J. Chem. Eng. Data **2003,** *48,* 241−248

Vapor Pressure and Dissolution Enthalpy Measurements in Ternary $\{H_2O + NaCl + Na_2SO_4\}$ System between 298 K and 363 K

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A nonisothermal static device was used to make measurements of vapor pressures in the ternary {NaCl (1) + Na_2SO_4 (2) + H_2O (3)} system between 298 K and 363 K with molality ratios $m_1/m_2 = 1/10$ and $m_1/m_2 = 1/1$. Experimental data were fitted using empirical relation proposed by Appelblat. Dissolution enthalpies of both anhydrous sodium chloride and sodium sulfate in water were also measured up to saturation conditions at 297.8 K, 317.5 K, and 332.4 K (with $m_1/m_2 = 1/10$, $m_1/m_2 = 1/1$, and $m_1/m_2 = 10/1$, respectively) by using a Setaram C80D differential calorimeter. These calorimetric data were used to establish the analytical expressions of Pitzer and NRTL electrolyte's parameters as a function of temperature. The ability of both models to represent both the dissolution enthalpies and the activities of water were tested.

1. Introduction

Because Na^+, Cl^-, and SO_4^{2-} are components of natural fluids, a knowledge of their thermodynamic properties in aqueous solutions is very important to understand various industrial and geochemical processes such as crystallization, evaporite formation and subsurfaces brine evolution. In particular, vapor−liquid equilibrium (VLE) data are needed to design separation processes such as distillation and evaporation but are also important thermodynamic properties. Calorimetric data, including enthalpies and heat capacities, are mainly used by industrials for the calculation of thermal effects linked to dissolution of solids in liquid phase and mixture or heating and crystallization. However, from a theoretical point of view, they are related to derivatives of equilibrium properties with respect to temperatures (according to the Gibbs − Helmoltz relationship) and are consequently very important for modeling thermodynamic properties of solutions.

Though numerous experimental and theoretical investigations have been reported on binaries {NaCl + H_2O} (see for example, Clarke and Glew[6]) and {Na2SO4 + H_2O} (see, for example, Marliacy et al.[7] and references therein), much less data exists on the {NaCl + Na_2SO_4 + H_2O} ternaries. Thus, Tischenko et al.[8] made measurements of mean activity coefficients of NaCl and Na_2SO_4 in water at various composition between 278 and 318 K. However, most VLE data on this system were reported at 298 K; the reports concern the determination of osmotic coefficients by isopiestic methods (Robinson et al.,[9] Platford,[10] and Wu et al.[11]) or the direct measurements of activity coefficients from electrochemical techniques (Synott and Buttler[12] and Lanier[13]). Similarly, calorimetric data of aqueous {Na_2SO_4 + NaCl} are very scarce; heats of mixing measurements of sodium sulfate and sodium chloride solutions were reported by Snra and Wood[14] at ambient temperature, and more recently, Conti et al.[15] measured isobaric heat capacities for aqueous solutions containing the system Na−K−Cl−SO4 from 333 K to 473 K.

The determination of activities of solutes (Na^+, Cl^-, and SO_4^{2-}) or activity of water can be made using isopiestic methods (Hefter et al.[16]) or by direct measurements of vapor pressures. Although less precise than the isopiestic method, the latter technique is often preferred especially when the volatility of electrolytes can be neglected and because it requires only a short time to reach equilibrium conditions. Vapor pressures in binary {NaCl + H_2O} systems were measured in this way with the help of a nonisothermal static device constructed in our laboratory (Hubert et al.[1]). The possible extension of this apparatus to a more complex system was tested in this work. We made vapor pressure measurements in the ternary {NaCl (1) + Na_2SO_4 (2) + H_2O (3)} system between (298 and 363) K with different molality ratios $m_1/m_2 = 1/10$ and $m_1/m_2 = 1/1$. Data obtained at constant composition could be easily used for determining coefficients of Appelblatt's correlation.[2]

Numerous experimental techniques have been proposed (Marsh and O'Hare[17]) to measure enthalpies of dissolution, enthalpies of dilution, or heat capacities. Particularly, it has been shown that dissolution enthalpy of sodium chloride (Hubert et al.[18]) and sodium sulfate (Hubert et al.[19]) performed in a mixing differential calorimeter can be used for expressing variations with respect to temperature of binary interaction parameters in an excess Gibbs energy model proposed by Pitzer.[3] The proposed methodology leads to a set of binary parameters which allows very accurate calculations of mean activity coefficients, activity of water and dissolution enthalpies for binary {H_2O + Na_2SO_4 or NaCl } systems (Marliacy et al.[20]). Similar results have been obtained with an NRTL electrolyte model proposed by Chen and co-workers (Chen et al.[4,5]) for binary {H_2O + Na_2SO_4} system (Marliacy et al.[7]). In the present paper, this method will be applied to more complex systems. Ternary interaction parameters of Pitzer and Chen's models will be determined using dissolution enthalpies of both anhydrous NaCl and Na_2SO_4 in pure water up to saturation at 297.75 K, 317.45 K, and 332.35 K (with molality ratios $m_1/m_2 = 1/10$, $m_1/m_2 = 1/1$, and $m_1/m_2 =$

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10.1021/je0200766 CCC: $25.00

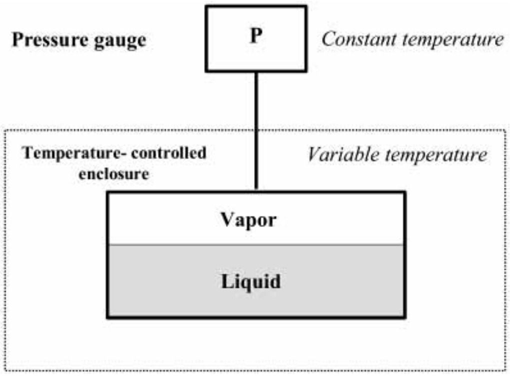

Figure 1. Schematic description of our non isothermal static device for measuring vapor pressure in electrolyte solutions.

10/1, respectively) and using solubility data at 298.15 K for the ternary system. Finally, we will test the thermodynamic consistency of our parameters by calculating both dissolution enthalpies and activities of water in the {NaCl (1) + Na_2SO_4 (2) + H_2O (3)} system. A systematic comparison of results obtained with both models will be performed.

2. Experimental Section

Reagent grade Na_2SO_4 and NaCl (Aldrich) were used with a purity greater than 99%. They were previously dried at 383.15 K and stored in a desiccator next to a vessel containing highly concentrated H_2SO_4. The water was demineralized and twice distilled.

2.1. Vapor Pressure Measurements. Vapor pressures were measured in a nonisothermal static device built in our laboratory.[1] A schematic description of this apparatus is shown in Figure 1. An aqueous electrolytes liquid solution of known composition is introduced into a thermostated cell. Then, the equilibrium pressure above the liquid solution is measured at different temperatures with a manometer placed in an external jacket thermostated at a high temperature (403.15 K) to ensure a good thermal stability of the sensor. With this type of apparatus pressure measurements were performed as a function of temperature at a constant liquid composition.

Temperature of the gas−liquid interface in the cell is measured within ±0.01 K with a Pt 100 thermometer. An absolute manometer (MKS Baratron 315 B, 0 to 1000 Torr) allows the determination of the pressure with an accuracy of ±0.1%. The composition of liquid mixture is determined at ±0.001 mol·kg^{-1} with a vibrating tube densimeter (ANTON PAAR, DMA 45).

Calibration of the densimeter was made at 298.15 ± 0.02 K using two different reference solutions in which $m_1 = m_2$ and $m_1/m_2 = 1/10$. For each type of solution, measurement of the vibrating period, τ, leads to the determination of molalities m_1 and m_2 according to

$$m_i = A_i(\tau - \tau_w) + B_i(\tau - \tau_w)^2 + C_i(\tau - \tau_w)^3 \qquad (1)$$

in which τ_w is the vibrating period of water and A_i, B_i, and C_i are constants fitted from compositions of reference solutions. Measurements of vapor pressures of pure water between (273.15 and 368.15) K were made to test the apparatus. The agreement between our experimental values and those reported by Haar et al.[21] is better than 0.1%.

Measurements were performed between (298 and 363) K with 8 solutions in which $m_1 = m_2$ (from 0.2625 to 1.04915 mol·kg^{-1}) and 7 solution with $m_1/m_2 = 1/10$ ($m_2 =$ 0.2448 to 1.3596 mol·kg^{-1}) corresponding to ionic strengths from 0.77 to 4.214 mol/kg^{-1}. Values of pressures are reported in Table 1.

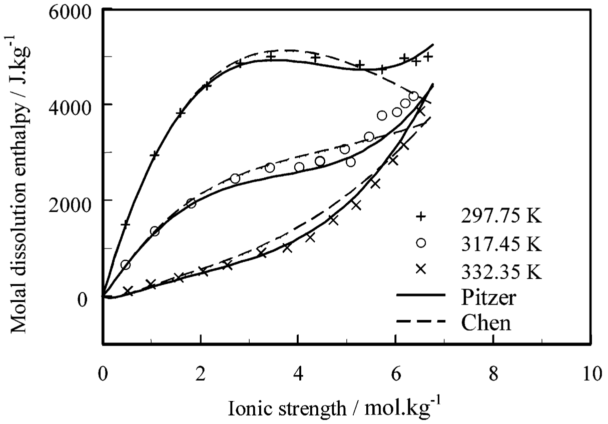

Figure 2. Molal dissolution enthalpy (J·kg^{-1}) of {NaCl (1) + Na_2SO_4 (2)} mixtures in water ($m_1/m_2 = 10/1$).

2.2. Dissolution Enthalpy Measurements. Dissolution enthalpies were measured using a SETARAM C80D differential calorimeter. Known masses of solid sodium chloride, solid sodium sulfate, and water were introduced in the two parts of the mixing cell. The reference cell was filled with a mass of water equal to the sum of three previous ones. The working temperature was fixed, and when thermal equilibrium was reached, the mixing was achieved using an inverting mechanism driven by an electric motor. The accuracy of the mass measurements was about of ±0.1 mg. The sensitivity of this calorimeter slightly decreases with temperature and is 31.5 μV·mW^{1-} at 290 K and 29.5 μV·mW^{1-} at 390 K.

The lower value of the salt molality was chosen according to the calorimeter's sensitivity. The reproducibility of the experiments has been tested using two series of measurements made with {H_2O + NaCl} in the molality range from 0.05 mol·kg^{-1} to 6.0 mol·kg^{-1} at 317.45 K. A relative mean deviation of about 1.5% was found between the two data sets.

Measurements were performed at respectively 297.8 K, 317.5 K, and 332.4 K in solutions of NaCl (1) and Na_2SO_4 (2) in which the ratio m_1/m_2 is respectively equal to 1/10 (with $m_2 \approx 0.41-3.0$ mol·kg^{-1}), to 1 (with $m_2 \approx 0.26-1.9$ mol·kg^{-1}), and to 10/1 (with $m_1 \approx 0.36-5.1$ mol·kg^{-1}) corresponding to ionic strengths from approximately 0.40 to 9.3 mol/kg^{-1}. The experimental results of our dissolution experiments are reported in Table 2. Molal dissolution enthalpies (in J/kg of water) at $m_1/m_2 = 10/1$, $m_1/m_2 = 1$, and $m_1/m_2 = 1/10$ are plotted against ionic strength in respectively Figures 2−4. Inspection of these data leads to the conclusion that values obtained in the ternary system 1/10 are nearly identical to those obtained in binary {Na_2SO_4 + H_2O};[7] this is due to the fact that ionic strength of the ternary solution strongly depends on the molality of sodium sulfate ($I = m_1 + 3m_2$). Moreover, dissolution of mixtures in which $m_1 > m_2$ are endothermic and at the opposite, solutions in which $m_2 > m_1$ present highly negative dissolution enthalpies.

3. Results and Discussions

3.1. Determination of Activity of Water from Pressure Measurements. It is possible to demonstrate (see for example[1]) that activity of water, a_w, in a nonvolatile electrolyte aqueous solution at temperature T can be directly related to equilibrium pressure above liquid, P, and

Table 1. Vapor Pressures P_{exp}, and Activities of Water, a_w, in {NaCl (1) + Na_2SO_4 (2) + H_2O (3)} with m_1/m_2 = 1/10 and m_1/m_2 = 1

T	P_{exp}		a_w	T	P_{exp}		a_w	T	P_{exp}		a_w	T	P_{exp}		a_w
K	Pa	a_w	Appelblat	K	Pa	a_w	Appelblat	K	Pa	a_w	Appelblat	K	Pa	a_w	Appelblat
m_1 = 0.13596 mol·kg^{-1}, m_2 = 1.3596 mol·kg^{-1} m_1/m_2 = 1/10															
298.67	3097.1	0.9487	0.9486	317.97	9001.6	0.9482	0.9476	337.58	23078	0.9468	0.9473	357.27	52902	0.9479	0.9475
303.46	4094.3	0.9484	0.9483	322.79	11486	0.9479	0.9475	342.52	28704	0.9468	0.9473	362.13	63835	0.9472	0.9476
308.32	5376.9	0.9475	0.9480	327.72	14612	0.9480	0.9474	347.40	35384	0.9476	0.9473				
313.14	6982.6	0.9473	0.9478	332.64	18412	0.9467	0.9473	352.33	43383	0.9475	0.9474				
m_1 = 0.12715 mol·kg^{-1}, m_2 = 1.2715 mol·kg^{-1} m_1/m_2 = 1/10															
298.56	3086.9	0.9513	0.9515	317.95	9022.3	0.9515	0.9512	337.31	22915	0.9516	0.9515	356.89	52363	0.9524	0.9524
303.40	4093.9	0.9514	0.9513	322.78	11513	0.9508	0.9512	342.24	28506	0.9519	0.9517	361.75	63237	0.9522	0.9527
308.22	5367.6	0.9514	0.9512	327.61	14582	0.9511	0.9513	347.08	35082	0.9522	0.9519				
313.06	6983.7	0.9514	0.9512	332.45	18334	0.9508	0.9514	352.00	43038	0.9526	0.9521				
m_1 = 0.08849 mol·kg^{-1}, m_2 = 0.8849 mol·kg^{-1} m_1/m_2 = 1/10															
298.82	3178.3	0.9647	0.9651	318.24	9289.9	0.9651	0.9649	337.69	23630	0.9647	0.9652	357.38	54174	0.9663	0.9658
303.66	4216.5	0.9655	0.9650	323.03	11829	0.9648	0.9649	342.63	29398	0.9651	0.9653	362.26	65403	0.9655	0.9660
308.49	5526.7	0.9649	0.9649	327.89	15004	0.9651	0.9650	347.49	36208	0.9658	0.9654				
313.35	7192.4	0.9649	0.9649	332.77	18871	0.9646	0.9650	352.43	44416	0.9660	0.9656				
m_1 = 0.08081 mol·kg^{-1}, m_2 = 0.8081 mol·kg^{-1} m_1/m_2 = 1/10															
298.38	3112.3	0.9697	0.9697	317.92	9178.0	0.9695	0.9689	337.44	23465	0.9686	0.9688	357.14	53806	0.9690	0.9690
303.27	4139.6	0.9694	0.9695	322.73	11704	0.9688	0.9688	342.39	29203	0.9689	0.9688	362.06	65137	0.9689	0.9692
308.08	5425.9	0.9690	0.9693	327.60	14852	0.9688	0.9688	347.28	36016	0.9692	0.9688				
312.97	7079.1	0.9692	0.9691	332.49	18700	0.9680	0.9688	352.22	44186	0.9692	0.9689				
m_1 = 0.05524 mol·kg^{-1}, m_2 = 0.5524 mol·kg^{-1} m_1/m_2 = 1/10															
298.47	3159.7	0.9791	0.9799	318.04	9336.0	0.9798	0.9793	337.56	23842	0.9791	0.9793	357.29	54764	0.9801	0.9798
303.39	4215.4	0.9802	0.9797	322.84	11896	0.9793	0.9793	342.51	29686	0.9794	0.9794	362.18	66174	0.9798	0.9800
308.27	5544.8	0.9796	0.9795	327.70	15081	0.9789	0.9793	347.42	36621	0.9797	0.9795				
313.12	7213.9	0.9798	0.9794	332.60	19000	0.9784	0.9793	352.36	44941	0.9799	0.9797				
m_1 = 0.04046 mol·kg^{-1}, m_2 = 0.4046 mol·kg^{-1} m_1/m_2 = 1/10															
298.64	3214.1	0.9858	0.9859	318.09	9410.0	0.9850	0.9848	337.61	24035	0.9847	0.9846	357.35	55160	0.9848	0.9851
303.50	4266.3	0.9857	0.9855	322.91	11997	0.9845	0.9847	342.58	29937	0.9850	0.9846	362.24	66666	0.9847	0.9853
308.36	5602.0	0.9852	0.9852	327.78	15219	0.9841	0.9846	347.47	36916	0.9855	0.9847				
313.21	7288.5	0.9850	0.985	332.66	19149	0.9836	0.9845	352.42	45302	0.9856	0.9849				
m_1 = 0.02484 mol·kg^{-1}, m_2 = 0.2484 mol·kg^{-1} m_1/m_2 = 1/10															
298.77	3252.8	0.9900	0.9901	318.17	9492.2	0.9896	0.9893	332.69	19278	0.9889	0.9892	352.35	45379	0.9899	0.9897
303.59	4308.0	0.9902	0.9899	322.97	12088	0.9890	0.9892	337.62	24156	0.9891	0.9893	357.29	55320	0.9901	0.9899
308.42	5647.5	0.9896	0.9896	327.81	15314	0.9891	0.9892	342.55	30042	0.9895	0.9894				
313.28	7346.8	0.9893	0.9895	327.81	15314	0.9891	0.9892	347.40	36980	0.9900	0.9895				
m_1 = 1.0495 mol·kg^{-1}, m_2 = 1.0495 mol·kg^{-1} m_1/m_2 = 1/1															
298.34	2967.5	0.9270	0.9271	317.66	8655.9	0.9265	0.9259	337.12	22108	0.9261	0.9262	356.70	50601	0.9276	0.9277
303.16	3931.0	0.9266	0.9266	322.50	11057	0.9260	0.9259	342.03	27493	0.9266	0.9265	361.59	61254	0.9283	0.9282
307.96	5150.7	0.9261	0.9263	327.34	14009	0.9258	0.9259	346.88	33851	0.9270	0.9268				
312.79	6700.0	0.9262	0.9260	332.22	17646	0.9254	0.9260	351.80	41531	0.9272	0.9272				
m_1 = 0.9775 mol·kg^{-1}, m_2 = 0.9775 mol·kg^{-1} m_1/m_2 = 1/1															
298.35	2992.0	0.9338	0.9338	317.77	8767.8	0.9332	0.9324	337.24	22358	0.9318	0.9323	356.89	51298	0.9331	0.9332
303.16	3960.5	0.9333	0.9333	322.59	11187	0.9326	0.9323	342.17	27831	0.9324	0.9324	361.84	62218	0.9337	0.9335
307.98	5193.9	0.9326	0.9329	327.43	14175	0.9323	0.9322	347.03	34282	0.9326	0.9326				
312.84	6764.7	0.9325	0.9326	332.30	17839	0.9320	0.9322	351.96	42073	0.9329	0.9329				
m_1 = 0.9617 mol·kg^{-1}, m_2 = 0.9617 mol·kg^{-1} m_1/m_2 = 1/1															
298.38	3004.3	0.9359	0.9360	317.85	8800.5	0.9327	0.9325	337.33	22440	0.9315	0.9316	357.04	51584	0.9328	0.9327
303.27	3991.8	0.9348	0.9348	322.65	11211	0.9321	0.9320	342.26	27921	0.9317	0.9317	361.97	62491	0.9332	0.9333
308.08	5228.3	0.9339	0.9339	327.51	14222	0.9318	0.9317	347.13	34406	0.9319	0.9319				
312.95	6806.2	0.9329	0.9331	332.40	17911	0.9312	0.9316	352.07	42230	0.9324	0.9323				
m_1 = 0.7901 mol·kg^{-1}, m_2 = 0.7901 mol·kg^{-1} m_1/m_2 = 1/1															
298.42	3042.9	0.9461	0.9460	317.79	8894.3	0.9456	0.9452	337.24	22689	0.9453	0.9455	356.97	52211	0.9467	0.9467
303.19	4019.7	0.9454	0.9457	322.61	11348	0.9455	0.9452	342.19	28255	0.9457	0.9458	361.87	63206	0.9471	0.9471
308.06	5289.1	0.9454	0.9455	327.45	14387	0.9452	0.9453	347.08	34856	0.9462	0.9460				
312.90	6878.1	0.9454	0.9453	332.33	18113	0.9450	0.9454	352.02	42789	0.9464	0.9464				
m_1 = 0.6651 mol·kg^{-1}, m_2 = 0.6651 mol·kg^{-1} m_1/m_2 = 1/1															
298.32	3052.1	0.9546	0.9548	317.75	8960.1	0.9545	0.9540	337.21	22870	0.9542	0.9544	356.90	52551	0.9554	0.9555
303.14	4045.1	0.9545	0.9545	322.57	11432	0.9539	0.9540	342.17	28495	0.9546	0.9546	361.83	63701	0.9560	0.9559
307.99	5317.5	0.9544	0.9543	327.42	14494	0.9540	0.9541	347.05	35135	0.9550	0.9549				
312.84	6923.6	0.9543	0.9541	332.28	18244	0.9537	0.9542	351.95	43077	0.9553	0.9552				
m_1 = 0.5204 mol·kg^{-1}, m_2 = 0.5204 mol·kg^{-1} m_1/m_2 = 1/1															
298.31	3082.9	0.9648	0.9651	317.67	9018.2	0.9648	0.9641	337.18	23079	0.9641	0.9646	356.93	53207	0.9661	0.9662
303.12	4082.7	0.9644	0.9647	322.51	11518	0.9641	0.9641	342.12	28744	0.9648	0.9649	361.87	64535	0.9669	0.9668
307.94	5357.7	0.9644	0.9644	327.35	14604	0.9641	0.9642	347.03	35488	0.9652	0.9653				
312.75	6965.3	0.9647	0.9642	332.23	18396	0.9639	0.9644	351.98	43620	0.9662	0.9658				
m_1 = 0.4073 mol·kg^{-1}, m_2 = 0.4073 mol·kg^{-1} m_1/m_2 = 1/1															
298.33	3107.2	0.9710	0.9707	317.69	9090.6	0.9718	0.9714	337.17	23260	0.9720	0.9721	356.81	53323	0.9729	0.9727
303.13	4112.9	0.9708	0.9709	322.53	11618	0.9715	0.9716	342.10	28945	0.9724	0.9722	361.65	64336	0.9721	0.9728
307.97	5403.4	0.9708	0.9711	327.37	14727	0.9715	0.9717	346.97	35669	0.9726	0.9724				
312.82	7036.0	0.9711	0.9712	332.25	18559	0.9717	0.9719	351.89	43772	0.9731	0.9725				
m_1 = 0.2625 mol·kg^{-1}, m_2 = 0.2625 mol·kg^{-1} m_1/m_2 = 1/1															
298.35	3149.4	0.9828	0.9825	317.71	9207.0	0.9831	0.9831	337.13	23497	0.9837	0.9837	356.81	53972	0.9846	0.9843
303.14	4166.9	0.9828	0.9827	322.51	11746	0.9830	0.9832	342.10	29296	0.9842	0.9838	361.64	65071	0.9835	0.9844
308.00	5479.2	0.9826	0.9828	327.35	14894	0.9832	0.9834	346.96	36092	0.9844	0.9840				
312.82	7120.8	0.9827	0.9829	332.21	18741	0.9831	0.9835	351.89	44294	0.9846	0.9841				

Table 2. Molal Dissolution Enthalpies $\Delta_{\mathrm{sol}}\hat{H}$ of NaCl (1) and Na_2SO_4 (2) in Water at 297.75 K, 317.45 K, and 332.35 K with $m_1/m_2 = 1/10$, $m_1/m_2 = 1$, and $m_1/m_2 = 10/1$'

mol·kg^{-1}			$\Delta_{\mathrm{sol}}\hat{H}$	mol·kg^{-1}			$\Delta_{\mathrm{sol}}\hat{H}$
m_1	m_2	m_1/m_2	J·kg^{-1}	m_1	m_2	m_1/m_2	J·kg^{-1}
$T = 297.75$ K							
0.0414	0.4139	1/10	−1038.3	0.2001	2.0000	1/10	−16644
0.0827	0.8264	1/10	−3782.2	0.2399	2.3992	1/10	−21779
0.1245	1.2447	1/10	−7733.2	0.2800	2.7999	1/10	−26740
0.1659	1.6587	1/10	−12609	0.3000	3.0002	1/10	−29011
$T = 317.45$ K							
0.0414	0.4139	1/10	−2311.5	0.2000	1.9995	1/10	−16195
0.0826	0.8263	1/10	−5235.2	0.2399	2.3991	1/10	−20136
0.1170	1.1702	1/10	−8330.5	0.2800	2.8001	1/10	−23259
0.1657	1.6567	1/10	−12839	0.3000	2.9996	1/10	−25268
$T = 332.35$ K							
0.0414	0.4137	1/10	−3145.1	0.2000	2.0003	1/10	−16149
0.0826	0.8264	1/10	−6367.9	0.2400	2.3994	1/10	−19291
0.1244	1.2444	1/10	−9767.6	0.2800	2.7997	1/10	−21923
0.1656	1.6559	1/10	−13190	0.3000	3.0005	1/10	−22484
$T = 297.75$ K							
0.2602	0.2602	1	339.87	1.2008	1.2008	1	−6566.2
0.5501	0.5500	1	−748.53	1.4001	1.4001	1	−8817.0
0.7721	0.7721	1	−2416.9	1.6507	1.6506	1	−11657
0.9896	0.9896	1	−4377.0	1.8513	1.8513	1	−13881
$T = 317.45$ K							
0.3000	0.3000	1	−1119.4	1.2461	1.2460	1	−7874.3
0.5501	0.5501	1	−2470.8	1.4521	1.4521	1	−9627.4
0.7917	0.7917	1	−4200.7	1.7010	1.7010	1	−11505
1.0194	1.0194	1	−6019.0	1.9008	1.9007	1	−12838
$T = 332.35$ K							
0.2429	0.2429	1	−1642.1	1.1595	1.1595	1	−7987.8
0.5001	0.5001	1	−3221.3	1.3812	1.3812	1	−9583.7
0.7203	0.7203	1	−4834.1	1.6012	1.6012	1	−10699
0.9404	0.9404	1	−6387.4	1.8002	1.8001	1	−11817
$T = 297.75$ K							
0.3596	0.0359	10/1	1497.7	3.3540	0.3353	10/1	4975.2
0.8215	0.0823	10/1	2937.6	4.0547	0.4055	10/1	4829.5
1.2323	0.1232	10/1	3822.9	4.4043	0.4404	10/1	4730.1
1.6408	0.1641	10/1	4386.0	4.7531	0.4752	10/1	4960.0
2.1670	0.2168	10/1	4857.2	4.9378	0.4938	10/1	4896.8
2.6521	0.2651	10/1	4988.1	5.1240	0.5124	10/1	4993.4
$T = 317.45$ K							
0.3579	0.0358	10/1	660.95	3.4265	0.3426	10/1	2833.7
0.8232	0.0823	10/1	1357.4	3.8141	0.3814	10/1	3074.0
1.3972	0.1397	10/1	1939.6	3.9082	0.3908	10/1	2810.7
2.0882	0.2088	10/1	2461.5	4.2001	0.4200	10/1	3333.5
2.6362	0.2635	10/1	2691.1	4.4026	0.4398	10/1	3776.5
3.1001	0.3100	10/1	2697.3	4.6385	0.4639	10/1	3847.2
3.4248	0.3426	10/1	2818.3	4.7686	0.4769	10/1	4034.4
				4.8997	0.4900	10/1	4181.8
$T = 332.35$ K							
0.4041	0.0404	10/1	109.18	3.2763	0.3276	10/1	1221.6
0.7642	0.0764	10/1	254.01	3.6389	0.3639	10/1	1585.7
1.2000	0.1200	10/1	388.87	4.0006	0.4001	10/1	1901.6
1.5873	0.1587	10/1	524.72	4.3012	0.4301	10/1	2348.7
1.9718	0.1972	10/1	651.48	4.5805	0.4581	10/1	2836.9
2.5003	0.2500	10/1	904.57	4.7502	0.4750	10/1	3160.0
2.9158	0.2916	10/1	1013.7	5.0074	0.5007	10/1	3858.5

vapor pressure of pure water at T, $P_{\mathrm{w}}^{\mathrm{s}}$, according to the relationship,

$$\ln a_{\mathrm{w}} = \ln\left(\frac{P}{P_{\mathrm{w}}^{\mathrm{s}}}\right) + \frac{(P - P_{\mathrm{w}}^{\mathrm{s}})}{RT}(B - v^{*}{}_{\mathrm{w}}) = \ln\left(\frac{P}{P_{\mathrm{w}}^{\mathrm{s}}}\right) + \delta \tag{2}$$

in which the corrective term δ is defined with B, the second virial coefficient of water (Le Fevre et al.[22]), and v_{w}^{*}, the molar volume of pure liquid water (Kell[23]). Values of δ are very small (they do not exceed 0.2% of the $P/P_{\mathrm{w}}^{\mathrm{s}}$) but must be taken into account because they have the same order of magnitude as our experimental accuracy (0.1%). Values of a_{w} obtained using eq 2 are reported together with experimental values of P in the Table 1.

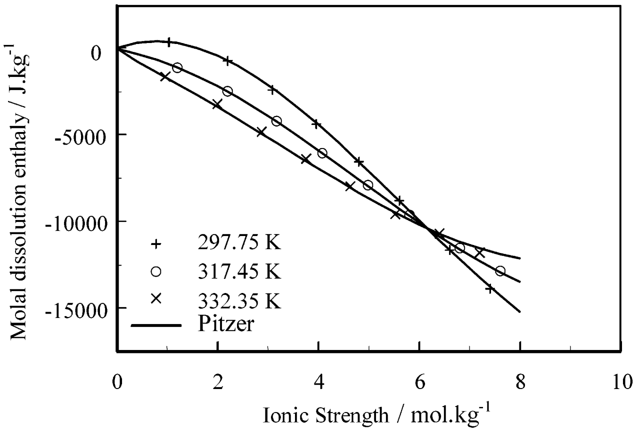

Figure 3. Molal dissolution enthalpy (J·kg^{-1}) of {NaCl (1) + Na_2SO_4 (2)} mixtures in water ($m_1/m_2 = 1/1$); comparison with model of Pitzer (calculation with Chen's model gives same results).

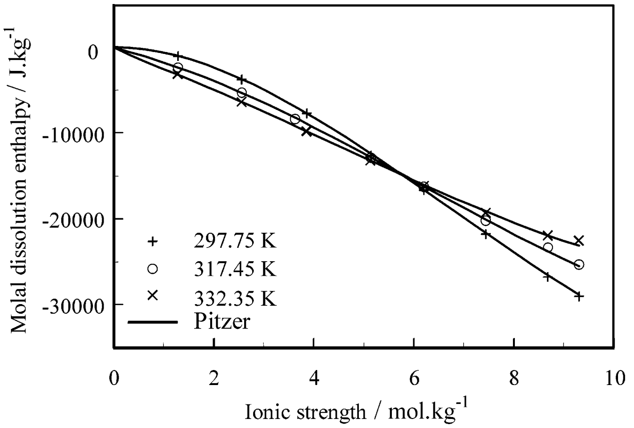

Figure 4. Molal dissolution enthalpy (J·kg^{-1}) of {NaCl (1) + Na_2SO_4 (2)} mixtures in water ($m_1/m_2 = 1/10$); comparison with model of Pitzer (calculation with Chen's model gives same results).

For each composition, experimental results can be regressed using the Appelblatt relation,[2] given by

$$\ln(P_{\mathrm{w}}^{\mathrm{s}} - P) = A + \frac{B}{T} + C\left(\ln(T) - \frac{T}{2T_{\mathrm{c}}}\right) \tag{3}$$

where T is absolute temperature in K, T_{c} is the critical temperature of water ($T_{\mathrm{c}} = 647.14$ K), and A, B, and C are adjustable parameters depending on liquid composition. Values of these parameters were regressed on our experimental values of pressure for each ternary composition studied and are reported in the Table 3. A strong correlation between these parameters can be observed. As it can be observed, deviations between experimental and calculated values of a_{w} are very low (<0.1%). It is also clearly evident that, for a given composition, the influence of temperature on activity of water is negligible.

3.2. Modeling with Pitzer and Chen Electrolyte Models. Thermodynamic Background. Excess Gibbs energy models for aqueous electrolyte solutions can be used to correlate our experimental dissolution enthalpy and activity of water data. The expressions proposed by Pitzer[3] and by Chen et al.[4,5] are extensively used in the literature and can be applied successfully in this work. In the two models, excess Gibbs energy of a solution can be considered as a sum of a Pitzer−Debye−Hückel term which expresses the effect of long-range interactions between ions and a second term accounting for the short-range interactions between solute species.

Table 3. *A*, *B*, and *C* Parameters of Appelblatt's Expression (eq 2) at Different Molalities of NaCl and Na_2SO_4 (with $m_1/m_2 = 1/10$ and $m_1/m_2 = 1$, Respectively)

m_1/mol·kg^{-1}	m_2/mol·kg^{-1}	m_1/m_2	A	B	C
0.13596	1.3596	1/10	109.76	−8604.18	−13.87
0.12715	1.2715	1/10	117.79	−8852.77	−15.40
0.08849	0.8849	1/10	118.73	−8901.34	−15.40
0.08081	0.8081	1/10	130.01	−9411.64	−17.17
0.05524	0.5524	1/10	162.55	−10655.61	−22.43
0.04046	0.4046	1/10	257.03	−14421.91	−37.47
0.02484	0.2484	1/10	309.35	−16421.00	−45.88
1.0495	1.0495	1	139.26	−9686.27	−18.53
0.9775	0.9775	1	131.88	−9432.49	−17.36
0.9617	0.9617	1	193.28	−11877.38	−27.09
0.7901	0.7901	1	140.09	−9723.56	−18.71
0.6651	0.6651	1	153.48	−10244.16	−20.88
0.5204	0.5204	1	209.46	−12395.12	−29.85
0.4073	0.4073	1	77.96	−7250.40	−8.98
0.2625	0.2625	1	95.29	−7886.04	−11.86

In the equation proposed by Pitzer,[3] the molal excess Gibbs energy (in J/kg of water), $\hat{G}^E$, is defined in molality scale and in unsymmetric convention like a function of m_c, m_{a1}, and m_{a2}, respectively, the molalities of cation Na^+, of anion Cl^-, and of anion SO_4^{2-} which can be easily calculated from the apparent molality of salt, m_1 and m_2,

$$m_c = m_1 + 2m_2, \quad m_{a1} = m_1, \quad \text{and } m_{a2} = m_2$$

if the hypothesis of complete dissociation of electrolytes is made. The short-range interactions term is a virial development of molalities of species.

The model of Chen and co-workers[5] is an expression of the molar excess Gibbs energy (in J/mol of true species), G_m^E, in unsymmetric convention and in molar fraction scale. Its second term is accounted for by the NRTL theory and is based on the local composition concept. Under the same hypothesis of complete dissociation, true molar fractions of Na^+, x_c, of Cl^-, x_{a1}, of SO_4^{2-}, x_{a2}, and of water, x_w, can also be expressed from apparent molalities of electrolytes,

$$x_w = \frac{\frac{1000}{M_W}}{\frac{1000}{M_w} + (m_1 + 2m_2) + m_1 + m_2},$$

$$x_c = \frac{m_1 + 2m_2}{\frac{1000}{M_w} + (m_1 + 2m_2) + m_1 + m_2}$$

$$x_{a1} = \frac{m_1}{\frac{1000}{M_w} + (m_1 + 2m_2) + m_1 + m_2},$$

$$x_{a2} = \frac{m_2}{\frac{1000}{M_w} + (m_1 + 2m_2) + m_1 + m_2}$$

In which $M_w = 18.0153$ g·mol^{-1} is the molar mass of water. Classical thermodynamic properties (such as activity and osmotic coefficients) can be derived from the expressions of G^E. They can be found in the papers of the authors.[1,5] However, some general equations can be given to precise how they can be obtained. Expression of thermodynamic properties usually depend on the choice of reference state. Thus, activity coefficients of species, γ_i, are obtained using the general relationship

$$RT \ln \gamma_i = \left(\frac{\partial G^E}{\partial n_i}\right)_{T,P,nj\neq i} \quad (4)$$

where n_i is the amount of species i.

In molar fraction scale (for Chen's model) :

$$G^E = (n_w + n_c + n_{a1} + n_{a2})G_m^E \quad (5)$$

In molality scale (for Pitzer's model):

$$G^E = n_w \frac{M_W}{1000} \hat{G}^E \quad (6)$$

Activity of water, a_w, is calculated from activity coefficient of water in the solution, γ_w:

In molar fraction scale (for Chen's model):

$$\ln a_w = \ln \gamma_w + \ln x_w \quad (7)$$

In molality scale (for Pitzer's model):

$$\ln a_w = \ln \gamma_w - \frac{M_W}{1000}(m_c + m_{a1} + m_{a2}) \quad (8)$$

The activity of water is usually expressed by the osmotic coefficient Φ,

$$\Phi = -\frac{1000}{M_w} \frac{\ln a_w}{m_c + m_{a1} + m_{a2}} \quad (9)$$

The thermal effect measured when n_1 moles of NaCl and n_2 moles of sodium sulfate are dissolved in $n_w = n_3$ moles of water, noted $\Delta_{sol}H$, is related to excess enthalpy defined in unsymmetric convention, H^E [18,19] according to

$$\Delta_{sol}H = n_1 \Delta_{sol}H^\infty_{m,1} + n_2 \Delta_{sol}H^\infty_{m,2} + H^E(n_1, n_2, n_w) \quad (10)$$

in which $\Delta_{sol}H^\infty_{m,1}$ and $\Delta_{sol}H^\infty_{m,2}$ are the molar dissolution enthalpy of NaCl and Na_2SO_4 at infinite dilution. Excess enthalpy can be calculated from the excess Gibbs energy models using the Gibbs−Helmholtz relationship,

$$H^E = -T^2 \left(\frac{\partial (G^E/T)}{\partial T}\right)_{P,n_i} \quad (11)$$

Finally, the molal dissolution enthalpy, $\Delta_{sol}\hat{H}$, i.e., excess enthalpy of an aqueous solution containing two electrolytes of apparent molalities m_1 and m_2 and 1 kg of water, is calculated by,

$$\Delta_{sol}\hat{H} = \frac{\Delta_{sol}H}{n_w \frac{M_w}{1000}} \quad (12)$$

Determination of Pitzer's and Chen's Parameters. Excess Gibbs energy models proposed either by Pitzer or by Chen and co-workers are under the dependence of some binary and ternary adjustable parameters.

Most of binary parameters are temperature dependent and must be fitted on thermodynamic properties of binary $\{NaCl + H_2O\}$ or $\{Na_2SO_4 + H_2O\}$. Temperature dependent binary parameters are respectively β^0_{NaCl}, β^1_{NaCl}, and C^Φ_{NaCl} and $\beta^0_{Na_2SO_4}$, $\beta^1_{Na_2SO_4}$, and $C^\Phi_{Na_2SO_4}$ in the case of Pitzer's model[3] and $\tau_{H2O,NaCl}$, $\tau_{NaCl,H2O}$, τ_{H2O,Na_2SO_4}, and $\tau_{Na_2SO_4,H2O}$ in the case of Chen's model.[5] Ternary parameters of both models are temperature dependent and must be fitted on data relative to ternary system $\{NaCl + Na_2SO_4 + H_2O\}$: $\theta_{Cl^-,SO_4{}^{2-}}$ and $\psi_{Na^+,Cl^-,SO_4{}^{2-}}$ for Pitzer's model and τ_{NaCl,Na_2SO_4} and $\tau_{Na_2SO_4,NaCl}$ for Chen's model.

Application of eqs 10 and 11 for the calculation of dissolution enthalpy brings out to expressions containing

Table 4. Pitzer's Model Parameters and Corresponding Dissolution Enthalpies at Infinite Dilutions (273.15 < T < 373.15 K). Coefficients for Parameters (Equation 14)

parameter	*a*	*b*	*c*	*d*
$\alpha1_{NaCl}$	2.0[a]	0	0	0
β^0_{NaCl}	7.65×10^{-2} [a]	-4.27875369×10^2	−1.21435198	0
β^1_{NaCl}	2.664×10^{-1} [a]	3.43262086×10^2	1.40203591	0
C^{ϕ}_{NaCl}	1.27×10^{-3} [a]	5.92892282×10^1	$1.65939470\ 10^{-1}$	0
$\alpha1_{Na_2SO_4}$	1.4[b]	0	0	0
$\beta^0_{Na_2SO_4}$	-1.727×10^{-2} [a]	-2.56047587×10^3	-1.35084958×10^1	$1.82451748 \times 10^{-2}$
$\beta_{Na_2SO_4}{}^1$	7.534×10^{-1} [a]	-1.77370056×10^4	-1.03209462×10^2	$1.53114111 \times 10^{-1}$
$C^{\phi}_{Na_2SO_4}$	1.1745×10^{-2} [a]	6.60777453×10^2	3.70285811	$-5.31023797 \times 10^{-3}$
$\theta_{Cl^-,SO_4{}^{2-}}$	2.0184×10^{-2}	3.48727912×10^2	1.16954282	0
$\Psi_{Na^+,Cl^-,SO_4{}^{2-}}$	1.4063×10^{-3}	-9.51831180×10^1	$-3.34556419 \times 10^{-1}$	0

Coefficients for Dissolution Enthalpy at Infinite Dilution (J. mol^{-1}) (Equation 13)

species	$\Delta_{sol}H^{\infty}_{m,i}(T_0)$	*e*	*f*
NaCl	3.89710455×10^3	-1.17772160×10^2	0
Na_2SO_4	-1.93467805×10^3	-9.99070349×10^2	1.12610282

[a] Ref. [3]. [b] Recommended by Holmes et al.[26]

Table 5. Chen's Model Parameters and Corresponding Dissolution Enthalpies at Infinite Dilutions (273.15 < T < 373.15 K). Coefficients for Parameters (eq 14)

parameter	*a*	*b*	*c*	*d*
τ_{NaCl,H_2O}	−4.551[a]	8.18477803×10^2	2.79814877	0
$\tau_{H_2O,NaCl}$	8.898[a]	-2.6537277×10^2	−1.96527693	0
$\tau_{Na_2SO_4,H_2O}$	−3.863[a]	-1.4800427×10^4	-8.9658312×10^1	$1.38606364 \times 10^{-1}$
τ_{H_2O,Na_2SO_4}	7.934[a]	4.11894735×10^4	$2.40738326\ 10^2$	$-3.60128428 \times 10^{-1}$
τ_{NaCl,Na_2SO_4}	1.43211775	-2.4582335×10^3	−7.20015676	0
$\tau_{Na_2SO_4,NaCl}$	$-5.06891535 \times 10^{-1}$	$-2.4534473 \times 10^{-1}$	−6.70352531	0

Coefficients for Dissolution Enthalpy at Infinite Dilution (J·mol^{-1}; eq 13)

species	$\Delta_{sol}H^{\infty}_{m,i}(T_0)$	*e*	*f*
NaCl	3.82018410×10^3	-1.16626473×10^2	0
Na_2SO_4	-2.40952023×10^3	-1.04303949×10^3	1.212529844

[a] Reference 24.

also the temperature derivatives of each temperature-dependent parameter.

In previous works,[18,19] the temperature dependence of binary Pitzer's parameters β^0_{ca}, β^1_{ca}, and C^{Φ}_{ca} has been fitted on molar dissolution enthalpy data considering that $\Delta_{sol}H^{\infty}_{m,i}$, $T^2(\partial\beta^0_{ca}/\partial T)$, $T^2(\partial\beta^1_{ca}/\partial T)$, and $T^2(\partial C^{\Phi}_{ca}/\partial T)$ as adjustable parameters at each temperature. Then, by integration, the temperature dependence was obtained. Similar procedure was recently adapted in the case of Chen's model (Marliacy et al.[7]) for determining variation of $\Delta_{sol}H^{\infty}_{m,i}$, $\tau_{ca,w}$ and $\tau_{w,ca}$ with temperature.

The same methodology was used in this present work to fit the expression of ternary parameters in the case of both models. First $T^2(\partial\theta_{Cl^-,SO_4{}^{2-}}/\partial T)$ and $T^2(\partial\psi_{Na^+,Cl^-,SO_4{}^{2-}}/\partial T)$ in the case of Pitzer's model and $T^2(\partial\tau_{NaCl,Na_2SO_4}/\partial T)$ and $T^2(\partial\tau_{Na_2SO_4NaCl}/\partial T)$ in the case of Chen's model were adjusted at each temperature on our experimental molal dissolution enthalpies reported in the Table 2. Then, the expression of each ternary parameter with respect to temperature could be obtained by integration.

Finally, each parameter and molar dissolution enthalpy at infinite dilution can be represented by

$$\Delta_{sol}H^{\infty}_{m,i} = \Delta_{sol}H^{\infty}_{m,i}(T_0) + e(T - T_0) + f(T^2 - T_0{}^2) \quad (13)$$

$$\text{parameter} = a + b\left(\frac{1}{T} - \frac{1}{T_0}\right) + c\ln\left(\frac{T}{T_0}\right) + \mathrm{d}(T - T_0) \quad (14)$$

in which T_0 is the reference temperature (298.15 K) and "parameter" is respectively binary and ternary parameters of Pitzer's and Chen's models. Coefficient "*a*" is the value of "parameter" at T_0 and coefficients *b*, *c*, *d*, *e*, *f*, and $\Delta_{sol}H^{\infty}_{m,i}(T_0)$ were determined by fitting enthalpy measurements as explained above. In the case of binary parameters, coefficient "*a*" was taken from literature[3,5] and *b*, *c*, *d*, *e*, *f*, and $\Delta_{sol}H^{\infty}_{m,i}(T_0)$ were fitted on the {NaCl + H_2O} data reported by Hubert et al.[19] and on {Na_2SO_4 + H_2O} data reported by Marliacy and co-workers.[7] In the case of ternary parameters, *b*, *c*, and *d* were determined on our experimental dissolution enthalpies in {NaCl + Na_2SO_4 + H_2O} and the value at T_0 could be determined by fitting experimental solubility data at T_0 in the ternary system (see Marliacy et al.[20]). The values of the coefficients are reported in Table 4 (Pitzer's model) and in Table 5 (Chen's model). Equations 13 and 14 used in this work are simpler than the complex and empirical functions proposed by the authors. However, their application is limited between (298 and 363) K.

Representation of the Thermodynamic Properties of {NaCl + Na_2SO_4 + H_2O}. As shown in Figures 2−4, experimental values of molal dissolution enthalpies are better represented by Pitzer's model than by Chen's model, particularly for systems rich in NaCl (Figure 2). Thus, we have obtained a relative mean deviation of 3.9% with Pitzer and of 6.8% with NRTL-electrolytes. It is interesting to test the influence of temperature dependence in ternary parameters for the calculation of dissolution enthalpy (Figure 5) assuming that ternary parameters are constant with temperature. It is evident that Pitzer's model allows a rather good estimation of data in the 10/1 ternary system; with this model, it seems not necessary to consider a

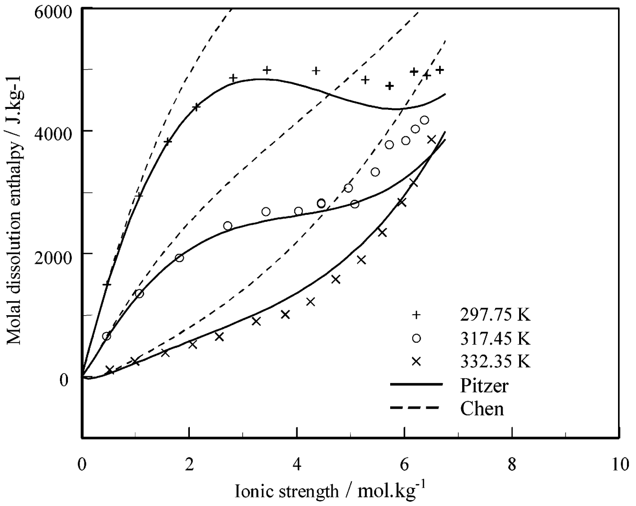

Figure 5. Molal dissolution enthalpy (J·kg^{-1}) of {NaCl (1) + Na_2SO_4 (2)} mixtures in water **(**m_1/m_2 = 10/1**)**; comparison with models of Pitzer and Chen in which ternary parameters are assumed to be constant.

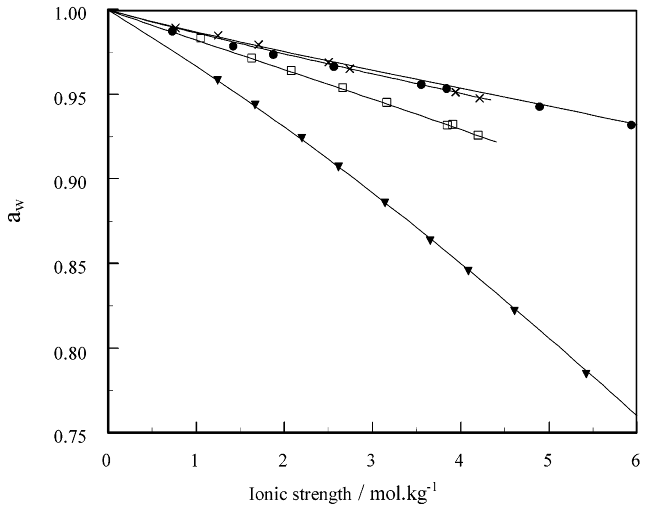

Figure 6. Activity of water a_w in {NaCl + Na_2SO_4 + H_2O+} system at 323.15 K:▼, NaCl ref 18; □, 1/1 ternary, this work; ×, 1/10 ternary, this work; ●, Na_2SO_4 ref 25; comparison between experimental data and values calculated with Pitzer's model.

temperature dependence for ternary parameters. At the opposite, the Chen's model cannot represent experimental values with a sufficient accuracy with constant ternary parameters.

We have also compared values of activities of water presented in Table 1 with those calculated using Pitzer's and Chen's model. Mean relative deviations are low (0.14% with Pitzer and 0.19% with NRTL-electrolytes). Figure 6 presents experimental data interpolated at 323.15 K using Appelblatt's relation (eq 2) and their representations with Pitzer's model in binary and ternary systems. Activity of water in the ternary is located between activity in {NaCl + H_2O} and in {Na_2SO_4 + H_2O}. It can be pointed that experimental values in the 1/10 ternary system and in the {NaCl + H_2O} are nearly the same at the same ionic strength.

Table 6. Deviations between Experimental and Calculated Values of Activity Coefficients and Osmotic Coefficients in {NaCl + Na_2SO_4 + H_2O} System

T/K	I/mol·kg^{-1}	data	Nb. points	Pitzer(%)	NRTL(%)	ref
298.15	1.0	$\gamma_{Na_2SO_4}$	10	2.9	4.7	12
298.15	6.47−8.16	ϕ	5	1.1	3.9	10
278.15	0.375−4.8	γ_{NaCl}	9	0.4	2.7	8
288.15	0.12−4.8	γ_{NaCl}	17	0.6	2.1	8
293.15	0.12−3.39	γ_{NaCl}	8	0.5	1.5	8
298.15	0.12−4.8	γ_{NaCl}	17	0.4	2.0	8
308.15	0.12−4.8	γ_{NaCl}	17	0.4	2.0	8
318.15	0.375−4.8	γ_{NaCl}	9	0.4	2.6	8

Pitzer and electrolyte-NRTL have been used to calculate activity coefficients of electrolytes and osmotic coefficients in the ternary system. The performances of two models are compared in Table 6 in which mean relative deviations between calculated values and experimental ones taken from literature are reported. Results obtained with Pitzer are satisfactorily excepting in the case of Synott et al.[12] data. It is evident that electrolyte-NRTL represents the data with a less good accuracy.

4. Conclusions

It was shown that our existing nonisothermal static device described previously[1] was able to measure vapor pressure in the ternary system {NaCl (1) + Na_2SO_4 (2) + H_2O(3)} between (298 and 363) K with different molality ratios m_1/m_2. As in binary systems, experimental values were fitted using Appelblatt's relation[2] (Table 1). That proves the possible of an extension of this apparatus to aqueous electrolyte systems that are more complex than binaries. Dissolution enthalpy measurements of {NaCl (1) + Na_2SO_4 (2)} system in water were also made for different value of m_1/m_2 at 297.8 K, 317.5 K, and 332.4 K. These experimental data (Table 2) were used to determine the temperature dependence of the electrolyte-NRTL and Pitzer model's ternary parameters. As previously shown,[7,18,19] binary parameters of both models could be fitted on dissolution enthalpy values measured in binary systems {salt + water}. Thus, it seems reasonable to claim that this method could be successfully used to fit parameters of numerous thermodynamic models in the case of complex aqueous electrolyte systems. Its main limitation concerns species that are poorly soluble in water, in this case solid−liquid equilibrium data must be preferred to determine the variation of the adjustable parameters with temperature. The resulting electrolyte-NRTL and Pitzer's parameters (Tables 4 and 5) lead to the simultaneous representation of our experimental values (Figures 2, 3, 4, and 6) and of some data taken from literature like osmotic coefficient and activity coefficient of both NaCl and Na_2SO_4 (Table 6). However, Pitzer's model is more capable of representing thermodynamic properties than electrolyte-NRTL. Particularly, the temperature dependence of ternary parameters of Pitzer's model was not necessary to calculate dissolution enthalpies with a good accuracy (Figure 5). In fact, the main advantage of Chen's model is its possible extension to mixed aqueous−organic solutions.

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Received for review April 26, 2002. Accepted October 26, 2002.

JE0200766