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Thermodynamics of the Calcium-Containing Brine Systems

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There are more than 700 salt lakes with area of more than 1km^2 on the Qinghai-Tibet Plateau of China. In recent years, an oilfield brine was also found in the Nanyishan Section of Qaidam Basin in the Qinghai-Tibet Plateau. The hydrochemistry of the oilfield brine is of the calcium chloride type with high concentrations of lithium, sodium, potassium, calcium and borate ions. The oilfield brine belongs to the complex seven-component system (Li^+, Na^+, K^+, Ca^{2+} //Cl^-, SO_4^{2-}, $B_4O_7^{2-}$–H_2O) (Fu et al., 2005). Although these oilfield brine resources are very abundant and valuable, nothing has been reported on its comprehensive utilization for lacking the relative solubility and phase diagrams of the calcium-bearing systems, especially the corresponding thermodynamic properties data.

In order to exploiting the oilfield brine resources in Nanyishan Section effectively, some work and corresponding investigations have been done till now. In previous work, more attentions were paid on calcium chloride because it is a major composition of natural aqueous systems and plays an important role in many industrial and biological areas (Ananthaswamyt and Atklnson, 1985). However, with the type of calcium brines are widely discovered in recent years, more works on the thermodynamic properties of those calcium compounds in the different systems at specific conditions such as isopiestic molalities, water activities, ionic strength, heat capacity, activity, enthalpies of dilution, heat of mixing, enthalpies, and so on were done under the specific conditions. The relative thermodynamic parameters for the calcium-containing systems investigated are shown in Table 1.

It is worth mentioning that Guendouzi (2009) from Université Hassan II Mohammedia had studied the quaternary aqueous solutions of chlorides charge-type 1-1, 2-1, and 2-1 with a cation (Na^+, NH_4^+, Mg^{2+}, Ca^{2+}) by the hygrometric method at 298.15 K and measured the water activities (a_w) and ratio ionic–strength (z) at the same time. The results showed that the obtained data allow the deduction of osmotic coefficients. In addition, to evaluate the mixing ionic parameters for quaternary systems, the ionic interaction model was established, the activity coefficients of different solutes in the quaternary aqueous solutions were calculated and the calculated values agreed well with experimental data. D. Saad et al. (1980) had reported activity coefficients and thermodynamics osmotic coefficients of the aqueous quaternary system (Na^+, K^+, Ca^{2+}//Cl^-–H_2O) at 298 K by the isopiestic measurements. The results showed good agreement with those obtained by pseudo-ternary transforms.

The thermodynamic data is essential to predict the

Table 1 The thermodynamic properties of the different systems under specific conditions

System	Thermodyn. property	Conditions	Refs
$MgCl_2$-$CaCl_2$	$\triangle H_{mix}$	I=3 T=298.03K	(Wood et al.,1966)
$CaCl_2$-$SrCl_2$	$\triangle H_{mix}$	I=3 T=298.03K	(Wood et al.,1966)
$CaCl_2$-$BaCl_2$	$\triangle H_{mix}$	I=3 T=298.03K	(Wood et al.,1966)
$MgBr_2$-$CaBr_2$	$\triangle H_{mix}$	I=3 T=298.03K	(Wood et al., 1966)
$CaCl_2$-$CaBr_2$	$\triangle H_{mix}$	I=3 T=298.03K	(Wood et al.,1966)
$MgCl_2$-$CaBr_2$	$\triangle H_{mix}$	I=3 T=298.03K	(Wood et al.,1966)
$CaCl_2$	C_p, Φ	P=17.5MPa, T=306-603K	(White et al., 1987)
$CaCl_2$	$\triangle_{dil}H_m$, Φ	P=7-40MPa, T=298-526K	(Holmes et al.,1994)
NaCl-$CaCl_2$	$\triangle_{dil}H_m$, Φ	P=21.5MPa, T=373-573K	(Oakes et al., 1998)
NH_4Cl-$MgCl_2$-$CaCl_2$-H_2O	Φ, a_w	T=298.15K	(Mohamed et al., 2009)
NaCl-$CaCl_2$- H_2O	Φ, a_w	T=308.15K	(Deng et al., 2010)
NaCl- KCl-$CaCl_2$-H_2O	Φ	I=0.9-5.7mole·kg^{-1} T=298.03K	(Saad et al., 1980)
$CaCl_2$	$\gamma_{\pm}$, Φ	C=0-10mol·kg^{-1} T=298.15K	(Bert et al., 1977)

Note: $\triangle H_{mix}$, heat of mixing; $C_{p,\Phi}$, heart capacity; $\triangle_{dil}H_m$, enthalpies; Φ, isopiestic molalities; a_w, water activities; I, ionic strength; T, temperature; p, Pressure; $\gamma_{\pm}$, mean activity.

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solubilities, and some relative works have been done by scientists. Greenberg and Moller (1989) had predicted the mineral solubilities in natural waters using a chemical equilibrium model for the Na^+, K^+, Ca^{2+}//Cl^-, SO_4^{2-}–H_2O system from zero to high ionic strength with the temperatures from 273 K to 523 K. Then the relative data parameterized through fitting available osmotic and solubility data in all common ion systems (Na^+, K^+//Cl^-–H_2O, Na^+, K^+//SO_4^{2-}–H_2O, K^+//Cl^-, SO_4^{2-}–H_2O, K^+, Ca^{2+}// Cl^-–H_2O and K^+, Ca^{2+} //SO_4^{2-}–H_2O). This model had been used to extend the Harvie et al.(1984) model for the Na^+, K^+, Ca^{2+}, Mg^{2+} //Cl^-, SO_4^{2-}, CO_3^{2-}–H_2O. Deng et al. (2010) had measured the isopiestic molalities and water activities for the systems (Na^+//Cl^-–H_2O, Ca^{2+}//Cl^-–H_2O and Na^+, Ca^{2+} //Cl^-–H_2O) at 308.15 K by the isopiestic method in the ranges of 0.5666–5.9265 mol/kg, 0.3943–5.5573 mol/ kg, and 0.6524–16.6631 mol/kg, respectively, calculated the saturated vapor pressures and the osmotic coefficients for the (Na^+, Ca^{2+}//Cl^- –H_2O) system, and obtained Pitzer single electrolyte parameters for $CaCl_2$ and Pitzer mixing ion-interaction parameters for the system (Na^+, Ca^{2+}//Cl^- – H_2O) with the multivariant linear regression method. The result shows that the osmotic coefficient values determined experimentally and these calculated by using Pitzer model agreed well.

The corresponding prediction of thermodynamic data is still scarce. However, these have established the foundation for the further solubility prediction of more different systems under specific conditions. The thermodynamic data plays an important role in constructing the complex thermodynamic model for the type of calcium-containing seawater and brine systems, so it is essential to measure and predict more corresponding data of the calcium-containing systems at different conditions to complete the thermodynamic data base in similar ways.

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