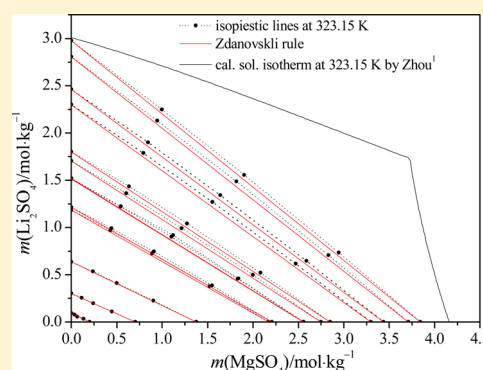


Isopiestic Measurements of Water Activity for the $\text{Li}_2\text{SO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ System at 323.15 and 373.15 KHaitang Yang,[†] Dewen Zeng,^{*,‡} Qingwei Wang,^{§,||} Yifeng Chen,[†] and Wolfgang Voigt[⊥][†]School of Metallurgical Engineering, Hunan University of Technology, Zhuzhou 412000, China[‡]College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China[§]Department of Environmental Engineering, School of Metallurgy and Environment, Central South University, Changsha 410083, China^{||}Chinese National Engineering Research Central for Control and Treatment of Heavy Metal Pollution, Changsha 410083, China[⊥]Department of Inorganic Chemistry, TU Bergakademie Freiberg, Freiberg 09596, Germany

S Supporting Information

ABSTRACT: The water activities for the binary $\text{Li}_2\text{SO}_4\text{--H}_2\text{O}$ and $\text{MgSO}_4\text{--H}_2\text{O}$, as well as the ternary $\text{Li}_2\text{SO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ systems at 323.15 and 373.15 K were elaborately determined by isopiestic measurements. The relative deviation of the isopiestic molality of parallel samples in each experimental run is better than 0.2%. The experimental water activities in the binary systems were compared with literature data and good agreement was found. The results obtained show that at salt concentration below 3 m the isopiestic composition lines of the $\text{Li}_2\text{SO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ system obey the Zdanovskii rule, whereas above 3 m the composition lines positively deviate from the Zdanovskii rule.



1. INTRODUCTION

The extraction of valuable resources (such as Li, K, Mg) from salt lake brines requires consulting many solubility diagrams containing the ions Li^+ , Na^+ , K^+ , Mg^{2+} , Cl^- , SO_4^{2-} , and H_2O over a wide temperature range. On account of the complexity of the phase diagrams of these systems, computational simulation is considered to be an indispensable tool. For the model parametrization, reliable thermodynamic information (especially water activities) of the basic binary and ternary systems from 273 to 373 K is especially important.

Until now, a number of measurements of water activities¹ have been reported at 298.15 K for the binary systems $\text{Li}_2\text{SO}_4\text{--H}_2\text{O}$ and $\text{MgSO}_4\text{--H}_2\text{O}$ and the ternary system $\text{Li}_2\text{SO}_4\text{--MgSO}_4\text{--H}_2\text{O}$. Few has been reported at higher temperatures, except the published water activities of the systems $\text{Li}_2\text{SO}_4\text{--H}_2\text{O}$ ^{2–4} and $\text{MgSO}_4\text{--H}_2\text{O}$ ^{5–7} at 323.15 and 373.15 K. For the ternary system $\text{Li}_2\text{SO}_4\text{--MgSO}_4\text{--H}_2\text{O}$, the water activities at temperatures higher than 298.15 K have never been reported. To close these gaps, we carried out isopiestic measurements of the system $\text{Li}_2\text{SO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ at 323.15 and 373.15 K. To verify the reliability of the experiment data in this work, we also measured the isopiestic data of water activity of the binary systems $\text{Li}_2\text{SO}_4\text{--H}_2\text{O}$ and $\text{MgSO}_4\text{--H}_2\text{O}$ at 323.15 and 373.15 K.

2. EXPERIMENTAL SECTION

2.1. Materials. The reference NaCl and CaCl_2 aqueous solution and to be measured MgSO_4 aqueous solutions were prepared by purifying the G. R. reagent by three times crystallization. The Li_2SO_4 aqueous solution was prepared by neutralizing Li_2CO_3 with H_2SO_4 and then purified by twice crystallization. The trace content of the metals in the stock solutions of NaCl(aq) , $\text{CaCl}_2\text{(aq)}$, $\text{MgSO}_4\text{(aq)}$, and $\text{Li}_2\text{SO}_4\text{(aq)}$ were quantified by ICP (atomic emission spectroscopy, Optima 5300 DV, PerkinElmer, U.S.A.). The total impurity levels on a trace metals basis were substantially less than 200 ppm.

The salt content of the reference solution NaCl(aq) and $\text{CaCl}_2\text{(aq)}$ were determined gravimetrically by precipitation with $\text{AgNO}_3\text{(aq)}$,⁸ whereas the contents of the stock solutions of $\text{Li}_2\text{SO}_4\text{(aq)}$ and $\text{MgSO}_4\text{(aq)}$ were determined gravimetrically by precipitation with $\text{BaCl}_2\text{(aq)}$.⁸ Five replicates were used in each analysis run and the mean relative deviations are $\leq 0.05\%$. At the same time, the composition of $\text{CaCl}_2\text{(aq)}$ and $\text{MgSO}_4\text{(aq)}$ solution were determined by gravimetric titration with EDTA (for Ca^{2+} and Mg^{2+}) as complement.⁸ The concentration of the stock solution and the studied solution were presented in Table 1. Ultrapure water ($\sigma \leq 1.1 \times 10^{-4}$ S/

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Table 1. Composition of Stock Solutions^a

	NaCl	CaCl ₂ ^c	CaCl ₂ ^e	Li ₂ SO ₄	MgSO ₄
m^b / mol·kg ⁻¹	2.0275	1.9275	6.7506	2.3504	2.2432
m^c / mol·kg ⁻¹		1.9279	6.7511		2.2413
pH ^f	7.0	6.5	6.5	6.5	6.5

^a $u_r(m) = 0.001$. ^bThe concentration of the solution determined by the method of precipitation. ^cThe concentration of the solution determined by the method of titration. ^dLow concentration reference solution. ^eHigh concentration reference solution. ^fpH values here were measured by a pH-meter (Sartorius PB-10) in this work.

m) was used in all the experiment processes. AgNO₃, BaCl₂, and EDTA were also used in the experiment. Table 2 gives the instructions of the chemical reagents used in this work.

Different mixed stock solutions $Y_{\text{Li}_2\text{SO}_4}$ ($Y_{\text{Li}_2\text{SO}_4} = m_{\text{Li}_2\text{SO}_4} / (m_{\text{Li}_2\text{SO}_4} + m_{\text{MgSO}_4})$) were prepared by mixing pure solution of Li₂SO₄ and MgSO₄ by using a mass buret,⁹ with $Y_1 = 0.4527$, $Y_2 = 1.0306$, $Y_3 = 1.6046$.

2.2. Apparatus. Isopiestic measurements were carried out in an equipment described in our previous paper.¹⁰ In the isopiestic chamber, there are 12 isopiestic cups.

2.3. Procedures. Most of the experiment processes are similar to our previous work,¹⁰ except for some special points: (1) after the isopiestic chamber had been closed, the chamber was pumped to 50 Pa and slowly heated to 373.15 K in 10 h, whereas the experimental is carried out at 323.15 K, the chamber is directly heated to 323.15 K; (2) the equilibrium time at 323.15 K was chosen as 168 h (a week), whereas at 373.15 K, it was reduced to 72–120 h; (3) after the equilibrium has reached, the sample cups were then closed in situ (at the equilibration temperature) and the apparatus has to cool to around 323.15 K in the thermostat bath before the apparatus removed from the thermostat bath.

The data-processing approaches, including the correction of the solution weighting and the water activity calculation, are the same as in our previous work,¹⁰ except the modified parameters of P_s^\ominus and B_2 . The parameters P_s^\ominus and B_2 are 12344.73 Pa and $-812 \text{ cm}^3/\text{mol}$ at 323.15 K and 101.32497 kPa and $-460 \text{ cm}^3/\text{mol}$ at 373.15 K, respectively.

2.4. Reference System. In this work, the system NaCl–H₂O was chosen as isopiestic reference systems at 323.15 and 373.15 K. For this system, reliable water activity data are available in the literature¹¹ from (273.15 to 373.15) K over an extensive concentration range. Tabled water activities of this reference system, a_w^* , as fitted to the polynomial eq 1

$$a_w^* = r_1 + r_2(m/\text{mol}\cdot\text{kg}^{-1})^{0.5} + r_3(m/\text{mol}\cdot\text{kg}^{-1}) + r_4(m/\text{mol}\cdot\text{kg}^{-1})^{1.5} + r_5(m/\text{mol}\cdot\text{kg}^{-1})^2 + r_6(m/\text{mol}\cdot\text{kg}^{-1})^{2.5} + r_7(m/\text{mol}\cdot\text{kg}^{-1})^3 + r_8(m/\text{mol}\cdot\text{kg}^{-1})^{3.5} \quad (1)$$

where the parameter values $r_1, r_2, r_3, r_4, r_5, r_6, r_7$, and r_8 are given in Table 3. As long as the molality of the references are known, the water activity of the reference systems and the test systems can be calculated.

Table 3. Fitted Parameters in eq 1 for NaCl References^a

parameters	NaCl	NaCl
T/K	323.15	373.15
r_1	1.00001	1.00001
r_2	-0.00034	-0.00038
r_3	-0.03271	-0.0323
r_4	0.00146	0.00155
r_5	-0.00141	-0.00146
r_6	-0.00056	-0.00088
r_7	0.00013	0.00039
r_8	0.00002	-0.00002
σ^b	1.0401×10^{-4}	0.6105×10^{-4}

^aFitting the water activity of NaCl in literature.¹⁰ ^bStandard deviation,

$$\sigma = \sqrt{\frac{\sum_i (a_w(\text{exp}) - a_w(\text{cal}))^2}{n-1}}$$

3. RESULTS AND DISCUSSION

3.1. Experimental Results. The determined water activities of the systems Li₂SO₄–H₂O, MgSO₄–H₂O and Li₂SO₄–MgSO₄–H₂O at 323.15 and 373.15 K are listed in Tables 4 and 5 and illustrated in Figures 1 and 2. The relative errors of the isopiestic molalities in Tables 4 and 5 do not exceed 0.4%, as discussed previously.¹⁰ In each isopiestic experiment, duplicate cups were used for each test system and the reference system. When the relative deviation of isopiestic molalities between the duplicate cups was less than 0.2%, the equilibrium state was thought to be reached and the average data for the duplicate cups were chosen as valid. Every single determined isopiestic concentration can be seen in the tables S₁ and S₂ in the supplement.

The distance of the experiment points to the saturation line of the system Li₂SO₄–MgSO₄–H₂O can be recognized from Figures 3 and 4. Due to lack of solubility data of this system at 373.15 K, the solubility isotherm was substituted by 348.15 K.

Table 2. Specifications of Chemicals Used in This Work

chemical name	source	initial mass fraction purity	purification method	final mass fraction purity	analysis method
sodium chloride	Sinopharm Chemical Reagent Co.	>0.9995	recrystallized four times	0.9999	ICP
calcium chloride	Sinopharm Chemical Reagent Co.	>0.999	recrystallized four times	0.9999	ICP
magnesium sulfate	Sinopharm Chemical Reagent Co.	>0.999	recrystallized three times	0.9999	ICP
lithium chloride	synthesized by ourselves		recrystallized four times	≥0.9999	ICP
lithium chlorate	Shanghai China-Lithium Industry	0.9995	none		ICP
hydrochloric acid	Sinopharm Chemical Reagent Co.	0.9998	none		ICP
sulfuric acid	Sinopharm Chemical Reagent Co.	0.9998	none		ICP
silver nitrate	Sinopharm Chemical Reagent Co.	0.9995	none		ICP
barium chloride	Sinopharm Chemical Reagent Co.	0.9995	none		ICP
disodium EDTA	Sinopharm Chemical Reagent Co.	0.9995	none		ICP
water			distilled three times	$\sigma \leq 1.1 \times 10^{-4} \text{ S/m}$	TDS

Table 4. Experimental Isopiestic Molalities, m , and Calculated Water Activities, a_w , of the Ternary System $\text{Li}_2\text{SO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ at $T = 323.15\text{ K}$ ^a

no.	$m_{\text{Li}_2\text{SO}_4}/\text{mol}\cdot\text{kg}^{-1}$	$m_{\text{MgSO}_4}/\text{mol}\cdot\text{kg}^{-1}$	no.	$m_{\text{Li}_2\text{SO}_4}/\text{mol}\cdot\text{kg}^{-1}$	$m_{\text{MgSO}_4}/\text{mol}\cdot\text{kg}^{-1}$
1	$m_{\text{NaCl}} = 0.01203, a_w = 0.9960^b$		8	$m_{\text{NaCl}} = 2.0506, a_w = 0.9288^b$	
	0	0.2019		0	2.7475
	0.03286	0.1315		0.4995	1.9981
	0.05430	0.06636		0.9929	1.2134
	0.07712	0.03421		1.3606	0.6035
	0.09343	0		1.7041	0
2	$m_{\text{NaCl}} = 0.3759, a_w = 0.9876^b$		9	$m_{\text{NaCl}} = 2.1753, a_w = 0.9241^b$	
	0	0.7045		0	2.8482
	0.1114	0.4457		0.5208	2.0834
	0.1969	0.2407		1.0423	1.2738
	0.2554	0.1133		1.4343	0.6362
	0.3019	0		1.8014	0
3	$m_{\text{NaCl}} = 0.7745, a_w = 0.9743^b$		10	$m_{\text{NaCl}} = 2.7969, a_w = 0.9000^b$	
	0	1.3735		0	3.2979
	0.2258	0.9033		0.6173	2.4695
	0.4098	0.5008		1.2702	1.5522
	0.5339	0.2368		1.7879	0.7930
	0.6373	0		2.2995	0
4	$m_{\text{NaCl}} = 1.4222, a_w = 0.9518^b$		11	$m_{\text{NaCl}} = 2.9975, a_w = 0.8920^b$	
	0	2.1716		0	3.4375
	0.3803	1.5214		0.6473	2.5894
	0.7267	0.8881		1.3416	1.6396
	0.9684	0.4295		1.9014	0.8434
	1.1839	0		2.4620	0
5	$m_{\text{NaCl}} = 1.4529, a_w = 0.9507^b$		12	$m_{\text{NaCl}} = 3.4472, a_w = 0.8737^b$	
	0	2.2073		0	3.7101
	0.3873	1.5493		0.7077	2.8312
	0.7437	0.9089		1.4870	1.8172
	0.9919	0.4400		2.1313	0.9454
	1.2143	0		2.8063	0
6	$m_{\text{NaCl}} = 1.8194, a_w = 0.9374^b$		13	$m_{\text{NaCl}} = 3.6666, a_w = 0.8646^b$	
	0	2.5516		0	3.8410
	0.4583	1.8336		0.7359	2.9440
	0.9009	1.1010		1.5569	1.9026
	1.2206	0.5414		2.2489	0.9975
	1.5135	0		2.9765	0
7	$m_{\text{NaCl}} = 1.8299, a_w = 0.9370^b$		14	$m_{\text{NaCl}} = 4.5677, a_w = 0.8262^b$	
	0	2.5581		0	4.3147
	0.4599	1.8400		0.8394	3.3582
	0.9186	1.1226		1.8206	2.2249
	1.2245	0.5431		3.6602	1.6235
	1.5209	0			

^a $u(T) = 0.05\text{ K}$, $u(a_w) = 0.00015$, $u_t(m) = 0.004$. ^bWater activity is calculated according to eq 1.

However, the solubility^{12,13} of pure $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ at 373.15 K should be near $(2.8 \pm 0.1)\text{ mol}\cdot\text{kg}^{-1}$, which means the last point in Table 5 could have been an supersaturated solution.

3.2. Comparison with Literature. In order to evaluate the accuracy of the data in this work, some comparison has been made of the experimental data with literature data. As mentioned above, some authors have reported the water activities for the binary systems $\text{Li}_2\text{SO}_4\text{--H}_2\text{O}$ ^{1–4} and $\text{MgSO}_4\text{--H}_2\text{O}$ ^{5–7} at 323.15 and 373.15 K by experimental or modeling methods.

For the system $\text{Li}_2\text{SO}_4\text{--H}_2\text{O}$, as shown in Figure 3, the experiment data at 323.15 K in this work agree well with the literature data reported by Rard,² Li³ and the model values calculated by Zhou.¹ Furthermore, the good agreement can also be found for this system at 373.15 K between our work and the

calculated results by Zhou¹ and Homles,⁴ as shown from Figure 4.

As shown in Figure 5, the experiment data of the system $\text{MgSO}_4\text{--H}_2\text{O}$ in this work at 323.15 K show good agreement with the literature data reported by Snipes⁵ and the model values calculated by Rard.⁶ However, up until now, no author reported the literature experimental water activity/osmotic coefficient data of this system at 373.15 K, except at 372.75 K. So the comparison was carried out between the experimental data in this work at 373.15 K and the literature experimental data at 372.75 K. As shown from Figure 6, due to the small difference between the temperature 373.15 and 372.75 K, the deviations only appeared at the salt concentrations higher than 2.5 m. Also, the data in this work is slightly lower than the literature data at any given concentration, which is full

Table 5. Experimental Isopiestic Molalities, m , and Calculated Water Activities, a_w , of the Ternary System $\text{Li}_2\text{SO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ at $T = 373.15\text{ K}^a$

no.	$m_{\text{Li}_2\text{SO}_4}/\text{mol}\cdot\text{kg}^{-1}$	$m_{\text{MgSO}_4}/\text{mol}\cdot\text{kg}^{-1}$	no.	$m_{\text{Li}_2\text{SO}_4}/\text{mol}\cdot\text{kg}^{-1}$	$m_{\text{MgSO}_4}/\text{mol}\cdot\text{kg}^{-1}$
1	$m_{\text{NaCl}} = 0.1244, a_w^b = 0.9959$		8	$m_{\text{NaCl}} = 1.4145, a_w^b = 0.9525$	
	0	0.2432		0	2.4430
	0.03806	0.1523		0.4152	1.6609
	0.06526	0.07975		0.7732	0.9449
	0.09037	0.04008		1.0094	0.4477
	0.1014	0		1.2092	0
2	$m_{\text{NaCl}} = 0.3615, a_w^b = 0.9882$		9	$m_{\text{NaCl}} = 1.7195, a_w^b = 0.9416$	
	0	0.7581		0	2.7029
	0.1145	0.4581		0.4748	1.8995
	0.1974	0.2413		0.9168	1.098
	0.2484	0.1102		1.2192	0.5367
	0.2910	0		1.4666	0
3	$m_{\text{NaCl}} = 0.3707, a_w^b = 0.9879$		10	$m_{\text{NaCl}} = 2.3118, a_w^b = 0.9197$	
	0	0.8141		0	3.3010
	0.1199	0.4795		0.5952	2.3811
	0.2128	0.2601		1.1819	1.4445
	0.2721	0.1207		1.6105	0.7143
	0.3293	0		1.9903	0
4	$m_{\text{NaCl}} = 0.5202, a_w^b = 0.9830$		11	$m_{\text{NaCl}} = 2.6796, a_w^b = 0.9057$	
	0	0.8227		0	3.5908
	0.1292	0.5170		0.6595	2.6386
	0.2209	0.2699		1.3296	1.6249
	0.2895	0.1284		1.8376	0.8151
	0.3486	0		2.3040	0
5	$m_{\text{NaCl}} = 0.6141, a_w^b = 0.9799$		12	$m_{\text{NaCl}} = 3.0038, a_w^b = 0.8931$	
	0	1.2715		0	3.8262
	0.1965	0.7862		0.7117	2.8474
	0.3421	0.4181		1.4560	1.7794
	0.4304	0.1909		2.0302	0.9005
	0.5048	0		2.5862	0
6	$m_{\text{NaCl}} = 0.8416, a_w^b = 0.9723$		13	$m_{\text{NaCl}} = 3.5416, a_w^b = 0.8718$	
	0	1.6697		0	4.1806
	0.2661	1.0645		0.7878	3.1517
	0.4712	0.5759		1.6685	2.0161
	0.5981	0.2653		2.3433	1.0394
	0.7032	0		3.0487	0
7	$m_{\text{NaCl}} = 1.1544, a_w^b = 0.9616$				
	0	2.1244			
	0.3528	1.4112			
	0.6418	0.7843			
	0.8250	0.3659			
	0.9782	0			

^a $u(T) = 0.05\text{ K}$, $u(a_w) = 0.00015$, $u_r(m) = 0.004$. ^bWater activity is calculated according to eq 1.

compliance with the thermodynamic properties of the solution. Moreover, we also compare the experimental data in this work at 373.15 K (Figure 6) and the literature calculated results by Rad⁶ data at 373.15 K, and the good agreement is also obtained.

In general, the comparison demonstrates the isopiestic procedures and apparatus applied in this work are reliable.

3.3. Discussion. The experimentally measured isopiestic points and equal water activity lines of the ternary system $\text{Li}_2\text{SO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ at 323.15 and 373.15 K are shown in Figures 1 and 2. All the isopiestic composition points in the $\text{Li}_2\text{SO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ system are found to be roughly in straight lines at salt concentrations below 3 m. This apparent behavior fully meets the Zdanovskii rule. However, at total molalities above 3, the isopiestic lines positively deviate from

the Zdanovskii rule line (dash lines in Figures 1 and 2) and these deviations grow with increasing concentration at both temperatures. This positive deviation phenomenon was also observed for the $\text{Li}_2\text{SO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ system at 298.15 K reported by Zhang.¹⁴

This represents a quite common phenomenon for strong electrolyte mixtures, which already proposed the equation to adapt the experimental data by Kirgintsev and Lukyanov.¹⁵ A recent thorough test of Zdanovskii's rule for many systems was performed by Rowland.¹⁶ A generalization of Zdanovskii's rule for modeling purposes was suggested by Clegg and Seinfeld,¹⁷ but this is out of the scope of the present work. The molecular reason in positive deviations can be assumed in liberation of hydration water when ions are forced to come into contact with each other at increasing concentration.

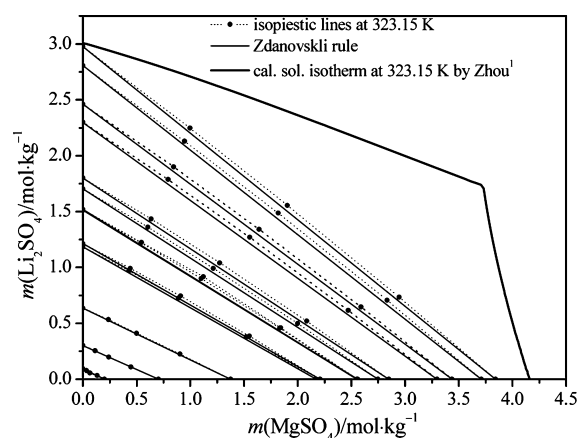


Figure 1. Experimental isopiestic lines in the $\text{Li}_2\text{SO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ at 323.15 K.

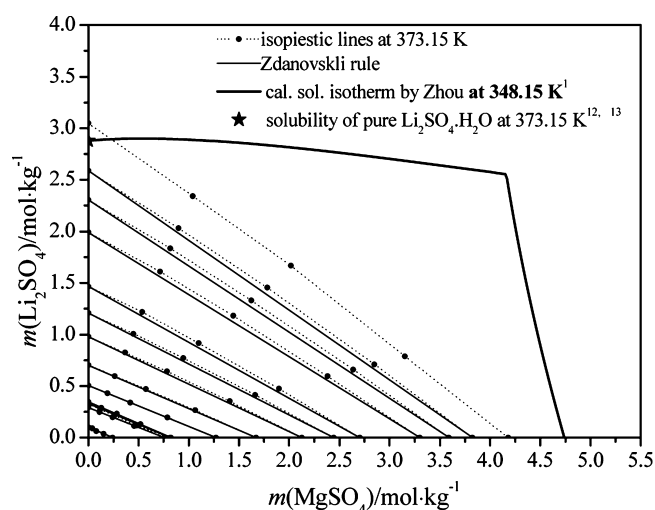


Figure 2. Experimental isopiestic lines in the $\text{Li}_2\text{SO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ at 373.15 K.

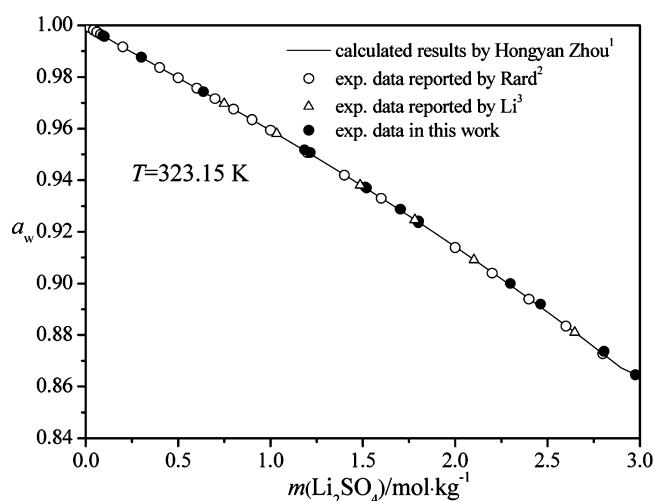


Figure 3. Isopiestic water activities (a_w) as a function of solute concentration for the binary system $\text{Li}_2\text{SO}_4\text{--H}_2\text{O}$ at 323.15 K.

4. CONCLUSIONS

The water activities of the ternary system $\text{Li}_2\text{SO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ and its sub-binary systems at 323.15 and 373.15 K were

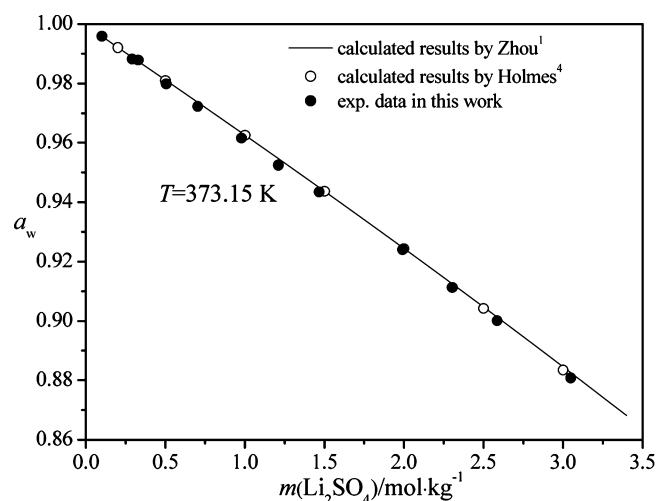


Figure 4. Isopiestic water activities (a_w) as a function of solute concentration for the binary system $\text{Li}_2\text{SO}_4\text{--H}_2\text{O}$ at 373.15 K.

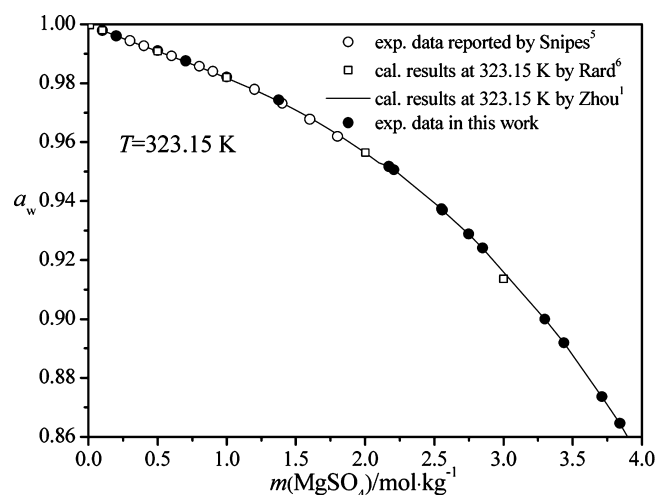


Figure 5. Isopiestic water activities (a_w) as a function of solute concentration for the binary system $\text{MgSO}_4\text{--H}_2\text{O}$ at 323.15 K.

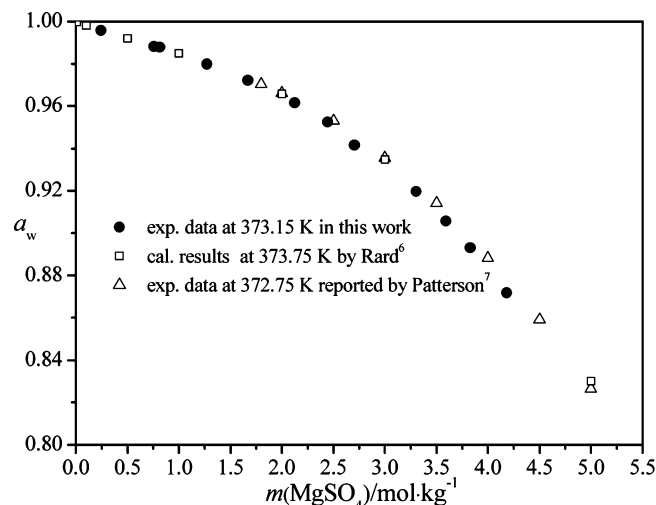


Figure 6. Isopiestic water activities (a_w) as a function of solute concentration for the binary system $\text{MgSO}_4\text{--H}_2\text{O}$ at 373.15 K.

elaborately measured by an isopiestic method. The experimental results of the systems $\text{Li}_2\text{SO}_4\text{--H}_2\text{O}$ and $\text{MgSO}_4\text{--H}_2\text{O}$ are agree well with the literature data. When the solution concentration is low, the isopiestic composition line in the $\text{Li}_2\text{SO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ system was found to obey the Zdanovskii rule. However, at high concentration, the isopiestic composition line was found to positively deviate the Zdanovskii rule. The measured water activities reported in this work can be used to parametrize thermodynamic models simulating the salt-lake chemical engineering processes.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.6b00239.

Original solution weights and the mass corrected weights. (PDF)

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Notes

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