

Extraction of Acetic Acid with Tri-*n*-octylamine: Physical Properties and Phase Equilibria

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The effect of sodium chloride, hydrochloric acid, and sodium acetate on the partitioning between aqueous solutions and tri-*n*-octylamine has been studied at 298 K. Physical properties (density, viscosity, and interfacial tension) have been determined for the salt-free systems. The equilibrium data of the simultaneous extraction of acetic acid and hydrochloric acid is described well with a model that includes the formation of organic complexes and the dissociation equilibria in the aqueous phase. The Pitzer equation was used for the aqueous phase and the Hildebrand and Scott solubility parameters were used to describe nonidealities in the organic phase.

Introduction

The extraction of organic acids with ternary amines has been widely studied for the treatment of fermentation broths and wastewater streams.^{1–6} Most of the investigations consider only the partitioning of acetic acid and impurities or cosolutes have been neglected. In fermentation broths and wastewater streams salts are also dissolved, which influence the extraction of the organic acid.

In the presence of sodium chloride, the extraction of acetate ions (Ac⁻) leads to a simultaneous extraction of chloride. The following aqueous species will influence the extraction process: HAc, NaAc, Ac⁻, Cl⁻, H⁺, and Na⁺. The equilibrium model based on chemical potential theory for such a complex system and the physical properties for the salt-free basic system are presented.

Experimental Section

Reagents. Hydrochloric acid (FIXANAL, Riedel de Haen), sodium chloride (ROTIPURAN, >99.5%), acetic acid (ROTIPURAN, >99.7%), and sodium acetate (Riedel de Haen, >99%) were used to prepare the acid solutions of various concentrations. Tri-*n*-octylamine (tri-*n*-octylamine, >95% by Henkel) was diluted in toluene (Riedel de Haen, >99.7%). The physical properties are given also for the solvent isododecane (EC Erdölchemie GmbH, purity >98%), which consists mainly of pentamethylheptane. All chemicals except tri-*n*-octylamine (washed once with aqueous NaOH solution) were used without further purification.

Methods. The determination of the acid concentration in the aqueous and organic solutions was performed with an autotitrator (METTLER DL25) with NaOH (FIXANAL, Riedel de Haen). The concentrations of the different anions were obtained (after titration) with an ion chromatography system (DIONEX DX500). To determine the fraction of the anions from the ratio of the peak area, an eluent of 0.05 N NaOH at a flow of 2 mL/min was used. The maximal

Table 1. Physical Properties of Tri-*n*-octylamine (1) and Toluene (2) at 298 K

x_1	$\rho/\text{kg m}^{-3}$	$\eta/\text{mPa s}$	x_1	$\rho/\text{kg m}^{-3}$	$\eta/\text{mPa s}$
0.000	861.8	0.556	0.075	848.9	0.775
0.015	859.1	0.595	0.231	832.7	1.405
0.033	855.7	0.646	1.000	808.4	8.325

Table 2. Physical Properties of Tri-*n*-octylamine (1) and Isododecane (2) at 298 K

x_1	$\rho/\text{kg m}^{-3}$	$\eta/\text{mPa s}$	x_1	$\rho/\text{kg m}^{-3}$	$\eta/\text{mPa s}$
0.000	743.6	1.217	0.173	764.3	1.982
0.052	752.1	1.424	0.527	789.0	4.260
0.110	758.2	1.675	1.000	808.4	8.325

relative error for the aqueous titration was 1% and for the organic one 2%. The ion chromatographic analysis was repeated three times, giving a relative error of 3%. The density was measured with a HERAEUS DMA 55 ($\pm 0.0001 \text{ g/cm}^3$) densimeter, the interfacial tension was measured with a LAUDA TVT 1 ($\pm 0.1 \text{ mN/m}$), and the viscosity of the solutions was measured with a LAUDA Viscoboy 2 ($\pm 0.5\%$).

For the equilibrium experiments, about 50 mL of the organic and aqueous phases (of known initial concentrations) are weighted into an Erlenmeyer flask, stirred for at least 24 h at 298 K, and centrifuged before analysis. The physical properties (density, viscosity, and interfacial tension) of the solutions were measured at 298 K.

Physical Properties. The density of mixtures of tri-*n*-octylamine (1) with toluene or isododecane (2) are given in Tables 1 and 2. The results can be described well with the equation for an ideal mixture in weight fractions, w_i :

$$\frac{1}{\rho_{\text{mix}}} = \frac{w_1}{\rho_1} + \frac{w_2}{\rho_2} \quad (1)$$

Aqueous solutions of acetic acid show (see Table 3) significant volumetric excess effects. The polynomial equation

$$\rho_{\text{mix}} = -93.37w_{\text{acid}}^2 + 141.14w_{\text{acid}} + \rho_{\text{water}} \quad (2)$$

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Table 3. Physical Properties of Acetic Acid (1) and Water (2) at 298 K

x_1	$\rho/\text{kg m}^{-3}$	$\eta/\text{mPa s}$	x_1	$\rho/\text{kg m}^{-3}$	$\eta/\text{mPa s}$
0.000	998.5	0.918	0.070	1023.8	1.254
0.016	1004.3	0.988	1.000	1046.3	1.125
0.034	1011.6	1.080			

Table 4. Binary Viscosity Parameters

$i-j$	G_{ij}
tri- <i>n</i> -octylamine + toluene	1.7260
tri- <i>n</i> -octylamine + isododecane	1.0037
acetic acid + water	4.6161

Table 5. Interfacial Tension of Tri-*n*-octylamine (1), Toluene (2), and Water (3)^a

$c_1/\text{mol kg}^{-1}$	$\sigma/\text{mN m}^{-1}$	$c_1/\text{mol kg}^{-1}$	$\sigma/\text{mN m}^{-1}$
0.00283	29.7 ^a	0.0569	21.8
0.00567	29.0 ^a	0.0569	20.6
0.102	18.3 ^a	0.102	17.7
0.229	16.4 ^a	0.149	16.5
1.21	13.1 ^a	0.229	15.6
0.00283	30.1	0.314	15.5
0.00567	29.1	0.699	13.3
0.0138	24.8	0.706	13.4
0.0138	26.2	1.212	12.0
0.0286	24.3		

^a Organic droplets.

fits the experimental data up to a mass fraction of 0.2 and gives the correct density for the pure acid. The measured viscosities of the mixtures (see Tables 1–3) can be described as follows:

$$\ln \eta_{\text{mix}} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \quad (3)$$

The estimated binary viscosity parameters G_{12} are listed in Table 4. The interfacial concentration of the adsorbed tri-*n*-octylamine can be calculated with the Gibbs equation (see Table 5). The concentration domain (molal units) investigated gives a fully saturated interface with $\Gamma_{\text{sat}} = 1.24 \text{ mmol/m}^2$.

$$\Gamma = -\frac{1}{RT} \frac{\partial \sigma}{\partial (\ln m_{\text{TOA}})} \quad (4)$$

Thermodynamic Model

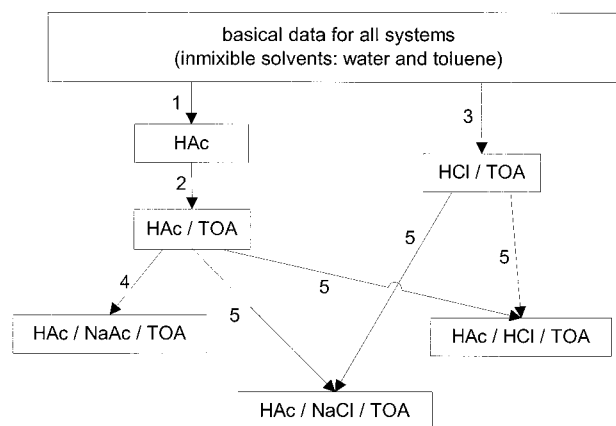
For the description of the liquid–liquid-phase equilibria, a model has been used, which combines chemical equilibria in both phases with physical interactions. In the aqueous phase the following dissociation reactions will occur:



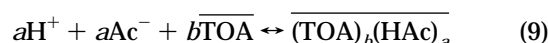
The dissociation constant for, for example, acetic acid is then

$$K_{\text{diss}} = \frac{m_{\text{H}^+} m_{\text{Ac}^-} \gamma_{\text{H}^+} \gamma_{\text{Ac}^-}}{m_{\text{HA}} \gamma_{\text{HA}}} \quad (8)$$

HCl and NaCl are totally dissociated and the dissociation constant of acetic acid is taken as $\text{p}K_a = 4.783$.⁵ The

**Figure 1.** Succession for estimating the parameters of the phase equilibria.

extraction equation for, for example, acetic acid is then (bar denotes organic species)



with the equilibrium constant

$$K_{ab} = \frac{m_{\overline{(\text{TOA})_b(\text{HAc})_a}} \gamma_{\overline{(\text{TOA})_b(\text{HAc})_a}}}{m_{\text{TOA}}^b m_{\text{H}^+}^a m_{\text{Ac}^-}^a \gamma_{\text{TOA}}^b \gamma_{\text{H}^+}^a \gamma_{\text{Ac}^-}^a} \quad (10)$$

This definition of equilibrium constant for the weak acetic acid is analogue to the formulation for hydrochloric acid, but can be transferred to the more common expression

$$K_{ab} = \frac{m_{\overline{(\text{TOA})_b(\text{HAc})_a}} \gamma_{\overline{(\text{TOA})_b(\text{HAc})_a}}}{m_{\text{TOA}}^b m_{\text{HAc}}^a \gamma_{\text{TOA}}^b \gamma_{\text{HAc}}^a} K_{\text{Diss}}^a \quad (11)$$

The distribution coefficient P is then for acetate

$$P_{\text{Ac}} = \frac{m_{\overline{\text{HAc}}}}{m_{\text{HAc}} + m_{\text{NaAc}}} \quad (12)$$

and for chloride

$$P_{\text{Cl}} = \frac{m_{\overline{\text{HCl}}}}{m_{\text{NaCl}}} \quad (13)$$

To calculate the activity coefficients γ_b , the Pitzer model⁷ is used for the aqueous phase and the Hildebrand–Scott solubility parameter model⁸ is used for the organic phase. Some of the Pitzer, equilibrium, and solubility parameters are taken from the literature.^{9–11} It could be shown¹³ with independent FTIR measurements that $\overline{\text{TOA} \cdot \text{HAc}}$ and $\overline{\text{TOA} \cdot (\text{HAc})_3}$ complexes prevail with toluene as the solvent. With the software of Baes,¹² the solubility parameters of the organic complexes and the equilibrium constants can be estimated stepwise to gain a consistent set of parameters according to Figure 1. Step 1 considers the physical solubility of HAc in toluene and steps 2 and 3 the reactive solubility of HAc and HCl due to tri-*n*-octylamine in toluene. With that basic data the behavior of the system H^+ , Na^+ , Ac^- , HAc, H_2O , and $\overline{\text{TOA}}$, $\overline{\text{TOA} \cdot \text{HAc}}$, $\overline{\text{TOA}(\text{HAc})_3}$, and toluene could be predicted (step 4). Because sodium cannot be extracted by the anion exchanger tri-*n*-octylamine, its influence is only on the aqueous phase and is correctly predicted by the Pitzer model. A difference is in step 5 with the system H^+ , Na^+ , Ac^- , Cl^- , HAc, H_2O , $\overline{\text{TOA}}$,

Table 6. Equilibrium Data for the System Acetic Acid (1), Tri-*n*-octylamine (2), Toluene (3), and Water (4) with and without Sodium Acetate (5)

aqu. conc. (mol kg ⁻¹)			org. conc. (mol kg ⁻¹)		P_{Acetate}
c_1	c_5	pH	c_2	c_1	
0.0729	0		0.149	0.0108	0.148
0.0256	0		0.314	0.0093	0.365
0.0263	0		0.314	0.0095	0.363
0.1068	0	3.49	0.707	0.0740	0.693
0.2116	0	3.21	0.707	0.1820	0.860
0.4640	0	2.89	0.707	0.5942	1.281
0.8974	0	2.63	0.707	1.3000	1.449
0.0267	0.203		0.314	0.0086	0.037
0.0270	0.203		0.314	0.0086	0.038
0.0538	0.125	5.06	0.707	0.0390	0.218
0.0550	0.282	5.39	0.707	0.0395	0.117
0.0497	0.532	5.72	0.707	0.0363	0.062
0.0542	0.561	5.63	0.707	0.0393	0.064
0.0541	1.040	6.01	0.707	0.0378	0.035
0.0555	2.003	6.37	0.707	0.0373	0.018
0.4717	0.133	4.11	0.707	0.5825	0.963
0.4661	0.269	4.40	0.707	0.5777	0.786
0.4559	0.518	4.72	0.707	0.5602	0.575
0.4693	1.099	5.10	0.707	0.5758	0.367
0.4756	2.022	5.47	0.707	0.5530	0.221

TOA·HAc, TOA·(HAc)₃, TOA(HCl), and toluene where the correlations proved insufficient, neglecting the occurrence of a mixed complex TOA·HCl·(HAc)₂. The parameter evaluation was done with the software SLXSQA,¹² which is available free through the Internet (<http://www.ornl.gov/divisions/casd/csg/sxlsqi/>). In addition to the data presented here, also HAc, H₂O, TOA, and toluene data from the literature¹¹ were used. The quality of the fit is expressed by the agreement factor σ (N_E is the number of the experimental data and N_P the number of adjustable parameters and σ_i denotes the experimental error):

$$\sigma = \left[\sum_{i=1}^{N_E} \left(\frac{1}{\sigma_i^2} (y_i - y_{i,\text{calc}})^2 \right) \frac{1}{N_E - N_P} \right]^{0.5} \quad (14)$$

Results and Conclusions

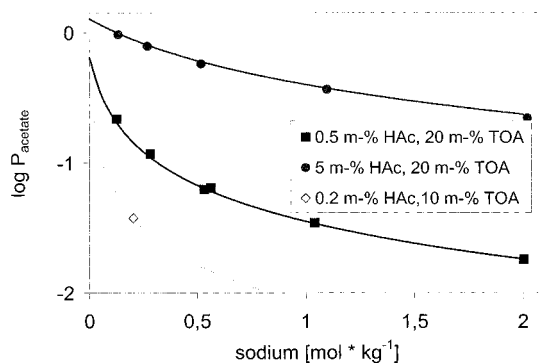
The equilibrium data for acetic acid and sodium acetate are given in Table 6. The pauschal molal acetate concentration, c_1 , in the aqueous phase is the sum of sodium acetate and acetic acid and in the organic phase the sum of the complexes TOA·HAc and TOA·(HAc)₃. In Table 7 the results of the admixture of sodium chloride are pre-

Table 7. Equilibrium Data for the System Acetic and Hydrochloric Acid (1), Tri-*n*-octylamine (2), Toluene (3), Water (4) with Sodium Salt (5)

aqu. conc. (mol kg ⁻¹)			org. conc. (mol kg ⁻¹)		X_{Cl}	P_{Acetate}	P_{Chloride}
c_1	c_5	pH	c_2	c_1			
0.5496	0		0.315	0.4526	0	0.824	
0.5496	0.006		0.315	0.4722	0.018	0.837	3.715
0.5493	0.009		0.315	0.4341	0.025	0.763	3.082
0.5476	0.009		0.315	0.4665	0.025	0.822	3.369
0.5485	0.016		0.315	0.4485	0.038	0.773	2.646
0.5490	0.022		0.315	0.4479	0.048	0.759	2.346
0.5531	0.046		0.315	0.4564	0.079	0.730	1.522
0.5437	0.106		0.315	0.4576	0.136	0.678	0.938
0.5333	0.219		0.315	0.4620	0.203	0.612	0.623
0.5121	0.481		0.315	0.5483	0.307	0.611	0.454
0.4951	0.987		0.315	0.5342	0.378	0.519	0.240
0.4650	1.994		0.315	0.5542	0.434	0.483	0.133
0.4367	0.112	3.62	0.703	0.6127	0.120	1.107	1.197
0.4268	0.214	3.79	0.703	0.6510	0.188	1.058	0.865
0.3846	0.559	4.00	0.703	0.6911	0.306	0.939	0.489
0.3551	1.058	4.07	0.703	0.7655	0.408	0.855	0.354
0.0434	0.149	4.20	0.703	0.0560	0.444	0.472	0.197
0.0425	0.196	4.25	0.703	0.0620	0.498	0.463	0.180
0.0335	0.516	4.44	0.703	0.0718	0.609	0.403	0.091
0.0275	1.026	4.59	0.703	0.0882	0.637	0.433	0.057
0.0096	0.500	4.88	0.707	0.0353	0.799	0.225	0.059
0.0312	0.501	4.62	0.707	0.0714	0.709	0.280	0.111
0.0673	0.501	4.47	0.707	0.1295	0.608	0.395	0.179
0.1490	0.501	4.34	0.707	0.2648	0.473	0.571	0.309
0.2908	0.502	4.22	0.707	0.5336	0.355	0.802	0.522
0.5457	0.503	4.04	0.707	0.9979	0.210	1.100	0.631
0.5651	0.503	4.04	0.707	1.0030	0.228	1.066	0.669
0.8068	0.502	3.85	0.707	1.3868	0.169	1.148	0.768
0.8828	0.504	3.85	0.707	1.3639	0.178	1.065	0.728
0.0835	0.523	2.81	0	0.0011		0.013	
0.0584	0.523	3.93	0.136	0.0327	0.697	0.133	0.045
0.0480	0.523	4.16	0.280	0.0483	0.679	0.218	0.066
0.0336	0.523	4.45	0.685	0.0681	0.686	0.323	0.095
0.0317	0.523	4.49	1.248	0.0984	0.694	0.456	0.140
0.0262	0.523	4.64	1.949	0.1296	0.715	0.568	0.191
0.8835	0.549	2.25	0	0.0235		0.027	
0.7040	0.550	3.35	0.151	0.2586	0.268	0.247	0.142
0.5557	0.550	3.70	0.345	0.4857	0.277	0.534	0.300
0.4024	0.551	4.03	0.673	0.6886	0.284	0.913	0.473
0.3226	0.551	4.22	1.204	0.9087	0.291	1.274	0.719
0.2989	0.552	4.31	1.869	1.2127	0.324	1.633	1.125

Table 8. Equilibrium Data for the System Hydrochloric Acid (1), Tri-*n*-octylamine (2), Toluene (3), and Water (4) with and without Acetic Acid (5)

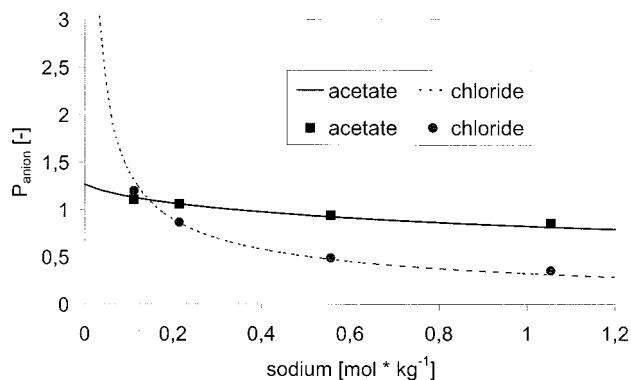
aqu. conc. (mol kg ⁻¹)			org. conc. (mol kg ⁻¹)				
$c_1 + c_5$	X_{Cl}	pH	c_2	$c_1 + c_5$	X_{Cl}	$P_{Acetate}$	$P_{Chloride}$
0.0025	1	2.57	0.313	0.0190	1		7.489
0.0043	1	2.34	0.313	0.0566	1		13.204
0.0060	1	2.20	0.313	0.1158	1		19.305
0.0105	1	1.94	0.313	0.2205	1		21.010
0.0710	1	1.24	0.313	0.3013	1		4.244
0.1646	1	0.97	0.313	0.3015	1		1.832
0.2699	1	0.80	0.313	0.3022	1		1.120
0.7842	1	0.51	0.313	0.3016	1		0.385
0.0012	1	3.03	0.703	0.0203	1		16.433
0.0013	1	2.76	0.707	0.0436	1		34.770
0.0024	1	2.52	0.707	0.0931	1		38.291
0.0025	1	2.62	0.703	0.0699	1		28.000
0.0026	1	2.42	0.707	0.1852	1		70.662
0.0034	1	2.44	0.703	0.1355	1		40.148
0.0045	1	2.20	0.707	0.3695	1		81.372
0.0046	1	2.44	0.707	0.2770	1		60.133
0.0046	1	2.29	0.703	0.2575	1		55.588
0.0058	1	2.31	0.707	0.4109	1		71.028
0.0086	1	2.12	0.707	0.5734	1		66.751
0.0413	1	1.23	0.707	0.6673	1		16.140
0.2306	1	0.90	0.707	0.7103	1		3.080
0.5548	1	0.32	0.707	0.6543	1		1.179
0.0149	0.333	2.68	0.706	0.0882	0.900	0.893	16.049
0.0161	0.475	2.40	0.706	0.3918	0.972	1.302	49.634
0.0277	0.315	2.40	0.706	0.4600	0.951	1.198	50.228
0.0321	0.182	2.72	0.706	0.0913	0.779	0.769	12.160
0.0577	0.167	2.43	0.706	0.4731	0.887	1.109	43.611
0.0599	0.110	2.72	0.706	0.1110	0.655	0.720	11.018
0.1105	0.091	2.41	0.706	0.5078	0.794	1.042	40.162
0.1156	0.062	2.65	0.706	0.1658	0.493	0.776	11.320
0.2080	0.047	2.38	0.706	0.5882	0.650	1.039	39.219
0.2127	0.040	2.71	0.706	0.2554	0.305	0.869	9.200
0.4770	0.025	2.62	0.706	0.6685	0.130	1.251	7.230
0.5116	0.025	2.27	0.706	0.9456	0.416	1.108	30.296
0.1230	0.085	2.24	0.707	0.4264	0.859	0.535	34.933
0.1263	0.061	2.47	0.707	0.2509	0.493	1.073	16.132
0.1266	0.054	2.56	0.707	0.1792	0.548	0.677	14.256
0.1287	0.042	2.76	0.707	0.1375	0.254	0.832	6.424
0.2148	0.400	0.98	0.707	0.7708	0.852	0.888	7.638
0.6423	0.803	0.35	0.707	0.7592	0.846	0.926	1.245

**Figure 2.** Comparison of measured and simulated distribution coefficients of acetic acid influenced by sodium acetate in water, tri-*n*-octylamine, and toluene.

sented. Here, c_1 is the pauschal molal concentration of acetic and hydrochloric acid and c_5 is the sum of sodium chloride and sodium acetate. X_{Cl} is the relative fraction of chloride derived from the integrated ion chromatographic peaks:

$$X_{Cl} = \frac{m_{Cl}}{m_{Cl} + m_{Ac}} \quad (15)$$

The results with hydrochloric acid (also combined with acetic acid) are given in Table 8. The addition of sodium

**Figure 3.** Comparison of measured and simulated distribution coefficients of acetic acid (5 m-%) influenced by sodium chloride in water and tri-*n*-octylamine (20 m-%)/toluene.

acetate reduces the distribution coefficient of acetate (see Figure 2), but the acid content in the organic phase does not change very much. The addition of sodium chloride reduces the distribution coefficient of acetate slightly (see Figure 3), while the distribution coefficient of chloride decreases significantly. At low NaCl concentrations the extraction of chloride is preferred. The distribution coefficients are also shown for a higher salt concentration in Figure 4. In all cases the extraction of acetate is preferred to the extraction of chloride. The estimated equilibrium constants and solubility parameters are given in Table 9,

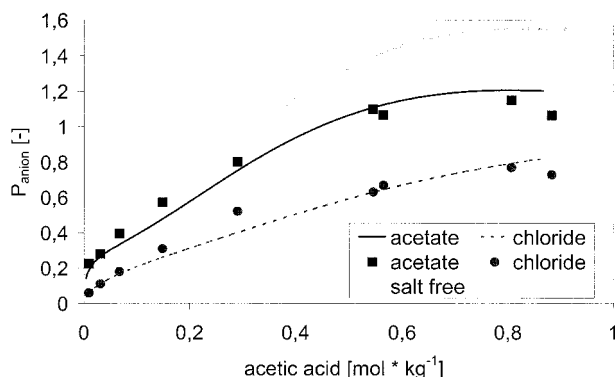


Figure 4. Comparison of measured and simulated distribution coefficients of acetic acid influenced by sodium chloride (0.55 mol/kg) in water and tri-*n*-octylamine (20 m-%)/toluene and the salt-free system.

Table 9. Equilibrium Constants and Solubility Parameters for the Organic Species¹³

<i>i</i>	p <i>K_i</i>	$\delta_i/\text{cal}^{1/2} \text{ cm}^{-3/2}$
toluene ¹³		8.9
TOA		9.2
HAc ¹³	2.7375	10.1
(HAc) ₂	7.4368	10.1
TOAHAc	4.7828	8.3637
TOA(HAc) ₃	14.952	8.4102
TOAHCl	3.9576	11.705
TOA(HAc) ₂ HCl	31.779	10.682

Table 10. Pitzer Parameters^{8,9}

<i>i-j</i>	$\beta_{ij}^{(0)}$	$\beta_{ij}^{(1)}$	C_{ij}^ϕ
Na ⁺ + Ac ⁻	0.1426	0.3237	0.00629
Na ⁺ + Cl ⁻	0.0765	0.2664	0.00127
H ⁺ + Cl ⁻	0.1775	0.2945	0.0008
HAc + HAc ⁹	0.0608		

and the Pitzer parameters used for modeling are given in Table 10. With those parameters, a good description of the measured simultaneous distribution coefficients of acetate and chloride is possible (see Figures 2–4).

In this work the physical properties and equilibrium concentrations for the extraction of chloride and acetate were investigated. The physical properties can be described with commonly used equations. The liquid interface is saturated with adsorbed tri-*n*-octylamine in an interesting

concentration range. Extraction equilibria of acetic acid in the presence of sodium acetate, sodium chloride, and hydrochloric acid have been measured. The experimental data could be described well with a model that assumes the formation of organic complexes and regards the dissociation equilibrium of acetic acid. On the basis of the binary systems acetate and chloride, a prediction of the equilibria of the mixed system considering a new mixed complex was possible. Nonidealities in both phases were considered.

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Received for review September 20, 2000. Accepted May 25, 2001.

JE000313+