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Determination of Phase Equilibria and Densities for the Quaternary System Toluene + Acetone + Phenol + Water

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The success of modeling mass transfer depends strongly on the accurate description of the physical properties of the system involved. In the case of two liquid phases the knowledge of the liquid−liquid equilibrium is of special importance. This knowledge gains importance when the transfer of multiple species is to be modeled, as more complex interactions have to be considered. These can only be described with advanced mass-transfer models, such as the Stefan−Maxwell model, with a high demand on accuracy in the description of physical properties. The quaternary system toluene + acetone + phenol + water is being considered as a possible new standard test system for the investigation of multicomponent mass transfer in liquid−liquid extraction. Equilibrium data are needed: experimentally determined tie-line data at 20 °C are now presented for this system. The results are correlated with the UNIQUAC model using different objective functions. The resulting calculated data sets are compared considering their accuracy and applicability to multicomponent mass-transfer description. The densities of various mixtures of the system have been measured and correlated.

Introduction

The description of mass transfer in liquid−liquid systems is mostly limited to the case of single-transferred species. But even in the most simple system in liquid−liquid extraction, that is, two solvents and one solute, multicomponent mass transfer is apparent as the solubilities of the solvents change with solute concentration. The investigation of these multicomponent effects on mass transfer in liquid−liquid extraction has been the subject of some recent studies (Zimmermann et al., 1995; Toutain et al., 1998; von Reden, 1998). To increase the value of further studies on the subject, both theoretical and experimental, it seems worthwhile to establish a quaternary standard test system, such as those available for ternary systems (Misek et al., 1985), as its use can significantly increase the comparability of results of different studies (Hartland and Steiner, 1983; Gourdon et al., 1991).

A proposed quaternary test system (toluene + acetone + phenol + water) was introduced by von Reden et al. (1996). It is based on the ternary test system toluene + acetone + water recommended by the European Federation of Chemical Engineering (EFCE), which is extended with the second solute, phenol. The solute combination phenol + acetone is involved in phenol/acetone production with the Hock process as well as being relevant to the industrial process of caprolactam manufacture.

The system investigated is a type II quaternary system and is represented schematically in Figure 1. Liquid−liquid equilibrium tie-line data are available for the ternary subsystem water + acetone + toluene from Sørensen and Arlt (1980), Vol. 5, Part 2. Binodal curves are available for the system water + acetone + phenol (Schreinemakers, 1900) (note the date!). The binary solubilities of the immiscible pairs toluene + water and phenol + water are also available from Sørensen and Arlt (1980), Vol. 5, Part 1, pp 448 and 356, respectively. The subsystem acetone + phenol + toluene is found to be completely miscible. No data are available for the fourth ternary subsystem or for the full quaternary system.

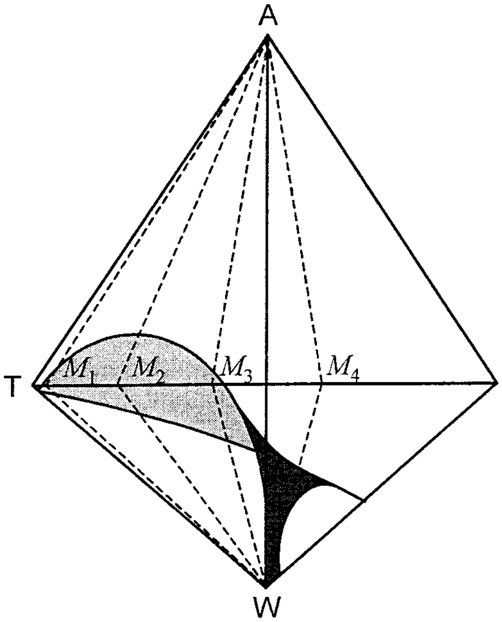

Figure 1. Schematic representation of the phase equilibrium of the quaternary system toluene (T) + acetone (A) + phenol (P) + water (W) at 20 °C; M_i denote quaternary sectional planes ($M = w_P/(w_P + w_T)$; $M_1 = 0.02$, $M_2 = 0.2$, $M_3 = 0.4$, $M_4 = 0.6$).

In preliminary studies literature parameters were used to model the solubility surface of the quaternary system. The resulting solute distribution coefficients showed unacceptably large errors of up to 80% when compared with results of preliminary distribution coefficient experiments

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(von Reden, 1998). A more detailed investigation was therefore necessary. The present study provides results for the liquid−liquid equilibrium of the full quaternary system, as well as the concentration dependency of the density of aqueous and organic mixtures of the constituents, both at 20 °C. The knowledge of both is essential for the success of any modeling attempt of the multicomponent mass-transfer process (von Reden, 1998).

Experimental Section

Chemicals and Equipment. The acetone, phenol, and toluene used in this study were obtained from Aldrich and were all HPLC grade (stated purity > 99%, which has been checked by Karl Fischer titration and gas chromatographic analysis). The acetone and toluene were used without further purification, while the phenol was dried over silica gel in a vacuum desiccator before use. Single-distilled water was used for the liquid−liquid equilibrium experiments, while for the density measurements double-distilled water was produced on the day of the experiment.

The glassware used in the experiments was meticulously cleaned by overnight soaking in a 5% Decon 90 solution (obtained from BDH Laboratory Supplies, U.K.) prior to repeated rinsing with distilled water and acetone. Clean glassware was dried in an oven at 90 °C and stored in a desiccator.

Liquid−Liquid Equilibrium Determination. Measurement Technique. Different methods of obtaining experimental phase equilibrium data are described in the literature, for example, Ruiz et al. (1985). Their usefulness depends strongly on the kind of system and the available analytical methods to measure solute concentrations. The method most often used for quaternary systems is the method of analysis, where one prepares a mixture in the heterogeneous concentration region, allows the phases to separate, and measures the concentrations of the minor components in each of the phases.

For this study the solute concentrations of acetone, phenol, and toluene were determined by gas chromatography (GC) with a Perkin-Elmer PE8300 gas chromatograph. The calibration was made with nonane (organic phase) and 2-propanol (aqueous phase) as internal standards. Each sample was analyzed three times, and a mean value has been used. The water content of the organic phase was determined by Karl Fischer (KF) titration with a Mettler DL18 automatic titrator with the use of Riedel-de-Haën's Hydranal solutions to allow for water determination in the presence of ketones. Each sample was analyzed twice, and the mean value was used.

The relative errors of the mass ratio measurements employed in this study were tested with mixtures of known concentration and lie between 1 and 5%, depending on species and concentration range.

The initial concentrations for the equilibrium experiments were chosen following the procedure for type II quaternary systems described by Ruiz et al. (1984), which is based on the method developed by Chang and Moulton (1953). The quaternary system toluene (T)−acetone (A)−water (W)−phenol (P) is schematically shown in Figure 1. To be able to accurately describe the full solubility surface, tie lines for different quaternary heterogeneous mixtures, which lie on four different planes, such as W + A + M, were determined.

The initial solutions were selected in order to distribute the resulting tie lines regularly over the heterogeneous region. The following rules were applied:

(i) M represents mixtures of toluene and phenol and, therefore, defines quaternary sectional planes of the tetrahedron. To cover the desired concentration range, M was chosen to be $M = w(w_P + w_T) = 0.04$, 0.2, 0.4, and 0.6, where w_i denote mass fractions.

(ii) The water concentration was chosen to be $w_W = w_P + w_T$.

(iii) The acetone mass fractions in the initial solutions L were chosen to be approximately $L = 0.05$, 0.10, 0.15, and 0.20.

This results in four different sets of four experiments each. All experimental sets were repeated once (except the fourth set with $M = 0.4$, which was not repeated).

For one set of experiments, four different mixtures of the four constituents were weighed in 50 mL separation funnels on a Mettler PJ300 balance with a precision of ±0.001 g and sealed. After intensive stirring of the mixtures with a Teflon-coated magnetic stirrer for about 4 h, the separation funnels were placed in a temperature controlled water bath at 20.0 °C (±0.1 °C) for at least 48 h. Preliminary experiments showed that this time was adequate for equilibrium to have been reached.

For the sampling procedure one separation funnel was removed from the water bath and unsealed. Approximately 20 mg of cooled nonane (the internal standard for the organic phase) was weighed in a 0.8 mL glass vial using a 25 μL micropipet. Approximately 0.6 g of organic phase was then taken from the separation funnel with a micropipet through the top opening, the sample was added to the vial, and the mass was recorded. The weighing of the internal standards and samples was done with a Mettler AC100 balance with a precision of ±0.0001 g. The vial was then sealed with a Teflon-coated crimp cap for analysis, and the whole process was repeated for a second sample, and the results were averaged. A 15 mL screw cap sample vial was then filled with organic phase using a 5 mL pipet. This sample was later used for water analysis by Karl Fisher titration.

Once the large sample was taken from the organic phase, the samples from the aqueous phase were immediately taken by filling two 1.5 mL plastic sample vials through the bottom opening of the separation funnel. A 0.8 mL glass vial was prepared by weighing 20 mg of 2-propanol (the internal standard for the aqueous phase) into it. Approximately 0.7 g of aqueous phase was then transferred from the plastic vial into the glass vial with a micropipet. Finally, the mass was recorded and the vial sealed for analysis. A second aqueous sample was prepared from the second plastic vial by following the same procedure, and the results were averaged.

By taking samples first from the organic phase and then from the aqueous phase through the two different openings of the separation funnel, cross-contamination between the two phases was minimized. Evaporation of volatile compounds (especially acetone) is minimized through the short duration of the procedure. Effects due to temperature changes of the mixture during the sampling process can be neglected for the same reason.

Density Measurements. Measurement Technique. The densities of the ternary systems toluene + acetone + phenol and water + acetone + phenol and their binary subsystems were determined using a Paar DMA 46 meter. The mixtures to be measured were chosen by considering the concentration range typically found in liquid−liquid extraction systems. As the phenol solubility in water is limited and decreases with increasing acetone concentration, mixtures that showed cloudiness were discarded.

Table 1. Comparison of Experimental and Literature Density Data at 20 °C

	ρ_{lit}/kg·m^{-3}	ρ_{exp}/kg·m^{-3}
water (calibration)	998.2	998.2
toluene	866.9	866.9
acetone	790.5	790.0

Table 2. Tie Lines for the Quaternary System Toluene + Acetone + Phenol + Water at 20 °C after Application of the Reconciliation Test by Gomis et al. (1997)[a]

organic phase				aqueous phase			
x_T	x_A	x_P	x_W	x_T	x_A	x_P	x_W
0.862	0.090	0.035	0.0130	0.0001	0.0172	0.0010	0.982
0.749	0.195	0.032	0.0239	0.0002	0.0415	0.0007	0.958
0.698	0.243	0.029	0.0301	0.0003	0.0532	0.0006	0.946
0.611	0.314	0.029	0.0456	0.0004	0.0734	0.0006	0.926
0.693	0.083	0.168	0.0563	0.0001	0.0053	0.0050	0.990
0.629	0.157	0.154	0.0597	0.0001	0.0164	0.0037	0.980
0.519	0.284	0.119	0.079	0.0003	0.0554	0.0030	0.941
0.686	0.099	0.162	0.052	0.0002	0.0072	0.0046	0.988
0.626	0.160	0.155	0.059	0.0002	0.0174	0.0037	0.979
0.496	0.296	0.122	0.086	0.0002	0.0464	0.0025	0.951
0.471	0.077	0.307	0.145	0.0001	0.0027	0.0080	0.989
0.432	0.142	0.284	0.142	0.0001	0.0076	0.0062	0.986
0.390	0.211	0.257	0.142	0.0001	0.0156	0.0046	0.980
0.336	0.286	0.222	0.156	0.0002	0.0326	0.0040	0.963
0.475	0.085	0.298	0.142	0.0001	0.0033	0.0082	0.988
0.434	0.144	0.283	0.139	0.0001	0.0078	0.0063	0.986
0.378	0.224	0.250	0.147	0.0002	0.0188	0.0045	0.977
0.345	0.278	0.223	0.153	0.0002	0.0324	0.0041	0.963
0.273	0.069	0.390	0.268	0.0001	0.0021	0.0104	0.987
0.289	0.129	0.357	0.225	0.0001	0.0057	0.0080	0.986
0.281	0.183	0.324	0.211	0.0001	0.0108	0.0063	0.983
0.864	0.088	0.035	0.0126	0.0002	0.0165	0.0011	0.982
0.744	0.205	0.029	0.0217	0.0002	0.0414	0.0006	0.958
0.691	0.252	0.028	0.0294	0.0004	0.0632	0.0007	0.936
0.556	0.365	0.027	0.0521	0.0005	0.0873	0.0006	0.912
0.937	0.059		0.0040	0.0001	0.0164		0.984
0.905	0.089		0.0054	0.0001	0.0233		0.977
0.810	0.174		0.0156	0.0002	0.0445		0.955
0.688	0.279		0.0334	0.0004	0.0721		0.928
0.447	0.480		0.0734	0.0010	0.129		0.870
		0.333	0.6670			0.0155	0.985
1.000			0.0001	0.0022			0.998

[a] The ternary data sets are taken from Sørensen and Arlt (1980), Vol. 5, Part 2, p 501. The solubilities of phenol and toluene in water are taken from Sørensen and Arlt (1980), Vol. 5, Part 1, pp 356 and 448, respectively.

The mixtures were weighed in a 15 mL sample bottle with a Mettler AC100 balance with a precision of ±0.0001 g. The most volatile compound was introduced last, and the sample bottle was immediately sealed with a Teflon crimp cap. Therefore, evaporation of the sample can be excluded and the accuracy of the weighing process is thought to be similar to the precision of the balance. For the density measurements calibration with air and water leads to an accuracy of $\pm 1 \times 10^{-4}$ g/cm^3 in the range 0.5–1.5 g/cm^3. The temperature of the system can be controlled via Peltier elements with a precision of ±0.01 K.

The samples were transferred from the sealed sample vials to the density meter via a glass syringe with a hypodermic needle attached. This allowed the transfer of the sample without loss of volatile components. For the actual measurement, about 5 mL of the sample was flushed through the measurement capillary to guarantee the removal of the previous sample. The final filling was observed visually to ensure the complete filling of the capillary. After filling, the open end of the capillary was closed with a Teflon plug and temperature equilibration was allowed until no change of the measured density value was observed with time. This typically took 3 min.

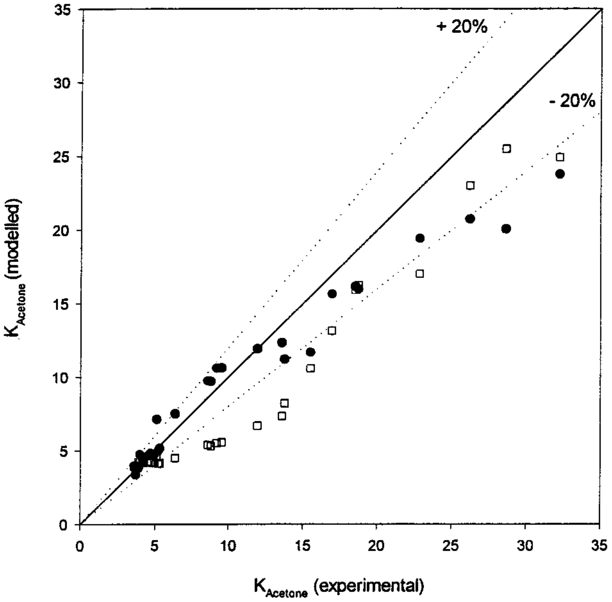

Figure 2. Comparison between experimental and calculated acetone distribution coefficients (□) calculated with UNIQUAC parameters from the literature (see von Reden (1998)); (●) calculated with UNIQUAC parameters from the new correlation.

Table 3. Deviations of LLE Correlations

objective function	mean deviation	β-dev (W)	β-dev (A)	β-dev (P)	β-dev (T)
f_I	0.0036	0.0920	0.2367	168.6	4.215
f_{II}	0.0101	0.1803	0.2317	0.1396	0.2162
f_{III}	0.0103	0.1965	0.1735	0.1015	0.1876
f_{IV}	0.0207	0.3530	0.8028	0.9110	0.1539

Table 4. UNIQUAC Parameter Set Resulting from Correlation with f_{III} (All Parameters are in K)

	water	acetone	phenol	toluene
water		−108.7	421.4	364.1
acetone	400.8		70.62	−133.4
phenol	−198.7	−300.8		−14.40
toluene	929.6	234.6	142.6	

The measurements were performed twice for each mixture in sets of 10 samples. A set was started with the confirmation of the calibration of the apparatus with the pure solvent (water or toluene) and air. After 10 measurements, the capillary was flushed with acetone and the density was measured for calibration. After the following measurement of air, the density measurements of the mixtures were repeated in reverse order. Finally the density of the pure solvent was measured again.

The results of the calibration checking experiments were always within one digit of previously measured data. In Table 1 the measured densities of pure acetone and toluene based on the calibration with double-distilled water are compared with literature values from Vargaftik (1975). The agreement is satisfactory.

Liquid−Liquid Equilibrium Modeling. The UNIQUAC model (Abrams and Prausnitz, 1975) is a suitable G^E model for describing the quaternary liquid−liquid equilibrium of the present type (Ruiz and Gomis, 1986). The quality of the modeling results depends on the quality of the binary interaction parameters available. Binary parameters regressed from experimental binary liquid−liquid equilibrium data will describe the binary LLE with the most accuracy. These parameters can also be used to predict ternary equilibria if the missing parameters of the other two binary pairs are added. The quality of these

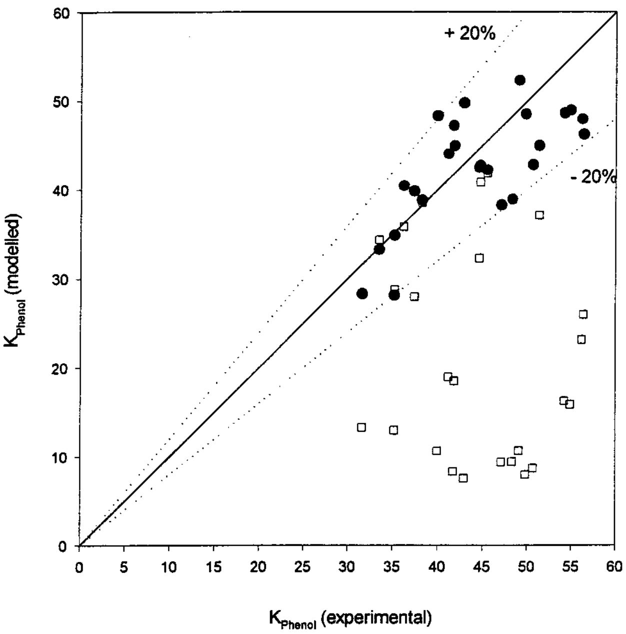

Figure 3. Comparison between experimental and calculated phenol distribution coefficients (□) calculated with UNIQUAC parameters from the literature (see von Reden (1998)); (●) calculated with UNIQUAC parameters from the new correlation.

Table 5. Density Data for the Organic Phase (Toluene + Acetone + Phenol)[a]

x_A	x_P	ρ_{exp}/kg·m^{-3}	ρ_{calc}/kg·m^{-3}	r (%)
0.0000	0.0000	866.9	866.9	0.00
1.0000	0.0000	790.0	790.0	0.00
0.0000	0.0029	867.3	867.4	0.01
0.0000	0.0109	868.7	868.9	0.01
0.0000	0.0978	884.6	884.7	0.02
0.0000	0.1953	902.2	903.0	0.09
0.0057	0.0000	866.6	866.6	0.01
0.0016	0.0000	866.7	866.8	0.01
0.0177	0.0000	866.0	866.1	0.01
0.0692	0.0000	863.4	863.7	0.03
0.1468	0.0000	859.5	859.7	0.02
0.3518	0.0000	847.3	847.3	0.00
0.6127	0.0000	828.4	827.6	0.10
0.0079	0.0048	867.4	867.4	0.00
0.0074	0.0098	868.3	868.4	0.00
0.0075	0.0976	884.4	884.4	0.00
0.0075	0.1950	902.7	902.8	0.01
0.0162	0.0048	867.0	867.1	0.00
0.0158	0.0099	868.0	868.0	0.00
0.0164	0.0981	884.2	884.2	0.00
0.0163	0.1929	902.2	902.2	0.00
0.0805	0.0048	863.9	864.0	0.02
0.0790	0.0097	864.2	865.0	0.09
0.0787	0.0958	881.8	881.5	0.03
0.0809	0.1902	900.3	900.0	0.03
0.1527	0.0047	860.2	860.3	0.01
0.1509	0.0093	861.2	861.3	0.02
0.1493	0.0908	877.8	877.6	0.02
0.1501	0.1860	897.3	897.0	0.03
0.3454	0.0042	848.7	848.7	0.00
0.3457	0.0088	849.7	849.7	0.00
0.3459	0.0857	866.7	866.7	0.00
0.3464	0.1718	885.9	886.1	0.01

[a] Relative difference $r = |\rho_{exp} - \rho_{calc}|/((\rho_{exp} + \rho_{calc})/2) \times 100\%$.

Table 6. Density Data for the Aqueous Phase (Acetone + Phenol + Water)[a]

x_A	x_P	ρ_{exp}/kg·m^{-3}	ρ_{calc}/kg·m^{-3}	r (%)
0.0000	0.0000	998.2	997.8	0.04
0.0000	0.0024	998.4	998.1	0.04
0.0000	0.0050	998.6	998.4	0.03
0.0000	0.0103	999.2	998.9	0.02
0.0000	0.0153	999.6	999.4	0.02
0.0000	0.0180	999.8	999.7	0.01
0.0000	0.0209	1000.2	1000.0	0.02
0.0000	0.0289	1000.9	1000.8	0.01
0.0000	0.0395	1002.0	1001.9	0.01
0.0000	0.0480	1002.7	1002.7	0.00
0.0021	0.0000	997.9	997.7	0.02
0.0045	0.0000	997.7	997.5	0.02
0.0077	0.0000	997.3	997.2	0.01
0.0080	0.0400	1001.2	1001.3	0.01
0.0080	0.0194	999.3	999.2	0.01
0.0087	0.0391	1001.1	1001.1	0.00
0.0092	0.0486	1002.0	1002.0	0.00
0.0147	0.0049	997.3	997.2	0.01
0.0154	0.0100	997.7	997.7	0.00
0.0171	0.0000	996.6	996.5	0.00
0.0285	0.0389	999.4	999.4	0.00
0.0295	0.0057	996.1	996.2	0.01
0.0298	0.0189	997.3	997.4	0.01
0.0319	0.0049	995.8	995.9	0.01
0.0322	0.0097	996.2	996.3	0.01
0.0323	0.0103	996.2	996.4	0.02
0.0334	0.0483	999.8	999.8	0.00
0.0351	0.0000	995.1	995.2	0.01
0.0591	0.0049	993.4	993.7	0.03
0.0714	0.0096	992.8	993.1	0.03
0.0731	0.0377	995.3	995.3	0.00
0.0741	0.0096	992.5	992.9	0.03
0.0756	0.0200	993.4	993.6	0.02
0.0776	0.0192	993.1	993.4	0.02
0.0790	0.0000	991.1	991.6	0.06
0.0848	0.0047	991.1	991.5	0.05
0.0879	0.0383	993.9	993.9	0.00
0.1213	0.0095	988.3	988.6	0.03
0.1367	0.0046	986.6	986.8	0.03
0.1401	0.0194	987.5	987.5	0.00
0.1515	0.0000	984.8	985.1	0.04
0.2360	0.0043	977.1	976.8	0.02
0.2858	0.0088	972.1	971.4	0.07
0.2886	0.0179	972.3	971.3	0.10
0.2892	0.0000	971.1	970.8	0.03
0.4874	0.0173	944.3	944.9	0.06

[a] Relative difference $r = |\rho_{exp} - \rho_{calc}|/((\rho_{exp} + \rho_{calc})/2) \times 100\%$.

modeling results will not be as high as the quality of the modeling results when binary parameters are used that are regressed from experimental ternary equilibrium data. The same principle can be transferred to the quaternary case. The best modeling results can be achieved by using binary parameters that are regressed from experimental quaternary equilibrium data, while modeling with binary parameters from ternary LLE, binary LLE, or VLE data will result in poorer accuracy. Complementary to the use of quaternary experimental tie-line data, it is advisable to add the solubilities of the binary systems to establish the correct limits of the solubility surface (Ruiz and Gomis, 1986).

Results and Discussion

Liquid–Liquid Equilibria. The determination of liquid–liquid equilibrium data has the disadvantage, compared with the determination of VLE data, that there is no such thing as a “thermodynamic consistency test” (Sørensen et al., 1979). Therefore, other ways of reconciliation of experimental data have to be found. One suitable method is to verify the mass balances for all components using the error of measurement inherent in each value. This method—a description of which can be found in Gomis et al. (1997)—was used here to confirm the correctness of the data. The application of this program leads to the rejection of three experimental tie lines. The concentrations (mole fractions, x) of the tie lines after application of the reconciliation test can be found in Table 2.

Table 7. Density Correlation Results

	organic phase				aqueous phase			
type of model	data pts	no. of param	S_R	max. rel diff (%)	data pts	no. of param	S_R	max. rel diff (%)
mixing rule (eq 5)	33	0	7.65	1.9	46	0	5.71	2.30
quadratic mixing rule (eq 6)	33	6	0.29	0.1	46	6	0.31	0.97
cubic mixing rule for ternary systems (eq 7)	33	10	0.51	0.2	46	10	0.05	0.01

Table 8. Parameters for the Quadratic Mixing Rule

	A_0	A_1	A_2	A_3	A_4	A_5
aq phase	997.811	−72.815	108.507	−71.069	−124.926	−277.667
org phase	866.900	−44.088	179.557	−32.812	27.056	113.239

The data set was then used to find four sets of binary UNIQUAC interaction parameters resulting from the minimization of four different objective functions, as follows:

Minimization of absolute difference:

$$f_{\mathrm{I}} = \sum_k \sum_i \sum_j (x_{\mathrm{exp}} - x_{\mathrm{cal}})^2 \quad (1)$$

Minimization of relative difference:

$$f_{\mathrm{II}} = \sum_k \sum_i \sum_j \left(\frac{x_{\mathrm{exp}} - x_{\mathrm{cal}}}{x_{\mathrm{exp}}} \right)^2 \quad (2)$$

Minimization of absolute distribution coefficients:

$$f_{\mathrm{III}} = \sum_k \sum_i \left(\frac{x_{\mathrm{exp}}^{\mathrm{org}}}{x_{\mathrm{exp}}^{\mathrm{aq}}} - \frac{x_{\mathrm{cal}}^{\mathrm{org}}}{x_{\mathrm{cal}}^{\mathrm{aq}}} \right)^2 \quad (3)$$

Minimization of relative distribution coefficients:

$$f_{\mathrm{IV}} = \sum_k \sum_i \left(\left(\frac{x_{\mathrm{exp}}^{\mathrm{org}}}{x_{\mathrm{exp}}^{\mathrm{aq}}} - \frac{x_{\mathrm{cal}}^{\mathrm{org}}}{x_{\mathrm{cal}}^{\mathrm{aq}}} \right) \Big/ \frac{x_{\mathrm{exp}}^{\mathrm{org}}}{x_{\mathrm{exp}}^{\mathrm{aq}}} \right)^2 \quad (4)$$

where i denotes the component, j the phase, and k the tie line.

The correlation procedure has been explained elsewhere (Ruiz and Gomis, 1986). For the correlation, additional binary and ternary data sets have been included from Sørensen and Arlt (1980) to represent the effects of the respective subsystems. These tie lines are shown in Table 2 as the final seven data sets.

A comparison of the four correlations regarding the mean deviations and distribution coefficient deviations (β-deviations) is shown in Table 3.

While f_{I} shows the lowest mean deviation, f_{III} gives the best correlation concerning the distribution coefficient deviations of the two solutes acetone and phenol. These are of great importance for the description of mass transfer, and f_{III} is therefore considered most suitable. The resulting parameter set is shown in Table 4.

The quality of the predictions is shown in Figures 2 and 3, where experimental and calculated distribution coefficient values of acetone and phenol are compared. Most calculated values have a relative deviation of less than 20%, much less than the prediction based on the literature parameters—especially in the case of phenol, as there were no experimental data previously available.

Density Measurements. Density Data. The results of the density measurements for the organic and the aqueous phase are presented in Tables 5 and 6.

To correlate the measured density data, the following equations were tested concerning their prediction quality:

Linear Mixing Rule—based on mass fractions w_i:

$$\rho_{\mathrm{mixture}} = w_1\rho_1 + w_2\rho_2 + w_3\rho_3 \quad (5)$$

Quadratic Mixing Rule—based on mole fractions x_i (Misek et al., 1985):

$$\rho_{\mathrm{mixture}} = A_0 + x_1A_1 + x_2A_2 + x_1^2A_3 + x_2^2A_4 + x_1x_2A_5 \quad (6)$$

Cubic Mixing Rule for a ternary system—based on mole fractions x_i (Paschke et al., 1993):

$$\rho_{\mathrm{mixture}} = x_1^3A_{01} + x_2^3A_{02} + x_3^3A_{03} + \sum_{i<j}(x_i^2x_jA_{iij} + x_ix_j^2A_{ijj}) + x_1x_2x_3A_{123} \quad (7)$$

The resulting accuracies of the correlations are shown in Table 7. The accuracy is demonstrated as the average deviation S_R, and additionally the largest relative difference between experimental and correlated values is shown.

$$S_R = \sqrt{\frac{\sum_{i=1}^{n}(\rho_{\mathrm{exp}} - \rho_{\mathrm{corr}})_i^2}{n - m}} \quad (8)$$

with n = number of data points and m = number of parameters.

While the simple mixing rule (eq 5) gives unsatisfactory correlation results with maximum relative errors larger than 2%, the quadratic mixing rule offers a good balance between accuracy and number of parameters. The parameters to correlate the mixtures are given in Table 8. The resulting density values are shown next to the experimental values in Tables 5 and 6.

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