Explanation and Exploration of the Isothermal Titration Curve for the NaCl + Na$_2$SO$_4$ + H$_2$O System at 298.15 K and 102.2 kPa

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ABSTRACT: Isothermal titration microcalorimetry (ITC) is a common and powerful tool in thermodynamics and related fields, and the connection between the solution behavior and raw titration curve is complex, important, and worth studying, so we try to discuss this problem using a complex solid−solid−liquid diagram. Although there are many experimental methods for studying ternary phase diagrams, ITC has been proven to be a simple, universal method at normal temperature and pressure. This method can be extended to investigate phase diagrams of multisalt aqueous solutions and related systems. Here, the phase equilibrium of one common ternary system (NaCl + Na$_2$SO$_4$ + H$_2$O) was determined using the ITC method with the aid of X-ray diffraction measurements. This isothermal and isobaric titration method can be used not only to determine the boundaries of different phase regions by analyzing changes in the slope of the observed heat vs solvent concentration plot but also to provide additional accurate data regarding the solid dissolution enthalpy and

the dilution enthalpy. The dissolution enthalpy of 1 mol NaCl (Na$_2$SO$_4$) solid dissolving in water to just form a saturated solution is measured at 1.92 kJ/mol (−15.60 kJ/mol), and the dissolution enthalpy of the mixed solids can be evaluated with these data. The dilution enthalpy is strongly dependent on the solute concentration (0.08−0.23 kJ/mol at the range of concentration studied), and for the same range concentration of a solute, the dilution enthalpy of Na$_2$SO$_4$ is positive and larger than that of NaCl. Therefore, the connection between the observed heat and the microscopic behavior and the separation between the dissolution and dilution data may result in the possibility to gain a clearer understanding about the solution behaviors.
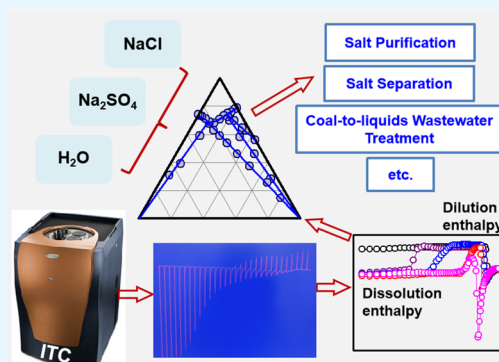
1. INTRODUCTION

A pseudo-ternary diagram is a convenient way to determine the solubility of salt as well as the compositions of stable microemulsions and macroemulsions. Additionally, phase equilibrium has a considerable basic groundwork in the metal smelting process, fractional crystallization, semiconductors, ceramics, salt separation, and purification in natural ores.[1,2] The construction of ternary equilibrium phase diagrams is at the basis of these applications. Thermal analysis is a very useful practical method for studying phase diagrams,[3−8] and calorimetric methods have been an invaluable tool for understanding the rich phase behaviors either in the early stages of process development or in phase equilibrium applications. Isothermal titration microcalorimetry (ITC) and reaction calorimetry are widely used calorimetric techniques alongside differential scanning calorimetry.

ITC has been used to study almost all types of physical and chemical binding processes in life sciences, in materials sciences, and within the pharmaceutical industry. ITC has also been traditionally used to study the solubilization or dissolution of solid compounds.[9−11] This approach shows considerable potential to simplify the description of the salt systems used in salt separation and purification in natural ores. The success or failure of the mirabilite treatment process will

directly affect the whole production of anhydrous sodium sulfate. In order to provide accurate calculations and guide the sodium sulfate production process, it is necessary to determine the saturated dissolution line of Na$_2$SO$_4$ and other salts, such as NaCl, with high-precision temperature control.[12−14] For this reason, the Na$_2$SO$_4$ + NaCl + H$_2$O ternary phase system is studied in this work and it is also of considerable importance to know their thermodynamic properties. Several examples of such investigations using ITC have been reported, and different calorimeters have been used. Grolier and co-workers used ITC to establish the solubility boundaries for the acquisition of thermodynamic data on phase equilibria in crystallization engineering.[9−11] Dhenain and co-workers used the isoplethic thermal analysis method to study the solid−liquid equilibrium in the NaCl−NaOH−H$_2$O ternary system for optimizing the operating conditions of an evaporator−
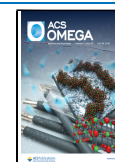
Table 1. Experimental Data Determined Using the ITC and IDE Methods for the NaCl−Na$_2$SO$_4$−H$_2$O Ternary System at 298.15 K and 102.2 kPa (Composition Shown as Mass Fraction, wt)^a

ITC method								IDE method			
Na$_2$SO$_4$ (wt)	H$_2$O (wt)	NaCl (wt)		Na$_2$SO$_4$ (wt)	H$_2$O (wt)	NaCl (wt)		Na$_2$SO$_4$ (wt)	H$_2$O (wt)	NaCl (wt)	
0.2122	0.7878	0.0000	[b,c]	0.2425	0.6964	0.0611	[j]	0.0000	0.7378	0.2622	[g]
0.2069	0.7801	0.0130	[b]	0.1941	0.7225	0.0834	[j,k]	0.0219	0.7252	0.2529	[g]
0.2026	0.7748	0.0226	[b]	0.6744	0.2842	0.0414	[k]	0.0420	0.7188	0.2392	[g]
0.1925	0.7590	0.0485	[b]	0.4871	0.4592	0.0537	[k]	0.0635	0.7058	0.2307	[g]
0.1761	0.7483	0.0756	[b]	0.3340	0.5820	0.0840	[k]	0.0850	0.7000	0.2150	[g]
0.1667	0.7324	0.1009	[b,d,e]	0.2124	0.6964	0.0912	[k]	0.1055	0.6993	0.1952	[d]
0.1581	0.7165	0.1253	[d]	0.8036	0.1471	0.0493	[l]	0.1290	0.7061	0.1649	[d]
0.1458	0.7088	0.1454	[d]	0.6675	0.2588	0.0737	[l]	0.1499	0.7143	0.1358	[d]
0.1352	0.6938	0.1710	[d]	0.5007	0.3732	0.1261	[l]	0.1611	0.7332	0.1057	[d]
0.1171	0.6923	0.1906	[d]	0.3788	0.4585	0.1627	[l]	0.1811	0.7589	0.0600	[b]
0.0957	0.6816	0.2227	[d,f,g]	0.2778	0.5364	0.1858	[l]	0.1910	0.7771	0.0319	[b]
0.0592	0.7068	0.2340	[g]	0.2051	0.5902	0.2047	[l]	0.2140	0.7860	0.0000	[b]
0.0285	0.7211	0.2504	[g]	0.1484	0.6291	0.2225	[l]				
0.0140	0.7263	0.2597	[g]	0.0974	0.6759	0.2267	[l,m]				
0.0000	0.7365	0.2635	[g,h]	0.0825	0.5907	0.3268	[m]				
0.4410	0.5590	0.0000	[i,j]	0.0620	0.3925	0.5455	[m]				
0.3505	0.6280	0.0215	[j]	0.0353	0.3080	0.6567	[m]				
0.3185	0.6464	0.0351	[j]								

^{a}The symbols S_1, S_2, and S_3 denote the NaCl, Na$_2$SO$_4$, and Na$_2$SO$_4$·10H$_2$O solids, respectively. The standard uncertainties are $u(T) = 0.01$ K (ITC) and 0.1 K (IDE) and $u(p) = 0.5$ kPa. The relative standard uncertainties of the ITC method are $u_r(w(NaCl)) = 0.03$, $u_r(w(H_2O)) = 0.03$, and $u_r(w(Na_2SO_4)) = 0.03$. The relative standard uncertainties of the IDE method are $u_r(w(NaCl)) = 0.07$, $u_r(w(H_2O)) = 0.07$, and $u_r(w(Na_2SO_4)) = 0.05$. ^{b}Lying on the boundary between the solid phase S_3 and the liquid phase. ^{c}A single saturated solution of sodium sulfate solution. ^{d}Lying on the boundary between the solid phase S_2 and the liquid phase. ^{e}A solution cosaturated with the solid phases ($S_2 + S_3$). ^{f}A solution cosaturated with the solid phases ($S_1 + S_2$). ^{g}Lying on the boundary between the solid phase S_1 and the liquid phase. ^{h}A single saturated solution of sodium chloride solution. ^{i}A composition of the solid phase S_3. ^{j}Lying on the boundary between the solid phase $S_3 + l$ region and the solid phase ($S_3 + S_2$) + l region. ^{k}Lying on the boundary between the solid phase ($S_3 + S_2$) + l region and the solid phase $S_2 + l$ region. ^{l}Lying on the boundary between the solid phase $S_2 + l$ region and the solid phase ($S_1 + S_2$) + l region. ^{m}Lying on the boundary between the solid phase ($S_1 + S_2$) + l region and the solid phase $S_1 + l$ region.

crystallizer used in the hydrazine extraction process.[15] The present study uses the ITC approach to study the Na$_2$SO$_4$ + NaCl + H$_2$O system, and the obtained thermodynamic parameters are of particular interest since they provide both a theoretical basis and fundamental data for the industrial utilization of natural soda to separate sodium salts.

A rigorous temperature control is essential in solubility phenomena, and the ITC technique is characterized by a constant temperature and a perfect control of precision. The thermodynamic study of the Na$_2$SO$_4$ + NaCl + H$_2$O system is focused on the determination of the maximum solubility of the solid solutes along the solid−liquid or solid−solid line of the ternary system. In this way, these lines, which represent the locus of the maximum solubility data points, are readily obtained by plotting these points. In our previous studies, ITC has been proved to be a feasible and convenient method to construct several types of phase diagrams of ternary systems.[16−18] As theoretical calculations providing an accurate prediction of the solubility limits of a solid component in binary mixtures are not yet available, experimental studies are necessary to determine the solid−liquid phase equilibria in ternary systems, such as the NaCl + Na$_2$SO$_4$ + H$_2$O system investigated in this paper. The Pitzer model is used to analyze the experimental data to determine the solid−liquid equilibrium.[19,20] This model is very efficient at predicting the behavior of electrolyte solutions ranging from infinitely diluted solutions to very concentrated ones; furthermore, the activity and osmotic coefficients as well as the activity product can be calculated using the corresponding Pitzer parameters. Experimental and theoretical evaluations of phase-equilibrium solubilities of multicomponent salt−water systems are of great importance in the fields of chemical engineering, saline chemistry, and thermodynamics.

2. RESULTS AND DISCUSSION

2.1. Drawing the Ternary Phase Diagram Using the ITC Method. The hydration and dissolution of inorganic salt usually result in the absorption or production of a large quantity of heat; thus, ITC is a reliable, convenient, and reproducible method to detect hydrate formation and determine the salt solubility. There is no hydrate of NaCl, and there are two types of hydrated crystalloid forms of Na$_2$SO$_4$ (Na$_2$SO$_4$·7H$_2$O and Na$_2$SO$_4$·10H$_2$O). Washburn and Klem determined the temperature of the transition from Na$_2$SO$_4$·7H$_2$O to Na$_2$SO$_4$ to be 23.46 °C.[21] Balarew and co-workers found that, at a low relative humidity (well-dried Na$_2$SO$_4$·7H$_2$O), the relative humidity of the system moved along the Na$_2$SO$_4$·7H$_2$O−anhydrous Na$_2$SO$_4$ phase boundary upon lowering the temperature and entered the stability zone of Na$_2$SO$_4$·7H$_2$O at a temperature of −9.75 °C.[22] Thus, the ternary phase diagram of the NaCl + Na$_2$SO$_4$ + H$_2$O system at 298.15 K was established without considering the heptahydrate.

Table 1 lists the experimental data of the NaCl + Na$_2$SO$_4$ + H$_2$O ternary system at 298.15 K and atmospheric pressure determined using the IDE and ITC methods, while Figure 1 shows the contrast curves of the two methods. It can be seen that the solubilities obtained from the IDE and ITC methods are similar. According to the literature, the solubility of NaCl is
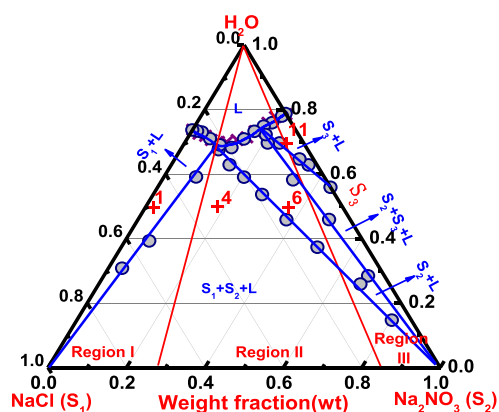
Figure 1. Phase diagram at 298.15 K and 102.2 kPa of the three-component system $NaCl-Na_2SO_4-H_2O$ obtained from the IDE and ITC methods. Purple "multiplication" symbols represent the IDE method, while blue "solid circle" symbols represent the ITC method. The compositions of samples 1, 4, 6, and 11 used in the subsequent X-ray diffraction measurements are indicated by the red "+" symbols. S_1, S_2, S_3, and L are the abbreviations for the NaCl solid, Na_2SO_4 solid, $Na_2SO_4 \cdot 10H_2O$ solid, and single liquid, respectively.

26.57[23] and 26.48%,[24] while the solubility of Na_2SO_4 is 21.9,[25] 22.7,[26] and 20.8%,[27] at a temperature of 25 °C. The solubilities of NaCl and Na_2SO_4 obtained in this work are 26.35 and 21.22%, respectively, as shown in Table 1, indicating that ITC is a reliable and relatively simple method to obtain the additional thermodynamic parameters. In other words, the ITC method is effective to determine the solubility of pure or mixed solids, and the phase diagram of the NaCl + Na_2SO_4 + H_2O system obtained via the ITC method is shown in Figure 1. What follows is a detailed description of the method to obtain these points lying on the boundaries of different phase regions from the ITC titration curves, including qualitative evaluation, quantitative analysis, phase boundary determination, interpretation, and discussion. We first discuss single-salt solutions and then present some analysis and discussion on mixed-salt solutions.

2.1.1. NaCl–H₂O System. The ITC thermogram for titrating distilled water into the pure NaCl solid at 298.15 K is shown in Figure 2. The observed enthalpy change (ΔH_{obs}) should first correspond to the dissolution enthalpy and then to the dilution enthalpy. The dissolution enthalpy is not a general

measure of the integral heat of solution or the differential heat of solution. In order to describe exactly the dissolution act or process, two methods were used, namely, the total heat of titrating 1 mol water into a solid system with excess salt and the total heat of 1 mol solid dissolving in water to form a saturated solution. When the titration process started, the same volume of water per titration was set to dissolve a constant mass of the NaCl solid. A sufficiently large quantity of solids was in an ampoule, resulting in the observed heats being almost constant. The dissolving process of NaCl is endothermic, as has been reported in refs 28−30. Only dilution of the NaCl solution was found to occur when water was added after the dissolution of the last crystal of NaCl, and ΔH_{obs} first decreased and then increased. This sharp decrease in ΔH_{obs} was used to determine the solubility of NaCl, as shown by the red arrow in Figure 2a. It is difficult to explain this sharp decrease, and we speculate that there may be a correlation with the transformation from the dissolution enthalpy to the dilution enthalpy. The dilution enthalpy of the NaCl solution is also an endothermic process but relatively small.

The plot of the accumulated heat as a function of the mole ratio, n_{H_2O}/n_{solute}, can also be employed for data treatment. Each curve of a system is composed of several parts (depending on the number of the different phase regions passed).[9−11] For the single-salt solution, no hydrated crystal exists, and each curve is composed of two parts. The first part of the solid dissolution process exhibits an approximately linear increase in $\Delta H/n_1$ according to

$$\Delta H/n_1 = A_1 \alpha \tag{1}$$

where ΔH is the cumulated titration heat, n_1 is the total number of moles of the solid, α is the mole ratio of the solvent to the solute, and A_1 is the total heat generated from titrating 1 mol water into a solid system with excess salt. When the solid has completely dissolved, the second part, which is simply related to the heat of dilution, is generally represented by a polynomial fitting:

$$\Delta H/n_1 = a + b\alpha + c\alpha^2 + \dots \tag{2}$$

where a, b, and c are coefficients that can be determined via linear regression, and the intersection of eqs 1 and 2 yields the enthalpy of dissolution for a given ratio α_S at saturation. From α_S, the composition of the binary or ternary system at saturation can be calculated using the concentration conversion method, and the result is in good agreement with the position of the red arrow in Figure 2a. For the binary $NaCl-H_2O$ system, the first part is undoubtedly linear, as shown in Figure 2b, and the slope is comparable with the solid dissolution enthalpy. The second part is also almost linear; that is, the c coefficient in eq 2 is approximately equal to 0, and the slope corresponds to the dilution enthalpy of the NaCl solution in the tested concentration.

The obtained dissolution enthalpy and dilution enthalpy are listed in Table 2, while the literature data at different concentrations are listed in Table S1. The averaged molar enthalpy of a solution containing NaCl in 1 mol water at 298.15 K was reported to be 2.16 kJ/mol,[28] while the molar enthalpy of NaCl dissolving in water and forming a saturated solution was reported to be 1.92 kJ/mol. The former includes the solid dissolution enthalpy and the subsequent dilution
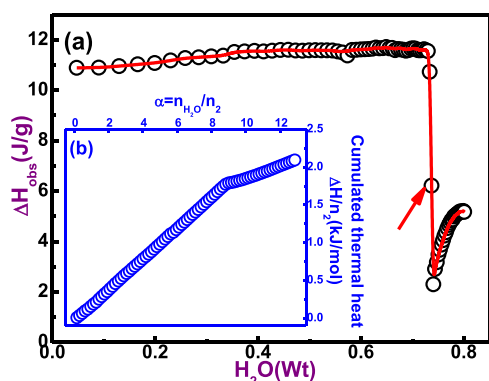

Figure 2. (a) ITC thermogram for titrating pure water into the NaCl solid at 298.15 K and 102.2 kPa. The red arrow indicates the position of the NaCl solubility. (b) Cumulative thermal effect $\Delta H/n_{solute}$ (in kJ/mol) as a function of $\alpha = n_{solvent}/n_{solute}$.

Table 2. Dissolution Enthalpy (Titrating 1 mol Water into a Solid System with Excess Salt or Titrating Water into 1 mol Solid or Mixed Solids To Form a Saturated Solution) and Dilution Enthalpy (Titrating 1 mol H_2O into the Salt Solution at a Certain Range of Concentration) Determined via the ITC Method at 298.15 K and 102.2 kPa[a]

mass ratio of NaCl to Na_2SO_4 in the ampoule[i]	dissolution enthalpy (kJ/mol)[b]					dilution enthalpy[h] (kJ/mol) in a certain range of water amount	H_2O (wt)
	$NaCl$[c]	$NaCl + Na_2SO_4$[c]	Na_2SO_4[c]	$Na_2SO_4 + Na_2SO_4 \cdot 10H_2O$[c]	$Na_2SO_4 \cdot 10H_2O$[c]		
0:10					−0.668 (−19.57[e,g])	0.2217	0.7878~0.8004
0.5:9.5		0.062[f]		−0.553 (−19.17[e,g])		0.1404	0.7801~0.8000
1:9		0.076		−0.552		0.1401	0.7748~0.7993
2:8		0.069[f] (0.67[e,g])		−0.555		0.1351	0.7590~0.8004
3:7		0.077	−0.392[d]	−0.491[f]		0.1148	0.7483~0.8009
4:6		0.077	−0.485[d]			0.1139	0.7324~0.8005
5:5		0.077	−0.422 (−15.60[e,g])			0.1103	0.7088~0.8001
6:4		0.077	−0.391[d]			0.1036	0.6923~0.8007
7:3	0.201[d]	0.077	−0.240[d,f]			0.0957	0.6816~0.8005
8:2	0.207 (1.92[e,g])	0.073				0.0929	0.7068~0.8004
9:1	0.217[d]	0.076				0.0926	0.7211~0.8007
9.5:0.5	0.205[d]	0.076				0.0905	0.7263~0.8008
10:0	0.205					0.0895	0.7365~0.8008

[a]The standard uncertainties are $u(T) = 0.01$ K and $u(p) = 0.5$ kPa. The relative standard uncertainties of dissolution enthalpies are $u_r(NaCl) = 0.05$, $u_r(NaCl+Na_2SO_4) = 0.06$, $u_r(Na_2SO_4) = 0.05$, $u_r(Na_2SO_4 + Na_2SO_4 \cdot 10H_2O) = 0.06$, and $u_r(Na_2SO_4 \cdot 10H_2O) = 0.05$. The relative standard uncertainty of dilution enthalpy is $u_r = 0.05$. The relative standard uncertainty of the automatic syringe is $u_r = 0.01$. The weighing error was ±0.01 mg. [b]Average total enthalpy of titrating 1 mol water into a solid system with excess salt(s), which means that the dissolved salt(s) is 1 mole and the added water is 1 mole. [c]The dissolved solid or the dissolved mixed solids proportionally when adding the water to the ampoule in the titration process, which also correspond(s) to the phase regions in Figure 1. The mass ratio of water to salts for each region can be read with the aid of Figure 1 and Table 2. [d]Average value due to the slightly changing concentration of the saturated salt solution. [e]Average molar enthalpy of the NaCl solid dissolving in water to form a saturated solution. [f]This value with a big error was not included when calculating the average value. [g]The total moles of mixed solids in solution is 1 mole using the saturated composition obtained from the ITC method. [h]Average dilution enthalpy of titrating 1 mol H_2O into the salt solution with no solid in the tested concentration. [i]It tells the readers that which titration curve is used to obtain the values in the same row.

enthalpy, while the latter only includes the solid dissolution enthalpy. In addition, the dilution heat does not represent the heat of a solution at infinite dilution, and the average of dilution enthalpy of titrating 1 mol H_2O into the salt solution with no solid in the tested concentration is listed in Table 2. Thus, the dissolution enthalpy obtained from the ITC method is reliable and does not change with the concentration of the solution, and the dilution enthalpy is relatively small as it is limited by the tested concentration.

2.1.2. $Na_2SO_4 \cdot 10H_2O$—H_2O System. For the determination of the solubility of Na_2SO_4, we used decahydrate to perform the experiment based on the probable hydration during the equilibrium time in an ampoule. For the mixed solids, there is no hydrate of Na_2SO_4 with the presence of a little water and it should be the region of $NaCl(s) + Na_2SO_4(s) + L$, which is also proved by the titration curves. The ITC thermogram for titrating distilled water into the pure $Na_2SO_4 \cdot 10H_2O$ crystal at 298.15 K is shown in Figure 3. Decahydrate was precipitated
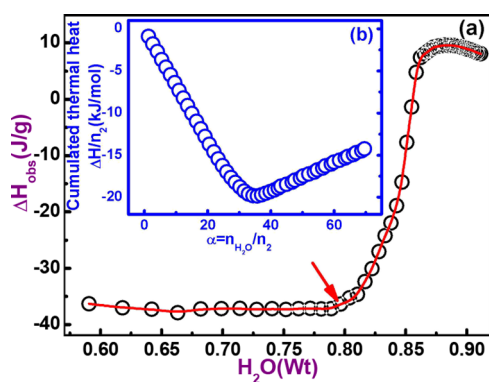

Figure 3. (a) ITC thermogram for titrating pure water into the pure $Na_2SO_4 \cdot 10H_2O$ solid at 298.15 K and 102.2 kPa. The red arrow indicates the position of the $Na_2SO_4 \cdot 10H_2O$ solubility. (b) Cumulative thermal effects $\Delta H / n_{solute}$ (in kJ/mol) as a function of $\alpha = n_{solvent} / n_{solute}$.

from its saturated solution. Without the hydration process, ΔH_{obs} corresponded initially to the dissolution enthalpy and then to the dilution enthalpy. The observed heats for the initial titrations were nearly constant, and their average value was used to determine the dissolution enthalpy of $Na_2SO_4 \cdot 10H_2O$. The dissolving process of $Na_2SO_4 \cdot 10H_2O$ is exothermic, and the thermal effect is relatively high. ΔH_{obs} exhibited a pronounced decrease at first followed by a slight increase. Therefore, the sharp increase in ΔH_{obs} was used to determine the solubility of $Na_2SO_4 \cdot 10H_2O$, as indicated by the red arrow in Figure 3a. The dilution process of the Na_2SO_4 solution is endothermic but relatively small.

The accumulated heat as a function of the mole ratio is shown in Figure 3b; this curve is composed of two parts. The intersection of these two parts can also be used to calculate the solubility, and the obtained result is in good agreement with the position indicated by the red arrow in Figure 3a. The solid dissolution enthalpy is determined by the slope of the first linear part, and the dilution enthalpy is obtained from the slope of the second nearly linear part. The obtained dissolution enthalpy and dilution enthalpy are listed in Table 2.

2.1.3. $NaCl$—Na_2SO_4—H_2O System. The ITC thermograms for titrating distilled water into the mixed $NaCl$—Na_2SO_4 solids with the desired composition at 298.15 K are illustrated in Figure 4a. There are both similarities and differences between

the binary and ternary systems, and the analyses of the curves in Figure 4a are relatively complex. In order to provide a comprehensive analysis of the curves and establishing connections between the curves and the phase behaviors, the curves are classified into three types (Figure 4b—d). The diagram was accordingly separated into three regions, namely, Regions I, II, and III, using the red lines shown in Figure 1.

Region I: the titration curves are shown in Figure 4b; it can be seen that the mass ratios of $NaCl$ and Na_2SO_4 are concentrated on the left-hand side of the phase diagram. The evolution of ΔH_{obs} with the water amount consists of a plateau, an increase, a plateau, a sharp decrease, and finally a smooth increase.

According to the calculations, the compositional point of the first plateau is situated at a two-solid region of $[NaCl(s) + Na_2SO_4(s) + L]$, and the concentrations of $NaCl$ and Na_2SO_4 in the saturated solution are fixed (i.e., 9.30% Na_2SO_4, 69.05% H_2O, and 21.65% $NaCl$). This means that the same volume of water per titration was set to dissolve the constant mass of the $NaCl + Na_2SO_4$ solids before the Na_2SO_4 solid was completely dissolved, resulting in almost constant observed heats, which corresponds to part 1 in Figure 4b. The higher the initial Na_2SO_4 content in the mixed solids, the longer the first plateau of ΔH_{obs}; this trend is easily understood and can be explained and calculated via quantitative analyses based on the lever rule. The phase transformation point is then obtained from the end of the plateau, see the first blue arrow in the inset in Figure 4b. The positive dissolving heat of $NaCl$ and the negative dissolving heat of Na_2SO_4 correspond to the relatively small value of the observed enthalpy change.

With water addition, the compositional point enters a one-solid region of $[NaCl(s) + L]$, which is accompanied by the ΔH_{obs} value increasing to reach another plateau. Similarly, the more the remaining $NaCl$ solid when the Na_2SO_4 solid is just dissolved, the shorter the second plateau of ΔH_{obs}, which corresponds to part 2 in Figure 4b. In the region of $[NaCl(s) + L]$, the solution is saturated with $NaCl$, and its concentration changes with the Na_2SO_4 content. Thus, the obtained dissolving heat of $NaCl$ is an average value and it has little effect on the dissolving heat due to the concentration of the saturated solution.

A further addition of water moves the system toward a single phase of the ternary unsaturated solution, and only dilution of the ternary aqueous solution is observed (part 3). The transition from part 2 to part 3 decreases more pronouncedly with the Na_2SO_4 content; additionally, the ΔH_{obs} value becomes negative, which is likely the reflection of the dissolution of Na_2SO_4. The phase transformation point is then obtained from the sharp decrease, see the second blue arrow in the inset in Figure 4b. This means that the titration curve passes through the intermediate point between the regions of $[NaCl(s) + L]$ and $[Na_2SO_4(s) + L]$, that is, a point near the cosaturated solution containing $NaCl$ and Na_2SO_4. The dilution process of the ternary solution is also endothermic, and the curve finally tends to become flat.

The plot of the accumulated heats as a function of the mole ratio, $n_{H_2O}/(n_{NaCl} + n_{Na_2SO_4})$, was also utilized for data treatment, and the obtained curves are displayed in Figure 5a. For better clarity, the curve corresponding to a mass ratio of $NaCl$ to Na_2SO_4 of 9:1 is shown in Figure 5b. It is found that each curve of the ternary solution is composed of three parts, which are related to the dissolution of $[NaCl(s) +$
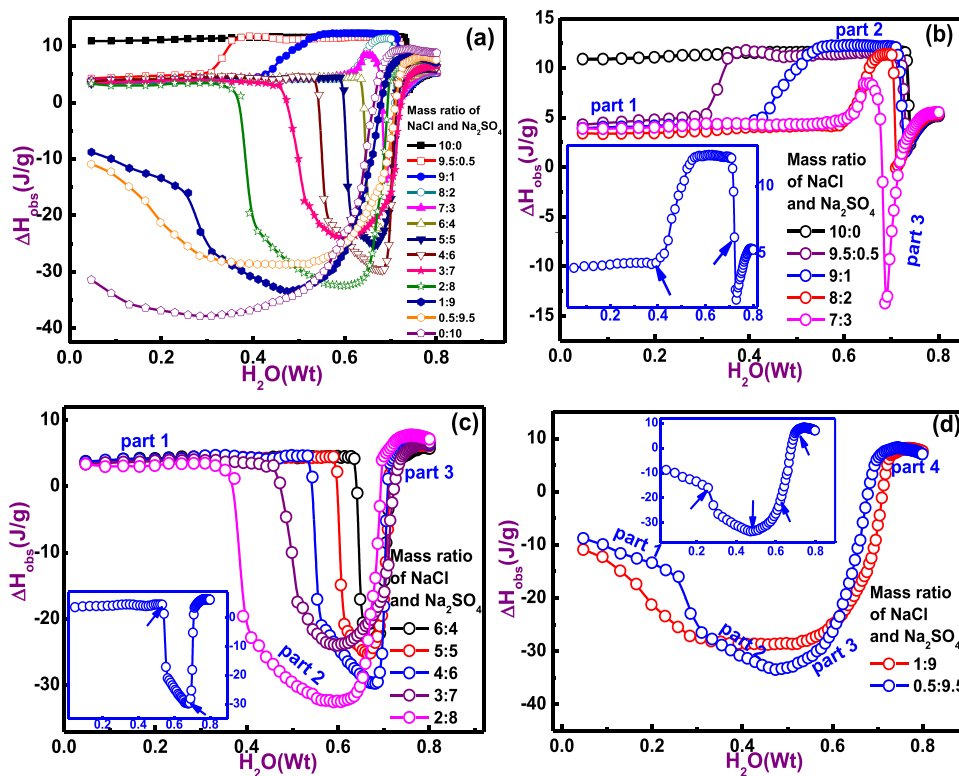
Figure 4. (a) Overall ITC thermogram for titrating pure water into pure NaCl, pure Na_2SO_4, or the mixed $NaCl/Na_2SO_4$ solid phase at 298.15 K and 102.2 kPa. The mass ratio of NaCl to Na_2SO_4 is fixed for each curve. (b) Comparison of the ITC curves for mass ratios of NaCl to Na_2SO_4 of 10:0, 9.5:0.5, 9:1, 8:2, and 7:3. (c) Comparison of the ITC curves for mass ratios of NaCl to Na_2SO_4 of 6:4, 5:5, 4:6, 3:7, and 2:8. (d) Comparison of the ITC curves for mass ratios of NaCl to Na_2SO_4 of 1:9, 0.5:9.5, and 0:10. The insets show the method to obtain the phase transformation points.
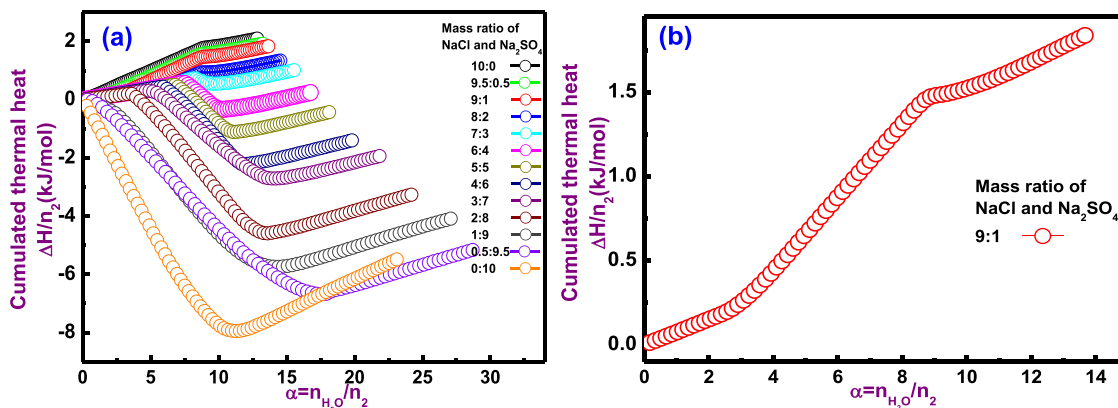

Figure 5. (a) Overall plots of the accumulated thermal effects $\Delta H/n_{solute}$ (in kJ/mol) as a function of $\alpha = n_{solvent}/n_{solute}$. (b) Specific plots of the accumulated thermal effects as a function of the molar ratio when the mass ratio of NaCl to Na_2SO_4 is 9:1.

$Na_2SO_4(s)$], the dissolution of NaCl(s), and the dilution of the ternary solution. These three parts are nearly linear; thus, the dissolution enthalpy and dilution enthalpy are also obtained and listed in Table 2.

Region II: the titration curves are shown in Figure 4c; it can be seen that the mass ratios of NaCl to Na_2SO_4 are concentrated in the middle region of the phase diagram. The evolution of ΔH_{obs} with the water amount consists of a plateau, a sharp decrease, a gradual decrease, a sharp increase, and finally a gradual variation.

Similar to Region I, in combination with the analysis of the ternary phase diagram, it is found that the compositional point of the initial plateau is situated at a two-solid region of

[NaCl(s) + Na_2SO_4(s) + L], and the liquid is a cosaturated point. The dissolution of the mixed solids with the same mass results in the observed heats being almost constant, which corresponds to part 1 in Figure 4c. The phase transformation point is then obtained from the end of the plateau, see the first blue arrow in the inset in Figure 4c. The higher the initial Na_2SO_4 content in the mixed solids, the shorter the plateau of ΔH_{obs}, which depends on the width of the first-phase region and can be calculated by quantitative analyses based on the lever rule.

With water addition, the compositional point begins to enter a one-solid region of [Na_2SO_4(s) + L]. The dissolution of the Na_2SO_4 solid is a clear exothermic process and thus induces a
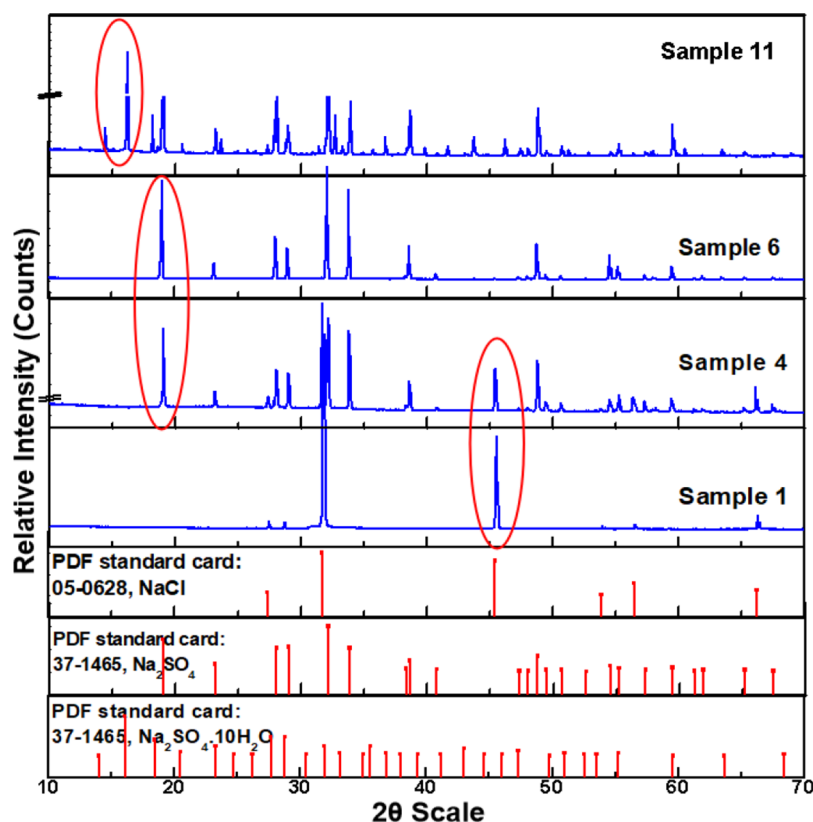
Figure 6. XRD patterns of samples 1, 4, 6, and 11. The reader is referred to the sample composition shown in Figure 1 by the red line and the "+" symbols.

sharp decrease and a subsequent gradual decrease in the ΔH_{obs} value. In the region of $[Na_2SO_4(s) + L]$, the solution is saturated with Na_2SO_4, and its concentration changes with the NaCl content. It is found that the observed heat of Na_2SO_4 per titration has an influence on the concentration of the saturated solution, which corresponds to the gradual decrease (part 2) in Figure 4c. Although the ΔH_{obs} value is not constant, the slope of the second linear part in Figure 5a can still be used to determine the average dissolution enthalpy of the Na_2SO_4 solid albeit only in a wide range. Similar to Region I, the more the remaining Na_2SO_4 solid when the NaCl solid is just dissolved, the more pronounced and wider the part 2 of ΔH_{obs} in Figure 4c.

A further addition of water moves the system toward a dilution process of the ternary aqueous solution (part 3). The transition from part 2 to part 3 increases significantly; such an increase is caused by the transformation from the dissolution enthalpy (exothermic process) to the dilution enthalpy (endothermic process); the phase transformation point is then obtained from the initial increase, taking the pure Na_2SO_4 solution as the reference, see the second blue arrow in the inset in Figure 4c. The dilution process of the ternary solution is endothermic, and the curve either reaches a constant value or decreases slightly.

Finally, we provide a detailed analysis for part 2 of the ITC curve when the mass ratio of NaCl to Na_2SO_4 is 2:8. In combination with the analysis of the ternary phase diagram, it can be seen that the titration curve goes through the regions of $[Na_2SO_4(s) + L]$, $[Na_2SO_4(s) + Na_2SO_4 \cdot 10H_2O(s) + L]$, and $[Na_2SO_4 \cdot 10H_2O(s) + L]$ with the amount of water addition. For the two-solid region of $[Na_2SO_4(s) + Na_2SO_4 \cdot 10H_2O +$

L], the liquid is a cosaturated point, and the ΔH_{obs} values should be nearly constant. Even if there are several points situated in this two-solid region, ΔH_{obs} is still reflected by the middle section of part 2 (the magenta line in Figure 4c). This change is beneficial not only to determine the phase points located on the boundary line but also to obtain the dissolution enthalpy of the mixed solids of $[Na_2SO_4(s) + Na_2SO_4 \cdot 10H_2O(s)]$.

Region III: the titration curves are shown in Figure 4d; it can be seen that the mass ratios of NaCl to Na_2SO_4 are concentrated on the right-hand side of the phase diagram. The evolution of ΔH_{obs} with the water amount consists of a gradual decrease, a plateau, a gradual increase, a sharp increase, and finally a gradual variation.

First, the titration curve goes through the phase region of $[NaCl(s) + Na_2SO_4(s) + L]$, and it should exhibit an endothermic plateau; however, the first several titrations are all exothermic and show a gradual decrease (part 1 in Figure 4d). It is likely that the composition of the ternary system quickly enters the subsequent region of $[Na_2SO_4(s) + L]$ due to water addition and the very small amount of NaCl; therefore, the titration peaks exhibit a behavior typical of the dissolution of the Na_2SO_4 solid. The phase transformation point is then obtained from the end of the plateau, see the first blue arrow in the inset in Figure 4d.

With water addition, the composition point begins to enter the region of $[Na_2SO_4(s) + Na_2SO_4 \cdot 10H_2O(s) + L]$, resulting in the observed heats being almost constant, which is well reflected in part 2 (the red line in Figure 4d) when the mass ratio of NaCl to Na_2SO_4 is 0.5:9.5.

Table 3. Comparison of the Compositions of the Liquid Phase and the Activity Product Obtained from the ITC Method and the Pitzer Model at 298.15 K and 102.2 kPa[a]

composition of the liquid phase obtained experimentally, wt			composition of the liquid phase obtained theoretically, wt			activity product		equilibrium solid phase
Na_2SO_4	H_2O	NaCl	Na_2SO_4	H_2O	NaCl	K_{ap}	averaged K_{ap}	
0.2069	0.7801	0.0130	0.2091	0.7778	0.0131	0.05869	0.06239 ± 0.00624	$Na_2SO_4 \cdot 10H_2O$
0.2026	0.7748	0.0226	0.2023	0.7752	0.0225	0.06029	0.06008[3)]	
0.1925	0.7590	0.0485	0.1960	0.7546	0.0494	0.06444		
0.1761	0.7483	0.0756	0.1708	0.7559	0.0733	0.06373		
0.1667	0.7324	0.1009	0.1600	0.7431	0.0969	0.06480		
						0.3452	0.6218 ± 0.0622	Na_2SO_4
0.1581	0.7165	0.1253	0.1608	0.7118	0.1274	0.4734	0.5180[34]	
0.1458	0.7088	0.1454	0.1439	0.7126	0.1435	0.5578		
0.1352	0.6938	0.1710	0.1290	0.7125	0.1585	0.7582		
0.1171	0.6923	0.1906	0.1152	0.7120	0.1728	0.7732		
0.0957	0.6816	0.2227	0.0877	0.7082	0.2041	0.8233		
						40.3973	38.1328 ± 3.8133	NaCl
0.0592	0.7068	0.2340	0.0595	0.7049	0.2356	37.2147	38.5390[34]	
0.0285	0.7211	0.2504	0.0287	0.7188	0.2525	36.9746		
0.0140	0.7263	0.2597	0.0140	0.7255	0.2605	37.9449		
0.2122	0.7878	0.0000	0.2213	0.7787	0.0000	0.05653	0.05653 ± 0.00565	$Na_2SO_4 \cdot 10H_2O$
0.0000	0.7365	0.2635	0.0000	0.7342	0.2658	36.8558	36.8558 ± 3.6856	NaCl

[a]The standard uncertainties are $u(T) = 0.01$ K and $u(p) = 0.5$ kPa. The relative standard uncertainties of ITC method are $u_r(w(NaCl)) = 0.03$, $u_r(w(H_2O)) = 0.03$, and $u_r(w(Na_2SO_4)) = 0.03$. The relative standard uncertainty of the averaged activity product is $u_r = 0.10$, and the standard uncertainty is listed in the above table.

A further addition of water moves the system toward a one-solid region of $[Na_2SO_4 \cdot 10H_2O(s) + L]$. The dissolution of $Na_2SO_4 \cdot 10H_2O$ is a clear exothermic process, and the NaCl content of the equilibrium saturated solution has a significant effect on the dissolution heat. Thus, the obtained dissolution enthalpy is an average value, and there is a gradual increase in ΔH_{obs} at the end of part 2 followed by a sharp increase, which is well reflected by part 3 of the blue line in Figure 4d when the mass ratio of NaCl to Na_2SO_4 is 1:9. Then, the phase transformation points are obtained from the initial increase and the changed slope from the gradual increase to the sharp increase, see the second and the third blue arrows in the inset in Figure 4d.

Finally, a further addition of water moves the system toward the dilution process of the ternary aqueous solution (part 4), and the dilution enthalpy is thus obtained. Then, the phase transformation point is determined from the highest value of ΔH_{obs} after the sharp increase, see the fourth blue arrow in the inset in Figure 4d. In summary, the titration curves in Region III should pass through five phase regions and are relatively complex; therefore, it is important to provide a comparative analysis. Even, the smaller titration water in some specific concentration range is needed to determine the phase point.

The above results demonstrate that ITC is an effective approach to determine the phase diagram of two solids and one solvent. The ITC method can be used to determine the compositional points on the boundary lines and supply additional information about solution behaviors with respect to thermodynamics. The phase diagram at 298.15 K in Figure 1 consists of six phase regions, including one liquid-phase region (L), three one-solid regions [NaCl(s) + L, Na_2SO_4(s) + L, and $Na_2SO_4 \cdot 10H_2O$(s) + L], and two two-solid regions [NaCl(s) + Na_2SO_4(s) + L and Na_2SO_4(s) + $Na_2SO_4 \cdot 10H_2O$(s) + L]. Most importantly, the data in Table 2 provide a clearer understanding of the dissolution and dilution

processes. Both the dissolution enthalpy and the dilution enthalpy of the Na_2SO_4 solid are greater than those of the NaCl solid; however, the thermal effect of NaCl should not be neglected.

2.2. X-ray Diffraction (XRD) Measurements. Several samples were chosen for the XRD measurements, and the sample compositions are indicated by the magenta circles in Figure S1. Most samples were found to have a similar water content, and the content of the equilibrium solid phase can be observed in Figure S2. The XRD patterns are shown in Figures 6 and S3. The XRD patterns shown in Figure 6 for samples 1, 4, 6, and 11 are compared to the standard XRD patterns of NaCl, Na_2SO_4, and $Na_2SO_4 \cdot 10H_2O$. The red elliptic circles indicate several characteristic peaks of NaCl, Na_2SO_4, and $Na_2SO_4 \cdot 10H_2O$. However, what needs to be explained is that the crystal of decahydrate is easily dehydrated in dry environments. For sample 11 and sample 12, Figure S2 shows the XRD pattern when we put the filtered crystal in the oven for 0, 10, and 30 min. It was found that a small ratio of decahydrate changed to anhydrous sodium carbonate after being dried 10 min, and decahydrate is nearly dehydrated after being dried 30 min. The results of the XRD measurements provide convincing evidence for the presence of the different phase regions obtained via the ITC method.

2.3. Calculation of the Thermodynamic Parameters Using the Pitzer Equation. The Pitzer model is a semiempirical model that is very important for understanding the behavior of ions dissolved in water.[19,20,31−35] This model is very efficient at predicting the behavior of electrolyte solutions ranging from infinitely diluted solutions to very concentrated ones. The algorithm is provided in the Supporting Information; the activity and osmotic coefficients as well as the activity product (K_{ap}) can be calculated using the corresponding Pitzer parameters, which are listed in Table S2. The K_{ap} value for a salt in an aqueous solution should be

constant at a constant temperature. In fact, there is a small discrepancy between the averaged K_{ap} values of NaCl, Na$_2$SO$_4$, and Na$_2$SO$_4$·10H$_2$O and those reported by theoretical studies.[35] The activity product of Na$_2$SO$_4$·10H$_2$O (NaCl) in single and mixed electrolytes is 0.05653 (34.1843) and 0.06239 (34.4708), which is close to a reported theoretical value of 0.06008 (38.5390);[35] the activity product of Na$_2$SO$_4$ is 0.6356 with the related mixed system, and the theoretical value is 0.5180.

Two factors are supposed to cause this discrepancy. On the one hand, there are some limitations associated with using the Pitzer model in the saturated liquid solution with a large concentration. On the other hand, there is a difference between the experimental and theoretical compositions of the liquid phase. The compositions of the saturated liquid solution can be calculated via backward deduction using the reported K_{ap} values and the Pitzer parameters; the corresponding results are tabulated in Table 3. For comparative purposes, the compositions of the liquid solution obtained from the ITC method and the Pitzer model are shown in Figure 7. The good
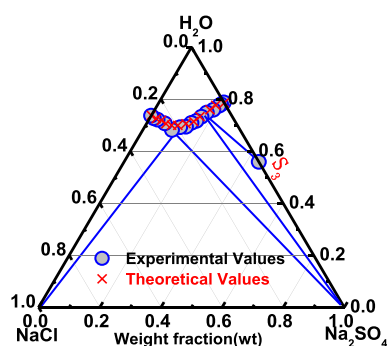

Figure 7. Comparison of the experimental ternary diagram of NaCl−Na$_2$SO$_4$−H$_2$O at 298.15 K and 102.2 kPa with the theoretical one: blue "●" symbols are experimental values obtained via ITC; red "×" symbols are values calculated using the Pitzer model.

agreement between the experimental and theoretical data proves the success of the ITC method and the Pitzer model for the NaCl + Na$_2$SO$_4$ + H$_2$O ternary system. In addition, comparison of the experimental solution composition and the literature resource[36] is shown in Figure 8, which can be referenced by the potential reader.
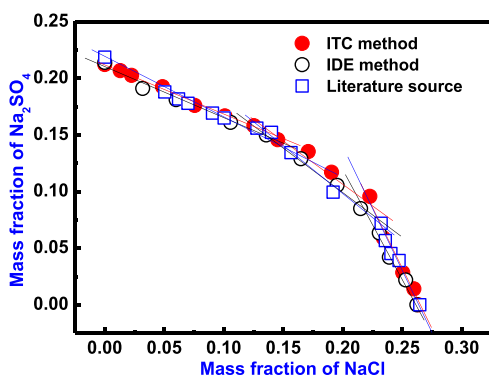

Figure 8. Comparison of the experimental solution composition obtained from different methods.

3. CONCLUSIONS

In this study, the ITC curve for titrating water into mixed solids was measured and the curve was complex, especially passing several phase regions. The results proved that the ITC method can be used to determine the global phase diagrams of the NaCl + Na$_2$SO$_4$ + H$_2$O system at 298.15 K, and the liquid compositions are in good agreement with the values reported in the literature; for example, the solubilities of NaCl and Na$_2$SO$_4$ obtained are 26.35 and 21.22%, which are close to the reported values (26.57 and 26.48% for NaCl and 21.9, 22.7, and 20.8% for Na$_2$SO$_4$).

ITC is considered as one of the most advantageous instruments for connecting the specific solution behavior, the raw titration curve, and the phase point. This method can provide not only heat information related to the phase transition but also separate data for the dissolution and dilution processes, thus permitting one to gain a clearer understanding of solution behaviors (crystal formation, ionic hydration, salt hydration, etc.). Judging from the heat amount, both the dissolution enthalpy and the dilution enthalpy of the Na$_2$SO$_4$ solid are greater than those of the NaCl solid. The dissolution processes of the Na$_2$SO$_4$ solid and the NaCl solid are endothermic and exothermic, respectively, and both their dilution processes are endothermic. The dissolution and dilution heats of the mixed solids are all between those of pure NaCl and pure Na$_2$SO$_4$. The good agreement between the liquid solution obtained from the ITC method and that obtained from the Pitzer model indicate that both these methods are suitable for modeling the NaCl + Na$_2$SO$_4$ + H$_2$O ternary system. It is envisaged that these methods will be used for the experimental determination and the theoretical calculation of the behaviors of mixed electrolytes. The research of the measurement, explanation, and analyzation of the curves is expected to transfer to other similar systems, which is beneficial for the development of solution thermodynamic theory and apparatus.

4. EXPERIMENTAL SECTION

4.1. Materials. The chemicals used are of analytical grade and were purchased from Beijing InnoChem Science & Technology Co., Ltd. The purity levels and CAS numbers of the chemicals used in this study are reported in Table 4. All chemicals were used without further purification. Sodium

Table 4. Information about the Chemicals

chemical	mass fraction purity[a]	CAS no.	purification method
sodium sulfate, anhydrous, Na$_2$SO$_4$	≥0.990	7757-82-6	used as received, stored in a desiccator
sodium chloride, anhydrous, NaCl	≥0.995	7647-14-5	
barium nitrate, Ba(NO$_3$)$_2$	≥0.999	10022-31-8	
silver nitrate, AgNO$_3$	≥0.998	7761-88-8	
sodium sulfate, decahydrate, Na$_2$SO$_4$·10H$_2$O	≥0.990	7757-82-6	used after filtration[b]

[a]As stated by the supplier. [b]Obtained from the single saturated solution of sodium sulfate solution; used after filtration and patted dried on the filter paper. If dried in an oven at 298.15 K, no more than 10 min.

chloride and sodium sulfate were dried in an electrothermal constant-temperature drybox (BPG-9050AH, Shanghai Yiheng Technology company) for 4 h at 423 K and stored in a desiccator. Triply distilled water of a specific conductivity (lower than 3 $\mu s \cdot cm^{-1}$) was used for preparing all solutions, cleaning all glassware, and conducting titration experiments.

4.2. ITC. Microcalorimetry was performed via a nanowatt-scale ITC (Thermal Activity Monitor IV, TA Instruments, USA). Approximately, 0.2 g of the NaCl solid (0.2 g of the Na_2SO_4 solid or 0.2 g of the mixed NaCl−Na_2SO_4 solids with the desired composition) was added to a 1 mL stainless-steel ampoule. Distilled water (10 μL per titration; 80 times; with a relative error smaller than ±1%) was injected into the stirred sample cell using a 500 L Hamilton syringe controlled by a Thermometric 612 Lund pump. The titration interval (50 min) was sufficiently long to allow the signal to return to the baseline, which ensures the titration equilibrium. Otherwise, the repeated experiment was conducted with an extended titration interval. The sample solution was stirred at 50 rpm with a gold propeller in the cell. All the experiments were repeated twice to achieve a reproducibility of the integrated heats within ±2%. The weighing error was ±0.01 mg and was neglected. Thus, the uncertainty budget for the determination of the phase equilibrium compositions was also controlled within ±2%. The temperature was controlled to be 298.15 ± 0.01 K.

4.3. Isothermal Dissolution Equilibrium Method (IDE). The classical IDE methodology was adopted as previously reported.[37,38] For each sample, dry sodium salts of NaCl and Na_2SO_4 in a selected quantity were weighed, mixed with triply distilled water, placed in sealed glass bottles, and finally placed in a thermostatic vibrator until equilibrium was attained. The temperature of the vibrator was fixed at 298.15 ± 0.1 K. The vibration process lasted 12 h. Then, the aqueous solutions of the two samples stayed under static conditions for 12 and 36 h. If the concentrations of Cl^- and SO_4^{2-} in the supernatant could be controlled within ±0.3%,[13,39] it indicated that 12 h was a sufficiently long time for statical separation and for the equilibrium to be reached.

A certain mass of the saturated supernatant (~5 g) was then accurately weighed into a centrifuge tube for quantitative analysis after equilibration. Step 1: an excess $Ba(NO_3)_2$ solution of known concentration was added. The solution was centrifuged for 30 min at a speed of 10,000 rpm. The $BaSO_4$ precipitate was washed and centrifuged to eliminate the surface adsorbate. The concentration of Na_2SO_4 can be calculated from the mass of the dried precipitate. Step 2: an excess $AgNO_3$ solution of known concentration was added to another supernatant. The concentration of NaCl can be calculated from the mass of the dried precipitate after centrifugation, washing, weighing, and deduction of the Ag_2SO_4 quality.

The isothermal filtration apparatus consisted of an oil-jacketed sand-core filter, and a filtering flask was employed to obtain the solid sample; the filtration temperature was controlled with an oil bath, which was also connected to an isothermal tank. The wet solid samples were dried at 298.15 K for more than 48 h and subsequently used for XRD (Rigaku, USA) measurements.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03339.

> Comparison phase diagram obtained from IDE and ITC methods; XRD patterns, composition, and appearance of all samples in XRD measurement; comparison of the calorimetric molar enthalpies of the solution of NaCl in water from the reference and from our measurement; activity and osmotic coefficients calculated using the Pitzer model and the corresponding calculation process (PDF)

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Notes

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