J. Chem. Eng. Data **1995,** *40,* 828–832

Thermodynamic Properties of the Na–K–Ca–Ba–Cl–H_2O System to 473.15 K and Solubility of Barium Chloride Hydrates

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Pitzer's ion interaction parameters for aqueous barium chloride are derived as a function of temperature from published parameter values for the activity coefficient and for the enthalpy at 298.15 K, and by fitting osmotic coefficients measured by Holmes and Mesmer (*J. Chem. Thermodyn.* **1981**, *13*, 1025) to 473.61 K. This allows the calculation of the thermodynamic properties of barium chloride solutions including the $BaCl_2(aq)$ activity coefficient and the activity of water. Barium chloride mono- and dihydrate solubilities in pure water are used to calculate their solubility products at various temperatures. Solubility data of barium chloride dihydrate in the Na–K–Ca–Ba–Cl–H_2O system are used to calculate Pitzer's mixing parameters. It is shown that the solubility of $BaCl_2{\cdot}2H_2O(s)$ in this system can be accurately predicted to high concentration using the resulting parameters.

Introduction

The accurate calculation of the thermodynamic properties of barium ion in natural waters requires characterization of its interaction with chloride, the most common anion found in natural aqueous solutions. A number of papers (*2, 4, 6, 7*) have already focused on the thermodynamic properties of aqueous barium chloride within the framework of Pitzer's ion interaction approach (*1*). These include Gibbs free energy (activity and osmotic coefficients) (*2, 4*), apparent molal enthalpy and related calorimetric measurements (heat of dilution and heat of solution) (*7*) at 298.15 K, and osmotic coefficients from isopiestic measurements up to 473 K (*6*). Despite these studies, no comprehensive model currently exists for correlating the available data for aqueous barium chloride over as large a temperature range as possible. In this paper such an expression is derived for $BaCl_2(aq)$ in order to calculate the thermodynamic properties (activity and osmotic coefficients) of aqueous barium chloride solutions as well as the solubility of barium chloride hydrates in electrolyte solutions. The solubility products of barium chloride mono- and dihydrates are calculated as a function of temperature from their solubilities in pure water. This information for barium chloride combined with Moller's (*17*) high-temperature model of the Na–K–Ca–Cl–H_2O system (*9–13*) allows a model for the solubility of barium chloride hydrates in this system to be built. It is used to calculate Pitzer's mixing parameters for Ba with Na, K, or Ca from solubility data in ternary systems with a common ion (*9–13*). The model is finally tested by comparing predicted and measured (*9–13*) solubilities of $BaCl_2{\cdot}2H_2O$ in the Na–Ca–Ba–Cl–H_2O and in the K–Ca–Ba–Cl–H_2O systems.

Activity and Osmotic Coefficients of Aqueous Barium Chloride in the $BaCl_2$–H_2O System

Pitzer's binary interaction parameters for $BaCl_2(aq)$ (i.e., $\beta^{(0)}_{BaCl}$, $\beta^{(1)}_{BaCl}$, and C^{Φ}_{BaCl}) at 298.15 K have been reported in two recent papers (*1, 4*). These parameters are based on two different sets of critically evaluated thermodynamic properties of aqueous solutions as a function of concentration: those of Robinson and Stokes (*3*) and of Goldberg and Nuttall (*5*). Pitzer (*1*) reports the values determined by Pitzer and Mayorga (*2*) from a fit to the older Robinson and Stokes (*3*) data, while Kim and Frederick (*4*) recently proposed a new set of parameters for $BaCl_2(aq)$ based on a fit of Goldberg and Nuttall's (*5*) data. The smoothed values reported by Goldberg and Nuttall are based on a critical evaluation of a broader data set than the one used by Robinson and Stokes. There is a slight difference between the Robinson and Stokes and the Goldberg and Nuttall resulting values, amounting to about 3% in the barium chloride activity coefficient in binary solutions. For example, Robinson and Stokes report a value of 0.439 for the $BaCl_2(aq)$ activity coefficient in a 1.6 $mol{\cdot}kg^{-1}$ solution, while Goldberg and Nuttall give 0.4273. This slight discrepancy leads to the differences in Pitzer's interaction parameters at 298.15 K reported by Pitzer and Mayorga and by Kim and Frederick. At higher temperatures, Holmes and Mesmer (*6*) report $BaCl_2(aq)$ interaction parameters at individual temperatures from 383 to 473 K based on fits of their own isopiestic measurements. The first derivatives with respect to temperature of Pitzer's ion interaction parameters for the activity and osmotic coefficients have been obtained for 298.15 K by Silvester and Pitzer (*7*) from calorimetric data (enthalpies of dilution and of dissolution).

The following empirical expression has been chosen here to represent the interaction parameters $\beta^{(0)}_{BaCl}$, $\beta^{(1)}_{BaCl}$, and C^{Φ}_{BaCl} as a function of temperature:

$$X(T) = X(T_0) + (\partial X/\partial T)_{T_0}(T - T_0) + p_1F_1(T) + p_2F_2(T) + p_3F_3(T) \quad (1)$$

with $X = \beta^{(0)}_{BaCl}$, $\beta^{(1)}_{BaCl}$, or C^{Φ}_{BaCl}, and

$$F_1(T) = \frac{T_0}{T} - 1 + \ln\left(\frac{T}{T_0}\right)$$

$$F_2(T) = 2T_0^{\,3}/T - 3T_0^{\,2} + T^2$$

$$F_3(T) = 3T_0^{\,4}/T - 4T_0^{\,3} + T^3$$

The F_i functions and their first derivatives with respect to temperature are zero at $T = T_0 = 298.15$ K. This allows known and well-determined values of $X(T_0)$ and of $(\partial X/\partial T)_{T_0}$ to be used in eq 1. In this work, $\beta^{(0)}_{BaCl}$, $\beta^{(1)}_{BaCl}$, and C^{Φ}_{BaCl} at 298.15 K are taken from Kim and Frederick (*4*) and

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Table 1. Coefficients of Eq 1 for $\beta^{(0)}_{\mathrm{BaCl}}$, $\beta^{(1)}_{\mathrm{BaCl}}$, and C^{Φ}_{BaCl}

	$X = \beta^{(0)}_{\mathrm{BaCl}}$	$X = \beta^{(1)}_{\mathrm{BaCl}}$	$X = C^{\Phi}_{\mathrm{BaCl}}$
$X(\mathrm{T}_0)^a$	0.29073	1.24998	−0.03046
$(\partial X/\partial T)_{\mathrm{T}_0}{}^b$	0.6375	3.225	−0.1537
$p_1{}^c$	−5.302131	15.87517	3.903953
$p_2{}^c$	4.608725×10^{-6}	-6.77403×10^{-6}	-1.10262×10^{-5}
$p_3{}^c$	0	0	8.761508×10^{-9}

[a] Reference 4. [b] Reference 7. [c] This work.

$\partial\beta^{(0)}_{\mathrm{BaCl}}/\partial T)_{T_0}$, $(\partial\beta^{(1)}_{\mathrm{BaCl}}/\partial T)_{T_0}$, and $\left(\partial C^{\Phi}_{\mathrm{BaCl}} / \partial T\right)_{T_0}$ are from Silvester and Pitzer (*7*). Raju and Atkinson (*19*) have chosen to equate $BaCl_2$(aq) properties at high temperature to those for calcium chloride. Instead, in this work, the parameters p_i in eq 1 are obtained by fitting osmotic coefficients of $BaCl_2$ solutions (*6*). Following the procedure used by Holmes and Mesmer (*6*), these osmotic coefficients have been calculated from the experimental isopiestic molalities and from the osmotic coefficients of the NaCl reference solutions calculated from the model of Silvester and Pitzer (*22*). All the coefficients of eq 1 are reported in Table 1.

The standard deviation of the fit of the whole data set (Goldberg−Nuttall and Holmes−Mesmer) with the parameters of Table 1 is 0.0025. The standard deviations in the global fit for the data sets at 383, 413, 444, and 473 K are, respectively, 0.0019, 0.0024, 0.0031, and 0.0044. These values are essentially the same as those obtained by fitting the data at each temperature (*6*) except for 383 K. For this temperature, the global fit gives a standard deviation in the osmotic coefficient of 0.0019 which is about twice that of the isothermal fit (0.0007).

Additional experimental data are reported by Apelblat (*14*) who derived the water activity of saturated barium chloride solutions (a_w) from vapor pressure measurements. At 298.15 K he reports a value of 0.912 for a_w while Goldberg and Nuttall give 0.9027 (the present model leads to 0.9032). The slight discrepancy between the solubilities given by the two researchers (1.785 versus 1.774 mol·kg^{-1}) cannot account for the difference in a_w. At temperatures above 298.15 K, Apelblat's water activities are larger than the values calculated in the present study (with a largest difference of 0.02 at 303 K), while they are lower at temperatures from 283 to 298 K (by about 0.022 at 283 K). The reasons for the difference between water activities reported by Apelblat and those generated in the present study are unclear.

Solubility Products of $BaCl_2{\cdot}2H_2O$(s) and of $BaCl_2{\cdot}H_2O$(s)

Barium chloride solubilities in pure water are given by Linke (*8*) who reports that $BaCl_2{\cdot}2H_2O$(s) dehydrates to the monohydrate $BaCl_2{\cdot}H_2O$(s) at 375 K. At 543 K it dehydrates again to give anhydrous barium chloride, but this is outside the temperature range within which eq 1 is valid. The solubilities reported in Linke at rounded temperatures to 453 K have been used together with eq 1 and the parameters of Table 1 to calculate the solubility products of the barium chloride mono- and dihydrates. These results are reported as a function of reciprocal temperature in Figure 1. The curvature of the two plots shows the influence of the heat capacity of the dissolution reaction.

If the heat capacity of the dissolution reaction is taken to be constant over the considered temperature range, integration of the Gibbs−Helmholtz equation gives

$$\ln K_{\mathrm{sp}} = A + B \ln(T/\mathrm{K}) + C/(T/\mathrm{K}) \qquad (2)$$

with

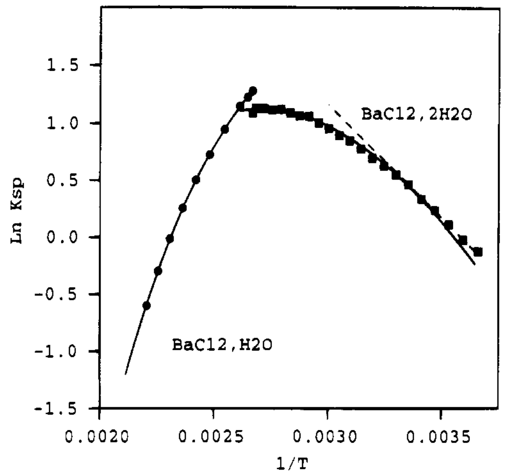

Figure 1. Arrhenius plot of the solubility products of barium chloride hydrates. The solid curves are calculated from eq 4 for the dihydrate and eq 5 for the monohydrate. The dashed line is calculated with $\Delta_r H^\circ = 16.52$ kJ·mol^{-1} (*15*) and $\Delta_r C_p^\circ = 0$.

$$A = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r C_p^\circ}{R}[1 + \ln(T_0/\mathrm{K})]$$

$$B = \Delta_r C_p^\circ / R$$

$$C = -\frac{\Delta_r H^\circ}{R} + \frac{T_0 \Delta_r C_p^\circ}{R}$$

It was not possible to fit the $BaCl_2{\cdot}2H_2O$(s) solubility product values between 273 and 395 K with eq 2, i.e., without including a temperature dependent heat capacity of reaction. A linear variation of the heat capacity of reaction is nevertheless sufficient to reproduce the solubility product values over the whole temperature range with a standard deviation of fit of 0.012 in $\ln K_{\mathrm{sp}}$. This leads to the following expression of the $BaCl_2{\cdot}2H_2O$(s) solubility product from 273.15 to 375.15 K:

$$\ln K_{\mathrm{sp}} = -613.6842 - 0.2069221(T/\mathrm{K}) + 12946.55/(T/\mathrm{K}) + 110.9967 \ln(T/\mathrm{K}) \qquad (3)$$

The values of the enthalpy and entropy of reaction derived from eq 3 are slightly different from the NBS values (Table 2).

When only the solubility product values between 298 and 395 K are considered, they can be fit with a standard deviation of 0.015 using eq 2 (constant heat capacity of reaction). It leads to the following expression:

$$\ln K_{\mathrm{sp}} = 194.2291 - 10303.78/(T/\mathrm{K}) - 27.94534 \ln(T/\mathrm{K}) \qquad (4)$$

The values of the enthalpy and entropy of the dissolution reaction obtained from eq 4 are in very good agreement with the NBS values (Table 2). The fact that the inclusion of the solubility product values between 273 and 298 K in the fit leads to this discrepancy in the standard thermodynamic properties of reaction when compared to the NBS data can be attributed either to a bias in the measured solubility (*8*) of $BaCl_2{\cdot}2H_2O$ below 298.15 K or to inadequate calculation of the thermodynamic properties of $BaCl_2$ solutions at these temperatures. This latter hypothesis would mean that the extrapolation of eq 1 to 273.15 K does not lead to accurate values of the $BaCl_2$(aq) activity coefficient and the activity of water of the binary solutions. This extrapolation is primarily constrainted by the values

Table 2. Standard (298.15 K, 1 bar) Thermodynamic Properties of the Dissolution Reaction of $BaCl_2{\cdot}2H_2O(s)$

	eq 3	eq 4	NBS (*15*)
Δ_rH° (kJ·mol^{-1})	14.6 ± 0.5	16.39 ± 0.04	16.52
Δ_rS°/R	6.3 ± 0.3	7.06 ± 0.02	7.6
$\Delta_rC_p^\circ/R$	−12.4 ± 0.3	−27.95 ± 0.01	

of $(\partial\beta^{(0)}_{BaCl}/\partial T)_{T_0}$, $(\partial\beta^{(1)}_{BaCl}/\partial T)_{T_0}$, and $(\partial C^{\Phi}_{BaCl}/\partial T)_{T_0}$ obtained from enthalpy data by Silvester and Pitzer (*7*). Nevertheless, this inaccuracy does not lead to a large uncertainty in the $BaCl{\cdot}2H_2O$ calculated solubility at temperatures below 298.15 K: for example, the value at 273.15 K calculated with eq 4 is 1.43 mol·kg^{-1}, which compares well with the measured values (*8*) of 1.50 mol·kg^{-1}.

The solubility product values of $BaCl_2{\cdot}H_2O(s)$ between 375.15 and 453.15 K are given by the following equation ($\sigma = 0.005$):

$$\ln K_{sp} = 334.1864 - 16071.20/(T/K) - 48.93717\ \ln(T/K) \quad (5)$$

In what follows, the solubility products of barium chloride hydrates and the thermodynamic model for $BaCl_2(aq)$ are used to calculate the solubilities of barium chloride hydrates in chloride solutions to high concentrations.

Na−Ba−Cl−H₂O System

In this system, the interaction between the two cations is unsymmetrical. It has been shown (*21*) that the contribution of higher-order electrostatic terms to the thermodynamic properties of unsymmetrical mixtures is important. θ_{ij}, the parameter representing the interaction between cations i and j, can be expressed in Pitzer's formalism as (*21*)

$$\theta_{ij} = {}^{s}\theta_{ij} + {}^{E}\theta_{ij}(I) \quad (6)$$

In this expression, ${}^{s}\theta_{ij}$ is an adjustable parameter while ${}^{E}\theta_{ij}(I)$ is a complex function of the ionic strength and of the charges of ions i and j (*21*). The influence of ${}^{E}\theta_{ij}(I)$ is here illustrated by solubility calculations for the Na−Ba−Cl−H_2O system.

Calculation of the barium chloride activity coefficient in NaCl solutions requires Pitzer's binary parameters for NaCl interactions. These are taken from Moller (*17*) who also reports values of ${}^{s}\theta_{NaBa}$ and ψ_{NaBaCl} to 523 K obtained from a fit of $BaSO_4$ (barite) solubility in sodium chloride solutions. ψN_{aBaCl} was set equal to zero, and ${}^{s}\theta_{NaBa}$ was found to vary with temperature. Pitzer's mixing parameters, such as ${}^{s}\theta_{NaBa}$ and ψ_{NaBaCl}, can be best retrieved from the thermodynamic properties of ternary systems with a common ion like Na−Ba−Cl−H_2O at high concentrations.

Lanier (*16*) used cation-sensitive electrodes to measure NaCl activity coefficients in $BaCl_2$ solutions to ionic strengths of 5 mol·kg^{-1}. Alternatively measurement of $BaCl_2{\cdot}2H_2O(s)$ solubility in sodium chloride solutions (*9*) can also be used to evaluate these mixing parameters. It was found that it was not possible to satisfactorily fit Lanier's data and the solubility data reported by Mozharova et al. (*9*) using a single set of parameters.

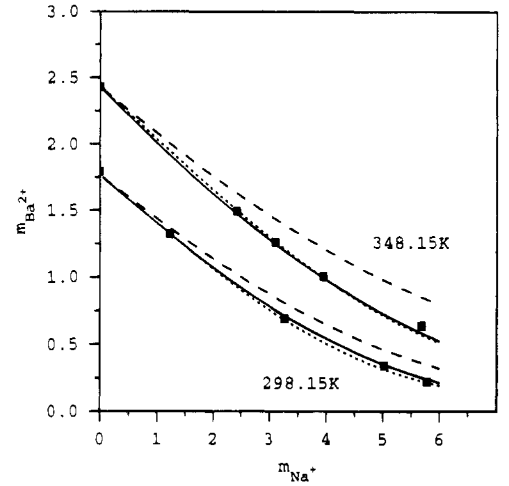

Figure 2. Solubility of barium chloride dihydrate in sodium chloride solutions: filled squares, measured values at 298.15 and 348.15 K (*9*); dotted curve, calculated from the sole binary parameters and without the higher-order electrostatic mixing terms ${}^{E}\theta(I)$; dashed curve, calculated with ${}^{s}\theta_{NaBa} = \psi_{NaBaCl} = 0$ and ${}^{E}\theta(I)$; solid curve, calculated with ${}^{s}\theta_{NaBa} = 0$, $\psi_{NaBaCl} = 0.0128$ and ${}^{E}\theta(I)$.

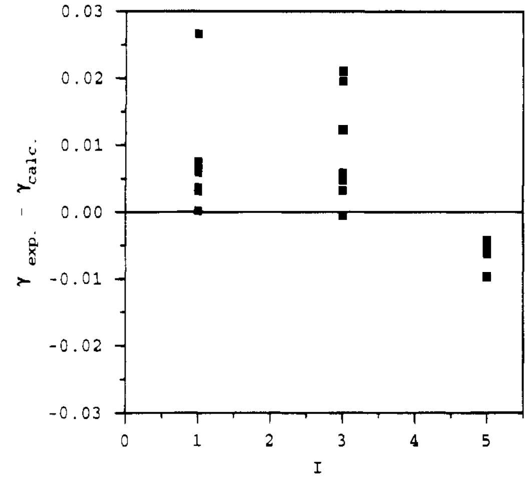

Figure 3. Difference between the activity coefficient of NaCl in barium chloride solutions measured by Lanier (*16*) and values calculated with ${}^{s}\theta$(Na,Ba) = 0.0 and ψ(Na,Ba,Cl) = 0.0128 versus the solution ionic strength.

Three types of solubility calculations were carried out: (1) $BaCl_2{\cdot}2H_2O(s)$ solubility calculated from the binary parameters alone (no ${}^{E}\theta(I)$ terms in the activity coefficient expression), (2) solubility calculated including ${}^{E}\theta(I)$ with ${}^{s}\theta_{NaBa}$ and ψ_{NaBaCl} set to zero, (3) solubility calculated including ${}^{E}\theta(I)$ with ${}^{s}\theta_{NaBa}$ and ψ_{NaBaCl} fitted to the data. In the case of the Na−Ba−Cl−H_2O system, the solubilities calculated from the binary parameters alone without ${}^{E}\theta_{ij}(I)$ are in good agreement with the measured values (dotted curves in Figure 2). The inclusion of the electrostatic terms ${}^{E}\theta(I)$ (*21*) has a large influence on the calculated solubilities, which are too high in this case (dashed curves in Figure 2). This difference can be compensated by keeping ${}^{s}\theta_{NaBa}$ equal to zero and by adjusting ψ_{NaBaCl} to the solubility data (*9*), as suggested by Pitzer (*1*). This gives $\psi_{NaBaCl} = 0.0128$. When these parameter values are used to calculate the activity coefficient of NaCl in $BaCl_2$ solutions, the plot of residuals (calculated minus measured values in Figure 3) shows that the results are a few percent higher than Lanier's measurements. It can be seen in Figure 2 that barium chloride dihydrate solubility in NaCl solutions at 348.15 K can be predicted with an excellent accuracy by keeping ${}^{s}\theta_{NaBa}$ and ψ_{NaBaCl} independent of temperature.

The same results as for 298.15 and 348.15 K have been found for the solubility data at 293.15 and 303.15 K (*8*): calculation of $BaCl_2{\cdot}2H_2O$ solubility is greatly improved by adopting ${}^{s}\theta_{NaBa} = 0$ and $\psi_{NaBaCl} = 0.0128$. These results are not reported in Figure 2 for clarity.

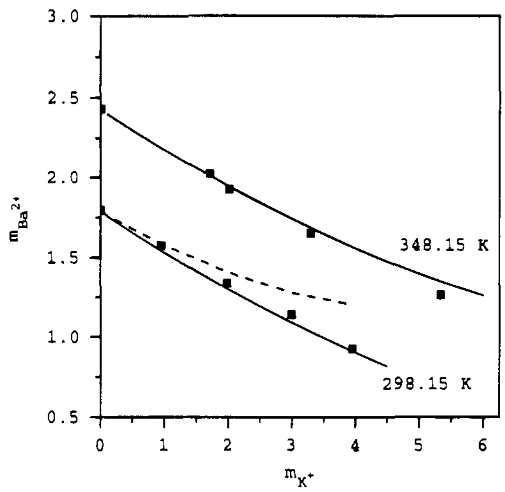

Figure 4. Solubility of barium chloride dihydrate in KCl solutions at 298.15 and 34815 K. The black squares are the measured values (*9*). The solid curves are calculated with ${}^s\theta(K,Ba) = \psi(K,Ba,Cl) = 0$. The dashed curve is calculated with $\theta(K,Ba) = 0.0304$ and $\psi(K,Ba,Cl) = -0.027$ (*20*).

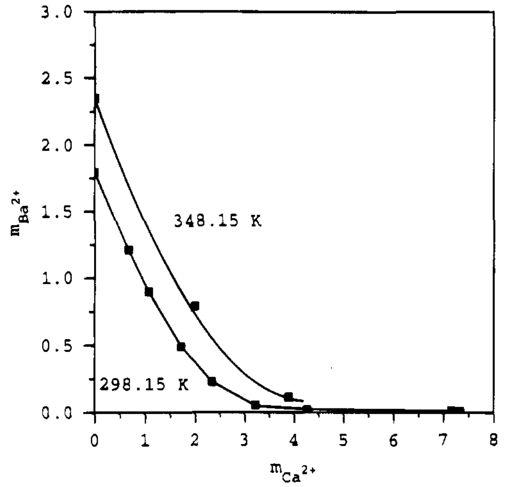

Figure 5. Solubility of barium chloride dihydrate in $CaCl_2$ solutions at 298.15 and 348.15 K. The black squares are the measured values (*10, 11*). The curves are calculated with ${}^s\theta(Ca,Ba) = \psi(Ca,Ba,Cl) = 0$.

K–Ba–Cl–H_2O, Ca–Ba–Cl–H_2O, K–Ca–Ba–Cl–H_2O, and Na–Ca–Ba–Cl–H_2O Systems

Again all the required binary parameters for KCl and $CaCl_2$ as well as the ternary parameters involving Na–Ca, K–Ca, etc. interactions are taken from Moller (*17*). The solubility of sodium, barium, and calcium chlorides in these systems are reported by Rashkovskaya et al. (*10–13*). These data can be used to determine the mixing parameters ${}^s\theta_{KBa}$, ψ_{KBaCl}, ${}^s\theta_{CaBa}$, and ψ_{CaBaCl}.

Figures 4 and 5 show that $BaCl_2{\cdot}2H_2O(s)$ solubility in potassium or calcium chloride solutions at 298.15 and 348.15 K can be predicted with a very good accuracy from the $BaCl_2{\cdot}2H_2)(s)$ solubility product and the sole binary interaction parameters for aqueous KCl, $CaCl_2$, and $BaCl_2$. The mixing parameters ${}^s\theta_{KBa}$, ψ_{KBaCl}, ${}^s\theta_{CaBa}$, and ψ_{CaBaCl} are set to zero in these calculations, but the ${}^E\theta(I)$ terms are included. Alternate values of ${}^s\theta_{KBa}$ and ψ_{KBaCl} have been obtained by Reddy and Ananthaswamy (*20*) from electromotive force (emf) measurements, but the $BaCl_2{\cdot}2H_2O(s)$ solubilities calculated with these values are in poor agreement with experimental data (Figure 4). Emf and solubility data lead to different values of the mixing parameters, as already found for the Na–Ba–Cl–H_2O system.

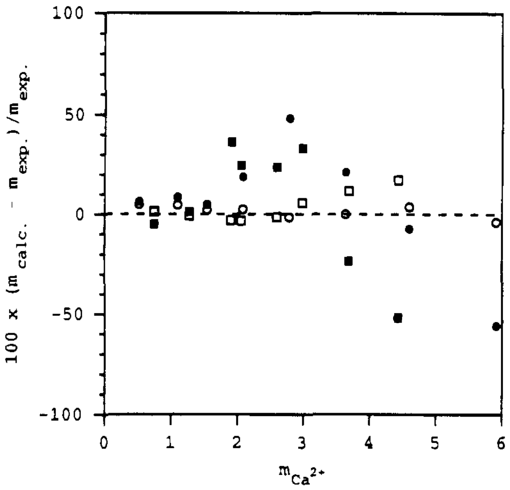

Figure 6. Difference between calculated and measured (*10, 11*) molalities of K (open symbols) and Ba (black symbols) for $CaCl_2$ solutions at equilibrium with $BaCl_2{\cdot}2H_2O(s)$ and KCl(s) at 298.15 (squares) and 348.15 K (circles).

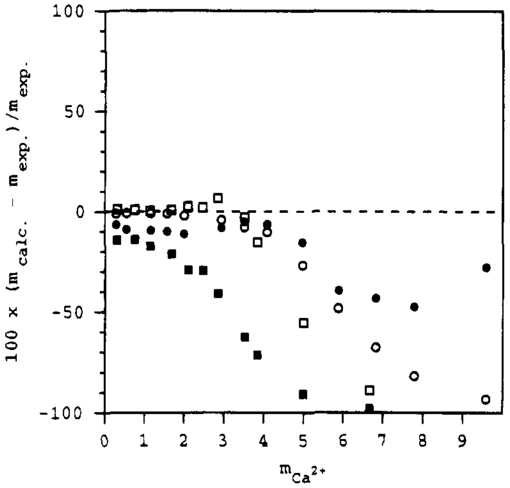

Figure 7. Difference between calculated and measured (*12, 13*) molalities of Na (open symbols) and Ba (black symbols) for $CaCl_2$ solutions at equilibrium with $BaCl_2{\cdot}2H_2O(s)$ and NaCl(s) at 298.15 (squares) and 348.15 K (circles).

It must be noted that the vertical scale of Figure 5 is misleading. It hides the deterioration of the accuracy of the calculated solubilities for $CaCl_2$ molalities above 4 mol·kg^{-1}. In fact for the two points at concentrations above 7 mol·kg^{-1}, the calculated solubilities are about 20 times lower than the measured values, which is not apparent in the figure due to the strong lowering of barium chloride solubility by the common ion effect. This discrepancy is due to the peculiar behavior of $CaCl_2$ above about 4 mol·kg^{-1} (*18*) which is not accounted for by Moller's model for this salt (*17*).

The solubilities of potassium, barium, calcium, and sodium chlorides in the K–Ca–Ba–Cl–H_2O system (*10, 11*) and in the Na–Ca–Ba–Cl–H_2O system (*12, 13*) have been measured at 298.15 and 348.15 K by Rashkovskaya et al. As these solubilities can be predicted from all the parameters determined above, they constitute a further test of the present model. The results are given in Figure 6 for the simultaneous solubilities of KCl and of $BaCl_2{\cdot}2H_2O$ in $CaCl_2$ solutions at 298.15 and 348.15 K. A close agreement can be seen between the measured and the calculated solubilities of KCl(s) in these systems at both 298.15 and 348.15 K. In contrast $BaCl_2{\cdot}2H_2O(s)$ solubility is poorly calculated at $CaCl_2$ concentrations in excess of 1.5 mol·kg^{-1}: the deviation from the measured values increases to about +50% at 3 mol·kg^{-1} and then decreases at greater calcium concentrations.

Figure 7 shows that the solubilities of NaCl at 298.15 and 348.15 K and of $BaCl_2·2H_2O(s)$ at 348.15 K in the Na−Ca−Ba−Cl−H_2O system are calculated within about 10% at calcium concentrations to 4 mol·kg^{-1}. As found for simpler systems, the discrepancy increases above this limit. At 348.15 K the calculated $BaCl_2·2H_2O(s)$ solubilities are too low when compared to the measured values, with the difference increasing with the Ca concentration.

Conclusions

Pitzer's ion interaction parameters for aqueous barium chloride derived in this study allow the calculation of the thermodynamic properties of $BaCl_2$ solutions to 473.15 K. The solubility products of barium chloride mono- and dihydrates have been obtained from their solubilities in pure water at various temperatures. It was necessary to only fit ψ_{NaBaCl} in order to accurately calculate $BaCl_2·2H_2O$ solubilities in ternary systems with a common ion (Na−Ba−Cl−H_2O, K−Ba−Cl−H_2O, Ca−Ba−Cl−H_2O) or in the more complex Na−Ca−Ba−Cl−H_2O and K−Ca−Ba−Cl−H_2O systems.

Acknowledgment

I would like to thank Professor K. S. Pitzer and Eric Oelkers for their comments on the paper and for language corrections.

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Received for review October 31, 1994. Revised February 24, 1995. Accepted March 21, 1995.[⊗]

JE940229S

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1995.