Reviews

Osmotic Coefficient of K_2SO_4(aq) in Supersaturated Solution at T = 298.15 K

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The Zdanovskii rule, in simple and modified form, was used for the estimation of supersaturated K_2SO_4(aq) osmotic coefficients at T = 298.15 K by treatment of the isopiestic data of the mixed electrolyte solutions. The results were compared with the predictions of the Åkerlöf−Thomas rule and of weighted averages. Estimated values by the Zdanovskii rule together with the K_2SO_4(aq) osmotic coefficient experimental data in unsaturated solution were used in fitting the data to the extended Pitzer equation. The reliability of the Zdanovskii rule estimation was tested on the prediction of the osmotic coefficients in several mixed electrolyte solutions containing K_2SO_4 and having an ionic strength much greater than the ionic strength of saturated K_2SO_4(aq) and on the osmotic coefficient estimation for supersaturated Na_2SO_4(aq) at T = 298.15 K.

Introduction

For treatment of the thermodynamic properties of mixed electrolyte solutions, it is necessary to know the properties of pure electrolyte solutions at the ionic strength of the mixture. Very often, the ionic strength of the mixed electrolyte solution significantly exceeds the ionic strength of the saturated pure solution of electrolyte, which is part of the mixture. Therefore, it is necessary to predict the thermodynamic properties of this pure electrolyte solution in the supersaturated region. There have been attempts to estimate the thermodynamic properties in the supersaturated concentration region of electrolyte solution. The prediction of the osmotic coefficients of K_2SO_4(aq) above the solubility limit $m = 0.7$ mol·kg^{-1} at T = 298.15 K, up to molalities of $m = 1.2$ mol·kg^{-1}, $m = 4.0$ mol·kg^{-1}, and $m = 2.3$ mol·kg^{-1}, was made by Robinson et al.[1], Kuschel and Seidel,[2] and Sangster et al.[3], respectively. Palmer et al.[4] evaluated the osmotic coefficients of supersaturated Rb_2SO_4(aq) and Cs_2SO_4(aq) by the Åkerlöf−Thomas rule.[5]

In this paper, the estimation of the osmotic coefficients of supersaturated K_2SO_4(aq) at T = 298.15 K was performed by applying the Zdanovskii rule,[6] in simple and modified form up to molalities of $m = 5.2$ mol·kg^{-1} and $m = 5.6$ mol·kg^{-1}, respectively. The results were compared with the predictions of the Åkerlöf−Thomas rule and of weighted averages. The Åkerlöf−Thomas rule was used with several electrolyte solutions that served as reference, and weighted averages estimation with some different salt combinations.

The osmotic coefficients predicted by the Zdanovskii rule together with the osmotic coefficient experimental data of Palmer et al.[7] for molalities of K_2SO_4(aq) lower than 0.7 mol·kg^{-1} were used in fitting the data in the extended Pitzer equation. The obtained parameters of the Pitzer equation were used for the prediction of the osmotic coefficients by the extended Pitzer equation for some mixed solutions having an ionic strength greater than 2.1 mol·kg^{-1}. In addition, the reliability of the Zdanovskii rule estimation was also tested on the osmotic coefficients for supersaturated Na_2SO_4(aq) at T = 298.15 K.

Treatment of Data. *Application of the Zdanovskii Rule.* An approximate relationship, known as the Zdanovskii rule, was first discovered empirically by Zdanovskii[6] and later derived independently by Stokes and Robinson.[8]

The Zdanovskii rule, applied to a mixed solution of electrolytes A and B is given by

$$m_A/m_{A0} + m_B/m_{B0} = 1 \tag{1}$$

where m_A and m_B are the molalities of electrolytes A and B in mixed solution at isopiestic equilibrium (e.g., the same solvent activity, a_w) with the pure electrolyte solutions having molalities m_{A0} and m_{B0}, respectively. The rule is valid, according to the Russian school,[9] for solutions where the interactions of ions and solvent are significant and the interactions between ions are negligible. Equation 1 for a constant solvent activity, a_w, represents a straight line in a plot of m_A against m_B.

To take account of deviations from Zdanovskii linearity and interaction between ions, eq 1 may be written in the following form:

$$m_A/m_{A0} + m_B/m_{B0} + bm_Am_B/(m_A + m_B) = 1 \tag{1a}$$

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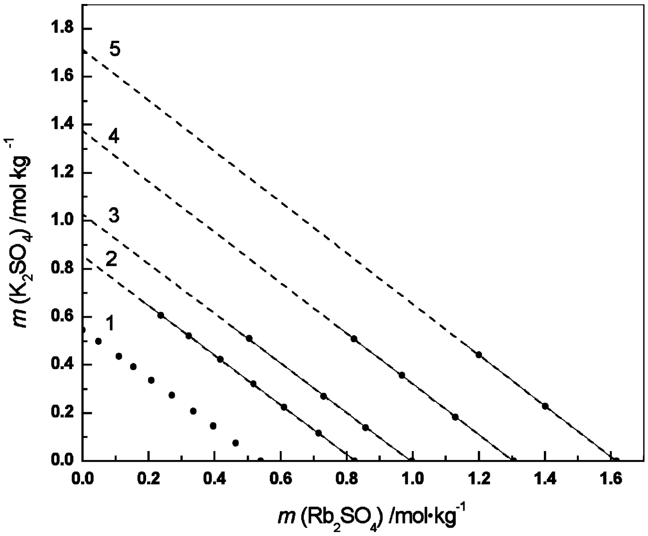

Figure 1. Zdanovskii rule applied to the system K_2SO_4 + Rb_2SO_4 + H_2O[10] (the dashed lines represent the extrapolation of isopiestic data): 1, $a_w = 0.9800$; 2, $a_w = 0.9706$; 3, $a_w = 0.9643$; 4, $a_w = 0.9535$; 5, $a_w = 0.9428$.

where b presents an empirical deviation parameter. Although many ternary systems obey eq 1 closely enough, the effect of even a small value of b can become quite marked at high concentrations.

When a_w exceeds the solubility limit of electrolyte A, the molality, m_{A0}, in the supersaturated solution of pure electrolyte A can be obtained by linear extrapolation (eq 1) of straight lines in the m_A against m_B plot, as illustrated in Figure 1. On the other hand, if m_{A0} is to be calculated from eq 1a, usually the average value of b, obtained from unsaturated solution data has to be extrapolated to supersaturated m_{A0}.

Once the molality, m_{A0}, in the supersaturated solution of A is determined, either by eq 1 or eq 1a, its osmotic coefficient, ϕ, is given by

$$\phi = -(1000/M_w)(\ln a_w/\nu_A m_{A0}) \qquad (2)$$

or from the fundamental equation for isopiestic equilibrium

$$\phi = \nu_R m_R \phi_R/\nu_A m_{A0} \qquad (3)$$

where M_w is the molar mass of solvent in grams per mole, ν_A is the stoichiometric ionization number of electrolyte A, and ν_R, m_R, and ϕ_R denote the corresponding quantities for the isopiestic reference standard. To obtain a better precision in linear extrapolation, it is favorable to have more isopiestic data for mixed solutions having a lower ionic strength fraction of A, for example, K_2SO_4, in the total ionic strength of the solutions (Figure 1).

The Zdanovskii rule (ZR) in the form of eq 1 and empirical modification of the Zdanovskii rule (MZR) in the form of eq 1a with the appropriate average value of b were used in treatment of the following ternary system data: (1) $K_2SO_4 + Li_2SO_4 + H_2O$, $b_{av} = -0.1873$; (2) $K_2SO_4 + Na_2SO_4 + H_2O$, $b_{av} = -0.0770$; (3) $K_2SO_4 + Rb_2SO_4 + H_2O$, $b_{av} = -0.0266$; (4) $K_2SO_4 + Cs_2SO_4 + H_2O$, $b_{av} = -0.0085$; and (5) $K_2SO_4 + (NH_4)_2SO_4 + H_2O$, $b_{av} = 0.0447$. The estimated osmotic coefficients and molalities of supersaturated K_2SO_4(aq) are listed in Table 1. The osmotic coefficients obtained from the ZR against the K_2SO_4(aq) molality are given in Figure 2. The osmotic coefficients originating from the MZR prediction are illustrated in Figure 3 together with the results of Sangster et al.[3] obtained from the ternary systems $K_2SO_4 + Na_2SO_4 + H_2O$, $K_2SO_4 + NaCl + H_2O$, and $K_2SO_4 + KCl + H_2O$ by the modified Zdanovskii rule.

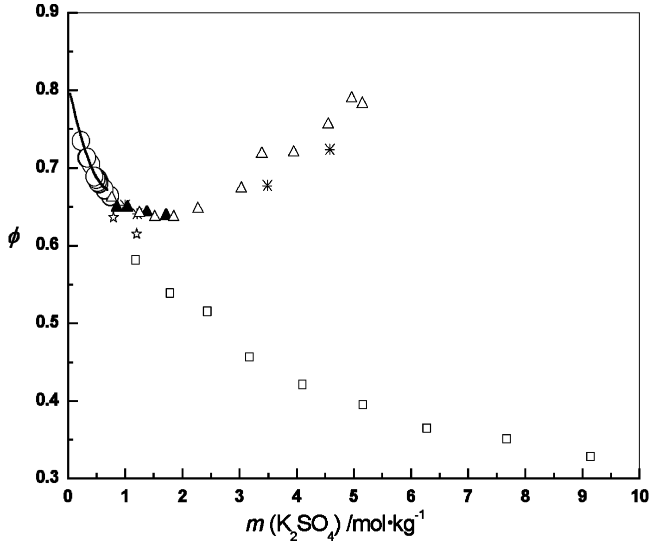

Figure 2. Osmotic coefficients of K_2SO_4(aq) at T = 298.15 K against the molality, obtained from different systems by the Zdanovskii rule (ZR): *, $K_2SO_4 + Cs_2SO_4 + H_2O$; □, $K_2SO_4 + Li_2SO_4 + H_2O$; ☆, $K_2SO_4 + Na_2SO_4 + H_2O$; ▲, $K_2SO_4 + Rb_2SO_4 + H_2O$; △, $K_2SO_4 + (NH_4)_2SO_4 + H_2O$; ○, experimental data of Palmer et al.[7] in the unsaturated region.

Application of the Åkerlöf–Thomas Rule and Method of Weighted Averages. Åkerlöf and Thomas[5] observed that the difference between the values of osmotic or activity coefficients for two different electrolytes of the same valence type is a linear function of the molality from low to fairly high molalities, where one of the electrolytes may be used as a reference for such a comparison. The corresponding form of the rule applied for the prediction of the osmotic coefficient values of K_2SO_4(aq) is

$$\Delta\phi = \phi(K_2SO_4) - \phi(R_2SO_4) = k_\phi m \qquad (4a)$$

$$R \equiv Rb, Cs, Li, Na, (NH_4)$$

$$\phi(K_2SO_4) = \phi(R_2SO_4) + k_\phi m \qquad (4b)$$

where $\phi(R_2SO_4)$ is the osmotic coefficient of the reference solution. The reference solutions, R_2SO_4(aq), were Rb_2SO_4(aq), Cs_2SO_4(aq), Li_2SO_4(aq), Na_2SO_4(aq), and $(NH_4)_2SO_4$(aq). In Table 2 are given the values of k_ϕ and ranges of molality in k_ϕ determination for referent solutions. The predicted osmotic coefficients by the Åkerlöf–Thomas rule are presented in Figure 4.

The method of weighted averages proposed by Robinson et al.[1] is based on the assumption that the osmotic coefficient of K_2SO_4(aq) "lays" on the same way between the osmotic coefficients of the other two "neighbor" electrolytes up to its solubility limit and above it.

That way,

$$\phi(K_2SO_4) = y\phi(A_2SO_4) + (1 - y)\phi(B_2SO_4) \qquad (5)$$

where $\phi(A_2SO_4)$ and $\phi(B_2SO_4)$ are the osmotic coefficients of the other two electrolytes and y and $(1 - y)$ are the fractions of the osmotic coefficients of A_2SO_4(aq) and B_2SO_4(aq), respectively, for a given molality.

The three electrolyte combinations used for the K_2SO_4(aq) osmotic coefficient estimation were the following: (1)

Table 1. Estimated Molalities, $m(K_2SO_4)$, and Osmotic Coefficients ϕ, in Supersaturated $K_2SO_4(aq)$ at T = 298.15 K, Obtained by the Zdanovskii Rule (ZR) or Its Empirical Modification (MZR) from the Following Three-Component Systems

	Zdanovskii rule (ZR)		modified Zdanovskii rule (MZR)		
system	$m(K_2SO_4)$/mol·kg^{-1}	ϕ^a	$m(K_2SO_4)$/mol·kg^{-1}	ϕ^a	source of data
$K_2SO_4 + Li_2SO_4 + H_2O^b$	1.1854	0.5812			Filippov et al.[11]
	1.7832	0.5387	1.5032	0.6391	
	2.4374	0.5152	1.9439	0.6458	
	3.1762	0.4565	2.2380	0.6481	
	4.1057	0.4209	2.5117	0.6883	
	5.1572	0.3949	2.7981	0.7276	
	6.2806	0.3647	3.0270	0.7564	
	7.6741	0.3511	3.2572	0.8271	
	9.1401	0.3279	3.4878	0.859	
$K_2SO_4 + Na_2SO_4 + H_2O$	0.7937	0.6363	0.7711	0.6593	Robinson et al.[1]
	1.2029	0.6151	1.1539	0.6446	
$K_2SO_4 + Rb_2SO_4 + H_2O$	0.8541	0.6486	0.8488	0.6595	Kalinkin and Rumyantsev[10]
	1.0391	0.6487	1.0072	0.6678	
	1.3748	0.6429	1.3395	0.6577	
	1.7133	0.6385	1.6554	0.6584	
$K_2SO_4 + Cs_2SO_4 + H_2O^b$	0.9947	0.6521			Filippov et al.[12]
	1.2127	0.6410	1.2114	0.6442	
	3.4863	0.6774	3.4037	0.6943	
	4.5797	0.7237	4.4377	0.7469	
$K_2SO_4 + (NH_4)_2SO_4 + H_2O$	0.7658	0.6613	0.7753	0.6532	Rumyantsev[c]
	1.2490	0.6418	1.2894	0.6217	
	1.5179	0.6368	1.5866	0.6092	
	1.8481	0.6365	1.9662	0.5983	
	2.2718	0.6473	2.4703	0.5953	
	3.0307	0.6732	3.4243	0.5958	
	3.3922	0.7182	3.9316	0.5968	
	3.9453	0.7199	4.6986	0.6045	
	4.5497	0.7558	5.6237	0.6115	
	4.9587	0.7891			
	5.1502	0.7824			

[a] For eq 3, the osmotic coefficients of the referent solutions NaCl(aq), KCl(aq), and $Na_2SO_4(aq)$ at T = 298.15 K are obtained by Archer[13,14] and Rard et al.,[15] respectively. [b] In the absence of isopiestic data for $K_2SO_4 + Li_2SO_4 + H_2O$ and $K_2SO_4 + Cs_2SO_4 + H_2O$ in the lower concentration region with available m_{A0} for $K_2SO_4(aq)$, the parameter b needed for the MZR is determined by extrapolated values of m_{A0} using Archer and Kirklin parameters[25] for $K_2SO_4(aq)$ valid up to m = 1.2 mol·kg^{-1} for the lowest available water isopiestic activities. [c] A. V. Rumyantsev, unpublished data.

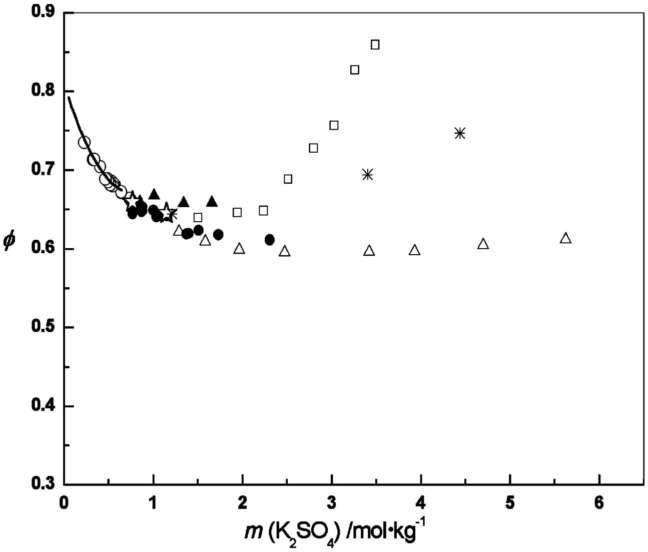

Figure 3. Osmotic coefficients of $K_2SO_4(aq)$ at T = 298.15 K against the molality, obtained from different systems by the modified Zdanovskii rule (MZR): *, $K_2SO_4 + Cs_2SO_4 + H_2O$; □, $K_2SO_4 + Li_2SO_4 + H_2O$; ☆, $K_2SO_4 + Na_2SO_4 + H_2O$; ▲, $K_2SO_4 + Rb_2SO_4 + H_2O$; △, $K_2SO_4 + (NH_4)_2SO_4 + H_2O$; ●, estimated values by Sangster et al.[3]; ○, experimental data of Palmer et al.[7] in the unsaturated region.

$(NH_4)_2SO_4(aq)/K_2SO_4(aq)/Rb_2SO_4(aq)$, (2) $(NH_4)_2SO_4(aq)/K_2SO_4(aq)/Cs_2SO_4(aq)$, and (3) $(NH_4)_2SO_4(aq)/K_2SO_4(aq)/Li_2SO_4(aq)$.

Fraction y, in function of molality, obeys the polynomial of the second order and therefore can be applied to different molality limits depending on the electrolyte combination in question: for combinations 1 and 2, up to a molality limit of $m \approx 1$ mol·kg^{-1}, and for combination 3, up to a molality limit of $m \approx 1.7$ mol·kg^{-1}. The results of osmotic coefficient evaluation are presented in Figure 5.

For the calculation of the osmotic coefficients of pure solutions that served as reference ones in the Åkerlöf–Thomas rule or the method of weighted averages Archer's extension[13,16,17] of Pitzer's model,[18] the following form for the solutions of 1:2 electrolyte was used:

$$\phi - 1 = -2A_\phi I^{1/2}/(1 + bI^{1/2}) + (^4/_3)mB^\phi + (^{16}/_3)m^2C^{T,\phi} \tag{6}$$

where

$$B^\phi = \beta^{(0)} + \beta^{(1)} \exp(-\alpha I^{1/2}) \tag{7}$$

$$C^{T\phi} = C^{(0)} + C^{(1)} \exp(-\omega I^{1/2}) \tag{8}$$

In eqs 6–8, I is the ionic strength of the solution ($I = 3m$), m is the stoichiometric molality, A_ϕ is the Debye–Hückel coefficient for the osmotic coefficient, which has the value 0.391 475 kg$^{1/2}$·mol$^{-1/2}$ for water solutions at T = 298.15 K, and b = 1.2 kg$^{1/2}$·mol$^{-1/2}$. The parameters defining the second (B^ϕ) and third ($C^{T\phi}$) virial coefficients are given in Table 2. The parameters α and ω have assigned values of 2.0 kg$^{1/2}$·mol$^{-1/2}$ and 2.5 kg$^{1/2}$·mol$^{-1/2}$, respectively.

Results and Discussion

The Zdanovskii rule can be an adequate approximation for the thermodynamic properties of alkali metal sulfate

Table 2. Parameters of the Extended Pitzer Equation for Pure Electrolyte Solutions at T = 298.15 K, Valid up to Maximum Molality, max m, with Standard Deviation of Fit, s, and Values of k_ϕ, with Ranges of Molality in Which k_ϕ Was Determined

	K_2SO_4(aq)[7]	Rb_2SO_4(aq)[4]	Cs_2SO_4(aq)[4]	Na_2SO_4(aq)[15]	$(NH_4)_2SO_4$(aq)[19]	Li_2SO_4(aq)[20 a]
$\beta^{(0)}/\text{mol·kg}^{-1}$	−0.004 6639	0.052 04	0.091 04	0.011 976	0.037 402 8	0.135 76
$\beta^{(1)}/\text{mol·kg}^{-1}$	0.774 728	0.6365	0.5659	0.951 276	0.534 514	1.2448
$C^{(0)}/\text{mol}^2\text{·kg}^{-2}$	$0.801\,034 \times 10^{-2}$	6.975×10^{-4}	3.683×10^{-5}	2.4359×10^{-3}	$-2.176\,17 \times 10^{-4}$	-1.3973×10^{-3}
$C^{(1)}/\text{mol}^2\text{·kg}^{-2}$	0.383 779	0.2124	0.076 69	0.236 044	0.164 263	5.4533×10^{-4}
max $m/\text{mol·kg}^{-1}$	0.7	2.018	3.1082	3.8140	5.5	3.0
s	0.002	0.0019	0.0009	0.000 91		
k_ϕ		−0.021 327	−0.046 362	−0.004 474 3	0.020 596	−0.156 63
range of $m/\text{mol·kg}^{-1}$ for k_ϕ		0.25−0.5	0.35−0.7	0.45−0.7	0.4−0.6	0.5−0.7

[a] Parameters obtained by the conversion of standard Pitzer parameters[20] by the method of Rard and Wijensinghe.[21]

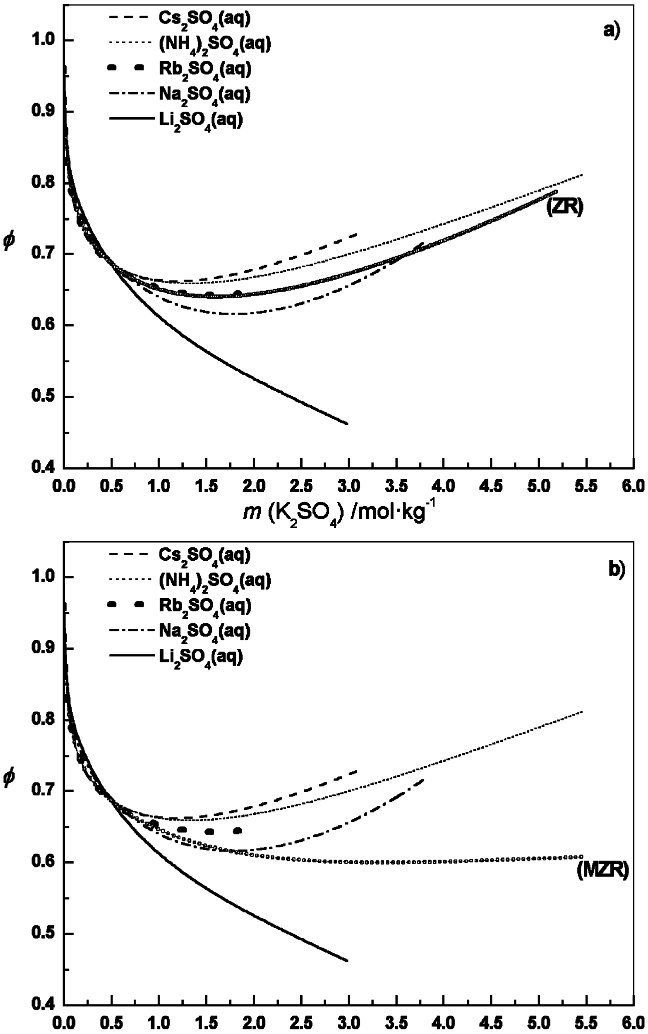

Figure 4. Predicted osmotic coefficients of K_2SO_4(aq) at T = 298.15 K by the Åkerlöf−Thomas rule for the different referent solutions noted in the graphic and fitted using values of extended Pitzer parameters: (a) from the ZR; (b) from the MZR.

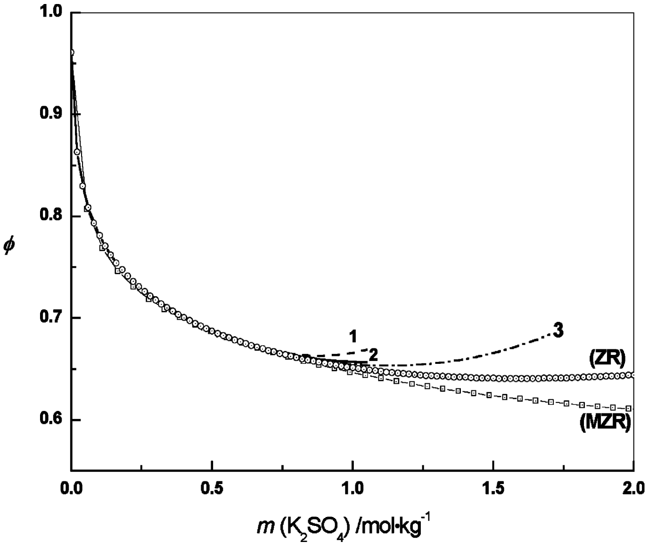

Figure 5. Estimated osmotic coefficients of K_2SO_4(aq) at T = 298.15 K by weighted averages for different electrolyte combinations: 1, $(NH_4)_2SO_4$(aq)/K_2SO_4(aq)/Cs_2SO_4(aq); 2, $(NH_4)_2SO_4$(aq)/K_2SO_4(aq)/Rb_2SO_4(aq); 3, $(NH_4)_2SO_4$(aq)/K_2SO_4(aq)/Li_2SO_4(aq); and fitted using values of extended Pitzer parameters from the ZR and from the MZR.

mixtures because nonideal mixing effects should be very small owing to the chemical similarity of the various 1:2 electrolyte solutions. This method can be assumed as a reliable way of obtaining supersaturated binary data in the absence of actual supersaturated values which are often difficult to obtain experimentally.[3,22]

The estimated osmotic coefficients of K_2SO_4(aq) in the supersaturated region obtained by the simple extrapolation of ternary system data (ZR) were generally consistent except for the estimation results from the system K_2SO_4 + Li_2SO_4 + H_2O (Figure 2). When the modified Zdanovskii relation (MZR), with inclusion of parameter b, was used in the estimation of the osmotic coefficients of K_2SO_4(aq), the results were consistent in the lower concentration region and showed a good mutual agreement with the results obtained by Sangster et al.[3] (Figure 3). In a more concentrated region, above the molality $m \approx 2.5$ mol·kg^{-1}, larger discrepancies in the osmotic coefficient estimation were obtained from the systems K_2SO_4 + Li_2SO_4 + H_2O and K_2SO_4 + $(NH_4)_2SO_4$ + H_2O. Low values of b_{av} were found in the systems K_2SO_4 + Cs_2SO_4 + H_2O (b_{av} = −0.0085), K_2SO_4 + Rb_2SO_4 + H_2O (b_{av} = −0.0266), and K_2SO_4 + $(NH_4)_2SO_4$ + H_2O (b_{av} = 0.0447), while the maximum value of b_{av} was found in the system K_2SO_4 + Li_2SO_4 + H_2O (b_{av} = −0.1873). Certain literature data[23,24] suggest that ion pair formation is more extensive in solution Li_2SO_4(aq) than in Rb_2SO_4(aq) and Cs_2SO_4(aq). Therefore, the estimation of K_2SO_4(aq) osmotic coefficients in the supersaturated region originating from the system K_2SO_4 + Li_2SO_4 + H_2O were consequently rejected in further treatment.

It has to be noted that the assumption of a constant b or its extrapolation as a function of a_w still contains a residue of arbitrariness. Misextrapolation of b's would be manifested as disagreements between the osmotic coefficients in the supersaturated region obtained via the different ternary systems. Conversely, agreement between estimation results provides a mutual check on their validity. Therefore, generally consistent estimation data together with experimental osmotic coefficients[7] were fitted in the extended Pitzer equation for pure electrolytes. Estimation

Table 3. Parameters of the Extended Pitzer Equation for K_2SO_4(aq) at $T = 298.15$ K (Using $\alpha = 2.0$ kg$^{1/2}$·mol$^{-1/2}$ and $\omega = 2.5$ kg$^{1/2}$·mol$^{-1/2}$), Valid up to Maximum Molality, max *m*

	parameters from this study		Kuschel and Seidel[2]	Archer and Kirklin[25]
	ZR	MZR		
$\beta^{(0)}$/mol·kg^{-1}	0.038 666	0.028 433	0.044 062	−0.004 663 9
$\beta^{(1)}$/mol·kg^{-1}	0.753 39	0.532 12	0.730 46	0.774 728
$C^{(0)}$/mol^2·kg^{-2}	0.000 393	−0.000 390	0.000 648 48	0.008 010 34
$C^{(1)}$/mol^2·kg^{-2}	0.093 221	0.412 14	−0.000 489 16	0.383 779
max m/mol·kg^{-1}	5.2	5.6	4.0	1.2

results in the supersaturated region used in treatment from the ZR prediction originate from the systems $K_2SO_4 + Rb_2SO_4 + H_2O$, $K_2SO_4 + Cs_2SO_4 + H_2O$, and $K_2SO_4 + (NH_4)_2SO_4 + H_2O$, while those used in treatment from the MZR prediction originate from the systems $K_2SO_4 + Rb_2SO_4 + H_2O$, $K_2SO_4 + (NH_4)_2SO_4 + H_2O$, and $K_2SO_4 + Na_2SO_4 + H_2O$ together with the estimation results obtained by Sangster et al.[3]

Evaluated parameters of the extended Pitzer model are listed in Table 3. The standard deviation of fit to the experimental data of Palmer et al.[7] (in the unsaturated region) is $s = 0.0019$ (ZR) and $s = 0.0024$ (MZR). Table 3 contains also the evaluated extended Pitzer parameters derived from Archer and Kirklin[25] and standard Pitzer parameters converted to extended form, by a procedure proposed by Rard and Wijesinghe,[21] originating from the study of Kuschel and Seidel.[2]

A comparison of the osmotic coefficient estimation of K_2SO_4(aq) in the supersaturated region by the Åkerlöf–Thomas rule and fitted values obtained from the Zdanovskii rule in Figure 4 shows mutual agreement for Rb_2SO_4(aq) as referent solution and the ZR estimation (Figure 4a) and for Na_2SO_4(aq) as referent solution and the MZR estimation up to $m = 2.0$ mol·kg^{-1} (Figure 4b). Generally, a better agreement of K_2SO_4(aq) osmotic coefficients is obtained between the ZR estimation and the Åkerlöf–Thomas rule prediction.

The method of weighted averages gives the same prediction results of K_2SO_4(aq) osmotic coefficients for the $(NH_4)_2SO_4$(aq)/K_2SO_4(aq)/Rb_2SO_4(aq) electrolyte combination and the Zdanovskii rule for the molalities up to $m = 1.0$ mol·kg^{-1} (Figure 5).

Figure 6 illustrates the fitted osmotic coefficients of K_2SO_4(aq) with parameters from Kuschel and Seidel,[2] Archer and Kirklin,[25] and the present work (Table 3) with estimated osmotic coefficients by Robinson et al.[1] and Sangster et al.[3] According to Figure 6, the fitted values from the present study are quite consistent with the estimated osmotic coefficients by weighted averages of Robinson et al.[1] for molalities up to 1.2 mol·kg^{-1} and with the values from Sangster et al.[3] up to 2.3 mol·kg^{-1}. Values of calculated osmotic coefficients with parameters from Kuschel and Seidel[2] and Archer and Kirklin[25] are generally higher in the more concentrated region.

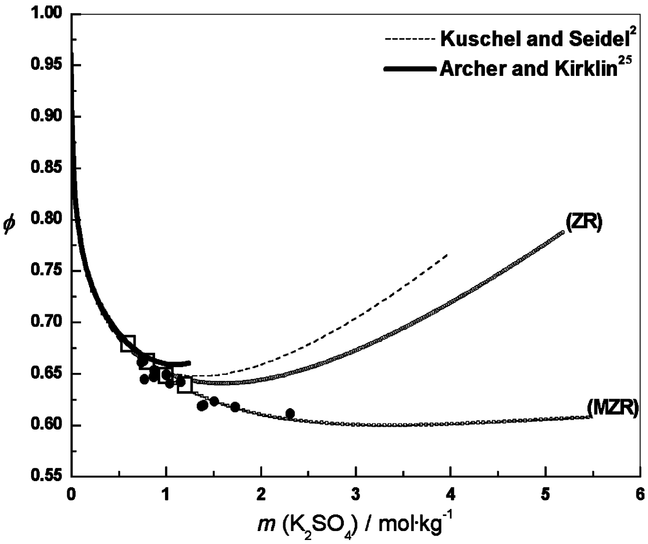

Figure 6. Osmotic coefficients of K_2SO_4(aq) at $T = 298.15$ K fitted using different values of extended Pitzer parameters noted in the picture: □, estimated by Robinson et al.[1]; ●, estimated by Sangster et al.[3]

The reliability of the Zdanovskii rule for the estimation of the osmotic coefficients for supersaturated solutions was checked in two different ways. The first test was to predict the osmotic coefficients of some studied ternary systems containing K_2SO_4, where the mixed electrolyte solution osmotic coefficients are between the osmotic coefficients of the pure solutions.

The extended Pitzer model, used by Clegg et al.,[26] for the osmotic coefficient of mixed electrolyte solution applied to systems of the type $K_2SO_4 + M_2SO_4 + H_2O$, where M ≡ Na, Rb, Cs, (NH_4), takes the form

$$\phi - 1 = \{2/(m(\mathrm{K}) + m(\mathrm{M}) + m(\mathrm{SO_4}))\}[-A_\phi I^{3/2}/(1 + bI^{1/2}) + m(\mathrm{K})m(\mathrm{SO_4})\{B^\phi(\mathrm{K_2SO_4}) + ZC^{T\phi}(\mathrm{K_2SO_4})\} + m(\mathrm{M})m(\mathrm{SO_4})\{B^\phi(\mathrm{M_2SO_4}) + ZC^{T\phi}(\mathrm{M_2SO_4})\}] \quad (9)$$

where

$$m(\mathrm{K}) = 2m(\mathrm{K_2SO_4}) \quad (10)$$

$$m(\mathrm{M}) = 2m(\mathrm{M_2SO_4}) \quad (11)$$

$$m(\mathrm{SO_4}) = m(\mathrm{K_2SO_4}) + m(\mathrm{M_2SO_4}) \quad (12)$$

$$I = 3[m(\mathrm{K_2SO_4}) + m(\mathrm{M_2SO_4})] \quad (13)$$

$$Z = \sum\nolimits_i (m_i|z_i|) = m(\mathrm{K}) + m(\mathrm{M}) + 2m(\mathrm{SO_4}) = 4[m(\mathrm{K_2SO_4}) + m(\mathrm{M_2SO_4})] \quad (14)$$

Standard deviations of predicted and experimental osmotic coefficients for different mixed electrolyte solutions, when the osmotic coefficients of K_2SO_4(aq) were determined by the ZR and MZR, are given in Table 4.

The maximum standard deviation for the ZR is found in the systems $K_2SO_4 + Cs_2SO_4 + H_2O$ and $K_2SO_4 + Na_2SO_4 + H_2O$. For the system containing Na_2SO_4, the same standard deviation ($s = 0.011$) is reported in a paper of Pitzer and Kim[28] in the treatment of Robinson et al.[1] data. Application of the modified Zdanovskii rule (MZR) reduces this standard deviation to the value $s = 0.0070$.

One of the reasons why the standard deviation of the fit from the ZR for the system $K_2SO_4 + Cs_2SO_4 + H_2O$ is larger compared to other systems is that the pure solution parameters for Cs_2SO_4(aq) at $T = 298.15$ K are taken from recent paper of Palmer et al.[4] Namely, Palmer et al.[4] rejected the experimental results of Fillipov et al.[12] and

Table 4. Standard Deviations between Experimental and Predicted Osmotic Coefficients of Ternary Systems at T = 298.15 K, When Predicted Values Were Obtained Using Parameters of the Extended Pitzer Equation for $K_2SO_4(aq)$ Determined by the ZR, s_1, and by the MZR, s_2, Range of Ionic Strength of the Mixed Solutions, I, Range of Ionic Strength Fraction of K_2SO_4 in Total Ionic Strength of the Mixed Solution, y, and Number of Experimental Data Treated, n

system	n	I/mol·kg^{-1}	y	s_1	s_2
$K_2SO_4 + Na_2SO_4 + H_2O$	6	2.3130−3.5619	0.3086−0.6530	0.0131	0.0070
$K_2SO_4 + Rb_2SO_4 + H_2O$	15	2.4942−4.9266	0.14−0.72	0.0030	0.0032
$K_2SO_4 + Cs_2SO_4 + H_2O$	22	2.7993−11.2260	0.04−0.50	0.0215	0.0018
$K_2SO_4 + (NH_4)_2SO_4 + H_2O$[a]	119	2.3037−16.9439	0.03−0.85	0.0039	0.0087
$K_2SO_4 + (NH_4)_2SO_4 + H_2O$[27] [b]	29	0.6−8.25	0.2−0.8	0.0025	0.0038

[a] A. V. Rumyantsev, unpublished data. [b] Osmotic coefficients obtained by the hygrometric method.

Table 5. Standard Deviations between Predicted and Experimental Osmotic Coefficients of Ternary Systems at T = 298.15 K, When Predicted Values Were Obtained Using Parameters of Rard et al.[15], s_1, Parameters from the ZR, s_2, and Parameters from the MZR, s_3, for $Na_2SO_4(aq)$, Ionic Strength Range of the Mixed Solutions, I, and Number of Experimental Data Treated, n

system	n	I/mol·kg^{-1}	s_1	s_2	s_3
$Na_2SO_4 + Rb_2SO_4 + H_2O$	42	7.7109−12.7197	0.0447	0.0310	0.0315
$Na_2SO_4 + Cs_2SO_4 + H_2O$	30	6.5166−16.3770	0.0776	0.0663	0.0581
$Na_2SO_4 + (NH_4)_2SO_4 + H_2O$	38	8.124−16.614	0.0138	0.0044	0.0038
$Na_2SO_4 + Li_2SO_4 + H_2O$	20	6.1536−8.7126	0.0118	0.0081	0.0081

this reflected in the calculation of the osmotic coefficients of the system $K_2SO_4 + Cs_2SO_4 + H_2O$. When the parameters of the standard Pitzer equation for $Cs_2SO_4(aq)$[29] are converted[21] to the parameters of the extended Pitzer form, the standard deviation of the calculated and experimental data of Fillipov et al.[12] is reduced from $s = 0.0215$ to $s = 0.0017$. The same reduction of standard deviation is accomplished when the modified Zdanovskii rule (MZR) is applied ($s = 0.0018$).

Another way of testing the reliability of the Zdanovskii rule application, in both ways (the ZR and MZR), was made for $Na_2SO_4(aq)$ at $T = 298.15$ K, for which the experimental values of the osmotic coefficient in supersaturated solution are available.[15] For this purpose, the Zdanovskii rule was applied to the following systems: (1) $Na_2SO_4 + Li_2SO_4 + H_2O$,[11] (2) $Na_2SO_4 + Rb_2SO_4 + H_2O$,[11] (3) $Na_2SO_4 + Cs_2SO_4 + H_2O$,[12] and (4) $Na_2SO_4 + (NH_4)_2SO_4 + H_2O$.[30] The following values of b for the MZR estimation were used: (1) $b_{av} = 0.0159$, (2) $b_{av} = -0.0866$, (3) $b = 0.1965 - 0.3055a_w$, and (4) $b_{av} = 0.0133$. The obtained results from the ZR and MZR estimation are illustrated in parts a and b of Figure 7, respectively, together with the experimental data from Rard et al.[15]

Figure 7 indicates that the estimated osmotic coefficients of $Na_2SO_4(aq)$ by the simple Zdanovskii rule (ZR) for the supersaturated region are slightly lower compared with the experimental data of Rard et al.,[15] except for the deviating results from $Na_2SO_4 + Cs_2SO_4 + H_2O$ (Figure 7a). When the modified Zdanovskii rule (MZR) was applied to this system, with parameter b as a function of a_w, then the estimated osmotic coefficients were in excellent agreement with the experimental values of Rard et al.[15] (Figure 7b). The experimental osmotic coefficient data of Rard et al. together with estimated values by the Zdanovskii rule in the supersaturated region for $Na_2SO_4(aq)$ at $T = 298.15$ K were fitted in the extended Pitzer equation for pure electrolytes. Evaluated parameters from the ZR estimation were $\beta^{(0)} = 0.012\,147$ kg·mol^{-1}, $\beta^{(1)} = 0.897\,78$ kg·mol^{-1}, $C^{(0)} = 0.002\,020\,9$ kg^2·mol^{-2}, and $C^{(1)} = 0.309\,04$ kg^2·mol^{-2}, valid up to a molality of $m \approx 4.5$ mol·kg^{-1}, and those from the MZR estimation were $\beta^{(0)} = 0.029\,553$ kg·mol^{-1}, $\beta^{(1)} = 1.0319$ kg·mol^{-1}, $C^{(0)} = 0.000\,869$ kg^2·mol^{-2}, and $C^{(1)} = -0.040\,99$ kg^2·mol^{-2}, valid up to a molality of $m \approx 5.2$ mol·kg^{-1}, with the parameters $b = 1.2$ kg$^{1/2}$·mol$^{-1/2}$, $\alpha = 2.0$ kg$^{1/2}$·mol$^{-1/2}$, and $\omega = 2.5$ kg$^{1/2}$·mol$^{-1/2}$. Differences

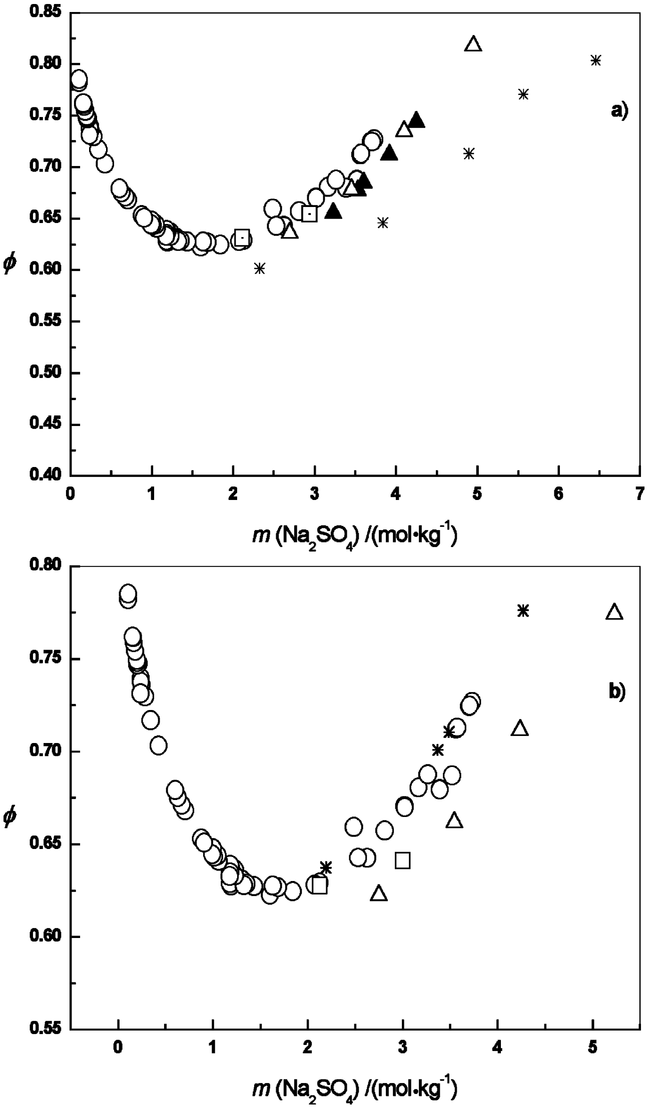

Figure 7. Estimated osmotic coefficients in supersaturated $Na_2SO_4(aq)$ at $T = 298.15$ K from different systems: *, $Na_2SO_4 + Cs_2SO_4 + H_2O$; □, $Na_2SO_4 + Li_2SO_4 + H_2O$; ▲, $Na_2SO_4 + Rb_2SO_4 + H_2O$; △, $Na_2SO_4 + (NH_4)_2SO_4 + H_2O$; ○, experimental data of Rard et al.[15]: (a) obtained by the Zdanovskii rule (ZR); (b) obtained by the modified Zdanovskii rule (MZR).

between the fitted osmotic coefficients of $Na_2SO_4(aq)$ with these parameters and the experimental data of Rard et al.[15] led to the overall standard deviations of fit of $s = 0.009$ (ZR) and $s = 0.0095$ (MZR).

The experimental osmotic coefficients of the systems $Na_2SO_4 + Li_2SO_4 + H_2O$,[11] $Na_2SO_4 + Rb_2SO_4 + H_2O$,[11] $Na_2SO_4 + (NH_4)_2SO_4 + H_2O$,[30] and $Na_2SO_4 + Cs_2SO_4 + H_2O$[12] were compared with the predicted values by the extended Pitzer model for mixed electrolyte solutions. In eqs 9−14, the following replacement is required: $K \equiv Na$ and $M \equiv Li, Rb, (NH_4)$. Table 5 contains the standard deviations between the experimental and calculated osmotic coefficients obtained by using Rard et al.[15] parameters from Table 2, s_1, and parameters from the present work obtained from the ZR, s_2, and from the MZR, s_3, together with the ionic strength range of the mixed solutions and the number of experimental points.

The standard deviations of the fit (s_2 and s_3) are systematically lower than s_1, probably due to the validity extension of Rard et al. parameters above an ionic strength of $\approx 11.4\ mol\cdot kg^{-1}$.

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