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Phase diagrams and thermochemical modeling of salt lake brine systems. III. $Li_2SO_4+H_2O$, $Na_2SO_4+H_2O$, $K_2SO_4+H_2O$, $MgSO_4+H_2O$ and $CaSO_4+H_2O$ systems

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ABSTRACT

This paper is part of a series of studies on the development of a multi-temperature thermodynamically consistent model for salt lake brine systems. Under the comprehensive thermodynamic framework proposed in our previous study, the thermodynamic and phase equilibria properties of the sulfate binary systems (i.e., $Li_2SO_4+H_2O$, $Na_2SO_4+H_2O$, $K_2SO_4+H_2O$, $MgSO_4+H_2O$ and $CaSO_4+H_2O$) were simulated using the Pitzer-Simonson-Clegg (PSC) model. Various type of thermodynamic properties (i.e., water activity, osmotic coefficient, mean ionic activity coefficient, enthalpy of dilution and solution, relative apparent molar enthalpy, heat capacity of aqueous phase and solid phases) were collected and fitted to the model equations. The thermodynamic properties of these systems can be well reproduced or predicted using the obtained model parameters. Comparisons with the experimental or model values in literature indicate that the model parameters determined in this study can describe all of the thermodynamic and phase equilibria properties of these binary sulfate systems from infinite dilution to saturation and freezing point temperature to approx. 500 K.

1. Introduction

Thermodynamic modeling of phase diagrams is of essential importance for revealing the natural brine evolution and designing chemical engineering process to extract valuable salts from salt lake brines by predicting their salt formation sequence. In previous studies [1,2], the Pitzer-Simonson-Clegg (PSC) model [3,4] was chosen to represent the aqueous properties of binary salt-water systems (i.e. $LiCl+H_2O$, $NaCl+H_2O$, $KCl+H_2O$, $MgCl_2+H_2O$ and $CaCl_2+H_2O$). To regress the model parameters as a function of temperature, various type of thermodynamic data (i.e., water activity a_w, ionic activity coefficients $\gamma_{\pm}$, heat capacity of solution and solid phases c_p, enthalpy of dilution $\Delta_{dil}H_m$, enthalpy of solution $\Delta_{sol}H_m$, relative apparent molar enthalpy ${}^{\phi}L_m$ and solubility) were used as constraint conditions to guarantee parameters reliability. In recent years, the importance of thermodynamic constraints among different types of thermodynamic property for activity coefficient model parameterization has been noted and valued by more and more researchers [5,6]. Emphasis was placed on the key role of the thermal quantities of the solid phases and the aqueous phase by the authors in the model parameterization under multi-temperature conditions. Under the parameterization framework, phase diagrams and thermodynamic properties of the binary systems $LiCl+H_2O$, $NaCl+H_2O$, $KCl+H_2O$, $MgCl_2+H_2O$ and $CaCl_2+H_2O$ were simulated in wide temperature and salt concentration ranges. To expand the modeling work for binary systems, which are the most important basis for the properties simulation and prediction of multi-component salt lake brine systems, herein binary sulfate systems $Li_2SO_4+H_2O$, $Na_2SO_4+H_2O$, $K_2SO_4+H_2O$, $MgSO_4+H_2O$ and $CaSO_4+H_2O$ involved in the salt lake brine system are modeled using our previous proposed thermodynamic framework [1,2] to assure the compatibility in the multi-component system modeling, although these systems have been simulated by many other researchers [6–15] either with simple solubility models or comprehensive thermodynamic consistency models.

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Table 1
Sources of experimental data used for parameterization of the binary systems $Li_2SO_4+H_2O$, $Na_2SO_4+H_2O$, $K_2SO_4+H_2O$, $MgSO_4+H_2O$ and $CaSO_4+H_2O$.

System	Data Property[a]	Number of data points	Temperature Range/K	Concentration Range/mol·kg^{-1}	Reference
$Li_2SO_4+H_2O$	Activity	99	383 – 498	0.54 – 3.18	[8]
	Activity	28	298.15	0.1 – 3.0	[21]
	Activity	120	298 – 323	0.1 – 2.8	[22]
	Activity	6	273.15	0.4 – 2.3	[23]
	Activity	7	323.15	0.75 – 3.1	[24]
	Activity	29	313.15	0.1 – 2.68	[25]
	Activity	17	298.15	0.7 – 2.87	[26]
	Thermal	10	303.15	0.17 – 0.92	[27]
	Thermal	19	298.15	0.15 – 3.0	[28]
	Thermal	10	298.15	0.0002 – 0.1	[29]
	SLE	11	251 – 487	0.38 – 3.38	[30]
	SLE	4	368 – 377	2.78 – 2.80	[31]
	SLE	4	253 – 323	2.97 – 3.40	[32]
	SLE	6	282 – 323	3.0 – 3.2	[33]
	SLE	1	298.15	3.16	[34]
	SLE	1	303.15	3.09	[35]
	SLE	19	257 – 376	2.83 – 3.42	[36]
	SLE	4	273 – 348	2.9 – 3.3	[37]
	SLE	7	258 – 373	2.79 – 3.36	[38]
$Na_2SO_4+H_2O$	Activity	80	383 – 498	0.55 – 3.42	[8]
	Activity	11	273.15	0.1 – 1.5	[40]
	Activity	96	298 – 323	0.1 – 3.73	[41]
	Activity	25	323 – 423	0.47 – 1.85	[42]
	Activity	13	318.15	0.7 – 3.5	[43]
	Activity	13	333.15	0.9 – 3.44	[44]
	Activity	30	353.15	0.7 – 2.97	[45]
	Activity	10	372.75	0.9 – 3.5	[46]
	Activity	6	298.15	0.5 – 3.0	[47]
	Activity	64	298.15	0.001 – 1.95	[48]
	Activity	6	298.15	0.05 – 1.0	[49]
	Thermal	6	303.15	0.18 – 1.0	[27]
	Thermal	14	298.15	0.25 – 3.0	[28]
	Thermal	20	313 – 353	0.07 – 1.6	[50]
	Thermal	25	373 – 423	0.02 – 2.14	[51]
	Thermal	9	298.15	0.05 – 1.27	[52]
	Thermal	11	298.15	0.01 – 1.5	[53]
	Thermal	34	304 – 413	0.05 – 2.63	[54]
	SLE	25	308 – 514	2.94 – 3.46	[39]
	SLE	11	330 – 371	3.03 – 3.60	[55]
	SLE	12	272 – 303	0.28 – 2.82	[58]
	SLE	16	298 – 303	1.95 – 2.98	[59]
	SLE	14	273 – 305	0.33 – 3.78	[60]
	SLE	5	288 – 298	0.91 – 1.93	[61]
	SLE	6	273 – 297	1.25 – 3.69	[62]
	SLE	2	313 – 323	3.26 – 3.38	[63]
$K_2SO_4+H_2O$	Activity	55	383 – 498	0.55 – 2.71	[8]
	Activity	53	298 – 323	0.2 – 0.96	[10]
	Activity	74	273 – 498	0.1 – 2.5	[10] [b]
	Activity	7	298.15	0.1 – 0.7	[21]
	Activity	50	298.15	0.001 – 0.6	[43]
	Activity	42	298.15	0.001 – 0.05	[64]
	Thermal	4	303.15	0.12 – 0.56	[27]
	Thermal	19	373 – 423	0.0025 – 0.65	[51]
	Thermal	9	298.15	0.06 – 0.65	[52]
	Thermal	8	298.15	0.01 – 0.65	[53]
	Thermal	22	298 – 373	0.03 – 0.4	[65]
	SLE	56	271.6 – 562.15	0.402 – 2.06	[66]
$MgSO_4+H_2O$	Activity	14	273.15	0.005 – 5.65	[40]
	Activity	6	372.75	2.0 – 4.5	[46]
	Activity	3	298.15	1.0 – 3.0	[47]
	Activity	30	273.15 – 373.15	0.72 – 5.65	[67]
	Activity	14	288.15	0.1 – 3.0	[68]
	Activity	48	298.15	0.1 – 3.6176	[69]
	Activity	17	298.15	0.1 – 3.0	[70]
	Activity	10	298.15	0.933 – 3.485	[71]
	Activity	9	298.15	1.48 – 2.98	[72]
	Activity	36	383.15 – 413.22	1.38 – 5.05	[73]
	Activity	13	298.15	0.005 – 0.149	[74]
	Thermal	6	303.15	0.341 – 1.059	[27]
	Thermal	16	313.15 – 353.15	0.1 – 1.968	[50]
	Thermal	30	373.15 – 423.65	0.002 – 2.712	[51]
	Thermal	41	348.15 – 473.15	0.1 – 2.186	[75]
	SLE	8	269.28 – 272.85	1.6739 – 2.1043	[76]
	SLE	32	273.15 – 363.15	2.195 – 5.732	[77]

(*continued on next page*)