Journal of the Korean Chemical Society
2010, *Vol. 54, No. 3*
Printed in the Republic of Korea
DOI 10.5012/jkcs.2010.54.3.269

$NaCl + CaCl_2 + H_2O$ 및 $KCl + CaCl_2 + H_2O$ 삼성분계에 대한 50 °C에서의 용해도 측정

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(접수 2009. 12. 29; 수정 2010. 3. 8; 게재확정 2010. 3. 17)

Measurement of Solubilities in the Ternary System $NaCl + CaCl_2 + H_2O$ and $KCl + CaCl_2 + H_2O$ at 50 °C

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(Received December 29, 2009; Revised March 8, 2010; Accepted March 17, 2010)

요약. $NaCl-CaCl_2-H_2O$와 $KCl-CaCl_2-H_2O$계의 용해도와 물리화학적 성질(굴절률)을 50 °C에서 측정하였으며, 그 결과를 상 평형 그림과 조성에 따른 물리화학적 성질에 대한 도표로 나타내었다. 삼성분계의 상 평형 그림은 불변점이 하나, 일변수 곡선이 둘, NaCl (또는 KCl) 및 $CaCl_2 \cdot 2H_2O$에 대응되는 결정화 지역이 두 개가 있음을 보여주었다. 이들 계에 대하여 혼합 파라미터인 $\theta_{M,Ca}$와 $\Psi_{M,Ca,Cl}$ (M = Na or K), 평형상수 K_{sp}를 최소제곱법을 이용하여 결정하였으며, 이때, NaCl, KCl 및 $CaCl_2$의 단일-염 Pitzer 파라미터 $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^{Φ}는 참고문헌을 통하여 직접 계산하였다. 이 결과들은 실험결과와 잘 일치하였다.

주제어: Pitzer 모델, 용해도 평형상수, 용해도 예측

ABSTRACT. The solubility and the physicochemical property (refractive index) in the $NaCl-CaCl_2-H_2O$ and $KCl-CaCl_2-H_2O$ systems were determined at 50 °C and the phase diagrams and the diagrams of physicochemical property *vs* composition were plotted. One invariant point, two univariant curves, and two crystallization zones, corresponding to sodium Chloride (or potassium chloride), dihydrate ($CaCl_2 \cdot 2H_2O$) showed up in the phase diagrams of the ternary systems. The mixing parameters $\theta_{M,Ca}$ and $\Psi_{M,Ca,Cl}$ (M = Na or K) and equilibrium constant K_{sp} were evaluated in $NaCl-CaCl_2-H_2O$ and $KCl-CaCl_2-H_2O$ systems by least-squares optimization procedure, in which the single-salt Pitzer parameters of NaCl, KCl and $CaCl_2$ $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^{Φ} were directly calculated from the literature. The results obtained were in good agreement with the experimental data.

Keywords: Pitzer model, Solubility equilibrium constant, Solubility prediction

INTRODUCTION

The prediction of the solubility in aqueous electrolyte solutions is important for a variety of applications in the chemical and geochemical processes, seawater systems, and evaporation as well as desalination. Salt solubility data are important as a tool for the design and simulation of unit operations such as drowning-out crystallization or liquid-liquid extraction. The investigation of the thermodynamics and phase diagram of the system is of theoretical and practical importance.[1,2] In the salt lakes of western China, these alkali metal salts coexist with other minerals containing boron, calcium, magnesium, and chloride.[3] To scientifically exploit these natural resources preliminary investigation of sodium, potassium and calcium salt solution chemistry is necessary. Thermodynamic properties of the ternary systems ($NaCl + CaCl_2 + H_2O$ and $KCl + CaCl_2 + H_2O$) are of essential importance in the extraction of sodium or potassium from natural salt brine mainly containing sodium, potassium, lithium, magnesium and calcium.

Pitzer's ion-interaction model[4] and its extended Harvie and Weare model[5-7] are very reliable for predicting the mineral solubility in natural water system with high ionic strengths over the wide temperature range from 0 to 300 ^{o}C.[8-11] The solubilities of calcium chloride and magnesium chloride were determined by prutton,[12] and calculating the activity coefficient and osmotic coefficients of electrolytes in seawater and synthetic salt lake brines were calculated by Song, P. S.[13,14] Li Ya-hong[15-17] reported. The solubility in the ternary $HCl-LiCl-H_2O$, $HCl-MgCl_2-H_2O$ and $LiCl-MgCl_2-H_2O$ systems at 273 and 293 K, using the ion-interaction Pitzer model and predicting the solubility isotherm of the $NaCl-RbCl-H_2O$, $KCl-CsCl-H_2O$ and $KBr-CsBr-H_2O$ systems at 298 K. Some other systems were also reported, such as $NaCH_3COO$ + NaCl + H_2O,[18] NaCl and KNO_3,[19] $LiCl-MgCl_2-H_2O$ system.[20] However, the application of the Pitzer model for predicting the component solubility of salt lake brine systems of NaCl + $CaCl_2$ + H_2O and KCl+$CaCl_2$+H_2O at 50 ^{o}C, has never been reported. Therefore, the solubility evaluation for the NaCl + $CaCl_2$ + H_2O and KCl + $CaCl_2$ + H_2O systems at 50 ^{o}C was performed in our lab.

In this paper, the solubility of the ternary systems NaCl + $CaCl_2$ + H_2O and KCl + $CaCl_2$ + H_2O was elaborately measured at 50 ^{o}C and an empirically Pitzer ion-interaction model was established based on those solubility data. The physicochemical properties (refractive index) of the equilibrium solutions were determined and a study on the prediction of the solubility was also performed.

EXPERIMENTAL SECTION

Apparatus and Reagents

A thermostatic shaker (model HS-4) whose temperature could be controlled to 0.02 K was used for the measurement of phase equilibrium. The chemicals used were of analytical grade and obtained from either the Tianjin Chemical Reagent Manufactory or the Shanghai Chemical Plant: calcium chloride ($CaCl_2{\cdot}6H_2O$, 99.5 mass %), sodium chloride (NaCl, g 99.8 mass %) and potassium chloride (KCl, g 99.5 mass %). Doubly deionized water was used to prepare the series of saturated solutions.

Experimental method

Various mixtures of salt and water were made by starting with a ground 250 cm^3 Erlenmeyer flask containing only one salt and water and in each subsequent run more of the second salt was added to the solution and solid left from the previous run. The flask was immersed in the thermostat and the solution and solid in the flask were stirred with a magnetic stirrer. Each sample was stirred at a specific constant temperature for 72 h, and then kept static for about 6 h. A sample of the saturated solution was then taken with a pipette. The sample was transferred to a weighed 30 cm^3 ground quartz beaker with cover. The salt concentration in pure saturated salt aqueous solution and the total salt concentration in the three component solutions were determined by evaporation to dryness, fusing, and weighing. The wet residuals were analyzed in the same way as for the solution. The composition of the solid phase in the wet residues was identified by the method of Schreinemaker.

Analytical method

The Cl^- ion concentration in the liquids and their corresponding wet residues of the solid phases were analyzed by titration with a standard solution of $AgNO_3$ in the presence of three drops of 0.1% (w/v) $KCrO_4$ as an indicator (precision within ± 0. 2 mass %. The Ca^{2+} ion concentration was determined by titration with EDTA standard solution in the presence of indicator of Eriochrome Black-T[21] (uncertainty of ± 0.2%). An Abbe refractometer (model WZS-1) was used to measure the refractive index (n_D) with an accuracy of ± 0.0001.

RUSULT AND DISCUSSION

The experimental data on the solubilities and refractive index of the ternary systems NaCl + $CaCl_2$ + H_2O and KCl + $CaCl_2$ + H_2O at 50 ^{o}C are presented in *Tables* 1 and 2, respectively. The electrolyte concentration values of the liquid phase in the equilibrium solution are expressed in mass fraction. According to the experimental data in *Tables* 1 and 2, the equilibrium phase diagrams of the systems NaCl + $CaCl_2$ + H_2O and KCl + $CaCl_2$ + H_2O are plotted, as shown in *Figs*. 1 and 2 at 50 ^{o}C, respectively. The solid phases in equilibrium with saturated solution are $CaCl_2{\cdot}2H_2O$ and MCl in the MCl (M = Na and K) + $CaCl_2$ + H_2O system at 50 ^{o}C.

In *Figs*. 1 and 2 with solid lines, points A and B are the solubilities of the single-salts of sodium chloride (or potassium chloride) and calcium chloride dihydrate. Point C is a eutectic point of sodium chloride(or potassium chloride) and calcium chloride dihydrate (NaCl + $CaCl_2{\cdot}2H_2O$ or KCl + $CaCl_2{\cdot}2H_2O$). There are two saturated curves corresponding to curves AC and BC, indicating the saturation of single salts. The phase diagram consists of two crystallization regions corresponding to the large area of NaCl (or KCl) and the relative small area of $CaCl_2{\cdot}2H_2O$. Obviously, the system belongs to the simple eutectic type, and neither double salts nor solid solutions are found.

On the basis of experimental data in *Tables* 1 and 2, relationship of the solution physicochemical property with the

***Table* 1.** Solubility data of the NaCl + $CaCl_2$+ H_2O system at 50 °C

Solution				Residue			Solid
W_{CaCl_2}%	W_{NaCl}%	W_{H_2O}%	n_D	W_{CaCl_2}%	W_{NaCl}%	W_{H_2O}%	phase
0.5634	0.0000	0.4366	1.4772	0.5502	0.0000	0.4498	$CaCl_2{\cdot}2H_2O$
0.5341	0.0343	0.4316	1.4787	0.5810	0.0279	0.3911	$CaCl_2{\cdot}2H_2O$
0.4454	0.1296	0.4249	1.4789	0.5010	0.1099	0.3891	$CaCl_2{\cdot}2H_2O$
0.4348	0.1435	0.4217	1.4787	0.4901	0.1179	0.3920	$CaCl_2{\cdot}2H_2O$
0.4182	0.1636	0.4183	1.4785	0.3487	0.2971	0.3542	$CaCl_22H_2O$ + NaCl
0.3818	0.1599	0.4583	1.4712	0.2245	0.4949	0.2806	NaCl
0.3705	0.1637	0.4658	1.4684				NaCl
0.3306	0.1446	0.5248	1.4605	0.1709	0.5647	0.2644	NaCl
0.2882	0.1363	0.5755	1.4461	0.1665	0.5966	0.2368	NaCl
0.2743	0.1343	0.5913	1.4425	0.1005	0.6635	0.2360	NaCl
0.1768	0.1418	0.6814	1.4081	0.0788	0.8183	0.1029	NaCl
0.1502	0.1550	0.6949	1.4007	0.0735	0.8399	0.0866	NaCl
0.1288	0.1683	0.7028	1.3958				NaCl
0.1148	0.1756	0.7096	1.3934	0.0304	0.8116	0.1580	NaCl
0.0924	0.1921	0.7155	1.3893	0.0254	0.8160	0.1586	NaCl
0.0514	0.2269	0.7217	1.3833	0.0148	0.8756	0.1096	NaCl
0.0285	0.2458	0.7257	1.3794	0.0096	0.8706	0.1198	NaCl
0.0000	0.2702	0.7298	1.3755	0.0000	0.8617	0.1383	NaCl

***Table* 2.** Solubility data of the KCl+ $CaCl_2$+ H_2O system at 50 °C

Solution				Residue			Solid
W_{CaCl_2}%	W_{NaCl}%	W_{H_2O}%	n_D	W_{CaCl_2}%	W_{NaCl}%	W_{H_2O}%	phase
0.5634	0.0000	0.4366	1.4772				$CaCl_2{\cdot}2H_2O$
0.5087	0.0772	0.4141	1.4776	0.6914	0.0216	0.2769	$CaCl_2{\cdot}2H_2O$
0.4611	0.1452	0.3931	1.4778	0.6628	0.0457	0.2915	$CaCl_2{\cdot}2H_2O$
0.4295	0.1978	0.3727	1.4781	0.5831	0.1064	0.3105	$CaCl_2{\cdot}2H_2O$
0.4196	0.2154	0.3650	1.4779	0.5678	0.1314	0.3008	$CaCl_2{\cdot}2H_2O$
0.3987	0.1948	0.4065	1.4761	0.4917	0.3159	0.1824	$CaCl_22H_2O$ + KCl
0.3759	0.2167	0.4074	1.4776	0.3227	0.3046	0.3227	KCl
0.3460	0.1887	0.4653	1.4652	0.2538	0.4116	0.3393	KCl
0.2857	0.1752	0.5491	1.4431				KCl
0.2126	0.1310	0.6564	1.4090	0.0780	0.6979	0.2241	KCl
0.1988	0.1246	0.6766	1.4045	0.0572	0.7576	0.1852	KCl
0.1372	0.1289	0.7339	1.3830	0.0233	0.8531	0.1236	KCl
0.0918	0.1367	0.7715	1.3783				KCl
0.0809	0.1547	0.7644	1.3750	0.0210	0.8959	0.0831	KCl
0.0339	0.2133	0.7528	1.3703	0.0128	0.8948	0.0924	KCl
0.0000	0.2595	0.7405	1.3689				KCl

concentration of calcium chloride is shown in *Figs*. 3 and 4. It can be found that the refractive indexes of the aqueous solutions in the ternary system, changed gradually and regularly with the content change of calcium chloride.

In *Figs*.1 and 2 with solid lines, points A and B are the solubilities of the single-salts of sodium chloride (or potassium chloride) and calcium chloride dihydrate. Point C is a eutectic point of sodium chloride (or potassium chloride) and calcium chloride dihydrate (NaCl + $CaCl_2{\cdot}2H_2O$ or KCl + $CaCl_2{\cdot}2H_2O$). There are two saturated curves corresponding to curves AC and BC, indicating the saturation of single salts. The phase diagram consists of two crystallization regions corresponding to the large area of NaCl (or KCl) and the relative small area of $CaCl_2{\cdot}2H_2O$. Obviously, the system belongs to the simple eutectic type, and neither double salts nor solid solutions are found.

On the basis of experimental data in *Tables* 1 and 2, relationship of the solution physicochemical property with the concentration of calcium chloride is shown in *Figs*. 3 and 4. It can be found that the refractive indexes of the aqueous

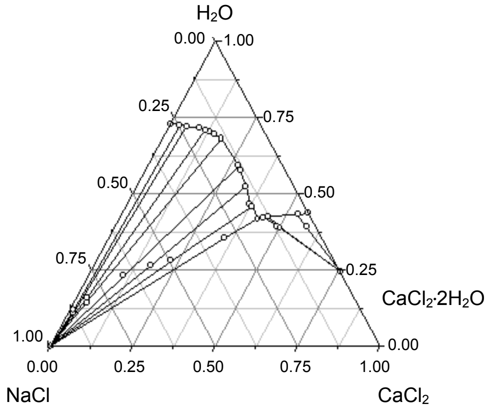

***Fig.* 1.** The phase diagram of the ternary system NaCl + $CaCl_2$ + H_2O at 50 °C.

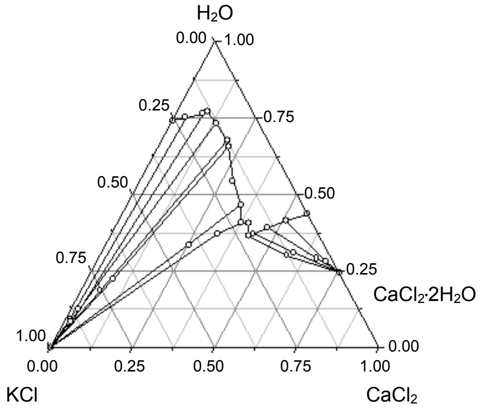

***Fig.* 2.** The phase diagram of the ternary system KCl + $CaCl_2$ + H_2O at 50 °C.

solutions in the ternary system, changed gradually and regularly with the content change of calcium chloride.

Calculation of the standard solubility product K_{MX}

The solubility of hydrated salt in concentrated electrolyte solutions can be calculated from thermodynamic considerations provided that equilibrium constants are known and activity coefficients can be obtained. For a hydrated salt $M_{vM}X_{vX}\cdot v_0H_2O$, the solubility equilibrium constant K_{sp}, at a de finite temperature and pressure for the dissolution reaction

$$M_{vM}X_{vX}\cdot v_0H_2O = v_M M^{+ZM} + v_X X^{-ZX} + v_0 H_2O \quad (1)$$

is expressed by

$$\ln K_{sp} = \upsilon_M \ln(m_M\gamma_M) + \upsilon_X \ln(m_X\gamma_X) + 2\ln r_{MX} + v_0 \ln a_W \quad (2)$$

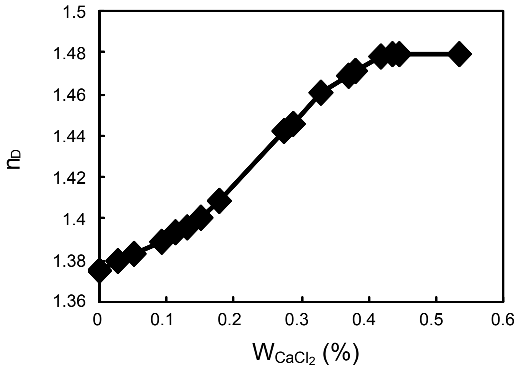

***Fig.* 3.** Physicochemical property *vs* composition in the ternary system ($NaCl$-$CaCl_2$-H_2O) at 50 °C.

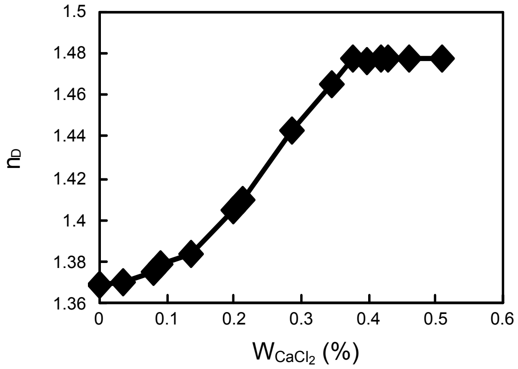

***Fig.* 4.** Physicochemical property *vs* composition in the ternary system (KCl-$CaCl_2$-H_2O) at 50 °C.

where m_i and γ_i represent the concentration expressed as molality and activity coefficient of the ions, respectively. The water activity a_W is related to the osmotic coefficient

$$\ln a_W = -\phi M_w \sum m_i \quad (3)$$

Here, M_w = 0.018015 kg·mol^{-1} is the molecular mass of water; ϕ is the osmotic coefficient.

Parameterization

Pitzer's binary parameters ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^{Φ}) for pure electrolytes of $CaCl_2$ + NaCl + H_2O and $CaCl_2$ + KCl + H_2O systems at 50 °C were available in the literature. The parameters of single-salt $CaCl_2$ were fitted from osmotic coefficients by least-square method. The parameters of single-salts NaCl and KCl were calculated by using the expressions of the temperature dependency of the ion interaction parameters. These values are listed in *Table* 3.

For the $CaCl_2$ + NaCl + H_2O and $CaCl_2$ + KCl + H_2O systems, the expression for the osmotic coefficient is

***Table* 3.** Pitzer's binary parameters for single electrolytes at 50 °C

	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{Φ}	SD	reference
NaCl	0.2172	0.5017	-1.0187	-0.0080	0.0001	18
KCl	0.0594	0.2493	0.0000	-0.0267	0.0005	22
$CaCl_2$	0.3485	1.8457	-0.2059	-0.0039	0.0043	23

$$\begin{aligned}\phi = {} & 1+(2/\sum_i m_i)(-A^{\phi}I^{3/2}/(1+1.2I^{1/2})+\\ & m_M\cdot m_{Cl}\{\beta^{(0)}_{M,Cl}+\beta^{(1)}_{M,Cl}\exp(-\alpha_1 I^{1/2})+\\ & \beta^{(1)}_{M,Cl}\exp(-\alpha_2 I^{1/2})+ZC^{\phi}_{M,Cl}/2\}+\\ & m_{Ca}\cdot m_{Cl}\{\beta^{(0)}_{Ca,Cl}+\beta^{(1)}_{Ca,Cl}\exp(-\alpha_1 I^{1/2})+\\ & \beta^{(1)}_{Ca,Cl}\exp(-\alpha_2 I^{1/2})+\sqrt{2}ZC^{\phi}_{Ca,Cl}/4\}+\\ & m_{Ca}m_{Cl}(\theta_{Ca,M}+m_{Cl}\psi_{M,Ca,Cl})\end{aligned} \tag{5}$$

where M is Na and K. $I = 1/2\sum_i m_i z_i^2$, and $Z = \sum_i m_i|z_i|$. The constants a_1 and a_2 are normally 1.4 and 2.0 $mol^{1/2}\cdot kg^{-1/2}$ respectively, $\theta_{M,Ca}$ and $\Psi_{Ca,M,Cl}$ are the mixing parameters.

The activity coefficients of MCl (M = Na or K) and $CaCl_2$ in the ternary mixture are

$$\begin{aligned}\ln\gamma_{MCl} = {} & F+(m_M+m_{Cl})B_{M,Cl}+0.5(m_M+m_{Cl})ZC_{M,Cl}\\ & +m_M m_{Cl}C_{M,Cl}+m_{Ca}B_{Ca,Cl}+0.5m_{Ca}ZC_{Ca,Cl}\\ & +0.5m_{Ca}m_{Cl}C_{Ca,Cl}+m_{Ca}\theta_{M,Ca}\\ & +0.5(m_M+m_{Cl})m_{Ca}\psi_{M,Ca,Cl}\end{aligned} \tag{6}$$

$$\begin{aligned}\ln\gamma_{CaCl2} = {} & 2F+\frac{2}{3}(2m_{Ca}+m_{Cl})B_{Ca,Cl}\\ & +\frac{1}{3}(2m_{Ca}+m_{Cl})ZC_{Ca,Cl}+\frac{4}{3}m_{Ca}m_{Cl}C_{Ca,Cl}\\ & +\frac{4}{3}m_M B_{M,Cl}+\frac{2}{3}Zm_M C_{M,Cl}+\frac{4}{3}m_M m_{Cl}C_{MLi,Cl}\\ & +\frac{2}{3}m_M\theta_{M,Ca}+\frac{1}{3}(2m_{Ca}+m_{Cl})m_M\psi_{Ca,M,Cl}\end{aligned} \tag{7}$$

The function F for the mixtures is given by:

$$\begin{aligned}F = {} & -A_{\phi}[(I)^{1/2}/\{1+b(I)^{1/2}\}+(2/b)\ln\{1+b(I)^{1/2}\}]\\ & +m_M m_{Cl}\beta^{(1)}_{M,Cl}g'(\alpha_1 I^{1/2})+m_M m_{Cl}\beta^{(2)}_{M,Cl}g'(\alpha_2 I^{1/2})\\ & +m_{Ca}m_{Cl}\beta^{(1)}_{Ca,Cl}g'(\alpha_1 I^{1/2})+m_{Ca}m_{Cl}\beta^{(2)}_{Ca,Cl}g'(\alpha_2 I^{1/2})\\ & +mMm_{Ca}\theta_{M,Ca}\end{aligned} \tag{8}$$

Here

***Table* 4.** Calculated logarithm of the solubility equilibrium constant

Salt	$\ln K^0_{sp}$	$m^s/(mol.kg^{-1})$
NaCl	3.364	6.334
KCl	2.179	5.106
$CaCl_2.2H_2O$	15.410	15.444

***Table* 5.** Pitzer mixing parameters for systems investigated at 50 °C

Salt	$\theta_{cc'}$	$\Psi_{cc'a}$	SD
$NaCl + CaCl_2 + H_2O$	0.0149	0.0027	0.0080
$KCl + CaCl_2 + H_2O$	0.0848	0.0082	0.0093

$$B_{M,Cl} = \beta^{(0)}_{M,Cl}+\beta^{(1)}_{M,Cl}g(-\alpha_1 I^{1/2})+\beta^{(2)}_{M,Cl}g(-\alpha_2 I^{1/2}) \tag{9}$$

$$B_{Ca,Cl} = \beta^{(0)}_{Ca,Cl}+\beta^{(1)}_{Ca,Cl}g(-\alpha_1 I^{1/2})+\beta^{(2)}_{Ca,Cl}g(-\alpha_2 I^{1/2}) \tag{10}$$

These equations contain the additional functions, which were described:[24]

$$g(x) = 2\{1-(1+x)\exp(-x)/x^2\} \tag{11}$$

$$g'(x) = \exp(-x)-g(x) \tag{12}$$

where b = 1.2 $mol.Kg^{-1}$. Value of the Debye-Hückel coefficient A_{φ} is 0.408 $kg^{1/2}.mol^{-1/2}$ at 50 °C.[25]

For $\theta_{M,Ca}$ and $\psi_{Ca,M,Cl}$ measurements of the activities of the complex salts in the system containing high concentrations of MCl (M = Na or K) and $CaCl_2$ are not available, hence the evaluation of the mixing parameters $\theta_{M,Ca}$ and $\psi_{Ca,M,Cl}$ relied on solubility data and solubility product of hydrated solid at 50 °C was obtained by a least-squares optimization procedure on the solubility data of corresponding ternary system. All of the parameters used in our calculations are listed in *Tables* 4 and 5.

Calculated Solubilities

The solubility data and the relevant physicochemical property data of the MCl (M = Na or K) + $CaCl_2$ + H_2O system at 50 °C were measured, and the results are shown in *Tables* 1 and 2, respectively. Using the chemical equilibrium model and the above parameters, the calculated results of the solu-

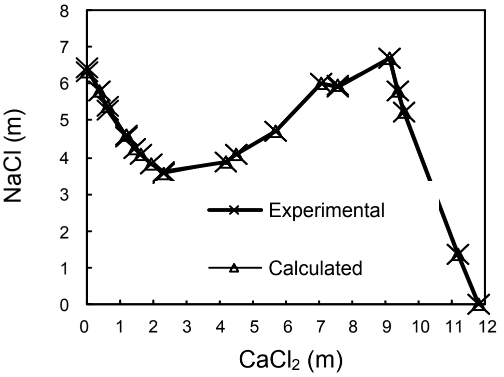

***Fig*. 5.** Calculated and experimental solution isotherms of NaCl + $CaCl_2 + H_2O$ at 50 °C.

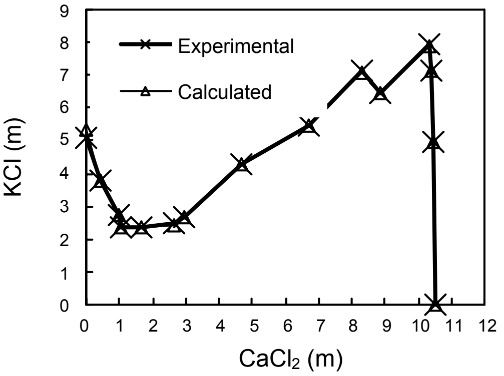

***Fig*. 6.** Calculated and experimental solution isotherms of KCl + $CaCl_2 + H_2O$ at 50 °C.

bility are shown in *Figs*. 5 and 6 at 50 °C, respectively. It is shown that the predicted values using the chemical equilibrium model agree well with experimental values. For the MCl (M = Na or K) + $CaCl_2 + H_2O$ system with high ionic strengths, this agreement indicates that the parameters obtained in this work are reliable and that the chemical equilibrium model of Harvie is capable of predicting equilibiria in the system studied.

CONCLUSION

The experimental solubility data and the relevant physicochemical property data of the aqueous systems NaCl + $CaCl_2 + H_2O$ and KCl + $CaCl_2 + H_2O$ at 50 °C were determined. Based on the solubility data measured, the isothermal phase diagram and diagram of physicochemical property *vs* composition are constructed. The single-salt Pitzer parameters of sodium chloride, potassium chloride and calcium chloride were calculated, and the mixing ion-interaction parameters of the NaCl + $CaCl_2 + H_2O$ and KCl + $CaCl_2 + H_2O$ systems could be fitted satisfactorily. The solubility product of NaCl, KCl and $CaCl_2 \cdot 2H_2O$ have been calculated. The calculated results agree well with the experimental values. This study could be useful for solubility prediction for more complicated systems and supply a theoretical basis for the exaction of sodium, potassium and calcium from salt lake brine.

Acknowledgments. The project was supported by the National Nature science Foundation of Shandong Province, China (Grant No. Y2007B47) and the Science Foundation of linyi Normal University, China (Grant No.XJS04064, HX07202).

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