Isopiestic Measurements of Thermodynamic properties for the aqueous system LiBr–$CaBr_2$–H_2O at 373.15 K

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ABSTRACT: The isopiestic molalities for the systems LiBr–H_2O, $CaBr_2$–H_2O and LiBr–$CaBr_2$–H_2O were measured at 373.15 K with the isopiestic method using the Oak Ridge National Laboratory (ORNL) high–temperature gravimetric isopiestic apparatus. The osmotic coefficients and water activities were determined based on the lithium chloride and sodium chloride reference standards. The behavior of the osmotic coefficients and the saturated vapor pressure for the ternary system as a function of molality was demonstrated. Good agreement has been found between the calculated vapor pressure and experimental results. The temperature-dependent equations for Pitzer binary parameters and the solubility product constants forLiBr–H_2O system from 273.15 to 523.15 K were obtained by combining our experimental results with other experimental data available in the literatures. The calculated solubilities for LiBr–H_2O system agree well with the reference data. The mixed ion–interaction parameters of $\theta_{\mathrm{Li,Ca}}$ and $\psi_{\mathrm{Li,Ca,Br}}$ were fitted for ionic strengths to 35.0 mol·kg^{-1} by using multiple linear regression method. The excellent agreement between the calculated water activities and experimental results indicates that the parameters obtained in this work are reliable. The thermodynamic data obtained in this study are essential for development of universal thermodynamic models for brine systems containing lithium bromide and calcium bromide.

***Keywords*:** Osmotic coefficients; Water activity; Lithium bromide; Calcium bromide; Thermodynamic model

1. INTRODUCTION

The oil field brines in Nanyishan District of the Qaidam Basin in Qinghai-Tibet Plateau of China, which mostly belong to the $CaCl_2$ type, have high lithium and bromine contents, with the concentration up to 0.98 $g \cdot L^{-1}$ for lithium and 0.28 $g \cdot L^{-1}$ for bromine, which mostly reach the industrial grade for comprehensive and single exploitation.[1,2] The thermodynamic properties of the ternary system $LiBr–CaBr_2–H_2O$including water activities and phase diagrams, are of theoretical and practical importance for effective exploitation for lithium and bromine resources from the brine. Phase diagrams at multiple temperatures are more effective in resources exploitation. The maximum temperature for the brine systems reported in the literature is up to 523.15 K.[3] Although a large number of thermodynamic properties and solubility data have been reported for the sub-binary systems,[4-6] and the phase diagrams of the system $LiBr–CaBr_2–H_2O$ at 298.15 K have been reported,[7] the water activities in the ternary system are still lacking in the literature.

Global thermodynamic models, even though they are largely empirical, provide convenient representations of thermodynamic properties for practical applications and for further research.[8] The Pitzer ion-interaction model and its extended Harvie-Weare (HW) formalism,[9,10] which gave a set of expressions for osmotic coefficients of the solution and mean activity coefficients of electrolytes in the solution, have been widely used in solubility predictions, thermodynamics properties calculations, and so on.[11,12] For the model parameterization, the water activities in the ternary system are a prerequisite. In this study, the thermodynamic properties of the ternary system $LiBr–CaBr_2–H_2O$,Pitzer and HW model for the thermodynamic property calculation were presented.

2. EXPERIMENTAL SECTION

2.1.Reagents and Apparatus. All the chemicals used in the experiment are listed in Table 1. All the chemicals used in this work were dried at 493 K under vacuum before use, without any further verification of purity. All the chemicals were thoroughly dried under this condition. The mass fraction of the salt on the metals was at least 0.998 for lithium bromide and 0.995 for calcium bromide. $CaBr_2 \cdot 6H_2O$ will be converted to $CaBr_2$ at about 400 K under atmospheric conditions, so $CaBr_2 \cdot 6H_2O$ will be fully converted to anhydrous $CaBr_2$ under vacuum with the pressure about 133 Pa. Distilled and deionized water, with conductivity less than 5.6×10^{-6} $S \cdot m^{-1}$. was boiled immediately before it was used in the isopiestic experiment. The ORNL high-temperature isopiestic apparatus has been described previously.[13,14] It is the only existing facility of this type that can be used at temperatures significantly above 373.15 K. The main feature of this apparatus is its internal electromagnetic balance, which makes it possible to monitor the mass of the sample cups without interruption of the equilibrium. The isopiestic chamber was surrounded by an air bath stirred by three fans. Temperature control of this location was stable to ± 0.01 K over periods of several months.

2.2. Experimental Method. The appropriate amounts of mixed dry salts with different lithium bromide mole fractions Y_{LiBr} ($Y_{LiBr} = n_{LiBr}/(n_{LiBr}+ n_{CaBr2})$, 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.67, 0.7, 0.8,0.9 and 1.0) were placed in weighed platinum isopiestic cups by mixing the two dry pure reagents of LiBr and $CaBr_2$. Sample cups were placed in a silver-lined stainless steel autoclave in a sample holder which could be rotated using a lever operated from the outside of the autoclave. After all of the sample cups were placed in the isopiestic chamber, the chamber was closed and slowly evacuated for about 6 h. After thourough evacuation, the cups containing dry salts were weighed on the internal balance (using the internal weight standards) yielding the total masses of dry salts in each cup. These results were in agreement with the masses of salts initially placed in the cups, obtained from the analytical balance, which shows that the salt $CaBr_2 \cdot 6H_2O$ thoroughly converted into $CaBr_2$. Distilled, deionized, and freshly boiled water was injected into the autoclave in steps via capillary tubing and a valve using polypropylene syringes. To verify complete equilibrium, the masses of the sample cups were weighed with the internal balance two times, with the intervals between two measurements usually more than 24h. If the difference between two mass measurements was within ± 0.0010 g, then the equilibrium state was achieved. The equilibration time becomes longer as the concentration of solution decreasing. It takes about 48 h to achieve the equilibrium at the beginning of the isopiestic experiments at high concentration, but more than 10d to get the equilibrium for dilute solution. No indication of incomplete equilibrium was found in the cases when measurements were repeated during several days. The final result was taken as an average of 2 weighings for each of these cups. The relative deviation for molalities of the salts calculated from the two mass measurements ($(m_1 - m_2)/(0.5\ m_1 + 0.5\ m_2)$) is less than 0.001. Combining the largest uncertainty from impurity, the total uncertainty of the measured salt concentration for LiBr, CaBr2, LiCl and NaCl should be no more than 0.003, 0.006, 0.011 and 0.001, respectively. The pressure inside of the isopiestic chamber was measured with a pressure probe inside, which is connected with the pressure gauges outside of the chamber. An automated data acquisition system sampled the pressures, temperatures, and balance currents (sample weights) simultaneously during (30 to 60) s to obtain one averaged weighing for each sample cup.

3. RESULTS AND DISCUSSION

Lithium chloride and sodium chloride were used for reference standards in this work. The osmotic coefficients ϕ for the NaCl and LiCl reference solutions from the literatures[16,17] were used to fit as a function of molality (m) using equation (1). The parameters a, b, c, d, e, f, g, and h in equation (1) are given in Table 2.

$$= a + b\left(\frac{\mathrm{m}}{\mathrm{mol}} \cdot \mathrm{kg}^{-1}\right)^{0.5} + c\left(\frac{\mathrm{m}}{\mathrm{mol}} \cdot \mathrm{kg}^{-1}\right)$$

$$+d\left(\frac{\mathrm{m}}{\mathrm{mol}}\cdot \mathrm{kg}^{-1}\right)^{1.5}+e\left(\frac{\mathrm{m}}{\mathrm{mol}}\cdot \mathrm{kg}^{-1}\right)^{2}$$

$$+f\left(\frac{\mathrm{m}}{\mathrm{mol}}\cdot \mathrm{kg}^{-1}\right)^{2.5}+g\left(\frac{\mathrm{m}}{\mathrm{mol}}\cdot \mathrm{kg}^{-1}\right)^{3}$$

$$+h(\mathrm{m}/\mathrm{mol}\cdot \mathrm{kg}^{-1})^{3.5}$$

(1)

The osmotic coefficient of these reference solutions can be calculated using equation (1). The water activity a_{w} of the reference solutions can be calculated by equation (2).

$$\ln a_{\mathrm{w}} = -M_{\mathrm{W}}\sum m_{\mathrm{i}} \qquad (3)$$

where M_{w} is the molar mass of water (kg·mol^{-1}), and the sum covers all the solute species. The osmotic coefficient of the ternary system can also be calculated by equation (2). The average deviation between the calculated osmotic coefficients for the same solution with NaCl and LiCl reference solutions is less than 0.01. The largest deviation between the water activities calculated with NaCl and LiCl reference solutions is less than 0.0012. Combining the accuracy of the balance (within ±0.0010 g) and the purity of the source chemicals, the largest deviation of water activities should be no more than 0.0020.

The experimental osmotic coefficients for LiCl–H_2O system with the concentration from 0.4479 mol·kg^{-1} to 3.2020 mol·kg^{-1} were reported by Campbell and Bhatnagar[20]. The average deviation between the calculated osmotic coefficients using equation (1) and the experimental data from Campbell and Bhatnagar[20] is 0.0028, which shows the equation (1) for LiCl–H_2O system is reliable with the concentration from 0.4479 mol·kg^{-1} to 3.2020 mol·kg^{-1}. NaCl was not dissolved in the isopiestic cups, when the water activity is small at the beginning of the isopiestic experiment. Therefore, the water activities with equation (2) were calculated with LiCl reference solutions in this study.

3.1. Pitzer Extended Model. Pitzer original model for binary system with only parameters $\beta^{(0)}$, $\beta^{(1)}$, $C^{\varnothing}$ were not suitable for the binary systems $CaCl_2$–H_2O and $CaBr_2$–H_2O,[8,13] especially at high concentration. Therefore, the extended model from Pitzer et al.[13] and from Archer[14,15] (denoted hereafter as Pitzer extended model) were used in this study. The present general models proposed by Pitzer et al.[13] for aqueous solutions of calcium bromide and lithium bromide are based on the modified ion-interaction (Pitzer) equations with a regular pattern of ionic-strength dependence for third virial coefficients. The term $D^{\varnothing}$ was not used in this study for the system systems LiBr–H_2O and $CaBr_2$–H_2O.

$$= 1 - \frac{|Z_M Z_X| A^{\phi} 1^{0.5}}{(1 + \mathrm{bl}^{0.5})} + m\left(\frac{2\upsilon_M \upsilon_X}{\upsilon}\right) B^{\phi}_{MX} + m^2\left(\frac{2(\upsilon_M \upsilon_X)^{1.5}}{\upsilon}\right) C^{\phi}_{MX} \tag{3}$$

$$B^{\phi}_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} \exp\left(-\alpha I^{0.5}\right) \tag{4}$$

$$C^{\phi}_{MX} = 2C^{(0)}_{MX} + 2C^{(1)}_{MX} \exp\left(-\omega_{MX} I\right) \tag{5}$$

In equations (3)–(5), b = 1.2 $\mathrm{kg}^{0.5}\cdot\mathrm{mol}^{-0.5}$, α = 2.0 $\mathrm{kg}^{0.5}\cdot\mathrm{mol}^{-0.5}$; Debye–Hückel parameter $A^{\o}$ = 0.460525 at 373.15 K obtained from the literature[21] was used for the parameter fitting. M denotes the cation and X the anion; z_M and z_X are the valences (with sign) of the cation and the anion, respectively; υ_M and υ_X are the numbers of M and X ions formed by the complete dissociation of one molecule of the solute, respectively; and $\upsilon = \upsilon_M + \upsilon_X$. The ion-interaction parameters $\beta^{(0)}$, $\beta^{(1)}$, $C^{(0)}$, and $C^{(1)}$ are fitted using experimental data. The constant x can also be fitted with the experimental osmotic coefficients.

An extended form of Archer's extended ion-interaction equation for the molality-based osmotic coefficient of a binary solution of an electrolyte were written as the following, which was presented in the literatures[16].

$$= 1 - \frac{|Z_M Z_X| A^{\phi} I^{0.5}}{(1 + \mathrm{bI}^{0.5})} + m\left(\frac{2\upsilon_M \upsilon_X}{\upsilon}\right) B^{\phi}_{MX} + m^2\left(\frac{4{\upsilon_M}^2 \upsilon_X z_M}{\upsilon}\right) C^{\phi}_{MX} \tag{6}$$

$$B^{\phi}_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} \exp\left(-\alpha I^{0.5}\right) \tag{7}$$

$$C^{\phi}_{MX} = C^{(0)}_{MX} + C^{(1)}_{MX} \exp\left(-\omega_{M,X} I^{0.5}\right) \tag{8}$$

Equation (6) is the same as equation (3) for the system LiBr–H_2O, but different for the system $CaBr_2$–H_2O. The parameters $\beta^{(0)}$, $\beta^{(1)}$, $C^{(0)}$, and $C^{(1)}$ for the two systems fitted with osmotic coefficients using the two extended models are different because of different equations. The constant ω is also different for the two extended models.

The following equation, which was given in the literatures from Pitzer[9] and Clegg et al[16], were used for the osmotic coefficient calculation for the ternary system LiBr–$CaBr_2$–H_2O. The equation for osmotic coefficient of the mixed system for the two Pitzer extended model has the form.

$$\phi = 1 + \frac{2}{\Sigma m_i}$$

$$\left[\frac{-A^{\phi}I^{1.5}}{(1+bI^{0.5})} + m_{Li}m_{Br}\left(B^{\phi}_{Li,Br} + ZC_{Li,Br}\right) + m_{Ca}m_{Br}\left(B^{\phi}_{Ca,Br} + ZC^{\phi}_{Ca,Br}\right) + m_{Li}m_{Ca}(\Phi^{\phi}_{Li,Ca} + m_{Br}\Psi_{Li,Ca,Br})\right] \tag{9}$$

$$\Phi_{Li,Ca} = \theta_{Li,Ca} + E\theta_{Li,Ca} + I^{E}\theta'_{Li,Ca} \tag{10}$$

According to the Pitzer model and Pitzer extended model from Pitzer et al.[13] and Archer,[14,15] the water activity and osmotic coefficients are parametric functions of $\beta^{(0)}$, $\beta^{(1)}$, $C^{(0)}$, $C^{(1)}$, $\theta_{cc'}$ and $\psi_{cc'a}$; $\beta^{(0)}$, $\beta^{(1)}$, $C^{(0)}$, and $C^{(1)}$ are the parameters of a single salt; $\theta_{cc'}$ represents the interaction between the two ions with the same sign, and $\psi_{cc'a}$ represents the interactions among the three ions, in which the sign of the third ion is different from the first two ions. The single salt and mixing parameters can be fitted using the water activity and osmotic coefficient data.

The experimental results of the ternary system LiBr–$CaBr_2$–H_2O at 373.15 K are listed in Table 1. The concentration of salts and the water activities were tabulated in each record of isopiestic experiment run. The water activities of all solutions in each set of isopiestic measurement were equal to the water activity of reference at isopiestic equilibrium. The water activities presented in Table 1 were calculated with the LiCl reference standard.

3.2. Saturated Vapor Pressure. The experimental equilibrium saturated vapor pressure was also presented in Table 1. The diagrams between vapor pressure and ionic strength in the ternary system

LiBr–CaBr$_2$–H$_2$O at different Y_{LiBr} in the mixed solution were plotted in Figure 1. The vapor pressure decreased with the increasing ionic strength and decreased with Y_{LiBr} increasing at the same ionic strength. The vapor pressure p can be calculated with the experimental water activities using the equation (11).[18-20]

$$ln\alpha_w = \ln\left(p/p_0\right) + B_T(P - P_0)/RT \tag{11}$$

where p_0 = 101325 Pa is the vapor pressure of pure water at 373.15 K, R = 8.314 Pa·m^3·mol^{-1}·K^{-1} , and B_{T}= -0.004527 m^3·mol^{-1} is the second virial coefficient taken from the literature.[21] The deviation between the experimental and calculated vapor pressure (Δp = calculated pressure – experimental pressure) is shown in Figure 2. The average deviation is about 353 Pa, which falls into the range of experimental error. The saturated vapor pressure data from the literature with w_t = 0.40 and 0.50 (in mass fraction) was plotted in Figure 1a. The comparisons show that the vapor pressure data from the literature agree well with those in this study. The results show shows the experimental pressures in this study are reliable.

3.3. LiBr–H$_2$O System. The osmotic coefficient diagram of LiBr–H$_2$O system was given in Figure 3. The osmotic coefficients in Figure 3 increase with the m_{LiBr} increasing. On the basis of Pitzer original model, the single salt parameters for LiBr at 373.15 K were fitted with the osmotic coefficients with the concentration ≤10.7478 mol·kg^{-1} and ≤14.1520 mol·kg^{-1}, as shown in Table 4. The comparison between the calculated osmotic coefficients with the three parameters and experimental data shows that the calculated data with the two sets of three parameters agree with the experimental data at low concentration, but show lager deviations at high concentration. The large deviation between the experimental data and calculated data with the parameters fitted at high concentration is more than 0.05, which shows the Pitzer original model with three parameters is not very suitable for the LiBr–

H_2O system.

On the basis of the Pitzer extended model from Pitzer et al,[13] and Archer,[14,15] the parameters $\beta^{(0)}$, $\beta^{(1)}$, $C^{(0)}$, and $C^{(1)}$ and constant ω were fitted with the experimental osmotic coefficients, as shown in Table 4. The maximum deviation between the calculated data with the two sets of four parameters and experimental results is less than 0.01. The calculated data with the two extended model are nearly the same because of the similar equations. The comparison in Fig. 2(b) shows the two models are more suitable for the LiBr–H_2O system.

3.4. $CaBr_2$–H_2O System. The measured osmotic coefficient diagram for the $CaBr_2$–H_2O system was shown in Fig. 3. The binary parameters for $CaBr_2$ were fitted with the measured osmotic coefficient on the basis of Pitzer original model, as shown in Table 5.With the same results as those for the LiBr–H_2O system, the Pitzer original model with three parameters is not suitable for the $CaBr_2$–H_2O system at high concentration. The parameters for $CaBr_2$ at 373.15 K can also be calculated with the temperature-dependent equations from Christov.[28] With the parameters from the literatures,[28] the osmotic coefficients were also calculated, as shown in Fig. 3(a). The calculated results are nearly the same as those with the parameters fitted at low concentration ($0 \sim 8.1363$ $mol\cdot kg^{-1}$), and also show remarkable deviation at high concentration. The experimental osmotic coefficients are quite different from those by Gruszkiewicz[8] in Fig. 3(a) especially at high concentration. The water activities were also calculated with the different sets of parameters as shown in Fig. 3(b). The maximum deviation is less than 0.01. Considering the water activities were usually used in solubility calculation, the binary three parameters for $CaBr_2$–H_2O system in this study and from Christov[28] are good enough for water activity calculation and can be used in solubility calculation.

The parameters fitted with the two Pitzer extended models were also listed in Table 5. The comparison between the experimental osmotic coefficient and calculated data with the two extend models were shown in Fig. 3(c). The maximum deviation for the two models is about 0.01 for the $CaBr_2$–H_2O system. The results show that the two extended models with four parameters are reliable for the osmotic coefficient calculation in the $CaBr_2$–H_2O system.

3.5. Libr−$CaBr_2$−H_2O System. The experimentally measured equal-water activity lines of the ternary system LiBr–$CaBr_2$–H_2O with different mole fraction for lithium bromide with Zdanovskii's rule are shown in Fig. 4, where composition points with the same water activity at low and middle salt concentrations form roughly straight lines. The lines with different water activity were nearly parallel. The dashed lines in Fig. 5 connect the composition points with the same Y_{LiBr}. The m_{CaBr2} decreases with the m_{LiBr} increasing in the lines with same water activity in Fig. 4.

The Pitzer extended models were used in the mixed system because of the remarkable deviation for the Pitzer original model at high concentration. With only the binary parameters fitted with the Pitzer extened model for Pitzer[13] in Tables 4 and 5, the osmotic coefficients ($ø_1$) and water activities (α_{w1}) of the LiBr–$CaBr_2$–H_2O system at 373.15 K were calculated and compared them with the experimental values ($ø$ and a_w), as shown in Fig. 5. The maximal and average deviation between experimental water activities and calculated data ($\Delta\alpha_{w1} = \alpha_{w1} - \alpha_w$) are −0.0178 and −0.0012. The ternary mixing parameters $\theta_{Li,Ca}$ and $\psi_{Li,Ca,Br}$ were obtained by fitting the osmotic coefficients in Table 3 measured in this work, as shown in Table 6. The maximal and average deviation between experimental water activities and calculated values (α_{w2}) ($\Delta\alpha_{w2} = \alpha_{w2} - \alpha_w$) with the binary parameters and mixing parameters are −0.0144 and −0.0007. The deviations of calculated data and experimental results are also shown in Fig. 5. Significant deviations occur mainly at high concentration. The deviations become smaller with the mixing parameters in Fig. 5. The mixing parameters can make better results in osmotic coefficient or water activity calculation, but it seems no remarkable improvement is achieved using the mixing parameters.

The Pitzer extended model from Archer[14,15] was also used to describe the mixed system. The mixing parameters fitted were tabulated in Table 6. The comparison for osmotic coefficients and water activities was shown in Fig. 6. The calculated results of osmotic coefficients and water activities with the two Pitzer extended model are nearly the same. The deviations from the extended model from Archer[14,15] are a little smaller than those with the model from Pitzer et al.[13] From Fig. 6, it shows that the Pitzer model with binary parameters is not very sufficient in representing the properties of the ternary system, and mixing parameters are needed to finish the task from Fig. 6 for this extended model.

From Figs. 5 and 6, the deviations between the osmotic coefficients are less than 0.01 at low concentration but more than 0.05 at high concentration in Figs. 5(a) and 6(a). It seems that equation (9) is not sufficient for osmotic coefficient calculation in the ternary system LiBr–$CaBr_2$–H_2O. The Pitzer model show large deviations for the system LiBr–$CaBr_2$–H_2O especially at high concentration. The results show that the ion interactions between Li^+, Ca^{2+} and Br^- in the ternary system are quite complicate; the Pitzer models are not very suitable for the mixed system. However, the results in Figs. 5(b) and 6(b) show that the mixing parameters $\theta_{Li,Ca}$ and $\psi_{Li,Ca,Br}$ fitted in this study are reliable and capable for water activity calculation. Because of the lack of the Pitzer model for the mixing parameters in the mixed system LiBr–$CaBr_2$–H_2O, the Pitzer extended model for the ternary system was not developed further.

The double salt $LiBr\cdot CaBr_2\cdot 5H_2O$ formed in the ternary system at 298.15 K,[7] so the double salt may form at 373.15 K. The solubility products lnK for $LiBr\cdot CaBr_2\cdot 5H_2O$ can't be obtained from the literatures. The parameters and solubility products for $LiBr\cdot H_2O$ and $CaBr_2\cdot 4H_2O$ at 373.15 K are known, but the solubility data of the system at 373.15 K can't be calculated.

4. CONCLUSIONS

The vapor pressure and osmotic coefficients of the systems $LiBr–H_2O$, $CaBr_2–H_2O$ and $LiBr–CaBr_2–H_2O$ at 373.15 K were investigated with the isopiestic method using the Oak Ridge National Laboratory (ORNL) high–temperature gravimetric isopiestic apparatus. The vapor pressure diagrams and osmotic coefficient diagrams at different mole fraction for LiBr were plotted. The calculated vapor pressure with water activities agree well with the experimental data. On the basis of Pitzer extended model, the Pitzer binary parameters $\beta^{(0)}$, $\beta^{(1)}$, $C^{(0)}$, and $C^{(1)}$ for the systems $LiBr–H_2O$ and $CaBr_2–H_2O$ and mixing parameters of $\theta_{\mathrm{Li,Ca}}$ and $\psi_{\mathrm{Li,Ca,Br}}$ were fitted with the measured osmotic coefficients. The calculated osmotic coefficients for systems like $LiBr–H_2O$ and $CaBr_2–H_2O$ agree well with the experimental data. The agreement between the calculated water activities and experimental results for the ternary system indicates that the parameters obtained in this work are reliable for water activity calculation. The thermodynamic data obtained in this study are essential for development of universal thermodynamic models for brine systems containing lithium bromide and calcium bromide.

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Notes

The authors declare no competing financial interest.

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■ ASSOCIATED CONTENT

Supporting Information

Information as mentioned in the text. This information is available free of charge via the Internet at http://pubs.acs.org.

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Captions

Table 1. Isopiestic Molalities and Water Activities of the Ternary System LiBr–$CaBr_2$–H_2O with LiCl (aq) and NaCl (aq) as a Reference at 3.15 K

Table 2. Pitzer Parameters of the Ternary System LiBr–$CaBr_2$–H_2O at 373.15 K

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Figure 1. Vapor pressures vs ionic strength of the LiBr–$CaBr_2$–H_2O system at 373.15 K.

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Figure 6. Phase diagram of LiBr–H_2O system from 222.4 K to 429.15 K. △,model values calculated from ref. 6; —, model values calculated with Pitzer and HW model in this work.

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Table 1.Isopiestic Molalities and Water Activities of the Ternary System LiBr–$CaBr_2$–H_2O with LiCl (aq) and NaCl (aq) as a Reference at 3.15 K

	1	2		3		4		5		6		7		8		9		10		11		12	13	14		
no.	m_{LiBr}	m_{LiBr}	m_{CaBr2}	m_{LiBr}	m_{CaBr2}	m_{LiBr}	m_{CaBr2}	m_{LiBr}	m_{CaBr2}	m_{LiBr}	m_{CaBr2}	m_{LiBr}	m_{CaBr2}	m_{LiBr}	m_{CaBr2}	m_{LiBr}	m_{CaBr2}	m_{LiBr}	m_{CaBr2}	m_{LiBr}	m_{CaBr2}	m_{CaBr2}	m_{LiCl}	m_{NaCl}	a_{w}	$P(10^5\mathrm{Pa})$
1	19.2104	17.16	1.9147	14.1552	3.575	11.8002	5.0014	11.0587	5.6464	9.7155	6.3458	7.3678	7.4935	5.5993	8.4299	4.2328	9.4985	2.6917	10.1009	1.4338	11.1046	11.7053	28.0251		0.1002	0.0788
2	18.2277	16.1875	1.8062	13.36	3.3742	11.0763	4.6946	10.4812	5.3515	9.0128	5.8868	6.8767	6.994	5.2515	7.9062	3.9773	8.9252	2.5335	9.5074	1.3445	10.4129	11.0575	25.9008		0.1165	0.0971
3	17.1131	15.1538	1.6909	12.4208	3.137	10.3038	4.3672	9.6928	4.949	8.4011	5.4873	6.4537	6.5638	4.911	7.3935	3.7099	8.3252	2.3712	8.8984	1.2543	9.7149	10.2679	23.7743		0.1369	0.1160
4	16.6535	14.7314	1.6437	12.3098	3.1089	10.1187	4.2887	9.4264	4.813	8.2369	5.38	6.2645	6.3714	4.7646	7.1731	3.6059	8.0917	2.3157	8.6898	1.2137	9.4001	9.963	22.8569		0.1472	0.1303
5	15.6509	13.7238	1.5313	11.3265	2.8606	9.3984	3.9834	8.7595	4.4725	7.5674	4.9427	5.7983	5.8972	4.3882	6.6065	3.33	7.4725	2.1146	7.9355	1.1134	8.6234	9.1463	20.7463		0.1746	0.1580
6	14.951	13.1125	1.4631	10.766	2.719	8.8931	3.7693	8.3139	4.245	7.209	4.7086	5.4884	5.582	4.1697	6.2776	3.1547	7.0793	2.0006	7.5075	1.0559	8.1778	8.6951	19.4483		0.1946	0.1774
7	14.152	12.3258	1.3753	10.0453	2.537	8.3381	3.534	7.7968	3.9809	6.7772	4.4266	5.145	5.2328	3.8948	5.8637	2.9333	6.5825	1.8692	7.0143	0.9873	7.6467	8.1363	17.8943		0.2225	0.2033
8	13.1248	11.403	1.2724	9.2849	2.345	7.6305	3.2341	7.1832	3.6676	6.1999	4.0495	4.745	4.8259	3.601	5.4214	2.718	6.0993	1.7268	6.4802	0.9076	7.0297	7.4885	16.1344		0.2608	0.2426
9	11.98	10.4008	1.1605	8.5011	2.147	7.0066	2.9697	6.4717	3.3044	5.6887	3.7156	4.3268	4.4007	3.2808	4.9393	2.4562	5.5117	1.5685	5.886	0.8228	6.3728	6.8039	14.2498		0.3122	0.2927
10	10.7478	9.298	1.0375	7.5514	1.9072	6.2608	2.6536	5.8068	2.9649	5.066	3.3089	3.8744	3.9405	2.942	4.4292	2.1968	4.9297	1.4033	5.2662	0.7371	5.7085	6.1266	12.436		0.3746	0.3528
11	10.3846	8.9471	0.9983	7.3169	1.8479	6.0561	2.5668	5.6325	2.8759	4.902	3.2018	3.7449	3.8088	2.8418	4.2783	2.1241	4.7665	1.3603	5.1046	0.7133	5.5247	5.8951	11.8667		0.3973	0.3835
12	9.7437	8.4189	0.9394	6.8894	1.7400	5.6569	2.3976	5.2594	2.6854	4.6163	3.0152	3.5021	3.5619	2.6668	4.0150	1.9941	4.4747	1.2936	4.8543	0.6725	5.2088	5.5931	11.0214		0.4337	0.4237
13	9.1878	7.9331	0.8852	6.4887	1.6388	5.3427	2.2644	4.9484	2.5266	4.352	2.8426	3.3242	3.381	2.5187	3.792	1.8861	4.2323	1.217	4.5668	0.634	4.91	5.2642	10.2349		0.4709	0.4626
14	8.6054	7.4164	0.8275	6.0895	1.538	5.024	2.1294	4.6524	2.3755	4.0943	2.6742	3.1181	3.1713	2.3584	3.5506	1.7649	3.9605	1.1405	4.2799	0.5943	4.6027	4.9614	9.5045		0.508	0.5071
15	8.068	6.9623	0.7769	5.7035	1.4405	4.7004	1.9922	4.3604	2.2264	3.8379	2.5068	2.936	2.9861	2.2311	3.3589	1.6668	3.7404	1.0785	4.0471	0.5621	4.3538	4.6794	8.8855		0.5413	0.5374
16	7.3364	6.3375	0.7071	5.2016	1.3137	4.2932	1.8196	3.9726	2.0283	3.5011	2.2868	2.6776	2.7233	2.0345	3.063	1.5238	3.4195	0.9854	3.698	0.5141	3.9818	4.2658	8.0003		0.5915	0.5904
17	6.8581	5.9269	0.6613	4.8766	1.2316	4.0376	1.7113	3.7418	1.9105	3.2968	2.1533	2.5215	2.5645	1.9176	2.8869	1.4346	3.2192	0.9278	3.4815	0.4841	3.7496	4.0155	7.4543		0.6236	0.6261
18	6.5855	5.6838	0.6342	4.6791	1.1818	3.8633	1.6374	3.5888	1.8324	3.1596	2.0638	2.4188	2.4601	1.8405	2.7709	1.3761	3.088	0.8879	3.3318	0.4642	3.5952	3.8664	7.1235		0.6434	0.6426
19	6.2506	5.3969	0.6022	4.4379	1.1208	3.673	1.5568	3.4133	1.7428	3.0007	1.9599	2.3034	2.3427	1.7505	2.6354	1.3106	2.941	0.8471	3.1788	0.4431	3.4316	3.6907	6.7487		0.666	0.6653
20	5.9532	5.1197	0.5713	4.2248	1.067	3.5003	1.4836	3.2519	1.6604	2.8647	1.8711	2.1933	2.2307	1.6716	2.5167	1.2521	2.8097	0.8116	3.0456	0.4233	3.2781	3.5304	6.4099		0.6865	0.6877
21	5.6959	4.9161	0.5485	4.0372	1.0196	3.3593	1.4238	3.1162	1.5911	2.7471	1.7943	2.1094	2.1454	1.6033	2.4139	1.202	2.6972	0.7784	2.921	0.4064	3.1478	3.3908	6.113		0.7045	0.7059
22	5.3129	4.5827	0.5113	3.7793	0.9545	3.1344	1.3285	2.9089	1.4853	2.5638	1.6746	1.9732	2.0068	1.5035	2.2636	1.1268	2.5285	0.7305	2.7415	0.3814	2.9537	3.173	5.6783		0.7307	0.7327
23	5.0726	4.3736	0.488	3.626	0.9158	3.0094	1.2755	2.787	1.423	2.45	1.6003	1.8897	1.922	1.4448	2.1751	1.0812	2.4262	0.6998	2.6261	0.3644	2.8223	3.05	5.4048	6.5300	0.7471	0.7501
24	4.5641	3.9489	0.4406	3.261	0.8236	2.7102	1.1487	2.5199	1.2866	2.2183	1.4489	1.7077	1.7368	1.3019	1.96	0.9766	2.1914	0.6324	2.373	0.3309	2.5629	2.759	4.8429	5.7465	0.7801	0.7848
25	4.1342	3.5887	0.4004	2.9652	0.7489	2.4698	1.0468	2.3025	1.1756	2.0252	1.3228	1.5615	1.5882	1.1959	1.8004	0.8956	2.0097	0.5814	2.1819	0.304	2.3548	2.536	4.4039	5.1058	0.8051	0.8112
26	3.6301	3.1437	0.3508	2.6176	0.6611	2.1821	0.9249	2.0244	1.0336	1.7903	1.1694	1.3854	1.4091	1.0604	1.5965	0.7943	1.7824	0.5162	1.9371	0.2704	2.0943	2.2523	3.8467	4.3782	0.8357	0.8426

27	3.2233	2.8014	0.3126	2.3309	0.5887	1.9468	0.8251	1.8068	0.9225	1.5979	1.0437	1.2392	1.2603	0.9495	1.4294	0.7119	1.5976	0.4632	1.7384	0.2429	1.8816	2.0357	3.4085	3.829	0.8587	0.8668
28	2.7518	2.3951	0.2672	1.9945	0.5037	1.6723	0.7088	1.5543	0.7936	1.3769	0.8994	1.0652	1.0833	0.818	1.2315	0.614	1.3779	0.399	1.4974	0.2099	1.6255	1.7588	2.8853	3.1965	0.8847	0.8944
29	2.2514	1.9582	0.2185	1.6394	0.4141	1.3802	0.585	1.2857	0.6565	1.1401	0.7447	0.884	0.8991	0.6804	1.0244	0.5124	1.1499	0.3346	1.2556	0.1757	1.3607	1.4761	2.3563	2.5593	0.9095	0.9181
30	1.9083	1.6664	0.1859	1.3945	0.3522	1.1738	0.4975	1.0953	0.5592	0.9723	0.6351	0.7581	0.771	0.5847	0.8803	0.4394	0.9861	0.2873	1.0783	0.1513	1.1718	1.2708	1.9895	2.1378	0.9256	0.9307
31	1.5353	1.3448	0.1501	1.1303	0.2855	0.9539	0.4043	0.8894	0.4541	0.7903	0.5162	0.6184	0.629	0.4773	0.7186	0.3596	0.8069	0.2353	0.8831	0.1241	0.9609	1.0437	1.5913	1.6867	0.9423	0.9497
32	1.2613	1.1061	0.1234	0.9338	0.2358	0.7875	0.3338	0.739	0.3773	0.6545	0.4275	0.5138	0.5225	0.3977	0.5987	0.3004	0.674	0.1969	0.7388	0.1039	0.8048	0.8745	1.3069	1.3654	0.9536	0.9673
33	1.0611	0.9326	0.1041	0.7876	0.1989	0.6668	0.2826	0.6206	0.3169	0.5545	0.3622	0.4338	0.4412	0.3358	0.5056	0.2531	0.5679	0.1661	0.6233	0.0877	0.6793	0.741	1.084	1.1348	0.9622	0.9755
34	0.8703	0.7649	0.0853	0.6466	0.1633	0.5485	0.2325	0.5143	0.2626	0.4569	0.2985	0.3606	0.3668	0.28	0.4215	0.2116	0.4749	0.1392	0.5224	0.0736	0.5698	0.6204	0.8967	0.9226	0.9692	0.9835
35	0.7434	0.6545	0.073	0.5537	0.1398	0.47	0.1992	0.44	0.2246	0.3917	0.2559	0.3084	0.3137	0.2395	0.3605	0.181	0.4062	0.1191	0.4468	0.0629	0.4872	0.5333	0.7589	0.7804	0.9742	0.9908
36	0.6472	0.5693	0.0635	0.4828	0.1219	0.4105	0.174	0.3861	0.1972	0.3428	0.2239	0.2721	0.2767	0.2116	0.3186	0.1602	0.3596	0.1056	0.3962	0.0559	0.4326	0.4707	0.6666	0.6765	0.9775	0.989
37	0.5723	0.5033	0.0562	0.4273	0.1079	0.3638	0.1542	0.3416	0.1744	0.3038	0.1984	0.241	0.2451	0.1875	0.2824	0.142	0.3187	0.0935	0.3508	0.0495	0.383	0.4179	0.5858	0.5953	0.9804	0.9985
38	0.5143	0.4521	0.0504	0.3839	0.097	0.3273	0.1387	0.3089	0.1577	0.2735	0.1787	0.2179	0.2216	0.1698	0.2556	0.1286	0.2886	0.0849	0.3186	0.0449	0.3481	0.3798	0.5297	0.5325	0.9823	1.002
39	0.462	0.4057	0.0453	0.3448	0.0871	0.2947	0.1249	0.2786	0.1422	0.2467	0.1611	0.1974	0.2008	0.154	0.2318	0.1168	0.262	0.077	0.2891	0.0408	0.3158	0.3433	0.4792	0.4785	0.9841	1.0031
40	0.4276	0.3767	0.042	0.3204	0.0809	0.2733	0.1158	0.2557	0.1305	0.2287	0.1494	0.1812	0.1843	0.1412	0.2126	0.1066	0.2393	0.0701	0.2632	0.0371	0.2877	0.315	0.4343	0.4402	0.9856	1.0052

Table 2. Pitzer Parameters of the Ternary System LiBr–$CaBr_2$–H_2O at 373.15 K

parameters	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	θ	ψ
LiBr	0.199195	0.212146	-0.002894		
$CaBr_2$	0.392885	-0.850955	-0.011123		
Li,Ca				0.136523	
Li,Ca,Br					-0.009101

Table 3. Values of the Fitting Coefficients *a* (eq5) for Pitzer Parameters and lnK_{sp} for LiBr–H_2O System

parameters	a_1	a_2	a_3	a_4
$\beta^{(0)}$(LiBr)	-57.334219	0.013541	-1651.603383	-9.756044
$\beta^{(1)}$(LiBr)	-330.567565	-0.090580	8141.268875	57.888453
C^{φ}(LiBr)	-10.954620	-0.002544	332.937772	1.859310
lnK(LiBr·H_2O)	-3784.643890	-0.628060	136626.252489	619.539862
lnK(LiBr·2H_2O)	-1423.358269	-0.264634	48652.607829	237.093924
lnK(LiBr·3H_2O)	802.973698	0.317685	-15153.014253	-146.952014

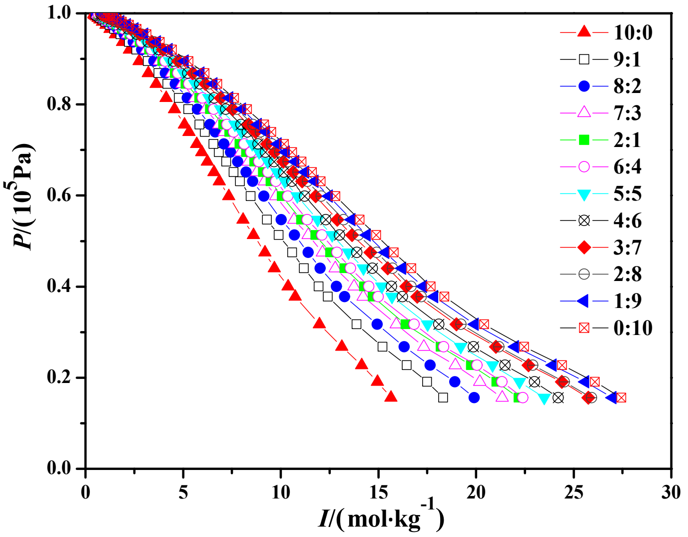


Figure 1. Vapor pressures vs ionic strength of the LiBr–$CaBr_2$–H_2O system at 373.15 K.

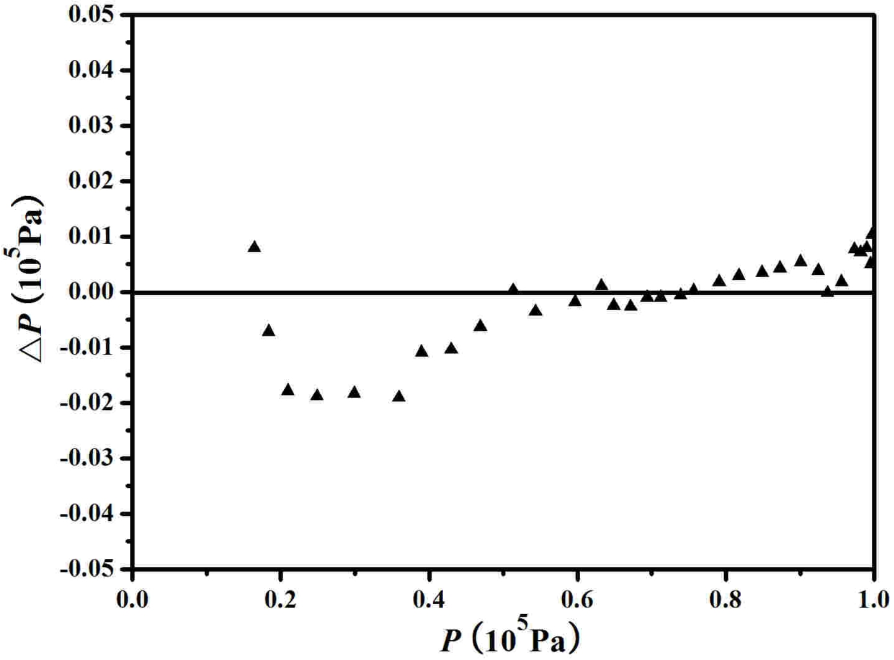


Figure 2. Deviation of experimental vapor pressure and calculated results in the ternary system calculated by equation (3) at 373.15 K.

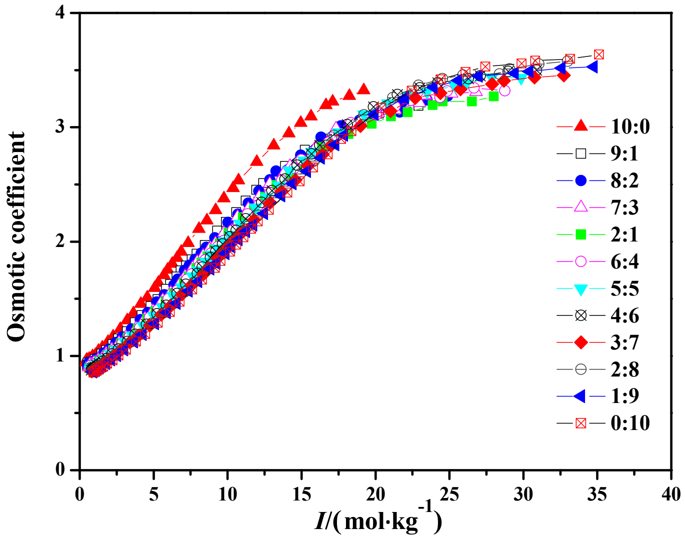


Figure 3. Measured osmotic coefficients of the LiBr–CaBr$_2$–H$_2$O system at 373.15 K.

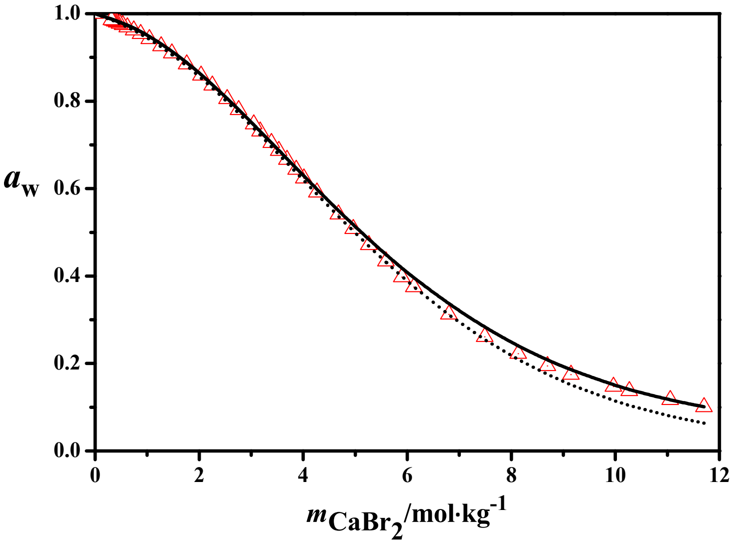


Figure 4. Water activities of the system CaBr$_2$–H$_2$O at 373.15 K.△,experimental data in this work; —, model values calculated with parameters in this work; …, model values calculated with parameters from ref. 18.

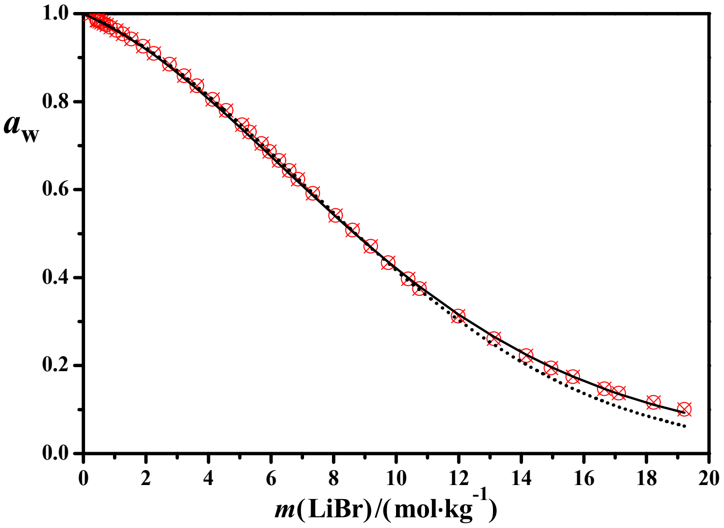


Figure 5. Water activities of the system LiBr–H_2O at 373.15 K. △, this work; —, model values calculated with parameters from Table 2 in this work; …, model values calculated with the fitted parameters from Table 3 in this work.

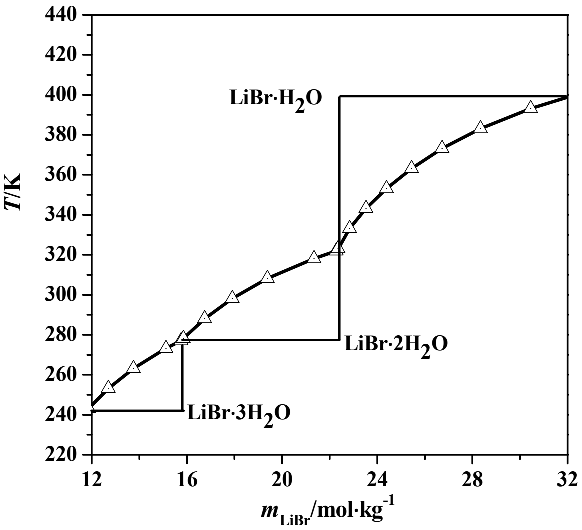


Figure 6. Phase diagram of LiBr–H_2O system from 222.4 K to 429.15 K. △, model values calculated from ref. 6; —, model values calculated with Pitzer and HW model in this work.

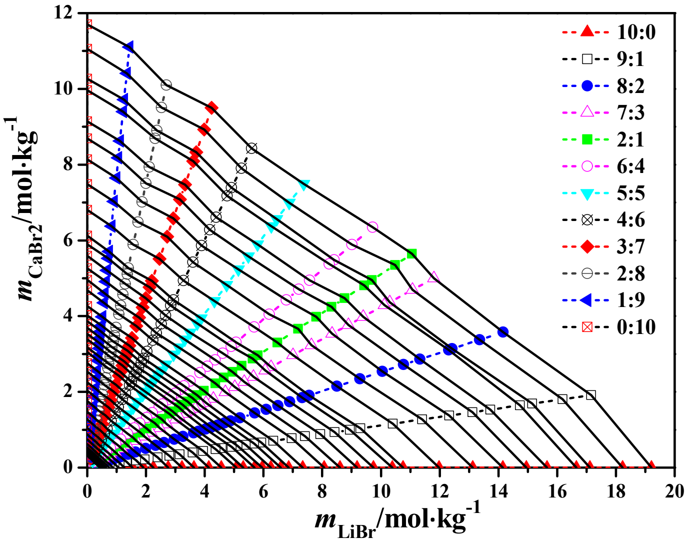


Figure 7. Experimental equal-water activity lines in theLiBr–$CaBr_2$–H_2O system at 373.15 K. —, lines with same water activity; …, lines with same Y_{LiBr}.

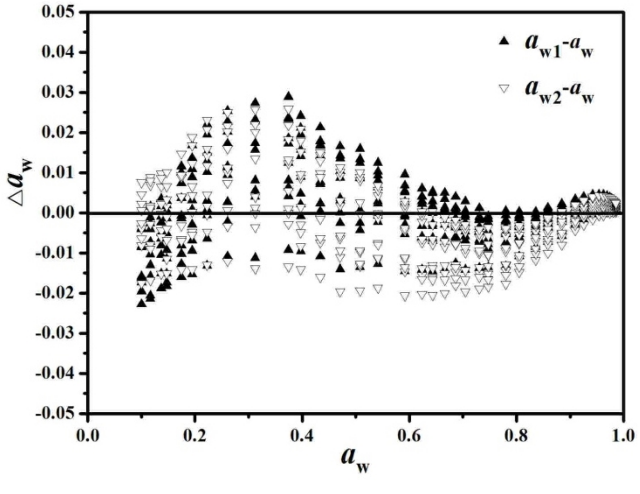
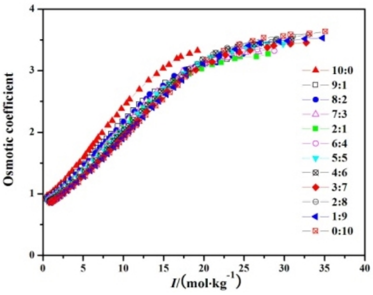


Figure 8. Deviation of experimental water activities and calculated results in the theLiBr–$CaBr_2$–H_2O system.▲, a_{w1}–a_w; ▽, a_{w2}–a_w.

TOC Graphic


Osmotic coefficient
0
1
2
3
4
0
5
10
15
20
25
30
35
40
I/(mol·kg^{-1})
10:0
9:1
8:2
7:3
2:1
6:4
5:5
4:6
3:7
2:8
1:9
0:10