häen Fixanal) was used in the range between 0 and 0.02 mol/L. On the organic side, the ion exchanger D2EHPA (Bayer AG, purity 97.3%) was diluted to between 0.005 and 0.2 mol/L in the solvent isododecane (EC Erdölchemie GmbH, purity > 98%), which consists mainly of pentamethylheptane. All chemicals were used without further purification.

Methods. The determination of zinc in aqueous and organic solutions was performed with a HITACHI AAS-spectrometer Z 8100, the density was measured with a HERAEUS DMA 55 densimeter, the interfacial tension was measured with a LAUDA TVT 1, and the viscosity of the solutions was measured with a LAUDA Viscoboy 2.

For the equilibrium experiments, 100 mL of the aqueous and the organic solutions, respectively, was mixed in a 250 mL vessel and stirred intensively for a minimum of 8 h, using a magnetic stirrer. After separation of the phases by centrifugation, the samples were analyzed with the methods mentioned above. The physical properties (density, viscosity, interfacial tension) of the equilibrium and starting solutions were measured at 298 K.

Model. When a two-phase, (1) and (2), system is at thermodynamic equilibrium, $T_1 = T_2$ (thermal), $p_1 = p_2$ (mechanical), $\mu_{i,1} = \mu_{i,2}$ (physical), and the total Gibb's free energy is minimum, $d(G_1 + G_2)_{T,p} = O$. Also, in systems with *k* chemical reactions

$$\sum_{i=1}^{n} \nu_{i,R} \cdot \mu_i = 0 \qquad R = 1, 2, ..., k \tag{1}$$

In an *n*-component system with *k* reactions, $\nu_{i,R}$ is the

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Table 1. Equilibrium Data for the System $ZnSO_4 + H_2SO_4$/D2EHPA in Isododecane at Low Zinc Concentrations

	total aqueous conc/mol L^{-1}			total org conc/mol L^{-1}	
no.	sulfate	zinc	pH	D2EHPA	zinc
1	0.0001	8.26×10^{-7}	3.66	0.005	9.92×10^{-5}
2	0.0001	4.74×10^{-7}	3.64	0.010	9.95×10^{-5}
3	0.0001	2.33×10^{-7}	3.59	0.015	9.98×10^{-5}
4	0.0001	1.02×10^{-7}	3.58	0.020	9.99×10^{-5}
5	0.0001	5.74×10^{-8}	3.62	0.030	9.99×10^{-5}
6	0.0001	2.44×10^{-8}	3.58	0.040	1.00×10^{-4}
7	0.0001	1.00×10^{-8}	3.50	0.060	1.00×10^{-4}
8	0.0001	1.00×10^{-8}	3.41	0.100	1.00×10^{-4}
9	0.0001	1.00×10^{-8}	3.32	0.200	1.00×10^{-4}
10	0.0006	1.75×10^{-5}	2.96	0.005	8.25×10^{-5}
11	0.0006	2.45×10^{-6}	2.95	0.020	9.76×10^{-5}
12	0.0006	2.24×10^{-6}	2.94	0.050	9.78×10^{-5}
13	0.0006	6.12×10^{-8}	3.00	0.100	9.99×10^{-5}
14	0.0006	2.04×10^{-8}	2.93	0.200	1.00×10^{-4}
15	0.0011	4.40×10^{-5}	2.72	0.005	5.60×10^{-5}
16	0.0011	6.73×10^{-6}	2.71	0.020	9.33×10^{-5}
17	0.0011	3.06×10^{-6}	2.68	0.050	9.69×10^{-5}
18	0.0011	2.91×10^{-6}	2.71	0.100	9.71×10^{-5}
19	0.0011	2.65×10^{-6}	2.73	0.200	9.73×10^{-5}
20	0.0101	4.97×10^{-5}	1.86	0.050	5.03×10^{-5}
21	0.0101	2.49×10^{-5}	1.87	0.100	7.51×10^{-5}
22	0.0101	1.06×10^{-5}	1.88	0.200	8.94×10^{-5}

Table 2. Equilibrium Data for the System $ZnSO_4 + H_2SO_4$/D2EHPA in Isododecane at Medium Zinc Concentrations

	total aqueous conc/mol L^{-1}			total org. conc/mol L^{-1}	
no.	sulfate	zinc	pH	D2EHPA	zinc
23	0.0050	0.0040	2.78	0.005	0.0010
24	0.0050	0.0031	2.53	0.010	0.0019
25	0.0050	0.0024	2.42	0.015	0.0026
26	0.0050	0.0020	2.35	0.020	0.0030
27	0.0050	0.0013	2.27	0.030	0.0037
28	0.0050	0.0009	2.22	0.040	0.0041
29	0.0050	0.0005	2.17	0.060	0.0045
30	0.0050	0.0002	2.19	0.100	0.0048
31	0.0050	0.0004	2.20	0.200	0.0046
32	0.0055	0.0041	2.60	0.005	0.0009
33	0.0055	0.0024	2.31	0.020	0.0026
34	0.0055	0.0009	2.15	0.050	0.0041
35	0.0055	0.0008	2.11	0.100	0.0042
36	0.0055	0.0001	2.20	0.200	0.0049
37	0.0060	0.0043	2.55	0.005	0.0007
38	0.0060	0.0027	2.29	0.020	0.0023
39	0.0060	0.0010	2.13	0.050	0.0040
40	0.0060	0.0003	2.08	0.100	0.0047
41	0.0060	0.0001	2.12	0.200	0.0049
42	0.0150	0.0044	1.85	0.020	0.0006
43	0.0150	0.0030	1.82	0.050	0.0020
44	0.0150	0.0017	1.77	0.100	0.0033
45	0.0150	0.0010	1.74	0.200	0.0040

Table 3. Equilibrium Data for the System $ZnSO_4 + H_2SO_4$/D2EHPA in Isododecane at High Zinc Concentrations

	total aqueous conc/mol L^{-1}			total org. conc/mol L^{-1}	
no.	sulfate	zinc	pH	D2EHPA	zinc
46	0.0500	0.0498	2.76	0.005	0.0002
47	0.0500	0.0459	2.55	0.010	0.0041
48	0.0500	0.0448	2.41	0.015	0.0052
49	0.0500	0.0427	2.30	0.020	0.0073
50	0.0500	0.0425	2.12	0.030	0.0075
51	0.0500	0.0407	2.05	0.040	0.0093
52	0.0500	0.0382	1.86	0.060	0.0118
53	0.0500	0.0343	1.73	0.100	0.0157
54	0.0500	0.0244	1.57	0.200	0.0256
55	0.0505	0.0466	2.33	0.020	0.0034
56	0.0505	0.0397	1.98	0.050	0.0103
57	0.0505	0.0322	1.76	0.100	0.0178
58	0.0505	0.0234	1.59	0.200	0.0266
59	0.0510	0.0485	2.23	0.020	0.0015
60	0.0510	0.0410	1.92	0.050	0.0090
61	0.0510	0.0334	1.73	0.100	0.0166
62	0.0510	0.0293	1.55	0.200	0.0207
63	0.0600	0.0483	1.92	0.020	0.0017
64	0.0600	0.0422	1.76	0.050	0.0078
65	0.0600	0.0352	1.62	0.100	0.0148
66	0.0600	0.0275	1.49	0.200	0.0225

Table 4. Equilibrium Data for the System $ZnCl_2 + HCl$/D2EHPA in Isododecane at Low Zinc Concentrations

	total aqueous conc/mol L^{-1}			total org conc/mol L^{-1}	
no.	chloride	zinc	pH	D2EHPA	zinc
1	0.0012	5.49×10^{-5}	2.97	0.002	4.51×10^{-5}
2	0.0012	3.66×10^{-5}	2.96	0.003	6.34×10^{-5}
3	0.0012	2.89×10^{-5}	2.95	0.004	7.11×10^{-5}
4	0.0012	1.40×10^{-5}	2.95	0.006	8.60×10^{-5}
5	0.0011	2.55×10^{-6}	2.98	0.010	4.75×10^{-5}
6	0.0012	5.61×10^{-6}	2.97	0.010	9.44×10^{-5}
7	0.0013	7.75×10^{-6}	2.95	0.010	1.17×10^{-4}
8	0.0013	1.17×10^{-5}	2.92	0.010	1.38×10^{-4}
9	0.0014	1.61×10^{-5}	2.88	0.010	1.84×10^{-4}
10	0.0016	3.10×10^{-5}	2.83	0.010	2.69×10^{-4}
11	0.0018	4.77×10^{-5}	2.79	0.010	3.52×10^{-4}
12	0.0022	9.72×10^{-5}	2.73	0.010	5.03×10^{-4}
13	0.0030	2.65×10^{-4}	2.65	0.010	7.35×10^{-4}
14	0.0101	4.20×10^{-5}	2.15	0.010	7.99×10^{-6}
15	0.0102	8.18×10^{-5}	2.11	0.010	1.82×10^{-5}
16	0.0104	1.60×10^{-4}	2.08	0.010	4.00×10^{-5}
17	0.0108	3.09×10^{-4}	2.08	0.010	9.14×10^{-5}
18	0.0022	1.80×10^{-5}	2.69	0.010	8.20×10^{-5}
19	0.0032	3.19×10^{-5}	2.53	0.010	6.81×10^{-5}
20	0.0042	4.25×10^{-5}	2.42	0.010	5.75×10^{-5}
21	0.0012	4.01×10^{-6}	2.96	0.020	9.60×10^{-5}

stoichiometric coefficient of compound i in the reaction R and μ_i is the chemical potential. As found in previous studies (Sainz-Diaz et al., 1996), zinc is extracted according to the following reaction equation confirming the stoichiometry of the organic complex, which has also been determined with FTIR technique:

$$Zn^{2+} + 1.5\overline{R_2H_2} \rightleftharpoons \overline{ZnR_2RH} + 2H^+ \tag{2}$$

The bar indicates organic species, and R_2H_2 is the D2EHPA dimer which is dominant in aliphatic diluents (Baes et al., 1958; Kolarik, 1982; Kunzmann, Kolarik, 1992). The equilibrium constant $K_{1,3}$ ($mol^{1/2}\ m^{-3/2}$) for this reaction is

$$K_{1,3} = \frac{[\overline{ZnR_2RH}]\cdot[H^+]^2}{[Zn^{2+}]\cdot[\overline{R_2H_2}]^{1.5}}\cdot\frac{\gamma_{\overline{Zn}}\cdot\gamma_H^2}{\gamma_{Zn}\cdot\gamma_{R_2H_2}^{1.5}} \tag{3}$$

γ_i is the activity coefficient of component i. To specify the total system, the formation of aqueous hydrogen sulfate has to be considered with the equilibrium constant K_{HS} ($m^3\ mol^{-1}$):

$$H^+ + SO_4^{\ 2-} \rightleftharpoons HSO_4^{\ -}$$

$$\text{with}\quad K_{HS} = \frac{\gamma_{HS}\cdot[HSO_4^{\ -}]}{\gamma_H\cdot[H^+]\cdot\gamma_S[SO_4^{\ 2-}]} \tag{4}$$

as described by Klocker et al. (1996). To evaluate the equilibria as defined above, one has to know the chemical potential of species i. The chemical potential in a mixture after Lewis is the sum of that of a reference state, μ_i^o, and a concentration dependent correction term.

$$\mu_i = \mu_i^0 + RT\ln(x_i\cdot\gamma_i) \tag{5}$$

To calculate the activity coefficients γ_i, the Pitzer model (Pitzer, 1973, 1975, 1977, 1979) is used for the aqueous phase and the Hildebrand−Scott solubility parameter (Hildebrand and Scott, 1950) is used for the organic phase.

Table 5. Equilibrium Data for the System $ZnCl_2$ + HCl/D2EHPA in Isododecane at Medium Zinc Concentrations

	total aqueous conc/mol L^{-1}			total org conc/mol L^{-1}	
no.	chloride	zinc	pH	D2EHPA	zinc
22	0.011	3.84×10^{-3}	2.54	0.006	1.16×10^{-3}
23	0.011	3.20×10^{-3}	2.45	0.010	1.80×10^{-3}
24	0.011	2.81×10^{-3}	2.31	0.015	2.19×10^{-3}
25	0.011	2.39×10^{-3}	2.26	0.020	2.61×10^{-3}
26	0.011	1.74×10^{-3}	2.20	0.030	3.26×10^{-3}
27	0.011	1.32×10^{-3}	2.21	0.040	3.68×10^{-3}
28	0.006	1.05×10^{-4}	2.36	0.060	1.89×10^{-3}
29	0.008	2.72×10^{-4}	2.22	0.060	2.73×10^{-3}
30	0.010	5.62×10^{-4}	2.14	0.060	3.44×10^{-3}
31	0.014	1.07×10^{-3}	2.12	0.060	3.93×10^{-3}
32	0.016	1.33×10^{-3}	2.02	0.060	3.67×10^{-3}
33	0.018	1.55×10^{-3}	1.94	0.060	3.45×10^{-3}
34	0.022	1.94×10^{-3}	1.90	0.060	3.06×10^{-3}
35	0.030	2.75×10^{-3}	1.76	0.060	2.25×10^{-3}
36	0.011	8.17×10^{-4}	2.10	0.060	4.18×10^{-3}
37	0.011	3.95×10^{-4}	2.09	0.100	4.60×10^{-3}
38	0.024	1.74×10^{-3}	1.80	0.100	5.26×10^{-3}

Table 6. Equilibrium Data for the System $ZnCl_2$ + HCl/D2EHPA in Isododecane at High Zinc Concentrations

	total aqueous conc/mol L^{-1}			total org. conc/mol L^{-1}	
no.	chloride	zinc	pH	D2EHPA	zinc
39	0.102	4.41×10^{-2}	1.99	0.02	5.95×10^{-3}
40	0.102	4.23×10^{-2}	1.87	0.03	7.73×10^{-3}
41	0.102	3.73×10^{-2}	1.69	0.06	1.27×10^{-2}
42	0.030	3.33×10^{-3}	1.74	0.10	6.67×10^{-3}
43	0.050	9.78×10^{-3}	1.65	0.10	1.02×10^{-2}
44	0.070	1.73×10^{-2}	1.58	0.10	1.27×10^{-2}
45	0.090	2.54×10^{-2}	1.51	0.10	1.46×10^{-2}
46	0.104	3.41×10^{-2}	1.56	0.10	1.59×10^{-2}
47	0.110	3.54×10^{-2}	1.52	0.10	1.46×10^{-2}
48	0.120	3.71×10^{-2}	1.46	0.10	1.29×10^{-2}
49	0.140	4.02×10^{-2}	1.36	0.10	9.82×10^{-3}
50	0.102	3.34×10^{-2}	1.58	0.10	1.66×10^{-2}
51	0.102	2.65×10^{-2}	1.43	0.20	2.35×10^{-2}

Table 7. Physical Properties of the Organic Phase

D2EHPA/mol L^{-1}	density/kg m^{-3}	viscosity/mm^2 s^{-1}
0.005	745.83	1.631
0.010	746.27	1.627
0.015	746.75	1.643
0.020	747.08	1.651
0.030	747.82	1.709
0.040	748.67	1.681
0.050	749.38	1.683
0.060	750.27	1.705
0.100	753.37	1.741
0.200	760.94	1.844

The Pitzer, Masson, and solubility parameters are taken from the literature (Barton, 1991). With the software of Baes et al. (1990), the solubility parameter of the organic complex and the equilibrium constant can be estimated. The quality of the fit is expressed by the agreement factor σ. The program is available free via the Internet (http://www.ornl.gov/divisions/casd/csg/sxlsqi/).

Results

The equilibrium data at low, medium, and high zinc concentrations are given in Tables 1−3 for sulfate and Tables 3−6 for chloride systems. As shown in previous studies (Sainz-Diaz et al., 1996) with KF titration, a coextraction of water does not occur.

The physical properties measured in the sulfate system are given in Table 7. D2EHPA is of medium viscosity and has a density of 976 kg/m^3 at 298 K. Isododecane is polymerized from isobutylene, leading to high-purity 2,2,4,6,6-pentamethylheptane with a density of 746 kg/m^3 at 298 K. The density and viscosity of D2EHPA diluted in isododecane have been described with the linear functions depicted in Table 8. Also, the interfacial tensions are given as a function of the total ion exchanger concentration for high, medium and low zinc concentrations.

Modeling both systems leads to the equilibrium constants $K_{1,3}$ and the solubility parameters δ of the organic complex, as shown in Table 9 together with the agreement factor σ for the calculations. A comparison of calculated values and experimental data shows the good quality of the mathematical description, which predicts the experiments within 10%. Figure 1 gives an example for the sulfate system. Basically, the interfacial reaction should be independent of the aqueous anion, and also the solubility parameter of the organic complex should be the same for both systems. This leads to the conclusion that equilibria of the chloride system should be predictable when using the solubility parameter for the organic complex and the equilibrium constants that have been estimated with the sulfate data. Such simulations have been carried out with the Pitzer parameters for the chloride system and the same solubility parameters and equilibrium constant as used for the sulfate system. Figure 2 shows the results. Experimental values, simulation data with the chloride parameters, and the prediction based on the sulfate data are in good accord.

The calculated activities have been used to create some shortcut correlations, as shown in Table 8. Equilibria for aqueous zinc concentrations up to 10^{-5} mol/L can be

Table 8. Shortcut Formula for Physical Properties and Activity Coefficients

property	unit	condition	formula
aq density	kg/m^3	sulfate system	$\rho_{aq} = 156.5 \cdot [ZnSO_4] + 997.2$
org density	kg/m^3		$\rho_{org} = 75.7 \cdot [D2EHPA] + 745.4$
org viscosity	mm^2/s		$\nu_{org} = 1.08 \cdot [D2EHPA] + 1.637$
interfacial tension	mN/m	[Zn] < 0.001	$\sigma_{low} = 17.23 \cdot [D2EHPA]^{-0.094}$
interfacial tension	mN/m	0.001< [Zn] < 0.01	$\sigma_{med} = 18.31 \cdot [D2EHPA]^{-0.088}$
interfacial tension	mN/m	[Zn] > 0.01	$\sigma_{high} = 18.61 \cdot [D2EHPA]^{-0.092}$
activity coeff Zn^{2+}		sulfate system	$\gamma_{Zn^{2+}} = -0.124 \cdot \ln[SO_4]_{tot} - 0.095$
activity coeff R_2H_2		sulfate system	$\gamma_{(RH)_2} = -0.972 \cdot [D2EHPA]_{tot} - 0.993$
activity coeff H^+		sulfate system	$\gamma_{H^+} = -0.055 \cdot \ln[SO_4]_{tot} - 0.579$
activity coeff Zn^{2+}		chloride system	$\gamma_{Zn^{2+}} = -0.114 \cdot \ln[Cl]_{tot} - 0.115$
activity coeff R_2H_2		chloride system	$\gamma_{(RH)_2} = -1.889 \cdot [D2EHPA]_{tot} - 1.005$
activity coeff H^+		chloride system	$\gamma_{H^+} = -0.045 \cdot \ln[Cl]_{tot} - 0.675$

Table 9. Simulation Data for Sulfate and for Chloride Systems

system	solubility parameter of $ZnR_2(RH)$/MPa$^{1/2}$	$\log_{10}(K_{1,3})$	σ
$ZnSO_4$/D2EHPA in isododecane	19.038	−1.1863	1.219
$ZnSO_4$/D2EHPA in heptane (Klocker et al., 1997)	18.591	−0.9441	1.648
$ZnCl_2$/D2EHPA in isododecane	24.272	−1.1178	1.046
$ZnCl_2$/D2EHPA predicted with sulfate parameters	19.038	−1.1863	1.811

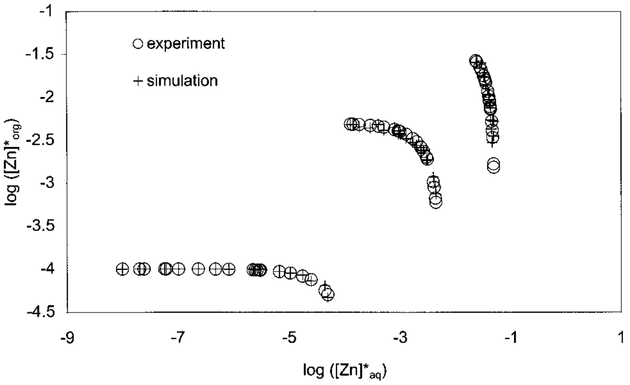

Figure 1. Comparison of calculated and simulated equilibria in the sulfate system.

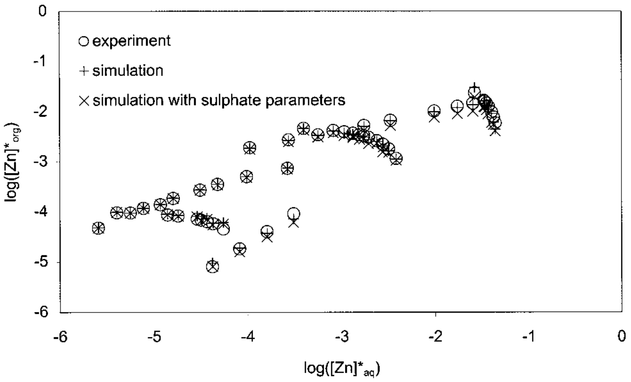

Figure 2. Comparison of calculated and simulated equilibria in the chloride system.

predicted without using the full model within 15%, if eq 3 is used, assuming all activity coefficients as $\gamma_i = 1$. For aqueous zinc concentrations between 10^{-5} mol/L and 10^{-3} mol/L, the use of the correlations is recommended. Equilibria for aqueous zinc concentrations $>10^{-3}$ mol/L cannot be predicted within an acceptable tolerance of error without using the full model.

Concluding Remarks

In this work, the physical properties and equilibrium concentrations for the systems $ZnSO_4 + H_2SO_4 +$ bis(2-ethylhexyl)phosphoric acid in isododecane and $ZnCl_2 + HCl +$ bis(2-ethylhexyl)phosphoric acid in isododecane were investigated. The experimental data of the sulfate system could be described well with a model that assumes the formation of one organic complex and regards the hydrogen sulfate equilibrium, if nonidealities are considered. With the same model, also the chloride system can be described. In addition, the derived model parameters of the sulfate system can be used to predict the equilibria of the chloride system. Shortcut formula are given to calculate physical properties and activity coefficients.

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