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Addition/Correction

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Addition to "Activity Coefficients of Fission Products in Highly Salinary Solutions of Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-}: Cs^+"

T. Scharge, A. G. Muñoz,* and H. C. Moog

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Supporting Information

In the published review we reported a set of binary and ternary interaction Pitzer parameters for Cs^+ in concentrated salt solutions of the hexary oceanic system Na−K−Mg−Ca−Cl−SO_4−H_2O at 25 °C. In that paper we advised against the inconsistency of reported solubility and isopiestic data for the system CsCl−$MgCl_2$−H_2O. For the systems CsCl−$CaCl_2$−H_2O and Cs_2SO_4−$MgSO_4$−H_2O, interaction parameters were calculated by taking only a few solubility data available in the literature. Recent isopiestic experiments carried out in our laboratories provided a more reliable basis for the determination of interaction parameters in relation to these three systems. Details of the measurement setup were reported elsewhere.[1] NaCl solutions (and $CaCl_2$ solutions for low water activities) were used as a reference. Highest available purity grades were used: CsCl (99.9 %, Applichem), Cs_2SO_4 (99.997 %, Alfar Aesar), $CaCl_2·4H_2O$ (99.995 %, Merck), $MgSO_4·7H_2O$ (99.5 % to 100.5 %, Riedel de Haen), $MgCl_2·6H_2O$ (99.0 % to 101.0 %, Merck), NaCl (99.99 %, Merck). Stock solutions were prepared and characterized with the initial weight (controlled by ash content method) (CsCl, Cs_2SO_4, NaCl, $MgSO_4$), density[2−4] ($CaCl_2$), and inductively coupled plasma mass spectrometry (ICP; $MgCl_2$).

Figure 1 shows the new obtained isoactivity lines along with solubility data already given in our review for the system CsCl−$MgCl_2$−H_2O. Numerical data are given in Table S1 of the Supporting Information. For the new set of Pitzer parameters, our isopiestic data and solubility data given by D'Ans and Busch[6] and Skripkin et al.[7] were taken into account (Table S3). Additionally, potentiometric data recently published by Hu et al.[5] were included in the calculus (see Table S2). Solubility data of Shevchuk and Vaisfel'd[8] as well as isopiestic data published

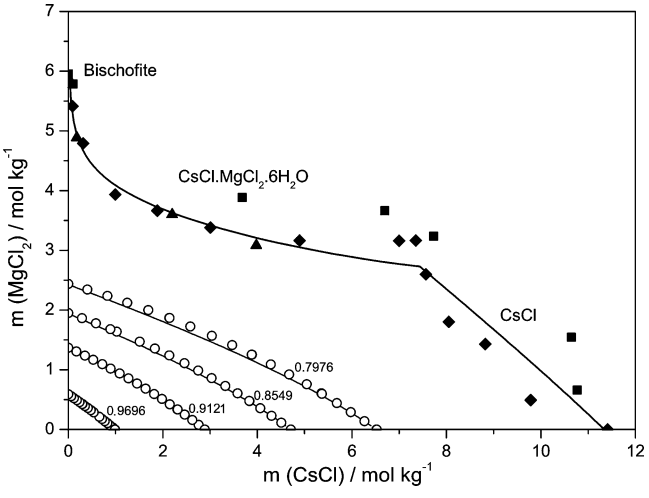

Figure 1. Equilibrium diagram of the ternary CsCl−$MgCl_2$−H_2O system at 25 °C. ■, ref 8; ▲, ref 6; ◆, ref 7; ○, this work; —, calculated.

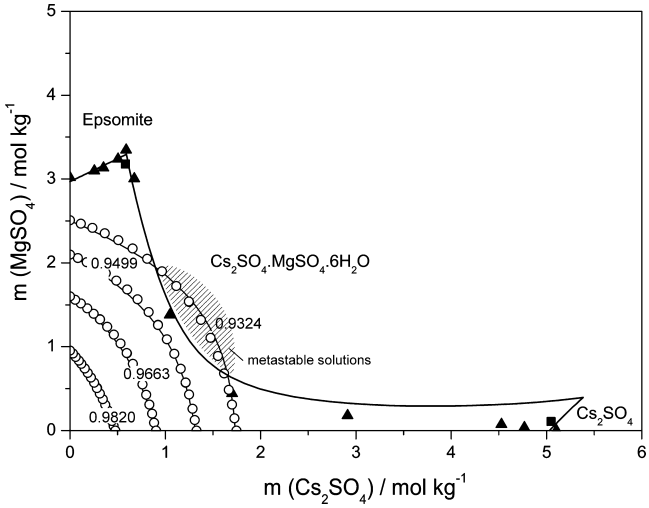

Figure 2. Equilibrium diagram of the ternary Cs_2SO_4−$MgSO_4$−H_2O system at 25 °C. ■, ref 9; ▲, ref 8; ○, this work; —, calculated.

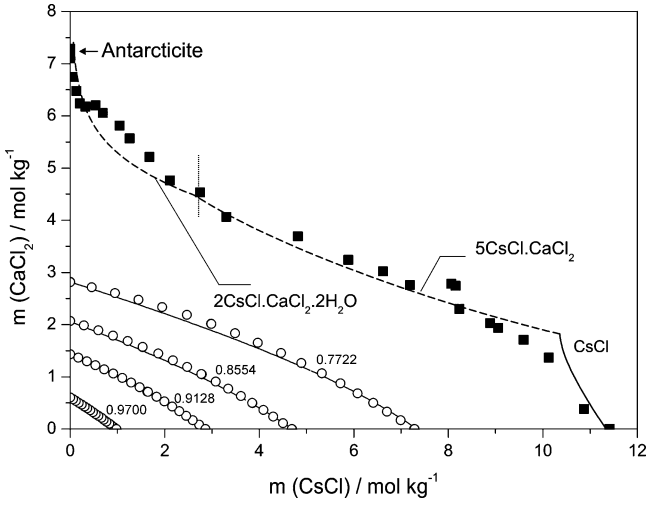

Figure 3. Equilibrium diagram of the ternary CsCl−$CaCl_2$−H_2O system at 25 °C. ■, ref 11; —, calculated, this work; ---, calculated, this work; ○, this work.

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Table 1. Recalculated Set of Pitzer Parameters[a]

M	c	X	θ_{M-c}	ψ_{M-c-X}
Cs^+	Na^+	Cl^-	−0.01676	−0.00485
Cs^+	Na^+	Cl^-	−0.01694[a]	−0.00480[a]
Cs^+	Na^+	SO_4^{2-}	−0.01676	−0.00012
Cs^+	Na^+	SO_4^{2-}	−0.01694[a]	−0.00008[a]
Cs^+	K^+	Cl^-	−0.00555	0.00020
Cs^+	K^+	Cl^-	−0.00893[a]	0.00079[a]
Cs^+	K^+	SO_4^{2-}	−0.00555	0.00306
Cs^+	K^+	SO_4^{2-}	−0.00893[a]	0.00420[a]
Cs^+	Mg^{2+}	Cl^-	−0.13117	−0.01033
Cs^+	Mg^{2+}	Cl^-	−0.05639[a]	−0.03650[a]
Cs^+	Mg^{2+}	SO_4^{2-}	−0.13117	−0.03584
Cs^+	Mg^{2+}	SO_4^{2-}	−0.05639[a]	−0.06391[a]
Cs^+	Ca^{2+}	Cl^-	−0.09812	−0.01171
Cs^+	Ca^{2+}	Cl^-	−0.00816[a]	−0.03518[a]
Cs^+	Cl^-	SO_4^{2-}	0.02	0.01039
Cs^+	Cl^-	SO_4^{2-}	0.02[a]	0.00829[a]

[a]These values are consistent with binary parameters of the CsCl−H_2O system (see original review) derived by setting $\alpha_1 = 2$ and $\alpha_2 = 12$ for their calculation (limited to a maximum concentration of 7 *m* CsCl).

by Skripkin et al.[7] were excluded. With the new set of Pitzer parameters the solubility constant of $CsCl{\cdot}MgCl_2{\cdot}6H_2O$

$$CsCl{\cdot}MgCl_2{\cdot}6H_2O \rightarrow Cs^+ + Mg^{2+} + 3Cl^- + 6H_2O(l)$$

was calculated as log K = 4.06. This value should replace the solubility constant given in our previous review.

Results from isopiestic measurements of the system $MgSO_4$−Cs_2SO_4−H_2O at 298.15 K are shown in Table S4 (Supporting Information) and depicted in Figure 2. Some of them were obtained within the metastable supersaturated region (hatched zone). The new set of Pitzer parameters was calculated by using new isopiestic data and already available solubility values[8,9] (Table S5). Figure 2 shows the isoactivity lines and the solubility curve calculated with the new set of parameters. Thus, the solubility constant of $Cs_2SO_4{\cdot}MgSO_4{\cdot}6H_2O$

$$Cs_2SO_4{\cdot}MgSO_4{\cdot}6H_2O \rightarrow 2Cs^+ + Mg^{2+} + 2SO_4^{2-} + 6H_2O(l)$$

was calculated as log K = −4.26, and this value should replace that in our previous review.

For the system CsCl−$CaCl_2$−H_2O results of isopiestic measurements (Table S6 of the Supporting Information) and electromotive force (emf) data reported recently by Hu et al.[10] (Table S7) were used with solubility data given by Plyushchev et al.[11] (Table S8) for calculating ternary interaction parameters. Figure 3 shows the calculated isoactivity lines and the solubility curve calculated with the new set of Pitzer parameters. Thus, solubility constants for the double salts $5CsCl{\cdot}CaCl_2$ log K = 10.08 and $2CsCl{\cdot}CaCl_2{\cdot}2H_2O$ log K = 6.31 can be calculated:

$$5CsCl{\cdot}CaCl_2 \rightarrow 5Cs^+ + Ca^{2+} + 7Cl^-$$

$$2CsCl{\cdot}CaCl_2{\cdot}2H_2O \rightarrow 2Cs^+ + Ca^{2+} + 4Cl^- + 2H_2O(l)$$

Table 1 lists all ternary Pitzer parameters for the system Cs−Na−K−Mg−Ca−Cl−SO_4−H_2O including parameters used for the recalculation of data in this addition. Because of the introduced changes, an overall optimized set of ternary parameters is now reported. The reader is encouraged to use reviewed ternary parameters given in Table 1 along with binary parameters reported in our previous review. These Pitzer parameters are consistent with all solubility constants given in our review apart from those which were recalculated in this addition. It is important to note that our data are consistent with solubility constants and Pitzer parameters for the hexary system of oceanic salts as given in our previously published review.

■ ASSOCIATED CONTENT

Supporting Information

Isopiestic, solubility, and potentiometric data for the determination of ternary parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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