HYDRATION ANALYSIS AND THE EXPANSION OF RELATIVE ACTIVITY COEFFICIENTS

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Of correlation methods for solubility in ternary systems, the method of expansion of relative activity coefficients and the hydration analysis are based on the thermodynamic condition of phase equilibria. Both of them require only reliable solubility data in the ternary system and corresponding binary systems. Correlation parameters of both of these methods are interrelated and the methods are compared on the system K_2SO_4–H_2SO_4–H_2O at 50 °C.
Key words: Solubility; Ternary systems; Hydration analysis; Phase equilibria; Thermodynamics; Solutions.

Let us consider a ternary system consisting of two electrolytes 1 and 2 having a common ion and water. The solution is saturated with component 1 and contains n_2 moles of component 2. If the electrolytes have a common anion, the method of expansion of relative activity[1] coefficients yields the correlation

$$\frac{1}{\alpha+\beta}\log\left[X_1^{\alpha}\left(X_1+\frac{\nu_{2-}m_{20}}{\nu_{1-}m_{10}}X_2\right)^{\beta}\right]=f\ , \qquad (1)$$

where $\alpha = \nu_{1+}$ is the number of cations in the molecule of 1, $\beta = \nu_{1-}$ is the number of anions in the molecule of 1, $X_i = m_i/m_{i0}$ is the relative molality of the *i*-th component and

$$f=-\log\frac{\gamma_i''}{\gamma_{i0}''}=Q_{12}m_2+Q_{122}m_2^2+Q_{1222}m_2^3 \qquad (2)$$

is a function of the relative activity coefficient, where γ_i'' is the activity coefficient of the *i*-th component in ternary liquid and γ_{i0}'' is the activity coefficient of the *i*-th component in saturated binary solution.

The hydration analysis[2,3] defines the parameter P as a mole fraction of water that has changed its properties under influence of the added component 2; in combination with a thermodynamic treatment, Eq. (*3*) holds[3]

$$P = \frac{w_0}{M_0\left(n_0 + n_1 + n_2\right)}\left(1 - \frac{\gamma''_{10}}{\gamma''_1}\right) = x_0\left(1 - \frac{\gamma''_{10}}{\gamma''_1}\right), \qquad (3)$$

where $n_i = w_i/M_i$ is the amount of the component i in corresponding solution, w_i is its mass and the subscript 0 denotes water or binary solution. It has been shown elsewhere[4] that the quantities P and f exhibit a similar character.

Another quantity, Ξ, has been introduced[5] for characterization of the interactions in the ternary system: it has been termed the residual Gibbs energy for the transfer of n_1 mole of electrolyte 1 from its saturated binary solution to a corresponding ternary solution.

$$\Xi = n_1 RT \ln \frac{\gamma''_1}{\gamma''_{10}} \qquad (4)$$

Starting from the definitions above, we can deduce the following relationships showing equivalency of the quantities characterizing both of the correlation methods:

$$P = x_0\left(1 - 10^f\right) \qquad (5)$$

$$f = \log\left(1 - \frac{P}{x_0}\right) \qquad (6)$$

$$\Xi = -2.303RTf\,. \qquad (7)$$

RESULTS AND DISCUSSION

Solubilities of the potassium sulfate in solutions containing sulfuric acid[6,7] have been chosen as an example. As can be seen from Fig. 1, the solubility of K_2SO_4 increases with addition of H_2SO_4. This may be explained by formation of associated ions in the ternary solution[4,7]. Treatment of experimental

data[7] by the method of expansion of relative activity coefficients (Eqs (*1*) and (*2*)) led to the interaction constants

Q_{12} = 0.394685, Q_{122} = –0.10277 and Q_{1222} = 0.01428.

Corresponding plots of the values of f and f/x_0 are shown in Fig. 2 and the smoothed solubilities are represented by the curve in Fig. 1.

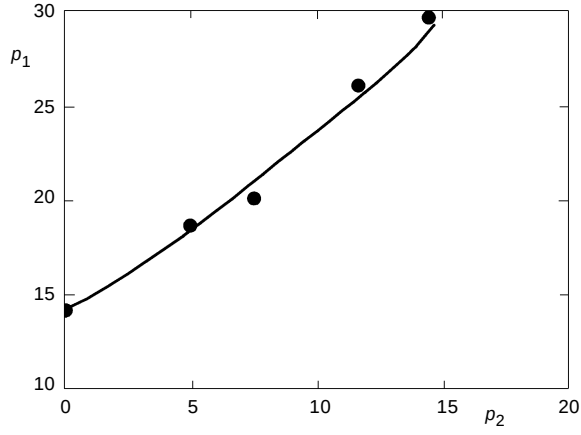

FIG. 1
Smoothed solubility in the system K_2SO_4–H_2SO_4–H_2O at 50 °C

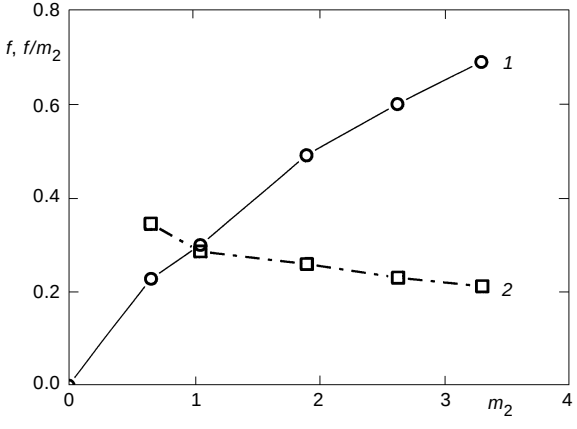

FIG. 2
Functions of relative activity coefficients f (*1*) and f/m_2 (*2*)

TABLE I
Comparison of correlation methods

p_1	p_2	x_0	P	f_{calc} γ_1''/γ_{10}'' (Eq.(*6*))	f γ_1''/γ_{10}'' (Eq.(*2*))	$\Delta f \cdot 10^4$ $\Delta(\gamma_1''/\gamma_{10}'') \cdot 10^3$
14.16	0	0.9832	0	0	0	0
				1	1	0
18.66	4.92	0.9643	–0.66	0.2266	0.2260	6
				0.593	0.594	–1
20.09	7.45	0.9546	–0.94	0.2979	0.2988	–9
				0.504	0.503	1
26.03	11.60	0.9282	–1.92	0.4872	0.4876	–4
				0.326	0.325	1
29.61	14.40	0.9075	–2.67	0.5961	0.5961	0
				0.253	0.253	0
32.80	16.40	0.8881	–3.41	0.6853	0.6847	6
				0.206	0.207	–1
						$\lvert\Phi\rvert$ = 4.2
						$\lvert\Delta(\gamma_1''/\gamma_{10}'')\rvert$ = 0.67

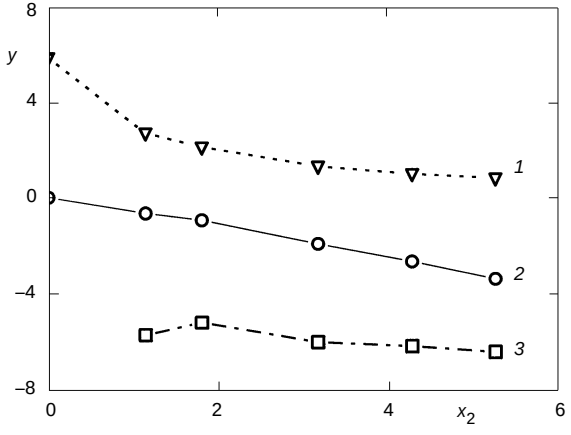

FIG. 3
Hydration analysis of the system K_2SO_4–H_2SO_4–H_2O at 50 °C: $1 \cdot 10^{-1}\ x_0/s$ (*1*), P (*2*), $1 \cdot 10^{-1}\ P/x_2$ (*3*)

On the other hand, the results of the hydration analysis are depicted in Fig. 3. It can be seen that the curve P (curve *2* in Fig. 3) decreases with increasing acid concentration, which (according to Eq. (*5*)) corresponds to the rising value of f in Fig. 2. Similarly, curves P/x_2 (Fig. 3) and f/m_2 (Fig. 2) are mirror images. Function f of relative activity coefficient can be obtained either by the method of expansion of relative activity coefficients (Eq. (*2*)) or by the hydration analysis method employing Eq. (*6*). A comparison of these values is shown in Table I; it can be seen that both methods yield identical values.

SYMBOLS

f	function of relative activity coefficient, Eq. (*2*)
M_i	molecular weight of the *i*-th substance
m_i	molality of the *i*-th substance
n_i	amount of the *i*-th substance, mole
P	mole fraction of water with changed properties (Eq. (*3*))
p_i	amount of the *i*-th substance, wt.%
$Q_{ij}, Q_{ijj}, Q_{ijjj}$	interaction constants
R	gas constant
s	amount of electrolyte components in solution, mole
T	temperature
w_i	mass of the *i*-th substance
X_i	relative molality of the *i*-th substance
x_0	mole fraction of water
α	number of cations in the *i*-th substance
β	number of anions in the *i*-th substance
γ_i''	activity coefficient of the *i*-th substance in solution
$\nu_\pm$	number of cations/anions in the *i*-th substance
Ξ	the residual Gibbs energy for the transfer of n_1 moles of electrolyte 1 from its saturated binary solution to a corresponding ternary solution

Subscripts

i, j	substance
0	water

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