HYDRATION ANALYSIS BASED CALCULATION OF SOLUTE ACTIVITY COEFFICIENTS IN TERNARY SATURATED SOLUTIONS

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Based on recently developed hydration analysis of solubility isotherms, a method for calculating activity coefficients of solute in ternary saturated solution is suggested. The method needs no adjustable parameters; it takes only solubility data and the value of the activity coefficient of the respective solute in its binary saturated solution under identical conditions as starting point. In the NaCl–KCl–H_2O model system, a comparison between the calculated activity coefficients and those obtained by de Lima and Pitzer from solution properties and from the solubility shows a good agreement over a wide temperature range.

As a part of the investigation of mutual connection between the shape of solubility isotherms and ionic processes in saturated ternary solutions, a computational treatment of solubility data called hydration analysis was developed[1]. During this analysis, solubility curves of the components (i.e. the branches of the solubility curve which begin with the solubility of the component) have been analyzed in systems consisting of water and two salts having a common ion. In each point of such solubility curve, the total amount of water present in the saturated solution has been splitted computationally in two terms: one of them refers to the water which preserved the properties of the water in binary saturated solution of the respective solute, the other term includes the water which changed its properties under the influence of the component added. Then a parameter P defined as mole fraction of water that has changed its properties if compared with the binary saturated solution is calculated in each point of the solubility curve. The dependence of the parameter P and related quantities on the amount of the non-saturating component serves as a source of information on ionic properties in the solution under consideration[1,2].

From the very definition of the approach, close relation between the hydration analysis parameter and activity coefficients is obvious. The aim of this paper is to express the relation analytically and compare the calculated activity coefficients with the literature data.

EQUATIONS

We are discussing ternary systems consisting of two salts having a common ion and water, i.e. M_pX_q–$M'_{p'}X_{q'}$–H_2O. For convenience we shall assume $p = q = p' = q' = 1$. We consider a binary system MX–H_2O with molality of the saturated solution m_0 (w_0 mass %) and ternary solution saturated with the same solute in the system MX–M′X–H_2O with molalities of the respective salts m_{MX} (w_{MX} mass %) and $m_{M'X}$ ($w_{M'X}$ mass %).

In hydration analysis, the amount of water which preserved in ternary solution the properties of the water in binary saturated solution of MX (the effective water w_{eff}) is calculated so that

$$m_0^2 = m_{MX}\,(m_{MX} + m_{M'X}) \quad . \tag{1}$$

This may be done by expressing the molalities via mass %:

$$\left(\frac{1\,000 w_0}{(M_r)_{MX}\,(w_w)_0}\right)^2 = \frac{1\,000 w_{MX}}{(M_r)_{MX} w_{eff}}\;\frac{1\,000}{w_{eff}}\left(\frac{w_{MX}}{(M_r)_{MX}} + \frac{w_{M'X}}{(M_r)_{M'X}}\right) , \tag{2}$$

where $(w_w)_0$ is the concentration of water (in mass %) in the binary saturated solution serving as our reference point. From Eq. (*2*),

$$w_{eff} = \frac{(w_w)_0\,(M_r)_{MX}}{w_0}\,[n_{MX}\,(n_{MX} + n_{M'X})]^{1/2} \quad , \tag{3}$$

where $n_i = w_i/(M_r)_i$ is the amount of substance of the component *i* in 100 g of the saturated solution.

According to the definition of the parameter *P*

$$P = \frac{w_{H_2O} - w_{eff}}{(M_r)_{H_2O}\,(n_{H_2O} + n_{MX} + n_{M'X})} \quad , \tag{4}$$

where $w_{H_2O} = 100 - w_{MX} - w_{M'X}$ answers to the concentration of water in ternary saturated solution under consideration (in mass %).

Forgetting the hydration analysis and Eqs (*1*) to (*4*) for a moment and using the usual description of the respective equilibrium with the aid of activity coefficients

$$\gamma_0^2 m_0^2 = \gamma_\pm^2\,(m_{MX} + m_{M'X})\,m_{MX} \quad . \tag{5}$$

Therefore

$$\frac{\gamma_\pm}{\gamma_0} = \left[\frac{m_0^2}{(m_{\mathrm{MX}} + m_{\mathrm{M'X}})\, m_{\mathrm{MX}}}\right]^{1/2} \quad . \tag{6}$$

Again, expressing molalities via mass % helps to find the relation to water concentrations:

$$\frac{\gamma_\pm}{\gamma_0} = \frac{w_{\mathrm{H_2O}}}{(w_w)_0}\; \frac{w_0}{[n_{\mathrm{MX}}\,(n_{\mathrm{MX}} + n_{\mathrm{M'X}})]^{1/2}\,(M_\mathrm{r})_{\mathrm{MX}}} \quad . \tag{7}$$

This thermodynamical treatment of the problem may be put into relation with the hydration analysis by substituting Eq. (*3*) into (*7*) which gives

$$\frac{\gamma_\pm}{\gamma_0} = \frac{w_{\mathrm{H_2O}}}{w_{\mathrm{eff}}} \quad . \tag{8}$$

Therefore

$$w_{\mathrm{eff}} = w_{\mathrm{H_2O}}\,\frac{\gamma_0}{\gamma_\pm} \tag{9}$$

and

$$P = \frac{w_{\mathrm{H_2O}}}{(M_\mathrm{r})_{\mathrm{H_2O}}\,(n_{\mathrm{H_2O}} + n_{\mathrm{MX}} + n_{\mathrm{M'X}})}\left(1 - \frac{\gamma_0}{\gamma_\pm}\right) = x_{\mathrm{H_2O}}\left(1 - \frac{\gamma_0}{\gamma_\pm}\right) \quad , \tag{10}$$

where $x_{\mathrm{H_2O}}$ is the mole fraction of water in the ternary saturated solution under consideration.

RESULTS AND DISCUSSION

In the NaCl–KCl–H_2O system at 20 – 190.6 °C, solubility curves measured by Cornec and Krombach[3] were treated by the above procedure taking the γ_0 values for NaCl and KCl from refs[4,5], respectively. Tables I to III give the results comparing the calculated activity coefficients with those reported by de Lima and Pitzer[5] based on solution properties and solubility for the same set of experimental data.

Considering Tables I – III we note that the agreement between the activity coefficients of de Lima and Pitzer[5] and those calculated in this paper is in general good. Therefore, in the system where the hydration analysis was performed, activity coefficient of the solute in ternary saturated solutions may be calculated simply according to the Eq. (*10*) provided the activity coefficient of the respective component in its binary saturated solution under identical conditions is known. Moreover, the established connection between the hydration analysis, the idea of which is yielding structural information on saturated solutions and activity coefficients as thermodynamical values may be stated both surprising and perspective.

TABLE I
Activity coefficients, $\gamma_{\pm}$, of NaCl in saturated aqueous mixture NaCl + KCl[a]; t is temperature; m_i is molality of the component i

t, °C	m_{NaCl}	m_{KCl}	$\gamma_{\pm}$		
			solution[5]	solubility[5]	this paper
20	5.50_8	1.33_0	1.013	0.995	0.991
20	5.81_6	0.659_0	1.004	0.995	0.991
40	5.40_9	1.73_3	1.039	1.025	1.021
40	5.80_1	0.870_0	1.030	1.024	1.015
60	5.33_8	2.16_8	1.025	1.016	1.008
60	5.82_3	1.08_9	1.017	1.014	1.003
80	5.20_3	2.87_1	0.983	0.978	0.976
80	5.82_8	1.43_3	0.977	0.974	0.961
100	4.94_0	4.08_6	0.920	0.917	0.911
100	4.79_1	4.02_4	0.909	0.942	0.910
120	5.34_6	3.68_0	0.839	0.837	0.832
120	6.05_5	1.90_2	0.842	0.838	0.832
140	5.47_2	4.17_1	0.760	0.753	0.745
140	6.26_6	2.03_1	0.696	0.706	0.751
169.5	5.55_6	5.42_1	0.605	0.610	0.617
169.5	6.24_4	3.29_1	0.624	0.618	0.627
169.5	6.78_5	1.78_0	0.633	0.625	0.634
189.6	5.77_6	6.16_6	0.505	0.513	0.507
189.6	6.31_6	4.12_9	0.528	0.525	0.518
189.6	6.98_7	2.07_1	0.544	0.536	0.528

[a] NaCl is present as the equilibrium solid phase.

TABLE II
Activity coefficients, $\gamma_\pm$, of KCl in saturated aqueous mixture NaCl + KCl[a]; t is temperature; m_i is molality of the component i

t, °C	m_{NaCl}	m_{KCl}	$\gamma_\pm$		
			solution[5]	solubility[5]	this paper
20	1.72_1	3.57_1	0.613	0.620	0.615
20	3.45_5	2.68_8	0.659	0.663	0.658
20	4.30_5	2.34_1	0.668	0.683	0.678
40	1.74_8	4.27_7	0.654	0.659	0.656
40	3.48_6	3.31_8	0.701	0.704	0.700
60	1.73_7	4.96_1	0.671	0.677	0.674
60	3.46_9	3.98_0	0.713	0.717	0.714
80	1.77_1	5.63_9	0.668	0.672	0.670
80	3.49_4	4.64_6	0.703	0.706	0.704
100	1.74_4	6.31_9	0.647	0.651	0.650
100	3.47_8	5.34_5	0.672	0.676	0.676
120	1.73_7	7.04_2	0.611	0.611	0.611
120	3.46_9	6.06_7	0.627	0.632	0.631
140	1.77_7	7.77_4	0.565	0.560	0.565
140	3.47_3	6.82_0	0.572	0.576	0.581
169.5	1.78_3	8.78_7	0.483	0.478	0.494
169.5	3.51_5	7.97_7	0.479	0.481	0.497
169.5	4.53_7	7.52_4	0.473	0.484	0.500
189.6	1.76_8	9.60_5	0.421	0.413	0.434
189.6	3.46_1	8.85_1	0.425	0.414	0.436
189.6	4.40_5	9.96_5	0.404	0.416	0.436

[a] KCl is present as the equilibrium solid phase.

TABLE III
Activity coefficients, $\gamma_\pm$, of NaCl and KCl in saturated aqueous mixture NaCl + KCl[a]; t is temperature; m_i is molality of the component i

t, °C	m_{NaCl}	m_{KCl}	$\gamma_\pm$			$\gamma_\pm$		
			b	*c*	*d*	*b*	*c*	*d*
20	5.06_7	2.06_0	1.007	1.016	1.031	0.737	0.704	0.729
40	5.00_8	2.62_7	1.048	1.030	1.021	0.752	0.747	0.743
60	4.86_2	3.29_8	1.036	1.021	1.013	0.751	0.752	0.749
80	4.74_9	4.02_7	0.991	0.981	0.980	0.729	0.730	0.728
100	4.70_8	4.73_4	0.922	0.918	0.913	0.685	0.697	0.694
120	4.70_8	5.46_9	0.835	0.840	0.835	0.637	0.644	0.644
140	4.82_2	6.18_2	0.738	0.746	0.744	0.574	0.585	0.591
169.5	5.04_8	7.31_3	0.582	0.603	0.612	0.470	0.485	0.501
189.5	5.38_1	8.19_7	0.473	0.499	0.492	0.393	0.409	0.430

[a] Both electrolytes are present as the equilibrium solid phase. [b] Solution data, ref.5. [c] Solubility, ref.5. [d] This paper.

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