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Phase Equilibrium of Aqueous Systems Containing 3-Methyl-1-vinylimidazolium Methyl Sulfate

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This paper reports experimental data for the activity of water in aqueous solutions of 3-methyl-1-vinylimidazolium methyl sulfate (QVI) at (298 and 338) K and the solid−liquid equilibrium for the ternary system (QVI + sodium sulfate + water) at the same temperatures. QVI is an ionic monomer which is gaining importance as a monomer for water-soluble polymers. The experimental data presented here are to contribute to a database which is needed to develop and test thermodynamic models for the description/prediction of phase equilibrium in aqueous solutions of such polyelectrolytes. The new experimental results for the activity of water are described by the VERS model of Gro*β*mann et al. for the excess Gibbs energy of aqueous solutions. Two interaction parameters were adjusted to correlate that data. The data set comprising the solid−liquid equilibrium was used for determining another set of interaction parameters (between that vinylimidazolium salt and sodium sulfate).

Introduction

The monomer 3-methyl-1-vinylimidazolium methyl sulfate quaternized with dimethyl sulfate (usually abbreviated by QVI) (cf. Figure 1) is a hydrophilic imidazolium salt that can be polymerized by free radical polymerization[1,2] to form water-soluble polymers. Copolymers of *N*,*N*-vinyl pyrrolidone and quaternary *N*-vinyl imidazole are especially utilized in the cosmetic industry particularly for conditioning and gelating products.[3] There are few publications on the synthesis and polymerization of vinylimidazolium salts. A reaction scheme to synthesize QVI from 1-vinyl imidazole and dimethyl sulfate is given in Figure 1. However, no information on physical and/or thermodynamic properties of systems containing such compounds could be found in the literature. QVI can behave like a "normal" organic salt[1] because its alkyl moiety is short.

The current publication presents experimental data for the activity of water in solutions of QVI as well as for the solid−liquid equilibrium of aqueous systems containing both QVI and sodium sulfate. The new experimental data are described by the semiempirical model VERS (viral equation with relative surface fractions)[4,5] for the excess Gibbs energy of aqueous electrolyte solutions that also contain polymers. That model was chosen as it is well suited to describe the liquid−liquid-phase equilibrium in aqueous mixtures of a strong electrolyte and a hydrophilic polymer (i.e., aqueous two-phase systems), and such systems will be investigated in the future.

Experimental Section

Materials. QVI was provided (as an aqueous solution with a mass fraction of QVI of 0.45) by BASF AG (Ludwigshafen a. Rh., Germany). The concentration was checked and verified by analyzing some samples by freeze drying, resulting in an average mass fraction of QVI of (0.46 ± 0.01).

Water-free sodium sulfate (mass fraction ≥ 0.99) was purchased from MERCK (Darmstadt, Germany) and used without further purification. Double distilled water was used for preparing all solutions.

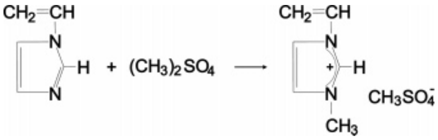

Figure 1. Schematic reaction of the synthesis of 3-methyl-1-vinylimidazolium methyl sulfate.

Vapor−Liquid Equilibrium Measurements. The activity of water in aqueous solutions of QVI was determined in isopiestic investigations at (298 and 338) K. The type of equipment and details of the experimental procedure were described previously.[4−7] The experimental arrangement consisted of 24 cells containing known amounts of either QVI or sodium chloride dissolved in water. Sodium chloride was used as a reference substance. At the beginning, the concentration of sodium chloride in at least two cells was below and in at least two other cells was above the expected equilibrium concentration. Vice versa, in two cells, the concentration of QVI was below and in another two cells was above the expected equilibrium concentration. These aqueous solutions were allowed to equilibrate through a common vapor phase at a constant temperature. Water is transferred between the cells in the equilibration process. The equilibrium is achieved when the activity of water attains the same value in all cells. After equilibration, the concentration of a solute in the aqueous solution in a cell is determined by weighting the cells. The activity of water is determined from the concentration of sodium chloride in the aqueous solutions using the correlation of Pitzer and Peiper[8] as a reference. The scattering in the activity of water from the equilibrated cells that contain aqueous solutions of sodium chloride was below 0.001, and the differences in the mass fractions of QVI in the corresponding, equilibrated aqueous solutions were below 0.002.

Solid−Liquid Equilibrium Measurements. This type of phase equilibrium investigation consisted of two parts. First, the cloud-point curve of the ternary system (QVI + Na_2SO_4 + H_2O) was determined at (298 and 338) K by turbidity measurements. Second, the composition of the liquid phase that coexists with

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solid sodium sulfate was determined. Both experimental procedures are described below.

For the determination of the cloud-point curve, about (5 to 7) g of aqueous solutions of 3-methyl-1-vinylimidazolium methyl sulfate (at mass fractions up to 0.45) were prepared in glass test tubes. A first estimate for the cloud-point line was determined in preliminary experiments. In the final experiment, somewhat less than the total amount of salt soluble in the liquid mixture was added, and afterward, small amounts (about (0.1 to 0.2) g) of pure sodium sulfate were stepwise added under stirring to such a solution. After each addition, the tubes were sealed and equilibrated in a thermostated water bath. Usually, turbidity is observed immediately after each salt addition. However, turbidity disappears within a couple of minutes when there is a single phase after equilibration. If the turbid phase persisted more than 1 h, it was assumed that the equilibrium state of the pertaining mixture lies in the two-phase region. To ensure that the equilibrium state was not in a single phase, such a turbid mixture was kept in the thermostated water bath for another 48 h under stirring, after which, if the mixture was turbid, it was assumed that the phase boundary had been crossed. Otherwise, the stepwise addition of sodium sulfate was continued, and the equilibration process was repeated.

The composition at the cloud-point was calculated from the amount of liquid solvent mixture in the test tube and the arithmetic mean of the added solid salt before and after the last addition. All masses were determined using a high-precision analytical balance (AE 240, Mettler-Toledo GmbH, Greifensee, Switzerland) with an uncertainty of $\pm\, 2\cdot10^{-4}$ g.

For the direct measurement of the solid−liquid equilibrium, about five feed solutions inside the solid−liquid two-phase region were prepared by dissolving solid sodium sulfate in an aqueous solution of QVI. The mixture was equilibrated in centrifuge tubes in a thermostated water bath for about 3 days at 298 K or 338 K. The uncertainty of that temperature was about ± 0.1 K. After equilibration, the solid phase was separated from the liquid phase in a thermostated centrifuge (model Rotina 48R, Hettich, Tuttlingen, Germany) at 3500 rpm for 90 min. Samples of the liquid phases were carefully withdrawn and analyzed for water and sodium sulfate. The water content was determined by freeze drying (model Lyovac GT 2, Amsco/Finn-Aqua, Hürth, Germany). For such an analysis, an exactly known amount (about 2 g) of the liquid phase was placed into an aluminum beaker. Then, that sample was diluted by about 20 g of water. The dilution of the samples was to ensure that a porous material was obtained by freeze drying. The solutions were put into a freezer where they were cooled to about −18 °C. Afterward, they were further cooled by liquid nitrogen to about −190 °C. The frozen samples were allowed to dry at 10^{-2} bar for (2 to 3) days to remove all water. The mass of the resulting solid sample was determined using the analytical balance described above, and the amount of water in the sample was calculated from the differences in the masses of the sample before and after freeze drying. The residues from the freeze drying process were put into a ceramic beaker and burned at about 800 °C in a muffle furnace (model Heraeus T 16A, Kendro GmbH, Hanau, Germany). The final residue consisted of sodium sulfate. The mass of that residue was again determined using the high-precision balance.

The absolute experimental error for the concentrations of sodium sulfate and QVI is approximately 15.5 % and 3.7 %, respectively.

Table 1. Activity of Water (1) in Aqueous Solutions with a w_2 Mass Fraction of 3-Methyl-1-vinylimidazolium Methyl Sulfate (2) at (298 and 338) K

$T = 298$ K		$T = 338$ K	
w_2	a_1	w_2	a_1
0.1055	0.9856	0.1257	0.9806
0.1169	0.9822	0.1303	0.9807
0.1561	0.9772	0.1476	0.9767
0.1772	0.9732	0.2277	0.9638
0.1893	0.9694	0.2749	0.9533
0.2179	0.9677	0.3155	0.9446
0.2272	0.9644	0.3482	0.9364
0.2469	0.9578		
0.2478	0.9599		
0.2690	0.9555		
0.2904	0.9509		
0.2954	0.9511		
0.3388	0.9405		
0.3584	0.9286		
0.3853	0.9269		
0.4015	0.9226		

Results and Discussion

Experimental Results. The experimental results for the activity of water (a_w) in aqueous solutions of QVI are given in Table 1. These experimental results were used to calculate the osmotic coefficient (Φ)

$$\Phi = \frac{\ln a_{\mathrm{w,real\ mixture}}}{\ln a_{\mathrm{w,ideal\ mixture}}} \tag{1}$$

The osmotic coefficient of an ideal solution is expressed using molality (moles per kilogram of water) for the composition of the aqueous solution and assuming that QVI is a completely dissociating 1:1 electrolyte

$$\ln a_{\mathrm{w,ideal\ mixture}} = -\frac{M_{\mathrm{w}}}{1000}\cdot 2(m_2/m^{\mathrm{o}}) \tag{1a}$$

where M_w is the relative molecular mass of water; m_2 is the molality of QVI; and $m^o = 1$ mol·kg^{-1} of water.

The osmotic coefficient is plotted versus the mass fraction of QVI in Figure 2. The vertical and horizontal bars in Figure 2 indicate the estimated experimental uncertainty which increases with decreasing solute concentration. The osmotic coefficient decreases only slightly when the temperature changes from (298 to 338) K. The small change is nearly within the uncertainty of the experimental data.

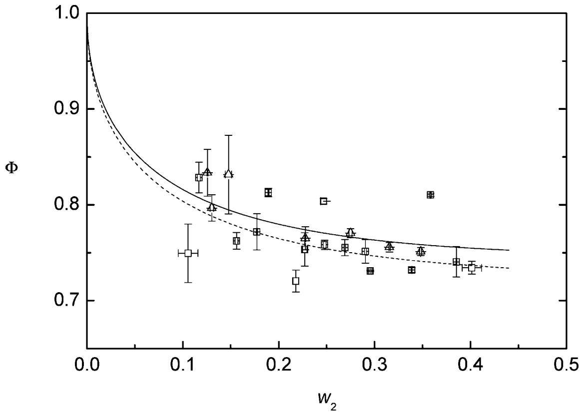

Figure 2. Osmotic coefficients of aqueous solutions of QVI. For 298.15 K: ■, experimental results; ____, correlation results. For 338.15 K: △, experimental results; -------, correlation results.

Table 2. Experimental Results for the Cloud-Point Curve in Aqueous Solutions of 3-Methyl-1-vinylimidazolium Methyl Sulfate (Mass Fraction w_2) and Sodium Sulfate (Mass Fraction w_3)

$T = 298$ K		$T = 338$ K	
w_2	w_3	w_2	w_3
0.4320	0.0443	0.4253	0.0588
0.3733	0.0658	0.3755	0.0745
0.3206	0.0748	0.3103	0.1033
0.2728	0.0943	0.1960	0.1685
0.1780	0.1306	0.1627	0.1900
0.1325	0.1540	0.1156	0.2092
0.1165	0.1803	0.0951	0.2383
0.0844	0.2074	0.0794	0.2381
0.0322	0.2595	0.0327	0.2951

Table 3. System (Water (1) + 3-Methyl-1-vinylimidazolium Methyl Sulfate (2) + Sodium Sulfate (3)): Compositions (Mass Fractions) of the Liquid Phase that Coexists with a Solid Phase at (298 and 338) K

feed solution		liquid phase	
w_2	w_3	w_2	w_3
$T = 298$ K (solid phase = sodium sulfate decahydrate)			
0.1311	0.2362	0.2304	0.0934
0.1656	0.1509	0.2040	0.1059
0.1880	0.1828	0.2717	0.0773
0.2682	0.1318	0.3333	0.0633
$T = 338$ K (solid phase = sodium sulfate)			
0.0984	0.2816	0.1125	0.2133
0.1466	0.2399	0.1583	0.1606
0.2010	0.1913	0.2048	0.1337
0.2041	0.2219	0.2246	0.1331
0.2622	0.2171	0.3215	0.0887

The experimental results for the cloud-point curve and the solid−liquid equilibrium of the ternary system (QVI + Na_2SO_4 + H_2O) are given in Tables 2 and 3 for (298 and 338) K. At temperatures below 305.4 K, sodium sulfate precipitates from aqueous solutions as sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$), whereas it precipitates as pure Na_2SO_4 at higher temperatures.[9] As is shown in Figure 3 for 298 K, the extrapolation of the line that connects the feed solution with the experimentally determined composition of the liquid phase hits the QVI-free side of the triangular diagram at a composition that corresponds to that of decahydrate. Furthermore, the experimental results for the cloud-point curve lie close to the phase boundary but in the two-phase region. That is typical for systems with high-molecular organic electrolytes. In such systems, one often observes metastable phases. Furthermore, as water-free sodium sulfate was added to the feed solution in the titration experiments (to determine the cloud-point curve), the water-free salt had to be dissolved and beyond the phase boundary had to be precipitated as decahydrate. Thus, in principle, the surplus of solid salt had to be converted from one speciation (metastable, water-free salt) to another (decahydrate) in a kinetically controlled process. Therefore, it is nearly impossible to reliably determine the phase boundary from cloud-point measurements. The solid−liquid phase equilibrium experiments are not as much influenced by the appearance of metastable states as they were carried out with much longer equilibrating times. At 338 K (cf. Figure 4), the differences between the experimental results for the cloud-point data and the experimental results for the composition of the equilibrated liquid phase become smaller. These differences are within the combined experimental uncertainties of both types of investigations. Figure 4 shows that for 338 K the extrapolation of the line that connects the feed solution with the experimentally determined composition of the liquid phase hits the corner that represents pure sodium sulfate. The experimental results for the composition of the precipitate are given neither in tabular nor in graphical form. The precipitate is always a heterogeneous mixture of the solid salt and some (more or less) coexisting liquid. A sample taken from that precipitate is also heterogeneous and does not represent the solid phase.

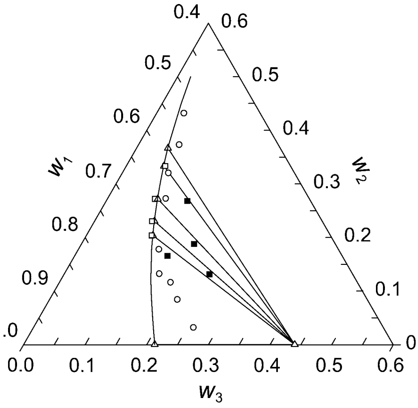

Figure 3. Solid−liquid equilibrium of the system (QVI + Na_2SO_4 + H_2O) at 298.15 K: ■, feed points; ○, exptl cloud points. Liquid phase in solid−liquid equilibrium: □, exptl; −△−, correlation of solid−liquid equilibrium with the VERS model.

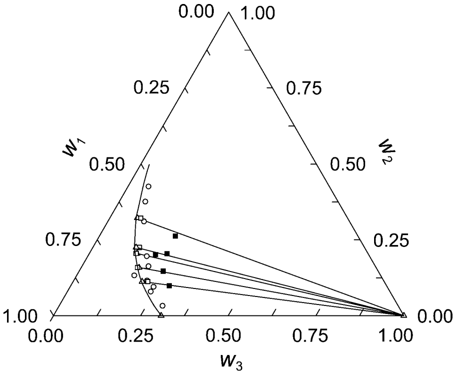

Figure 4. Solid−liquid equilibrium of the system (QVI + Na_2SO_4 + H_2O) at 338.15 K: ■, feed points; ○, exptl cloud points. Liquid phase in solid−liquid equilibrium: □, exptl; −△−, prediction of solid−liquid equilibrium.

Modeling. The thermodynamic properties studied in the present work are described by the virial equation with relative surface fractions (VERS) model.[4,5] The VERS model is an extension of Pitzer's[10] equation for the excess Gibbs energy of aqueous electrolyte solutions. The extension consists of two steps: a group contribution approach is introduced to allow for the treatment of polymers, and a surface-based concentration scale is used instead of the molality scale. As in Pitzer's equation, in the VERS model thermodynamic activities are normalized according to the asymmetric convention: the reference state for the solvent (i.e., water) is pure liquid at the system's temperature and pressure, whereas for a solute component, the reference state is a hypothetical solution of the solute in pure water (amount of substance of a solute: unit concentration; interactions of the solute with the solvent as in infinite dilution) at the system's temperature and pressure. However, the influence of pressure is neglected here. A normalized surface fraction (solute's surface fraction Θ_i is normalized by the surface fraction of water Θ_w) is used to describe the solute concentration.

$$\Theta_i = \frac{m_i Q_i}{\sum_{\text{all comp.}j} m_j Q_j} \tag{2}$$

where Q_i and m_i are the surface parameter and the molality of solute i, respectively. That surface parameter is calculated from the number of groups of type k in that solute, $\nu_k^{(i)}$, and the surface parameter q_k of group k.

$$Q_i = \sum_{\text{all groups } k} \nu_k^{(i)} q_k \tag{3}$$

The equation for the activity of water from the VERS model is

$$\ln a_\text{w} = -\frac{M_\text{w}}{1000}\left[\sum_{j\neq\text{w}} m_j - 2A_\varphi \frac{I_m^{1.5}}{1 + b\sqrt{I_m}}\right] - \left(\frac{1000}{M_\text{w}}\right)\sum_{i\neq\text{w}}\sum_{j\neq\text{w}} \frac{\Theta_i}{\Theta_\text{w}}\frac{\Theta_j}{\Theta_\text{w}}\,[A_{i,j}^{(0)} + A_{i,j}^{(1)}\exp\{-\alpha\sqrt{I_m}\}] - 2\left(\frac{1000}{M_\text{w}}\right)^2 \sum_{i\neq\text{w}}\sum_{j\neq\text{w}}\sum_{k\neq\text{w}} \frac{\Theta_i}{\Theta_\text{w}}\frac{\Theta_j}{\Theta_\text{w}}\frac{\Theta_k}{\Theta_\text{w}} B_{i,j,k} \tag{4}$$

M_w is the (dimensionless) molecular weight of water and A_φ is the Debye−Hückel constant. I_m is the ionic strength on the molality scale

$$I_m = \frac{1}{2}\sum_{i=1}^{S} m_i z_i^2 \tag{5}$$

$A_{i,j}^{(0)}$, $A_{i,j}^{(1)}$, and $B_{i,j,k}$ are (two) binary and (one) ternary parameters for interactions between solute species i, j, and k, respectively. Similar to Pitzer's equation for aqueous solutions of strong electrolytes, the second osmotic virial coefficient depends on temperature and on ionic strength. $A_{i,j}^{(0)}$ is the part of the second osmotic virial coefficient that does not depend on ionic strength, and $A_{i,j}^{(1)}$ is used to describe the influence of ionic strength. Parameters b and α were introduced by Pitzer and adopted from that work (Pitzer[10] (1973)): $b = 1.2$; $\alpha = 2.0$.

The binary and ternary interaction parameters ($A_{i,j}^{(0)}$, $A_{i,j}^{(1)}$, and $B_{i,j,k}$) are also expressed using a group contribution approach

$$A_{i,j}^{(d)} = \sum_{\text{all groups } k}\sum_{\text{all groups } l} \vartheta_k^{(i)}\vartheta_l^{(j)} a_{k,l}^{(d)} \quad \text{for } d = 0 \text{ and } 1 \tag{6}$$

$$B_{i,j,k} = \sum_{\text{all groups } k}\sum_{\text{all groups } l}\sum_{\text{all groups } m} \vartheta_k^{(i)}\vartheta_l^{(j)}\vartheta_m^{(k)} b_{k,l,m} \tag{7}$$

where $\vartheta_k^{(i)}$is the relative contribution of group k to the surface parameter Q_i of species i

$$\vartheta_k^{(i)} = \frac{\nu_k^{(i)} q_k}{Q_i} \tag{8}$$

$a_{k,l}^{(d)}$ and $b_{k,l,m}$ are binary and ternary interaction parameters between groups, respectively.

The equation for the activity of a solute from the VERS model is

$$\ln a_{i,m}^{*} = \ln m_i - A_\varphi z_i^2\left[\frac{\sqrt{I_m}}{1 + b\sqrt{I_m}} + \frac{2}{b}\ln(1 + b\sqrt{I_m})\right] + 2\left(\frac{1000}{M_\text{w}}\right)\frac{q_i}{q_\text{w}}\sum_{j\neq\text{w}}\frac{\Theta_j}{\Theta_\text{w}}[A_{i,j}^{(0)} + A_{i,j}^{(1)} f_2(I_m)] - z_i^2 f_3\,(I_m)\left(\frac{1000}{M_\text{w}}\right)^2 \sum_{j\neq\text{w}}\sum_{k\neq\text{w}}\frac{\Theta_j}{\Theta_\text{w}}\frac{\Theta_k}{\Theta_\text{w}} A_{j,k}^{(1)} + 3\left(\frac{1000}{M_\text{w}}\right)^2 \frac{q_i}{q_\text{w}}\sum_{j\neq\text{w}}\sum_{k\neq\text{w}}\frac{\Theta_j}{\Theta_\text{w}}\frac{\Theta_k}{\Theta_\text{w}} B_{i,j,k} \tag{9}$$

with

$$f_2(I_m) = \frac{2}{\alpha^2 I_m}[1 - (1 + \alpha\sqrt{I_m})\exp\{-\alpha\sqrt{I_m}\}] \tag{10}$$

$$f_3(I_m) = \frac{1}{\alpha^2 I_m^2}\left[1 - \left(1 + \alpha\sqrt{I_m} + \frac{\alpha^2 I_m}{2}\right)\exp\{-\alpha\sqrt{I_m}\}\right] \tag{11}$$

The summations in eqs 4 and 9 are over all solute species. Generally, all interaction parameters between solute species carrying the net charges of the same sign are neglected.

The expressions for the activities (eqs 4 and 9) require the Debye−Hückel parameter (A_φ) for water (at 298.15 K, $A_\varphi = 0.391466$, and at 338.15 K, $A_\varphi = 0.42358$),[11] surface parameters of groups k (q_k), and binary ($a_{i,j}^{(0)}, a_{i,j}^{(1)}$) as well as ternary ($\text{b}_{i,j,k}$) parameters for interactions between solute species.

It is assumed that the QVI molecule dissociates completely in water to ionic species (see Figure 1) abbreviated here by QVI^+ and MS^- (methyl sulfate, CH_3SO_4^-). Similarly, it is assumed that sodium sulfate is completely dissociated resulting in sodium ions and sulfate ions. The formation of bisulfate as well as the autoprotolysis of water are neglected. The number for the surface parameter of water ($q_\text{w} = 1.4$) was also assigned to Na^+ and $\text{SO}_4^=$. Thus, for the system ($\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$), the VERS model reduces to Pitzer's equation for the Gibbs excess energy of an aqueous solution of sodium sulfate, and the binary and ternary parameters for interaction between sodium and sulfate ions can be taken from Rogers and Pitzer.[12] QVI^+ and MS^- are treated as single groups. The surface parameters were estimated from the method of Bondi:[13] $q_{\text{QVI}^+} = 3.62$ and $q_{\text{MS}^-} = 3.128$. When all ternary parameters in the VERS model are neglected, there are still six parameters which are required: two parameters for interactions between QVI^+ and MS^- ($a_{\text{QVI}^+,\text{MS}^-}^{(0)} = A_{\text{QVI}^+,\text{MS}^-}^{(0)}$ and $a_{\text{QVI}^+,\text{MS}^-}^{(1)} = A_{\text{QVI}^+,\text{MS}^-}^{(1)}$) and four parameters for interactions between QVI^+ or Na^+ on one side and MS^- or $\text{SO}_4^=$ on the other side ($a_{\text{QVI}^+,\text{SO}_4^=}^{(0)}$, $a_{\text{QVI}^+,\text{SO}_4^=}^{(1)}$, $a_{\text{Na}^+,\text{MS}^-}^{(0)}$, and $a_{\text{Na}^+,\text{MS}^-}^{(1)}$). However, as due to stoichiometric considerations, there are only two independent parameters

$$A_{\text{Na}_2\text{SO}_4,\text{QVI}}^{(0)} = \frac{q_{\text{QVI}^+}}{2} a_{\text{QVI}^+,\text{SO}_4^=}^{(0)} + q_{\text{MS}^-} a_{\text{MS}^-,\,\text{Na}^+}^{(0)} \tag{12}$$

and

$$A_{\text{Na}_2\text{SO}_4,\text{QVI}}^{(1)} = \frac{q_{\text{QVI}^+}}{2} a_{\text{QVI}^+,\text{SO}_4^=}^{(1)} + q_{\text{MS}^-} a_{\text{MS}^-,\,\text{Na}^+}^{(1)} \tag{13}$$

Therefore, in total, four parameters are required. The binary parameters for interactions between the cations and the anions

Table 4. Interaction Parameters for the VERS Model

	lit. source	298 K	338 K
$a^{(0)}_{\mathrm{QVI^+,MS^-}}$	this work	$8.98 \cdot 10^{-5}$	$8.98 \cdot 10^{-5}$
$a^{(1)}_{\mathrm{QVI^+,MS^-}}$	this work	−0.0486	−0.0486
$a^{(0)}_{\mathrm{QVI^+,SO_4^=}}$	this work	0.3095	0.3095
$a^{(1)}_{\mathrm{QVI^+,SO_4^=}}$	this work	−0.0172	−0.0172
$a^{(0)}_{\mathrm{Na^+,SO_4^=}}$	Rogers and Pitzer[12]	0.01869	0.07983
$a^{(1)}_{\mathrm{Na^+,SO_4^=}}$	Rogers and Pitzer[12]	1.0994	1.2639
$b_{\mathrm{Na^+,Na^+,SO_4^=}}$	Rogers and Pitzer[12]	0.00131	−0.00152

of QVI ($a^{(0)}_{\mathrm{QVI^+,MS^-}}$ and $a^{(1)}_{\mathrm{QVI^+,MS^-}}$) were fitted to the new experimental data for the activity of water in aqueous solutions of QVI at (298 and 338) K, neglecting any influence of temperature on these parameters. The numerical values for these parameters are given in Table 4. The correlation results for the osmotic pressure of aqueous solutions of QVI are shown in Figure 2. The remaining parameters for interactions between $\mathrm{QVI^+}$ and $\mathrm{SO_4^=}$ ($a^{(0)}_{\mathrm{QVI^+,SO_4^=}}$ and $a^{(1)}_{\mathrm{QVI^+,SO_4^=}}$) were fitted to the new experimental data for the solid−liquid equilibrium in aqueous solutions of QVI and sodium sulfate at 298 K. They are also given in Table 4. The interactions between $\mathrm{MS^-}$ and $\mathrm{Na^+}$ were set to zero because, as mentioned before, the parameters between resulting species from QVI and $\mathrm{Na_2SO_4}$ dissociation are coupled. The experimental results for that phase equilibrium at 338 K were only used to test the model for its ability for predictions at that temperature. In the solid−liquid-phase equilibrium measurements, the precipitating substance was sodium sulfate decahydrate at 298 K and water-free sodium sulfate at 338 K, respectively. The condition for that phase equilibrium is: at 298 K

$$K^{\mathrm{s}}_{\mathrm{Na_2SO_4 \cdot 10H_2O}}(T) = a^2_{\mathrm{Na^+}} a_{\mathrm{SO_4^=}} a^{10}_{\mathrm{w}} \tag{14a}$$

and at 338 K

$$K^{\mathrm{s}}_{\mathrm{Na_2SO_4}}(T) = a^2_{\mathrm{Na^+}} a_{\mathrm{SO_4^=}} \tag{14b}$$

$K^{\mathrm{s}}_{\mathrm{Na_2SO_4}}$ and $K^{\mathrm{s}}_{\mathrm{Na_2SO_4 \cdot 10H_2O}}$ are the solubility constants of sodium sulfate and sodium sulfate decahydrate in water, respectively. Both constants were taken from the literature[14−16] ($K^{\mathrm{s}}_{\mathrm{Na_2SO_4 \cdot 10H_2O}}$ (298 K) = 0.0580; $K^{\mathrm{s}}_{\mathrm{Na_2SO_4}}$ (338 K) = 0.3438), and it is assumed that pressure has no influence on these constants. The calculation results using the VERS model are compared to the experimental data in Figures 3 and 4. It must be mentioned that only the experimental solid−liquid equilibrium data at 298 K were used to determine the parameters for interactions between sodium sulfate on one side and QVI on the other side. The experimental results for the cloud-points were not employed. The correlation results for the composition of the liquid phase reasonably agree with the experimental data. The predictions for the composition of the liquid phase that coexists at 338 K with pure sodium sulfate agree well with the new experimental data.

Conclusions

New experimental data for the activity of water of the binary system (water + 3-methyl-1-vinylimidazolium methyl sulfate (i.e., QVI)) and for the solid−liquid equilibrium of the ternary system (QVI + sodium sulfate + water) at (298 and 338) K are presented. The phase equilibrium data are correlated with the VERS model assuming that QVI is completely dissociated in an aqueous phase at around room temperature. Parameters for interactions between QVI were adjusted to the experimental results for the activity of water in the binary system ($\mathrm{H_2O}$ + QVI). Parameters for interactions between sodium sulfate and QVI were fitted to the experimental results for the solid−liquid equilibrium (SLE) at 298 K. With that set of parameters, the SLE of the ternary system ($\mathrm{Na_2SO_4}$ + QVI + $\mathrm{H_2O}$) at 338 K was successfully predicted.

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