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Modeling of phosphoric acid purification contaminated by magnesium and cadmium

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ABSTRACT

The present study brings to light modeling of the purification of phosphoric acid, which is obtained through the wet process route. The said wet process inevitably is used to remove the impurities, mainly the heavy metal cations such as Mg^{2+}, Cd^{2+}, etc., which are initially present in the phosphate rocks and it is imperative that these impurities be removed . For the very same purpose, liquid–liquid extraction has proven to be one of the most reliable techniques and hence it is again considered, basing the model on the purely theoretical considerations of thermodynamics and mass transfer. The developed model was tested on two systems with $Mg^{2+}$and Cd^{2+} as the contaminants and dinonylnaphthalene sulfonic acid and di (2-ethylhexyl) dithiophosphoric acid as complexing agents, both diluted in kerosene and dodecane, respectively. A parametric study was carried out, to investigate the effect of certain key parameters such as the phosphoric acid and the extractant initial concentrations.

Keywords: Phosphoric acid purification; Extraction; Magnesium; Cadmium; Phosphate; Complexing agent

1. Introduction

Many important industrial fields, such as pharmaceuticals, food, soap and detergents, and fertilizers, involve the use of phosphoric acid [1]. The use of phosphoric acid has paved the way for the development of phosphoric-acid-based production processes such as evaporation, fixation on land filtration, precipitation, adsorption or liquid–liquid extraction, with the last mentioned serving as the main topic of the present study [1–5]. However, a great majority of these works are purely of an experimental nature, hence motivating the modeling of this process.

In fact, phosphoric acid is produced in the wet process which consists of sulfuric acid attack on the phosphate rock. However, a major drawback of this production route is that the obtained phosphoric acid inevitably contains impurities such as organic matter and heavy metal cations such as Cu^{2+}, Cd^{2+}, and Zn^{2+}. These species are initially present in the phosphate rock and then migrate into produced phos-

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phoric acid solutions from where it is imperative that they be eliminated.

2. Thermodynamic modeling

As mentioned above and to remove heavy metal ions, with a view to purifying the phosphoric acid, the liquid–liquid extraction technique, involving an organic solvent, is employed. However a priori, metallic cations are made to enter into complexes using a carefully chosen complexing agent. The purification process then combines a chemical step (complexation and acid dissociation reactions) and a physical step (a mass transfer of the formed complex into the organic phase to ensure phase equilibria). The aim of the proposed model for phosphoric acid purification by the liquid–liquid extraction technique is to calculate the mole fractions of the different species present in both phases.

The phase equilibria are calculated using the UNIQUAC model which is modified to suit the case when the electrolytes are present in the system. However, this method requires interaction parameters, which are also calculated using the experimental data reported in the literature [6,7].

2.1. Chemical equilibria

The model is based on the method proposed by Devore [8], which is briefly described in the present section. The electrolyte dissociation and complex formation take place according to the following reaction series:

$$A \leftrightarrow B + C \quad K_1 \tag{1a}$$

$$B \leftrightarrow D + C \quad K_2 \tag{1b}$$

$$F \leftrightarrow G + H \quad K_i \tag{1c}$$

with $K_1, K_2, \ldots, K_i$, the equilibrium dissociation constants.

The initial concentrations of the different species in the reaction mixture are specified, while those of the species resulting from the dissociation of phosphoric acid are initially considered as zero. If $[A]^i$, $[B]^i$, etc., represent the molar concentrations of the reactants at the ith iteration, their values at the next iteration $(i+1)$th will be calculated from the equilibrium equations, considering the following general chemical equilibrium:

$$A \leftrightarrow B + C$$

The concentrations are:

at ith iteration	$[A]^i$	$[B]^i$	$[C]^i$
at $(i+1)$th iteration	$[A]^i - \Delta$	$[B]^i + \Delta$	$[C]^i + \Delta$

let:

$$[A]^{i+1} = [A]^i - \Delta \tag{1d}$$

$$[B]^{i+1} = [B]^i + \Delta \tag{1e}$$

$$[C]^{i+1} = [C]^i + \Delta \tag{1f}$$

with Δ the concentration step change. The equilibrium constant at the ith iteration is given by:

$$K_i = \frac{([C]^i + \Delta)([B]^i + \Delta)}{([A]^i - \Delta)} \tag{1g}$$

Neglecting the terms in Δ of power higher than 1 gives:

$$\Delta_1 = \frac{K_1[A]^i - [B]^i[C]^i}{[C]^i[B]^i + K_1} \tag{1h}$$

The concentrations of the species are then adjusted several times during one iterative cycle. If a negative concentration is generated, the corresponding reaction is skipped until the next iteration.

In the present study, the purification of phosphoric acid, contaminated with magnesium and cadmium, by the liquid–liquid extraction technique is considered using two complexing agents namely the dinonylnaphthalene sulfonic acid (DNNSA) and the di (2-ethylhexyl) dithiophosphoric acid (D_2EHDTPA) as well as kerosene and dodecane, as diluents, respectively. The experimental study for the two systems was reported in [6,7].

The different chemical equilibrium and reactions taking place in the aqueous phase are the following:

Dissociation reactions [9]

$$H_3PO_4 \leftrightarrow H_3PO_4^- + H^+ \quad K_1 = 7.107 \times 10^{-3} \tag{R1}$$

$$H_2PO_4^- \leftrightarrow HPO_4^{2-} + H^+ \quad K_2 = 4.275 \times 10^{-7} \tag{R2}$$

$$HPO_4^{2-} \leftrightarrow PO_4^{3-} + H^+ \quad K_3 = 1.15{\times}10^{-12} \tag{R3}$$

$$H_3PO_4 + H_2PO_4^- \leftrightarrow H_5P_2O_8^- \quad K_4 = 1.263 \tag{R4}$$

$$H^+ + H_5P_2O_8^- \leftrightarrow H_6P_2O_8 \quad K_5 = 0.3 \tag{R5}$$

$$H_2O \leftrightarrow H^+ + OH^- \quad K_6 = 10^{-14} \tag{R6}$$

Complexation reactions [6,7]:

$$Mg^{2+} + (HA)_8 \leftrightarrow (MgA_2{\cdot}6HA) + 2H^+ \quad K_7 = 59.6 \tag{R7}$$

$$Cd^{2+} + 2HR \leftrightarrow CdR_2 + 2H^+ \quad K_8 = 11{\times}10^6 \tag{R8}$$

Substituting into Eq. (1h) gives:

$$\Delta_1 = \frac{K_1[H_3PO_4] - [H_2PO_4^-][H]^+}{[H_2PO_4^-] + [H^+] + K_1} \tag{2a}$$

$$\Delta_2 = \frac{K_2[H_2PO_4^-] - [HPO_4^{2-}][H^+]}{[HPO_4^{2-}] + [H^+] + [K_2]} \tag{2b}$$

$$\Delta_3 = \frac{K_3[HPO_4^{2-}] - [PO_4^{3-}][H^+]}{[PO_4^{3-}] + [H^+] + K_3} \tag{2c}$$

$$\Delta_4 = \frac{K_4[H_3PO_4][H_2PO_4^-] - [H_5P_2O_8^-]}{1 + K_4[H_3PO_4] + K_4[H_2PO_4^-]} \tag{2d}$$

$$\Delta_5 = \frac{K_5[H^+][H_5P_2O_8^-] - [H_6P_2O_8]}{1 + K_5[H^+] + K_5[H_5P_2O_8^-]} \tag{2e}$$

$$\Delta_6 = \frac{K_6 - [H^+][OH^-]}{K_6 + [H^+] + [OH^-]} \tag{2f}$$

$$\Delta_7 = \frac{K_7[Mg^{2+}][(HA)_8] - [(MgA_2{\cdot}6HA)][H^+]^2}{K_7[(HA)_8] + K_7[Mg^{2+}] + 4[H^+][(MgA_2{\cdot}6HA)] + [H^+]^2} \tag{2g}$$

$$\Delta_8 = \frac{K_8[Cd^{2+}][HR]^2 - [CdR_2][H^+]^2}{K_8[HR]^2 + 4K_8[Cd^{2+}][HR] + 4[H^+][CdR_2] + [H^+]^2} \tag{2h}$$

The concentrations of the different species in the mixture are calculated by solving Eqs. (2a)–(2h) simultaneously.

2.2. Liquid phase equilibria

The calculation of liquid–liquid equilibria is based on the estimation of the activity coefficients according to a thermodynamic model activity such as NRTL, UNIFAC, UNIQUAC, etc. In the present study, the UNIQUAC model is employed under its modified version to take into account the presence of electrolytes and it is expressed as follows [10]:

$$Ln\gamma_n = Ln\gamma_n^{DH} + Ln\gamma_n^{C} + Ln\gamma_n^{R} \tag{3}$$

$$Ln\gamma_b^* = Ln\gamma_b^{*,DH} + Ln\gamma_b^{*,C}n + Ln\gamma_b^{*,R} \tag{4}$$

where n and b denote the solvent and the ion, respectively. $Ln\gamma_n^{DH}, Ln\gamma_n^{C}$, and $Ln\gamma_n^{R}$ are the Debye–Huckel, the combinatorial, and the residual contributions to the activity coefficient of solvent n or ion b, respectively, and are expressed as follows:

2.2.1. The Dubye–Huckel term

$$Ln\gamma_n^{DH} = M_n \frac{2A}{b^3}(1 + bI^{1/2} - 1/(1 + bI^{1/2})) - 2ln(1 + bI^{1/2}) \tag{5}$$

$$Ln\gamma_b^{*,DH} = -Z_b^2 A \frac{I^{1/2}}{1 + bI^{1/2}} \tag{6}$$

2.2.2. The combinatorial term

$$Ln\gamma_n^{C} = Ln\frac{\phi_n}{x_n} + 1 - \frac{\phi_n}{x_n} - \frac{1}{2}zq_n\left(Ln\frac{\phi_n}{\theta_n} + 1 - \frac{\phi_n}{\theta_n}\right) \tag{7}$$

$$Ln\gamma_{\mathrm{b}}^{*,\mathrm{C}} = Ln\frac{\phi_{\mathrm{b}}}{x_{\mathrm{b}}} - \frac{\phi_{\mathrm{b}}}{x_{\mathrm{b}}} - Ln\frac{r_{\mathrm{b}}}{r_{\mathrm{w}}} + \frac{r_{\mathrm{b}}}{r_{\mathrm{w}}} - \frac{1}{2}zq_{\mathrm{b}}\left(Ln\frac{\phi_{\mathrm{b}}}{\theta_{\mathrm{b}}} - \frac{\phi_{\mathrm{b}}}{\theta_{\mathrm{b}}} - Ln\frac{r_{\mathrm{b}}q_{\mathrm{w}}}{r_{\mathrm{w}}q_{\mathrm{b}}} + \frac{r_{\mathrm{b}}q_{\mathrm{w}}}{r_{\mathrm{w}}q_{\mathrm{b}}}\right) \tag{8}$$

where r_{w} and q_{w} are the surface area and volume parameters, Z is the coordination number set equal to 10, θ_{b}, ϕ_{b}, and ϕ_{n} are calculated from the following expressions:

$$\theta_i = \frac{x_i q_i}{\sum_{\mathrm{l}} x_{\mathrm{l}} q_{\mathrm{l}}} \tag{9}$$

$$\phi_i = \frac{x_i r_i}{\sum_{\mathrm{l}} x_{\mathrm{l}} r_{\mathrm{l}}} \tag{10}$$

2.2.3. The residual term

$$Ln\gamma_{\mathrm{n}}^{\mathrm{R}} = q_{\mathrm{n}}\left(1 - Lns_{\mathrm{n}} - A_{\mathrm{n}} - \frac{2}{T}B\right) \tag{11}$$

$$Ln\gamma_{\mathrm{b}}^{*,\mathrm{R}} = q_{\mathrm{b}}\left(-Lns_{\mathrm{b}} - A_{\mathrm{b}} + \frac{1}{T}(D_{\mathrm{b}} + E_{\mathrm{b}} - 2B) + Ln\psi\psi_{\mathrm{w,b}}^{\infty,\mathrm{w}} + \psi\psi_{\mathrm{b,w}}^{\infty,\mathrm{w}}\right) \tag{12}$$

where:

$$s_{\mathrm{l}} = \sum_{\mathrm{k}} \theta_{\mathrm{k}}\psi_{\mathrm{kl}} \tag{13}$$

$$C_{\mathrm{kl}} = \frac{\psi_{\mathrm{kl}}}{S_{\mathrm{l}}} \tag{14}$$

$$A_{\mathrm{k}} = \sum_{\mathrm{l}} \theta_{\mathrm{l}} C_{\mathrm{kl}} \tag{15}$$

$$D_{\mathrm{b}} = \sum_{i\neq \mathrm{b}} \sum_{\mathrm{m}} \theta_i^2 \theta_m \delta_{i\mathrm{b,m}}(C_{i\mathrm{m}} + C_{\mathrm{m}i}) \tag{16}$$

$$E_{\mathrm{b}} = \sum_{\mathrm{m}} \theta_{\mathrm{m}} f_{\mathrm{bm}}(C_{\mathrm{bm}} + C_{\mathrm{mb}}) \tag{17}$$

$$f_{\mathrm{bm}} = \theta_{\mathrm{b}} \sum_{i\neq \mathrm{b}} \delta_{\mathrm{b}i,\mathrm{m}} \theta_i \tag{18}$$

$$B = \sum_i \theta_i E_i \tag{19}$$

$\psi_{\mathrm{w,b}}^{\infty,\mathrm{w}}$ and $\psi_{\mathrm{b,w}}^{\infty,\mathrm{w}}$ are the values of $\psi_{\mathrm{w,b}}$ and $\psi_{\mathrm{b,w}}$ in water pure. $\sum_{\mathrm{k}}$ and $\sum_{\mathrm{l}}$ are sums over all the species in the system.

$$\psi_{\mathrm{kl}} = \exp\left(-\frac{a_{\mathrm{kl}}}{T}\right) \tag{20}$$

In this case, a_{kl} is the interaction parameter between species k and l.

A priori, the interaction parameters of the modified UNIQUAC model can be determined from the minimization of an objective function which can be written as follows:

$$F = \sum_i \sum_j [\ln(\gamma_j x_j)^{\mathrm{I}} - \ln(\gamma_j x_j)^{\mathrm{II}}]^2 \tag{21}$$

where $(\gamma_j x_j)^{\mathrm{I}}$ and $(\gamma_j x_j)^{\mathrm{II}}$ are the activities of the constituent j in phases I and II, and this is taken for all tie lines.

The objective function F is minimized by the simplex method of optimization developed by Nelder and Mead in 1965 [11].

3. Results and discussion

The proposed model is tested for the two systems which are shown in Table 1.

A priori, for a given initial concentration of the complexing agent, the total amount of complex formed should be calculated, and hence a complexation ratio R that is defined as the total amount of complex formed over that of an initial free metal concentration (before complexation) [9]. In other words, R gives an idea of the extent of complexation.

An assessment of the developed computer code was carried out by comparing the calculated results with the experimental values, as shown in Fig. 1, from which it can be seen that the model is more reliable for the second system than the first one where the agreement is more qualitative than quantitative.

Fig. 2 shows the effect of the concentration of complexing agent on the complexation ratio. For a given concentration of phosphoric acid and different concentrations of the metal, it is noted that the ratio of

Table 1
Systems tested

System	Acid	Metallic ion	Complexing agent	Organic diluent
1	H_3PO_4	Mg^{2+}	Dinonylnaphthalene sulfonic acid (DNNSA)	Kerosene
2	H_3PO_4	Cd^{2+}	Di (2-ethylhexyl) dithiophosphoric acid ($D_2EHDTPA$)	Dodecane

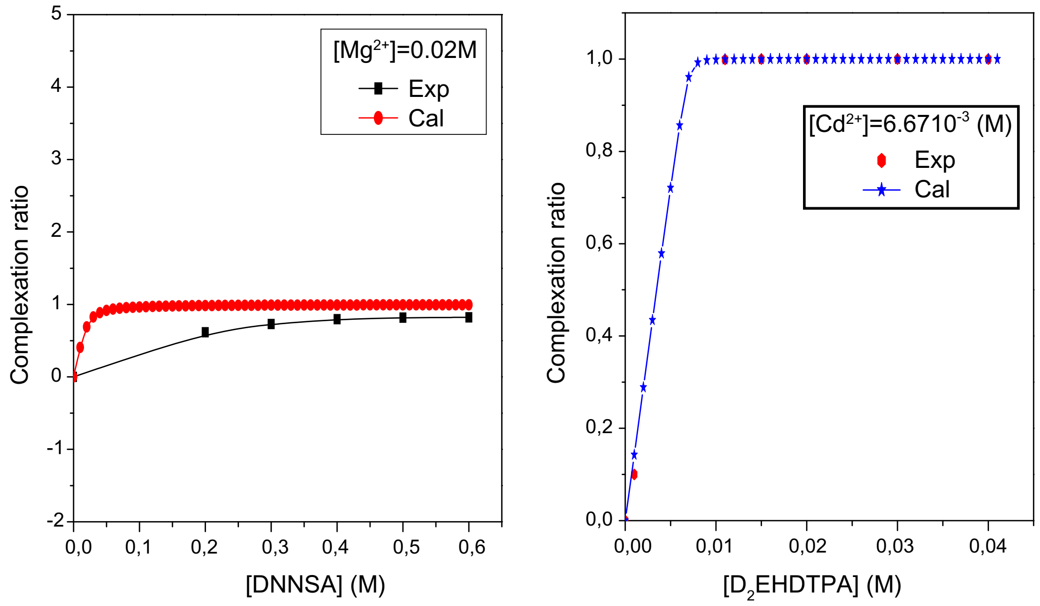

Fig. 1. Comparison between the calculated and experimental results for both systems.

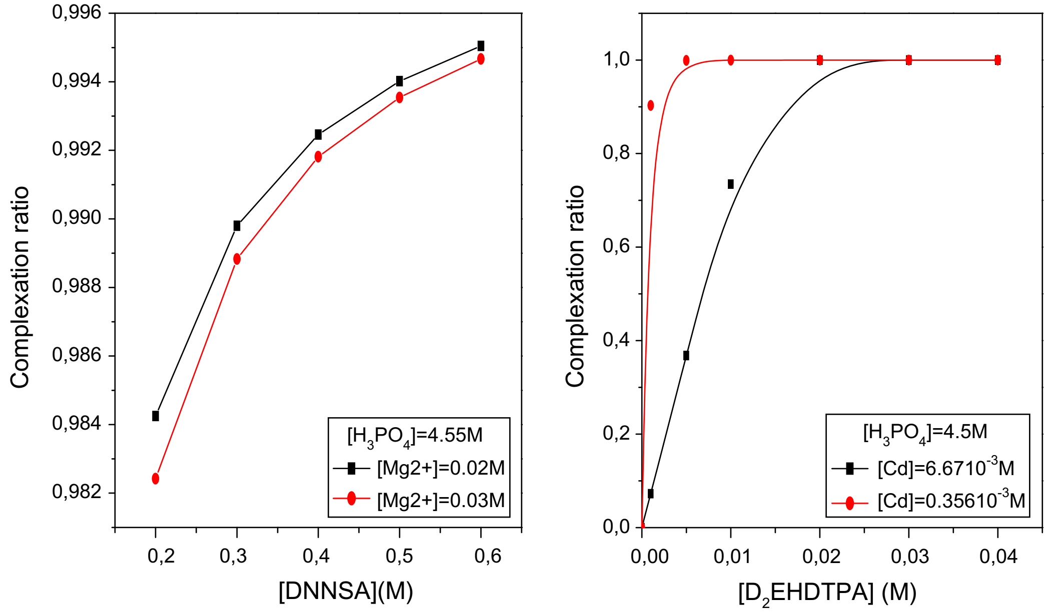

Fig. 2. The effect of the concentration of a complexing agent on the complexation ratio for different concentrations of the metal for both systems.

complexation increases with increasing concentration of the complexing agent, particularly for low values of the metal concentrations. This may be regarded as a direct consequence of the definition of the complexation ratio.

Fig. 3 shows that the increase of metal concentration has a negative effect on complexation ratio and that too whatever the concentration of phosphoric acid.

Applying the thermodynamic approach described above, a huge matrix of interaction parameters has been obtained (see Appendix), where all the values have been used to simulate the distribution of different species between the aqueous and the organic phases. A comparison between the metal mole fraction values in the two phases obtained from the complexation model based on the reported experimental data and those obtained using the modified UNIQUAC model, is given in Table 2.

4. Conclusion

The present study shows a model based on a combination of chemical and physical equilibria, through an application to the purification of phosphoric acid by the liquid–liquid extraction.

A computer code was developed and tested with two systems where phosphoric acid was contaminated with cadmium and magnesium ions, respectively. The proposed model was also used to investigate the effect of certain parameters on the complexation such as the effect of concentration of the complexing agent and the effect of the acidity of the medium. The comparison between the calculated and experimental results

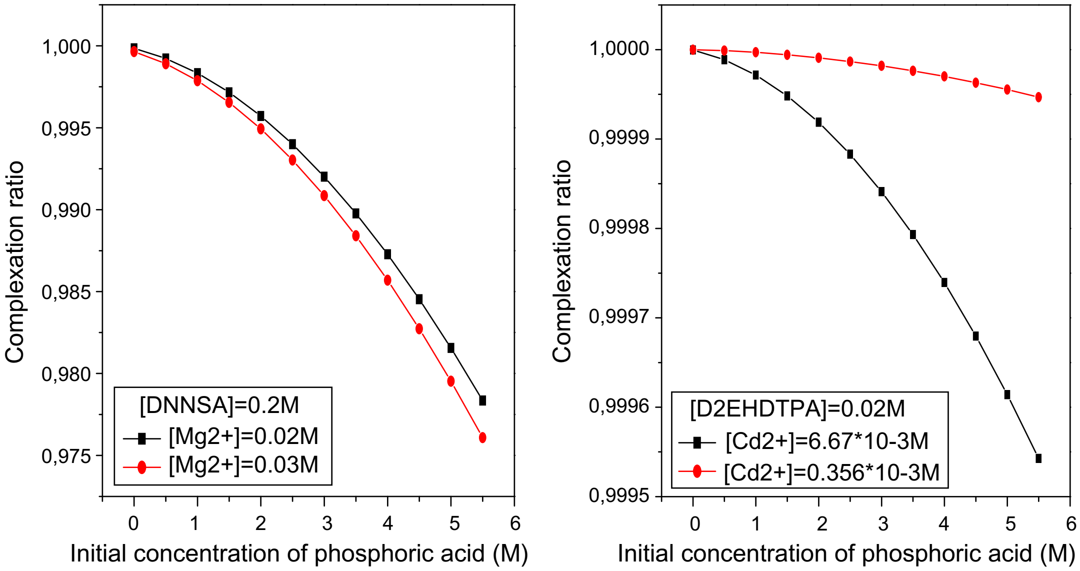

Fig. 3. The effect of an initial concentration of phosphoric acid on the report of complexation for both systems.

Table 2
A comparison between the experimental and calculated values

System		Experimental fraction f_1	Calculated fraction model f_2	Error $(\%) = \frac{\lvert(f_1 - f_2)\rvert \times 100}{f_1}$
1	X_1	2.7796018×10^{-6}	2.6509272×10^{-6}	4.63
	X_2	3.7509361×10^{-3}	3.5189835×10^{-3}	6.18
2	X_1	1.3202921×10^{-4}	1.3785210×10^{-4}	4.41
	X_2	2.0828463×10^{-4}	2.176644×10^{-4}	4.5

With X_1 and X_2 the metal and the complex mole fractions after equilibrium in the aqueous and organic phases, respectively. It can be seen that a good agreement is obtained.

for both systems gave a good agreement, particularly for the second system.

The results were also used for the determination of interaction parameters for the modified UNIQUAC model used for the activity coefficient calculations.

In conclusion, the present study should be seen as an attempt to model the liquid–liquid extraction starting from purely theoretical considerations of thermodynamics and mass transfer.

List of symbols

A,b	Debye–Huckel parameters
F	objective function
I	ionic strength
K	equilibrium constant
M_m	molecular weight of solvent m
n	number of moles
N	number of components
q	surface area parameter
r	volume parameter
R	complexation ratio
T	temperature
x_i	mole fraction
z	UNIQUAC parameter
Z_i	number of change of ion i

Greek letters

Δ	concentration step
γ	activity coefficient
γ_i^*	activity coefficient of non-symmetric component
δ	interaction parameter
θ	surface area fraction of component
μ	chemical potential
ϕ_i	volume fraction component

Subscripts

C	combinatorial
D–H	Debye–Huckel
ion	ion
sol	solvent
R	residual
UNI	UNIQUAC

Superscripts

$^\circ$,$*$	reference state
∞	infinite dilution

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Appendix

Table A1
UNIQUAC interaction parameters a^*_{ij}-system 1

	H_2O	Kerosene	H_2PO_4	$H_2PO_4^-$	HPO_4^{2-}	PO_46^{3-}	H^+	OH^-	$H_5P_2O_8^-$	$H_6P_2O_8$	Mg^{2+}	HA	$MgA_2{\cdot}6HA$	SO_4^{2-}
H_2O	0	165.176	159.853	−346.857	59.275	100.788	19.958	2.993	3.991	4.989	5.988	6.986	7.984	8.982
Kerosene	113.500	0	111.835	233.641	−1314.524	108.608	−167.685	240.619	3420.554	326.634	480.565	521.667	2,237.480	299.306
H_3PO_4	−250.073	104.686	0	70.038	591.605	250.160	241.229	983.086	410.421	−215.215	602.133	811.965	40.195	579.049
$H_2PO_4^-$	504.555	3,908.088	8,199.156	0	798.828	2,412.537	250.173	3,921.242	510.162	24.387	5.436	7,786.426	362.195	1,357.778
HPO_4^{2-}	487.573	20.002	280.285	295.302	0	26.809	10.171	−20.352	34.547	40.264	50.536	62.469	25.037	10.011
PO_4^{3-}	155.183	497.206	358.266	793.733	250.168	0	313.051	399.344	2,973.017	9,811.078	3,112.664	4,016.695	213.245	4,219.056
H^+	2,260.690	617.149	268.093	7,006.286	250.073	−910.921	0	592.564	243.066	904.310	526.990	644.760	357.6789	365.687
OH^-	445.526	49.014	248.822	59.726	250.143	250.168	992.002	0	903.996	191.190	−110.035	903.993	200.064	300.324
$H_5P_2O_8^-$	301.788	229.183	298.104	540.555	480.484	730.775	560.178	891.933	0	263.174	65.691	952.060	460.259	24.927
$H_6P_2O_8$	150.108	110.031	801.821	250.465	133.159	855.594	465.548	445.526	254.893	0	−620.239	510.517	1,026.005	250.173
Mg^{2+}	50.046	4,096.573	25.008	601.132	800.952	174.340	58.465	501.552	305.127	891.920	0	280.264	250.160	250.173
HA	400.301	510.163	275.280	551.051	902.689	637.502	356.666	48.082	20.002	233.234	293.299	0	250.073	250.173
$MgA_2{\cdot}6HA$	1,318.960	610.175	24.927	911.074	601.074	25.037	10.011	15.026	500.210	35.910	800.441	250.168	0	350.246
SO_4^{2-}	39.944	250.073	981.398	310.548	401.738	2,223.450	421.792	228.427	611.143	268.093	700.365	250.073	1,000.020	0

Table A2
$\delta_{ij,m}$ parameters

	H_3PO_4	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}	H^+	OH^-	$H_5P_2O_8^-$	$H_6P_2O_8$	Mg^{2+}	HA	$MgA_2{\cdot}6HA$	SO_4^{2-}
H_2O												
H_3PO_4	0	520.483	250.073	910.317	526.990	647.764	357.679	365.687	44.078	49.014	248.822	600.315
$H_2PO_4^-$	250.143	0	250.168	100.032	98.097	20.002	110.035	10.003	200.064	300.324	3,024.813	229.183
HPO_4^{2-}	300.106	60.015	0	50.016	30.003	560.179	90.028	26.909	657.355	91.093	460.259	250.173
PO_4^{3-}	150.108	1511.596	810.931	0	2,553.024	136.163	855.597	461.544	444.525	240.837	660.685	590.604
H^+	250.160	29.933	914.008	410.421	0	25.008	601.132	80.148	74.233	579.049	50.059	305.127
OH^-	90.040	720.746	250.160	250.173	400.301	0	510.163	241.243	551.051	902.689	36.840	356.666
$H_5P_2O_8^-$	48.082	110.103	243.245	30.013	250.073	250.173	0	1,318.960	610.175	24.927	911.699	601.073
$H_6P_2O_8$	25.037	10.011	15.026	500.210	35.910	800.441	250.168	0	350.246	39.944	250.073	981.398
Mg^{2+}	310.548	401.738	21.032	421.792	228.427	611.143	268.093	700.365	0	250.073	100.010	59.967
HA	250.073	910.317	526.990	64.121	37.321	365.687	44.078	49.014	248.822	0	600.315	29.903
MgA_26HA	250.168	100.032	94.093	110.103	110.035	20.014	200.064	30.023	321.810	28.964	0	300.106
SO_4^{2-}	60.015	50.016	30.003	560.179	90.028	227.133	657.355	10.004	460.259	250.173	150.108	0
Kerosene												
H_3PO_4	0	110.031	−802.822	250.465	13.024	855.597	46.080	44.078	24.597	70.038	60.027	250.160
$H_2PO_4^-$	250.173	0	70.068	−556.741	986.972	99.849	574.728	244.808	238.826	2388.254	106.528	1,033.361
HPO_4^{2-}	189.367	300.332	0	47.052	23.025	14.015	159.176	32.035	36.039	1.001	147.162	12.013
PO_4^{3-}	10.011	20.022	84.093	0	865.958	632.700	95.105	14.015	45.049	250.277	74.082	15.016
H^+	52.057	40.044	98.108	35.038	0	79.087	100.110	20.022	45.049	30.033	80.088	156.172
OH^-	423.468	368.407	269.298	248.274	321.355	0	148.164	75.083	42.046	159.176	78.086	322.356
$H_5P_2O_8^-$	47.052	23.025	14.015	159.176	32.035	36.039	0	1.001	147.162	12.013	10.011	20.022
$H_6P_2O_8$	84.093	24.927	150.108	110.031	801.821	250.465	133.159	0	855.597	465.548	445.526	254.853
Mg^{2+}	−620.639	510.517	1026.005	250.173	50.046	4096.573	25.008	165.721	0	160.376	−347.985	59.466
HA	101.111	20.022	3.003	4.004	5.005	6.006	7.007	8.008	9.009	0	444.525	240.837
MgA_26HA	660.685	590.604	252.160	29.933	914.008	410.421	25.008	601.132	80.148	74.233	0	579.049
SO_4^{2-}	50.059	1,938.570	1,889.273	1,378.756	1,689.128	2,359.594	2,456.899	218.742	4,103.042	578.081	237.966	0

Table B1
UNIQUAC interaction parameters a_{ij}^{*}-system 2

	H_2O	Dodecane	H_3PO_4	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}	H^+	OH^-	$H_5P_2O_8^-$	$H_6P_2O_8$	Cd^{2+}	HR	CdR_2	SO_4^{2-}
H_2O	0	20.493	10.975	67.849	19.956	69.848	94.796	35.923	71.849	12.973	72.849	12.973	2.993	28.942
Dodecane	141.841	0	11.687	23.334	41.919	103.293	−117.273	240.629	3420.683	326.647	480.583	123.141	225.235	199.134
H_3PO_4	−250.083	4.586	0	620.662	541.570	250.169	241.239	983.124	410.437	−215.223	602.156	511.651	404.6,163	58.468
$H_2PO_4^-$	504.574	3,908.235	8,199.470	0	798.858	2,412.628	250.183	3,921.392	510.183	24.388	5.436	17.720	362.209	1,237.699
HPO_4^{2-}	487.591	20.003	240.251	250.262	0	26.811	10.172	458.525	341.902	140.379	30.515	62.472	25.038	10.012
PO_4^{3-}	125.155	397.107	3526.921	793.463	250.178	0	313.063	359.312	298.342	9811.444	3,112.782	4,016.845	213.253	4,219.217
H^+	2,260.776	617.173	268.103	7,006.548	250.083	−910.956	0	592.5872	243.075	904.345	527.010	644.785	357.693	365.702
OH^-	445.543	49.016	248.831	59.728	250.153	250.178	992.039	0	904.031	191.197	−110.039	904.028	200.072	300.336
$H_5P_2O_8^-$	301.800	229.192	298.116	540.576	480.503	730.803	560.199	891.968	0	263.184	65.694	952.096	460.277	24.929
$H_6P_2O_8$	150.113	110.035	801.851	250.474	133.165	855.629	465.566	445.543	254.862	0	−620.662	510.536	1,026.043	250.1829
Cd^{2+}	50.047	4096.730	25.009	601.154	800.983	174.346	58.468	501.571	305.139	891.954	0	280.275	250.169	250.1830
HR	400.316	510.183	275.290	551.072	902.723	637.526	356.680	48.085	20.003	233.243	293.311	0	250.083	250.1830
CdR_2	1,319.010	610.198	24.928	911.733	601.097	25.038	10.011	15.027	500.229	35.911	800.472	250.178	0	350.2592
SO_4^{2-}	39.946	250.0829	981.436	310.560	401.753	2,223.532	421.808	228.435	744.0	268.103	700.391	250.083	1,000.058	0

Table B2
$\delta_{ij,m}$ parameters

	H_3PO_4	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}	H^+	OH^-		$H_5P_2O_8^-$	$H_6P_2O_8$	$Cd2^+$	HR	CdR_2
H_2O												
H_3PO_4	0	520.503	250.082	910.352	527.010	647.788	H_3PO_4	357.692	365.701	44.080	49.016	248.831
$H_2PO_4^-$	250.153	0	250.178	100.036	98.101	20.002	$H_2PO_4^-$	110.039	10.003	200.072	300.335	3,024.928
HPO_4^{2-}	300.118	60.017	0	50.018	30.004	560.199	HPO_4^{2-}	90.032	26.910	657.379	91.097	460.276
PO_4^{3-}	150.113	1511.653	810.861	0	2,553.121	136.168	PO_4^{3-}	855.629	461.561	444.542	240.846	660.710
H^+	250.169	29.934	914.043	410.436	0	25.009	H^+	601.154	80.151	74.235	579.071	50.061
OH^-	90.043	720.773	250.169	250.183	400.316	0	OH^-	510.183	241.252	551.072	902.723	36.841
$H_5P_2O_8^-$	48.084	110.107	243.254	30.0149	250.082	250.183	$H_5P_2O_8^-$	0	1,319.010	610.198	24.928	911.733
$H_6P_2O_8$	25.038	10.011	15.026	500.229	35.911	800.472	$H_6P_2O_8$	250.178	0	350.259	39.946	250.083
Cd^{2+}	310.560	401.753	21.033	421.807	228.435	611.166	Cd^{2+}	268.103	700.391	0	250.083	100.013
HR	250.083	910.352	527.010	64.124	37.322	365.701	HR	44.080	49.016	248.831	0	600.337
CdR_2	250.178	100.036	94.096	110.107	110.039	20.015	CdR_2	200.072	30.024	321.823	28.965	0
SO_4^{2-}	60.017	50.018	30.004	560.199	90.032	227.142	SO_4^{2-}	657.379	10.005	460.277	250.182	150.113
Dodecane												
	H_3PO_4	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}	H^+	OH^-	$H_5P_2O_8^-$	$H_6P_2O_8$	Cd^{2+}	HR	CdR_2	SO_4^{2-}
H_3PO_4	0	110.035	−802.852	250.474	13.024	855.629	46.082	44.080	24.598	70.041	60.029	250.169
$H_2PO_4^-$	250.182	0	70.070	−556.763	987.010	99.853	574.749	244.817	238.835	2,388.344	106.532	1,033.400
HPO_4^{2-}	189.374	300.343	0	47.053	23.0263	14.0160	159.182	32.036	36.041	1.001	147.168	12.013
PO_4^{2-}	10.011	20.022	84.096	0	865.991	632.724	95.108	14.016	45.051	250.286	74.084	15.017
H^+	52.059	40.045	98.112	35.040	0	79.090	100.114	20.022	45.051	30.034	80.091	156.178
OH^-	423.484	368.421	269.308	248.284	321.367	0	148.169	75.085	42.048	159.182	78.089	322.369
$H_5P_2O_8^-$	47.053	23.026	14.016	159.182	32.036	36.041	0	1.001	147.168	12.013	10.011	20.022
$H_6P_2O_8$	84.096	24.928	150.113	110.035	801.851	250.474	133.164	0	855.620	358.410	445.948	214.816
Cd^{2+}	−620.662	580.614	104.619	260.194	420.467	2,094.410	25.009	15.557	0	147.366	347.998	59.468
HR	101.115	20.002	3.003	4.004	5.005	6.006	$H_5P_2O_8^-$	$H_6P_2O_8$	Cd^{2+}	HR	CdR_2	SO_4^{2-}
CdR_2	660.710	590.625	250.169	29.934	914.042	410.436	46.082	44.080	24.598	70.041	60.029	250.169
SO_4^{2-}	50.060	1,938.642	1,889.343	1,378.807	1,689.193	2,359.682	574.749	244.817	238.835	2,388.344	106.532	1,033.400