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Activity of Water in Aqueous Solutions of Sodium Citrate and in Aqueous Solutions of (An Inorganic Salt and Citric Acid) at 298.15 K

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Modeling the reactive extraction of carboxylic acids in the presence of inorganic salts requires experimental data for the thermodynamic properties of aqueous solutions of the single salts as well as of aqueous solutions of (salt + carboxylic acid) mixtures. The activity of water in such solutions was determined by isopiestic measurements at 298.15 K for the binary mixture (water + sodium citrate) and the ternary mixtures of (water + citric acid + salt) for the salts sodium chloride, sodium nitrate, sodium sulfate, and sodium citrate. The experimental data are correlated with Pitzer's Gibbs excess energy model for aqueous electrolyte solutions.

Introduction

Carboxylic acids are commonly recovered from diluted aqueous solutions by reactive extraction with a water-insoluble organic amine. The liquid−liquid phase equilibrium in such systems is strongly influenced by inorganic salts. The development and parametrization of a model for correlating and predicting such liquid−liquid phase equilibria requires not only experimental data for the partitioning of carboxylic acids to aqueous/organic two-phase systems in the presence of a chemical extractant and some inorganic salts, but also of the properties of subsystems. Here, experimental results are presented for the activity of water in aqueous solutions of a single salt (sodium citrate) as well as in aqueous solutions of citric acid which also contain a single sodium salt (chloride, nitrate, sulfate, citrate) at 298.15 K. The experimental results are used to determine parameters of Pitzer's equation for the Gibbs excess energy of electrolyte solutions.

Experimental Section

The activity of water in aqueous solutions of nonvolatile solutes at 298.15 K was determined in isopiestic investigations using aqueous solutions of sodium chloride as references. The experimental techniques and the equipment are similar to those used in previous investigations on aqueous solutions of polymers (Groβmann et al.,[1] Hasse et al.,[2] Kany et al.[3]). Therefore, the experimental details are not repeated here. The experimental uncertainties are ±0.1 K for the temperature and ±0.35% in the molality of a solute. Aqueous solutions of sodium chloride were used as references. The correlation of Pitzer et al.[4] was used to convert the experimental results for the molality of sodium chloride in the reference solution to the activity of water. The absolute uncertainty of the experimental results for the activity of water is estimated to ±0.0005. However, that number does not include any contribution that might result from a bias of the correlation of Pitzer et al.[4] (cf. Clark and Glew,[5] Archer,[6] and Archer and Carter[7]).

Materials. Citric acid monohydrate (min. 99.8%), sodium nitrate, sodium chloride, and sodium sulfate (min. 99.5%) were purchased from Riedel-de Haën, Seelze, Germany. Sodium citrate (min. 99%) was purchased from Merck, Darmstadt, Germany. Deionized water was used in all experiments.

Table 1. Survey of the Experimental Investigations (Minimum and Maximum Molalities of Solutes)

salt	$(\tilde{m}_{H_3Cit})_{min}$	$(\tilde{m}_{H_3Cit})_{max}$	$(\tilde{m}_{salt})_{min}$	$(\tilde{m}_{salt})_{max}$
Na_3Cit			0.5	1.7
Na_3Cit	0.08	3.6	0.05	1.6
NaCl	0.1	5.7	0.5	3.0
$NaNO_3$	0.2	3.9	0.2	3.0
Na_2SO_4	0.2	3.5	0.2	2.4

Table 2. Activity of Water in Aqueous Solutions of Sodium Citrate at 298.15 K

$\tilde{m}_{Na_3Cit}$ / mol·kg^{-1}	$m^{(ref)}_{NaCl}$ / mol·kg^{-1}	a_w^{exp}	$\Delta a_w^{(exp-corr)} \times 10^4$
0.465	0.653	0.9785	1.6
0.758	1.059	0.9648	−1.5
0.804	1.120	0.9627	−0.7
1.018	1.429	0.9520	0.5
1.136	1.609	0.9457	0.8
1.137	1.610	0.9456	0.8
1.185	1.698	0.9425	−4.6
1.298	1.851	0.9370	3.1
1.457	2.106	0.9277	1.2
1.605	2.338	0.9190	0.9
1.683	2.465	0.9142	−1.0

Experimental Results. Table 1 gives a summary of the compositions of the aqueous solutions. The stoichiometric molality of citric acid $\tilde{m}_{H_3Cit}$ was typically varied between 0.1 and 4, while the stoichiometric molality of the salt $\tilde{m}_{salt}$ ranged from about 0.1 to 3.0. The activity of water a_w was as low as 0.89. The experimental results are given in Table 2 (for aqueous solutions of sodium citrate), Table 3 (aqueous solutions of citric acid and sodium chloride), Table 4 (aqueous solutions of citric acid and sodium nitrate), Table 5 (aqueous solutions of citric acid and sodium citrate), and Table 6 (aqueous solutions of citric acid and sodium sulfate). The tables with the experimental results also contain the stoichiometric molality of sodium chloride $\tilde{m}^{(ref)}_{NaCl}$ in the reference solution (used to determine the activity of water). Additionally, the experimental results for the activity of water in aqueous solutions of sodium

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Table 3. Activity of Water in Aqueous Solutions of Sodium Chloride and Citric Acid at 298.15 K

$\tilde{m}_{NaCl}$ mol·kg^{-1}	$\tilde{m}_{H_3Cit}$ mol·kg^{-1}	$\tilde{m}^{(ref)}_{NaCl}$ mol·kg^{-1}	a_w^{exp}	$\Delta a_w^{(exp-corr)} \times 10^4$
0.506	0.101	0.596	0.9804	−1.0
0.498	0.103	0.544	0.9821	5.7
0.499	0.301	0.666	0.9779	2.9
0.499	0.502	0.758	0.9750	12
0.498	0.973	1.103	0.9633	−9.3
0.503	1.562	1.492	0.9498	−18
0.503	2.514	2.033	0.9303	2.8
0.499	2.993	2.341	0.9188	2.3
0.498	3.486	2.651	0.9070	7.0
0.499	3.580	2.752	0.9030	−7.8
0.502	4.009	3.029	0.8921	−4.4
0.498	4.489	3.299	0.8811	14
0.500	5.034	3.715	0.8639	−4.9
0.501	5.517	4.031	0.8503	−0.3
0.988	0.493	1.285	0.9571	−3.3
0.995	1.492	1.865	0.9365	3.0
0.987	2.171	2.295	0.9206	−6.0
0.997	2.506	2.513	0.9125	−4.0
0.988	2.471	2.476	0.9137	−3.3
0.970	2.918	2.752	0.9030	−8.2
0.995	3.483	3.163	0.8895	7.9
0.997	4.737	3.922	0.8550	1.0
0.986	4.939	4.031	0.8503	7.2
0.999	5.647	4.525	0.8286	0.4
2.001	0.500	2.296	0.9206	−5.6
1.985	1.503	2.786	0.9017	15
1.946	1.945	3.029	0.8921	5.0
1.974	2.469	3.393	0.8773	−8.6
1.944	2.907	3.596	0.8689	3.1
1.946	3.410	3.922	0.8550	−6.5
1.981	3.964	4.248	0.8409	11
1.981	4.447	4.525	0.8286	19
2.984	0.675	3.299	0.8811	17
2.975	1.393	3.715	0.8639	−3.2
2.931	1.954	4.001	0.8513	−18
2.939	2.450	4.248	0.8409	−1.0
2.924	2.955	4.516	0.8290	−1.2

citrate are shown in Figure 1. Figure 2 shows, as a typical example, the activity of water in aqueous solutions of sodium chloride and citric acid. As it is expected, the activity of water decreases with increasing concentration of sodium chloride as well as with increasing concentration of citric acid.

Correlation

Model. Pitzer's equation[8,9] for the excess Gibbs energy of an aqueous electrolyte solution is used to describe the experimental data.

That equation gives for the activity of water (when pure liquid water is the reference state)

$$\ln a_w = \frac{M_w}{1000}\left[2A_\varphi I_m \frac{(I_m)^{1/2}}{(1 + b(I_m)^{1/2})} - \sum_{i=1}^{S}\sum_{j=1}^{S} \beta^{(0)}_{i,j} m_i m_j - \exp(-\alpha(I_m)^{1/2}) \sum_{i=1}^{S}\sum_{j=1}^{S} \beta^{(1)}_{i,j} m_i m_j - 2\sum_{i=1}^{S}\sum_{j=1}^{S}\sum_{k=1}^{S} \tau_{i,j,k} m_i m_j m_k - \sum_{i=1}^{S} m_i\right] \quad (1)$$

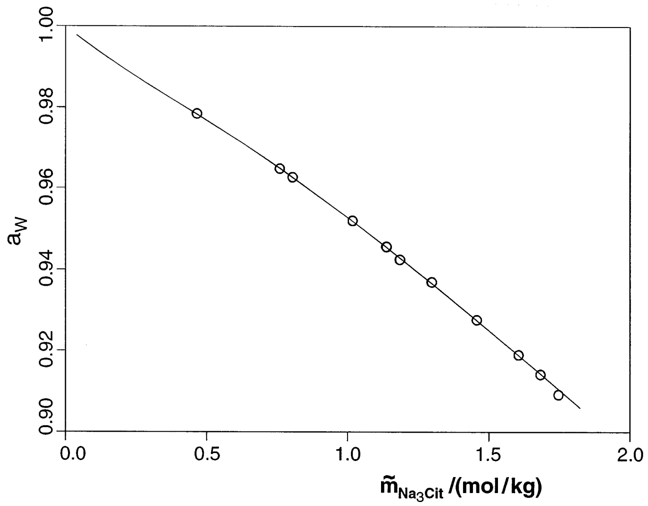

Figure 1. The activity of water in aqueous solution of sodium citrate at 298.15 K. ○, experimental data; solid line, correlation results.

Table 4. Activity of Water in Aqueous Solutions of Sodium Nitrate and Citric Acid at 298.15 K

$\tilde{m}_{NaNO_3}$ mol·kg^{-1}	$\tilde{m}_{H_3Cit}$ mol·kg^{-1}	$\tilde{m}^{(ref)}_{NaCl}$ mol·kg^{-1}	a_w^{exp}	$\Delta a_w^{(exp-corr)} \times 10^4$
0.194	1.742	1.223	0.9592	5.5
0.296	1.599	1.223	0.9592	6.2
0.379	1.507	1.223	0.9592	12
0.447	1.389	1.223	0.9592	7.1
0.542	1.250	1.223	0.9592	6.5
0.620	1.134	1.223	0.9592	5.9
0.782	0.892	1.223	0.9592	4.4
0.840	0.807	1.223	0.9592	4.5
0.907	0.706	1.223	0.9592	3.7
1.001	0.561	1.223	0.9592	2.4
1.105	0.399	1.223	0.9592	1.0
1.203	0.247	1.223	0.9592	0.1
0.519	2.663	2.102	0.9287	7.0
0.602	2.560	2.102	0.9287	7.2
0.719	2.419	2.102	0.9287	8.4
0.928	2.155	2.102	0.9287	8.2
1.136	1.884	2.102	0.9287	6.9
1.226	1.768	2.102	0.9287	6.6
1.335	1.623	2.102	0.9287	5.9
1.410	1.521	2.102	0.9287	5.1
1.631	1.221	2.102	0.9287	3.2
1.815	0.962	2.102	0.9287	0.5
2.030	0.658	2.102	0.9287	−1.4
0.506	3.861	2.870	0.8984	−4.2
0.711	3.638	2.870	0.8984	−2.5
0.903	3.420	2.870	0.8984	−3.1
1.107	3.203	2.870	0.8984	0.2
1.312	2.975	2.870	0.8984	1.4
1.500	2.758	2.870	0.8984	0.6
1.915	2.261	2.870	0.8984	2.4
2.094	2.043	2.870	0.8984	3.8
2.290	1.796	2.870	0.8984	−5.9
2.480	1.552	2.870	0.8984	−8.1
2.715	1.257	2.870	0.8984	−8.4
2.906	1.005	2.870	0.8984	−9.7

A_φ is the Debye−Hückel parameter of water (A_φ(25 °C) = 0.392), b is a size parameter ($b = 1.2$), α is a numerical value ($\alpha = 2$), m_i is the molality of solute i, and $\beta^{(0)}_{i,j}$, $\beta^{(1)}_{i,j}$, and $\tau_{i,j,k}$ are parameters for interactions between solute species i, j, and k. These parameters are symmetric, e.g., $\beta^{(0)}_{i,j} = \beta^{(0)}_{j,i}$. M_w is the molar mass of water; I_m is the ionic strength

$$I_m = \frac{1}{2}\sum_{i=1}^{S} m_i z_i^2 \quad (2)$$

z_i is the charge number of solute i, and S is the number of solute species in the aqueous phase. When citric acid and a salt (e.g., sodium citrate) are simultaneously dissolved

Table 5. Activity of Water in Aqueous Solutions of Sodium Citrate and Citric Acid at 298.15 K

$\tilde{m}_{\mathrm{NaCit}}$ mol·kg^{-1}	$\tilde{m}_{\mathrm{H_3Cit}}$ mol·kg^{-1}	$\tilde{m}^{(\mathrm{ref})}_{\mathrm{NaCl}}$ mol·kg^{-1}	$a_w^{\mathrm{exp.}}$	$\Delta a_w^{(\mathrm{exp-corr})} \times 10^4$
0.032	1.052	0.653	0.9785	1.7
0.063	0.986	0.653	0.9785	0.9
0.100	0.900	0.653	0.9785	0.4
0.130	0.826	0.653	0.9785	0.2
0.162	0.743	0.653	0.9785	0.2
0.197	0.652	0.653	0.9785	0.4
0.226	0.571	0.653	0.9785	−0.7
0.261	0.481	0.653	0.9785	−2.1
0.297	0.386	0.653	0.9785	−6.0
0.327	0.307	0.653	0.9785	−0.1
0.396	0.140	0.653	0.9785	−8.4
0.130	1.315	0.919	0.9696	1.5
0.237	1.081	0.919	0.9696	2.5
0.325	0.867	0.919	0.9696	3.9
0.392	0.689	0.919	0.9696	1.2
0.448	0.536	0.919	0.9696	−4.4
0.484	0.443	0.919	0.9696	−8.7
0.519	0.347	0.919	0.9696	−14
0.554	0.256	0.919	0.9696	−13
0.590	0.166	0.919	0.9696	−4.5
0.626	0.080	0.919	0.9696	<0.1
0.134	1.345	0.948	0.9686	−1.0
0.245	1.105	0.948	0.9686	0.4
0.331	0.895	0.948	0.9686	1.6
0.402	0.711	0.948	0.9686	−0.5
0.462	0.551	0.948	0.9686	−5.6
0.497	0.455	0.948	0.9686	−11
0.606	0.173	0.948	0.9686	−6.0
0.644	0.083	0.948	0.9686	−1.7
0.132	1.844	1.226	0.9591	2.4
0.252	1.634	1.226	0.9591	3.0
0.356	1.424	1.226	0.9591	6.5
0.445	1.224	1.226	0.9591	9.7
0.518	1.038	1.226	0.9591	9.4
0.581	0.872	1.226	0.9591	7.2
0.632	0.731	1.226	0.9591	3.2
0.678	0.594	1.226	0.9591	−2.9
0.715	0.484	1.226	0.9591	−8.6
0.752	0.374	1.226	0.9591	−10
0.782	0.284	1.226	0.9591	−4.3
0.051	2.048	1.284	0.9571	2.0
0.137	1.922	1.284	0.9571	0.2
0.264	1.708	1.284	0.9571	1.0
0.376	1.488	1.284	0.9571	5.2
0.466	1.291	1.284	0.9571	9.0
0.613	0.919	1.284	0.9571	8.6
0.667	0.768	1.284	0.9571	4.7
0.715	0.620	1.284	0.9571	−2.9
0.755	0.506	1.284	0.9571	−7.1
0.794	0.389	1.284	0.9571	−8.6
0.822	0.296	1.284	0.9571	−3.4
0.856	0.200	1.284	0.9571	1.5
0.101	2.501	1.609	0.9457	2.0
0.200	2.375	1.609	0.9457	0.6
0.298	2.240	1.609	0.9457	2.0
0.404	2.070	1.609	0.9457	4.6
0.933	0.757	1.609	0.9457	4.2
0.977	0.613	1.609	0.9457	−2.0
1.061	0.289	1.609	0.9457	2.2
0.164	2.961	1.954	0.9332	−1.6
0.441	2.641	1.954	0.9332	1.8
0.345	2.761	1.954	0.9332	−0.4
0.293	2.823	1.954	0.9332	−1.1
0.234	2.893	1.954	0.9332	−0.2
0.171	2.961	1.954	0.9332	<0.1
0.108	3.021	1.954	0.9332	−0.4
0.050	3.075	1.954	0.9332	−0.4
0.049	3.093	1.971	0.9326	−1.6
0.111	3.038	1.971	0.9326	−1.7
0.162	2.988	1.971	0.9326	−2.1
0.239	2.910	1.971	0.9326	−1.4
0.301	2.837	1.971	0.9326	−1.9
0.354	2.774	1.971	0.9326	−1.5
0.443	2.660	1.971	0.9326	0.2
1.191	0.845	1.971	0.9326	6.2
1.246	0.625	1.971	0.9326	−1.2
1.288	0.427	1.971	0.9326	4.3
1.321	0.265	1.971	0.9326	5.5
1.353	0.120	1.971	0.9326	6.0
0.264	2.901	1.983	0.9322	−1.4
0.516	2.581	1.983	0.9322	3.2
1.197	0.855	1.983	0.9322	6.2
1.247	0.623	1.983	0.9322	−4.9
1.296	0.432	1.983	0.9322	4.6
1.330	0.266	1.983	0.9322	6.3
1.360	0.124	1.983	0.9322	6.3
0.049	3.643	2.338	0.9190	−1.5
0.101	3.609	2.338	0.9190	<0.1
0.153	3.567	2.338	0.9190	0.2
0.202	3.528	2.338	0.9190	0.9
0.264	3.476	2.338	0.9190	1.5
0.310	3.435	2.338	0.9190	1.9
0.373	3.371	2.338	0.9190	0.9
0.462	3.287	2.338	0.9190	2.8
1.455	0.895	2.338	0.9190	1.9
1.494	0.695	2.338	0.9190	−2.6
1.531	0.470	2.338	0.9190	1.7
1.578	0.183	2.338	0.9190	3.3
1.547	0.891	2.465	0.9142	−2.8
1.570	0.760	2.465	0.9142	−0.6
1.590	0.628	2.465	0.9142	−3.7
1.607	0.526	2.465	0.9142	−1.0
1.624	0.407	2.465	0.9142	<0.1
1.642	0.299	2.465	0.9142	1.8
1.655	0.197	2.465	0.9142	0.1
1.670	0.096	2.465	0.9142	<0.1

in water, some citric acid dissociates according to

$$H_3Cit + H_2O \rightleftharpoons H_2Cit^- + H_3O^+ \quad \text{(I)}$$

$$H_2Cit^- + H_2O \rightleftharpoons HCit^{2-} + H_3O^+ \quad \text{(II)}$$

$$HCit^{2-} + H_2O \rightleftharpoons Cit^{3-} + H_3O^+ \quad \text{(III)}$$

When sodium sulfate is the dissolved salt, the formation of hydrogensulfate has to be taken into account. This is done here through the following reaction

$$HSO_4^- + H_2O \rightleftharpoons SO_4^{2-} + H_3O^+ \quad \text{(IV)}$$

Furthermore, the autoprotolysis of water has to be considered

$$2H_2O \rightleftharpoons OH^- + H_3O^+ \quad \text{(V)}$$

Chemical reaction equilibrium is taken into account through chemical reaction equilibrium constants $K_R^{(m)}(T,p)$ for R = I, II, ..., V. Neglecting the influence of pressure p on the chemical reaction equilibrium constant results in

$$K_R^{(m)}(T) = \exp\left[-\frac{1}{RT}\sum_{i=1}^{S_R} \nu_{i,R}\mu_i^{(\mathrm{ref})}\right] = \prod_{i=1}^{S_R} [a_i]^{\nu_{i,R}} \quad (3)$$

T stands for the thermodynamic temperature. Superscript "(m)" indicates that the molality scale is used to express

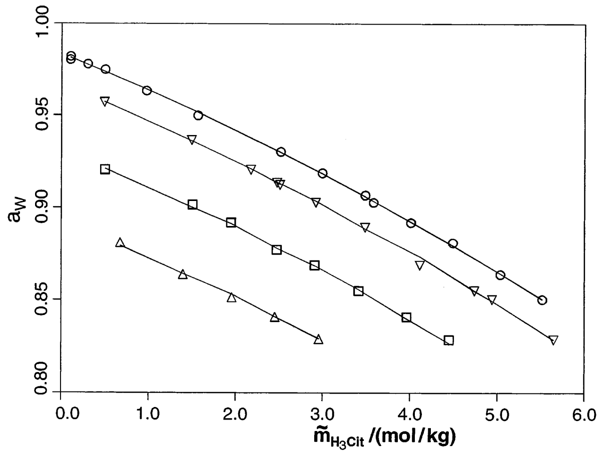

Figure 2. The activity of water in aqueous solution of sodium chloride and citric acid at 298.15 K: Experimental data for $\tilde{m}_{NaCl}/(\mathrm{mol \cdot kg^{-1}})$ = ○, 0.5 molal; ▽ 1.0 molal; □, 2.0 molal; △, 3.0 molal; solid lines, correlation results.

Table 6. Activity of Water in Aqueous Solutions of Sodium Sulfate and Citric Acid at 298.15 K

$\tilde{m}_{Na_2SO_4}$ mol·kg^{-1}	$\tilde{m}_{H_3Cit}$ mol·kg^{-1}	$\tilde{m}^{(ref)}_{NaCl}$ mol·kg^{-1}	a_w^{exp}	$\Delta a_w^{(exp-corr)} \times 10^4$
0.213	1.677	1.233	0.9589	4.0
0.311	1.514	1.233	0.9589	4.9
0.410	1.357	1.233	0.9589	7.1
0.517	1.175	1.233	0.9589	7.9
0.609	1.024	1.233	0.9589	7.8
0.726	0.821	1.233	0.9589	6.1
0.816	0.662	1.233	0.9589	4.0
0.916	0.492	1.233	0.9589	2.4
1.001	0.348	1.233	0.9589	0.3
1.095	0.199	1.233	0.9589	−0.8
0.542	2.655	2.137	0.9265	1.7
0.641	2.506	2.137	0.9265	0.1
0.736	2.374	2.137	0.9265	1.8
0.850	2.219	2.137	0.9265	5.6
1.044	1.915	2.137	0.9265	5.3
1.224	1.625	2.137	0.9265	5.2
1.319	1.472	2.137	0.9265	5.5
1.410	1.317	2.137	0.9265	4.2
1.574	1.039	2.137	0.9265	2.6
1.754	0.731	2.137	0.9265	−0.9
1.841	0.585	2.137	0.9265	−2.8
1.934	0.436	2.137	0.9265	−3.8
2.027	0.293	2.137	0.9265	−4.0
0.682	3.541	2.820	0.9004	−14
0.936	3.219	2.820	0.9004	−11
1.234	2.804	2.820	0.9004	−6.7
1.487	2.423	2.820	0.9004	−2.0
1.666	2.141	2.820	0.9004	2.2
1.901	1.736	2.820	0.9004	3.1
2.060	1.455	2.820	0.9004	3.1
2.201	1.198	2.820	0.9004	1.2
2.346	0.933	2.820	0.9004	−2.3
2.480	0.698	2.820	0.9004	−4.5

the concentration of a solute species and the reference state for its chemical potential is selected to be a hypothetical ideal solution of one mol of species i per kilogram of water at the systems temperature and pressure. S_R is the number of species involved in reaction R. $\nu_{i,R}$ is the stoichiometric factor of species i in reaction R ($\nu_{i,R}$ is positive for products and negative for educts), and $\mu_i^{(ref)}$ is the chemical potential of species i in its reference state. Numbers for the chemical reaction equilibrium constants were taken from the literature. They are given in Table 7.

The activity of a solute species a_i is

$$a_i = m_i \gamma_i \tag{4}$$

Table 7. Aqueous Phase Chemical Reaction Equilibrium Constants at 298.15 K

chemical reaction equilibrium constant	source
$\log K_{I}^{(m)} = -3.128$	Bates and Pinching[10]
$\log K_{II}^{(m)} = -4.761$	Bates and Pinching[10]
$\log K_{III}^{(m)} = -6.396$	Bates and Pinching[10]
$\log K_{IV}^{(m)} = -1.9788$	Pitzer et al.[11]
$\log K_{V}^{(m)} = -14.0$	Schmidt[12]

The activity coefficient of a solute i is

$$\ln \gamma_i = -z_i^2 A_\varphi \left[\frac{2}{b} \ln(1 + b(I_m)^{1/2}) + \frac{(I_m)^{1/2}}{(1 + b(I_m)^{1/2})} \right] - \frac{z_i^2}{\alpha^2 I_m^2} \sum_{i=1}^{S} \sum_{j=1}^{S} \beta_{i,j}^{(1)} m_i m_j + \frac{z_i^2}{\alpha^2 I_m^2} \exp(-\alpha (I_m)^{1/2}) \left[1 + \alpha (I_m)^{1/2} + \frac{\alpha^2 I_m}{2} \right] \sum_{i=1}^{S} \sum_{j=1}^{S} \beta_{i,j}^{(1)} m_i m_j + 2 \sum_{j=1}^{S} m_j \left\{ \beta_{i,j}^{(0)} + \beta_{i,j}^{(1)} \frac{2}{\alpha^2 I_m} [1 - (1 + \alpha (I_m)^{1/2}) \exp(-\alpha (I_m)^{1/2})] \right\} + 3 \sum_{j=1}^{S} \sum_{k=1}^{S} \tau_{i,j,k} m_j m_k \tag{5}$$

For preset temperature and stoichiometric composition (i.e., molalities of salt and/or citric acid), the composition of the liquid solution (and the activity of the water) is determined by minimizing the Gibbs energy G of the liquid phase

$$G(T, n_i) = \sum_i n_i \mu_i \tag{6}$$

taking the side conditions (mass balance for the components water, salt, and citric acid, chemical reaction equilibrium) into account. n_i and μ_i are the number of moles and the chemical potential of component i, respectively. The calculations require information on binary and ternary interaction parameters of the Pitzer model at 298.15 K. As usual, parameters for interactions between cations and cations as well as between anions and anions were set to zero. The parameters for interactions between sodium ions on one side and chloride ions, nitrate ions, and sulfate ions on the other side were taken from Silvester and Pitzer[13] (Na^+/Cl^-), Pitzer[14] (Na^+/NO_3^-), and Rogers and Pitzer[15] (Na^+/SO_4^{2-}), respectively. Parameters for interactions between sulfate and bisulfite ions on one side and hydrogenium ions on the other side were taken from Pitzer et al.[11] Only a single binary parameter was considered for interactions between citric acid molecules. That parameter was taken from Kirsch et al.[16] All non-neglected parameters are given in Table 8.

Three parameters for interactions between sodium ions and citrate ions ($\beta^{(0)}_{Na^+,Cit^{3-}}$, $\beta^{(1)}_{Na^+,Cit^{3-}}$, and $\tau_{Na^+,Na^+,Cit^{3-}}$ were fitted to the new experimental data. They are given in Table 8. Figure 1 and Table 2 also give a comparison between the experimental data and the correlation. The deviations between the experimental results and the correlation for the activity of water $\Delta a_w^{(exp-corr)}$ are typically about $\pm 10^{-4}$; the maximum absolute deviation is below 0.005.

The experimental results for the activity of water in aqueous solutions of sodium citrate and citric acid were

Table 8. Parameters of the Pitzer Model for Interactions in the Aqueous Phase at 298.15 K

electrolyte	parameter		source
NaCl	$\beta^{(0)}_{Na^+,Cl^-}$	0.0765	Silvester and Pitzer[13]
	$\beta^{(1)}_{Na^+,Cl^-}$	0.2664	
	τ_{Na^+,Na^+,Cl^-}	0.00042	
$NaNO_3$	$\beta^{(0)}_{Na^+,NO_3^-}$	0.0039	Pitzer[14]
	$\beta^{(1)}_{Na^+,NO_3^-}$	0.2115	
	τ_{Na^+,Na^+,NO_3^-}	−0.00002	
Na_2SO_4	$\beta^{(0)}_{Na^+,SO_4^{2-}}$	0.01869	Rogers and Pitzer[15]
	$\beta^{(1)}_{Na^+,SO_4^{2-}}$	1.0994	
	$\tau_{Na^+,Na^+,SO_4^{2-}}$	0.00131	
H_2SO_4	$\beta^{(0)}_{H_3O^+,SO_4^{2-}}$	0.0027	Pitzer et al.[11]
	$\beta^{(0)}_{H_3O^+,HSO_4^-}$	0.2103	
	$\beta^{(1)}_{H_3O^+,HSO_4^-}$	0.4711	
	$\tau_{H_3O^+,H_3O^+,SO_4^{2-}}$	0.0098	
H_3Cit	$\beta^{(0)}_{H_3Cit,H_3Cit}$	0.0767	Kirsch et al.[16]
Na_3Cit	$\beta^{(0)}_{H_3O^+,Cit^{3-}}$	0.2744	this work
	$\beta^{(1)}_{Na^+,Cit^{3-}}$	5.3772	
	$\tau_{Na^+,Na^+,Cit^{3-}}$	−0.00525	
$Na_3Cit + H_3Cit$	$\beta^{(0)}_{Na^+,HCit^{2-}}$	0.09133	this work
	$\beta^{(1)}_{Na^+,HCit^{2-}}$	−0.2265	
	$\tau_{Na^+,Na^+,HCit^{2-}}$	−0.00205	
	$\beta^{(0)}_{H_3Cit,H_2Cit^-}$	−0.09143	
	$\beta^{(1)}_{H_3Cit,H_2Cit^-}$	-0.1530	
	$\tau_{H^3Cit,H_3Cit,H_2Cit^-}$	0.00757	
$NaCl + H_3Cit$	$\beta^{(0)}_{H_3Cit,Cl^-}$	0.03435	this work
$NaNO_3 + H_3Cit$	$\beta^{(0)}_{H_3Cit,NO_3^-}$	0.00661	this work
$Na_2SO_4 + H_3Cit$	$\beta^{(0)}_{H_3Cit,SO_4^{2-}}$	0.02418	this work
	$\tau_{H_3Cit,H_3Cit,SO_4^{2-}}$	0.01430	

used to determine additional parameters for interactions between sodium ions and citric acid on one side and different citrate ions on the other side. Parameter studies revealed that a good agreement with the experimental results is achieved with three additional parameters for interactions between sodium ions and $HCit^{2-}$ ($\beta^{(0)}_{Na^+,HCit^2}$, $\beta,^{(1)}_{Na^+HCit^2}$, and $\tau_{Na^+,Na^+,HCit^{2-}}$) and three additional parameters for interactions between citric acid and H_2Cit^- ($\beta^{(0)}_{H_3Cit,H_2Cit^-}$, $\beta^{(1)}_{H_3Cit,H_2Cit^-}$, and $\tau_{H_3Cit,H_3Cit,H_2Cit^-}$). These parameters have no influence on the activity of water in aqueous solutions of sodium citrate, as there the concentrations of molecular citric acid and univalent as well as divalent citrate ions are very small. The parameters are also given in Table 8. As is shown in Table 5, the deviations between the experimental data for the activity of water and the correlation are not as small as they are for the system sodium citrate + water. Nevertheless, in most cases, the calculated numbers for the activity of water agree with the experimental data within the experimental uncertainty (±0.0005), but in a few cases, the deviations are larger by up to a factor of 3.

The experimental results for the activity of water in aqueous solutions of sodium chloride and citric acid were used to determine the binary parameter $\beta^{(0)}_{H_3Cit,Cl^-}$ for interactions between citric acid and chloride ions (the corresponding parameter $\beta^{(0)}_{H_3Cit,Na^+}$ for interactions between sodium ions and citric acid is set to zero; this is no simplification, as in a binary mixture of sodium chloride and citric acid these parameters always appear as a sum). In a similar way, the experimental results for the activity of water in aqueous solutions of sodium nitrate and citric acid were used to determine the binary parameter $\beta^{(0)}_{H_3Cit,NO_3^-}$ for interactions between citric acid and nitrate ions. Both parameters are given in Table 8. The comparisons between calculated and experimental data for the activity of water reveal a similar picture as mentioned before for aqueous solutions of sodium chloride and citric acid. As is shown in Tables 3 and 4, most calculated numbers for the activity of water agree with the experimental results within experimental uncertainty, but the maximum deviation surmounts the experimental uncertainty by a factor of about four.

Finally, the experimental results for the activity of water in aqueous solutions of sodium sulfate and citric acid were used to determine a binary ($\beta^{(0)}_{H_3Cit,SO_4^2}$) and a ternary ($\tau_{H_3Cit,H_3Cit,SO_4^{2-}}$) parameter for interactions between citric acid on one side and sulfate ions on the other side. Again, the final correlation reproduces the experimental data for the activity of water in nearly all cases within experimental uncertainty (cf. Table 6).

A comparison with literature data is not possible, as to the best of our knowledge, no such data are available.

Conclusions

The new experimental data and the new interaction parameters for Pitzer's model for the excess Gibbs energy of aqueous electrolyte solutions of citric acid are used in ongoing work on the liquid−liquid-phase equilibrium encountered in the extraction of carboxylic acids from aqueous electrolyte solutions in the presence of a chemical extractant.

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