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EXTENSION OF THE EQ3/6 COMPUTER CODES
TO GEOCHEMICAL MODELING OF BRINES

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EXTENSION OF THE EQ3/6 COMPUTER CODES TO GEOCHEMICAL MODELING OF BRINES

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ABSTRACT

Recent modifications to the EQ3/6 geochemical modeling software package* [1-3] provide for the use of Pitzer's [4] equations to calculate the activity coefficients of aqueous species and the activity of water. These changes extend the range of solute concentrations over which the codes can be used to dependably calculate equilibria in geochemical systems, and permit the inclusion of ion pairs, complexes, and undissociated acids and bases as explicit component species in the Pitzer model. Comparisons of calculations made by the EQ3NR and EQ6 computer codes with experimental data confirm that the modifications not only allow the codes to accurately evaluate activity coefficients in concentrated solutions, but also permit prediction of solubility limits of evaporite minerals in brines at 25°C and elevated temperatures. Calculations for a few salts can be made at temperatures up to ~300°C, but the temperature range for most electrolytes is constrained by the availability of requisite data to values $\leq 100^\circ\text{C}$. The implementation of Pitzer's equations in EQ3/6 allows application of these codes to problems involving calculation of geochemical equilibria in brines; such as evaluation of the chemical environment which might be anticipated for nuclear waste canisters located in a salt repository.

INTRODUCTION

Accurate evaluation of activity coefficients is necessary in order to relate the thermodynamic activities of electrolyte species used in geochemical calculations to their corresponding concentrations. Because many naturally occurring aqueous solutions have ionic strengths too high to model with the simple or extended Debye-Hückel equations commonly used to calculate activity coefficients in dilute solutions [5,6], it is necessary to appeal to a more sophisticated method for their evaluation. Pitzer's [4, 7-12] algorithms for calculating the activity of water and activity coefficients of aqueous species have been used previously by Harvie and co-workers [13-16] to accurately model geochemical processes involving brines and evaporite minerals. This set of equations and

*The EQ3/6 software package is comprised of a family of computer codes and supporting data bases designed for calculation of the equilibrium distribution of species in an aqueous solution and to model the interaction of this fluid with mineral phases, a gas phase, or another aqueous solution. The EQ3NR and EQ6 codes are the central features of this software package. EQ3NR performs aqueous speciation and solubility calculations [6], and EQ6 models reaction paths for aqueous geochemical systems [2].

supporting data have been incorporated into the EQ3/6 geochemical modeling software package [1,3] and greatly extend the range of ionic strengths over which activity coefficients can be calculated accurately by EQ3NR and EQ6. Consequently, these codes can now be used to model geochemical processes which they were previously unable to accurately describe owing to the high ionic strengths of the solutions involved. For example, in order to calculate the concentrations of the major dissolved species in equilibrium with evaporite deposits or to reproduce experimentally determined solubilities of such highly soluble mineral phases as halite and sylvite, it is necessary to evaluate activity coefficients in solutions with ionic strengths as high as ~ 6 [17-19]. The test runs outlined below not only document the ability of EQ3/6 to approximate the activity coefficients of solute species and the activity of water in high ionic strength solutions, but also illustrate sample solubility calculations for various evaporite minerals.

Versions of the EQ3NR and EQ6 codes described in this paper represent the first publicly available set of computer programs for geochemical modeling which incorporate a fully general capability for using Pitzer's equations to calculate activity coefficients.

Osmotic Coefficient and Activity Coefficient Calculations

Previously published [3] comparisons of the results of sample EQ3/6 calculations illustrate that the codes reproduce experimentally determined osmotic coefficient* and mean molal activity coefficient data, and serve to assure that the coding is in accordance with the formulation of these parameters as represented by Pitzer [4,7]. Secondly, agreement between values computed by EQ3/6 and experimental data for the activity coefficients of solutes in multicomponent systems and for the solubility of solids in mixed electrolytes ensures the validity of extending these calculations into more complex compositional systems.

To illustrate the first point, values of the mean molal activity coefficients (γ_{\pm}) for aqueous solutions of $MgSO_4$ and $AlCl_3$ calculated by EQ3/6 using Pitzer's [7] interaction parameters are plotted as a function of molality together with experimentally determined values of γ_{\pm} in figure 1a and 1b. For both electrolytes, the agreement between experimental and calculated values is quite good throughout the range of available data. Similar agreement between calculations and measurements can be illustrated for the osmotic coefficient data [3].

*The osmotic coefficient (ϕ) is related to the activity of water (a_w) by the expression

$$\phi = -(\omega/\sum m) \ln a_w$$

where ω is the number of moles of water in one kg of pure solvent ($\omega = 55.51$) and $\sum m$ represents the sum of the molalities of solute species. In high ionic strength solutions the activity of water may differ substantially from unity and must be explicitly included in mass action expressions in order to accurately describe chemical equilibrium relationships.

Because the activity coefficient behavior of MgSO_4 is notoriously difficult to model [20] due to its apparent large deviation from the Debye-Hückel limiting law even at low concentrations, the excellent fit to the data provided by Pitzer's equations as calculated by EQ3NR is particularly worth noting.

In addition, it should be noted that activity coefficient values calculated by EQ3/6 using the recently added algorithms represent a significant improvement over the capability of previous versions of the codes which were limited to the use of an extended form of the Debye-Hückel equation (the B-dot equation [5]). The B-dot equation is intended to be used only for estimating γ_{\pm} in relatively dilute solutions, however, and is not likely to dependably model γ_{\pm} at high ionic strengths [5,6]. The deviation of activity coefficient values calculated by the B-dot equation from experimental values at moderate concentrations is illustrated by the dashed curve in Figure 1-b. In fact, in some cases, this equation predicts values which diverge from the data even in quite dilute solutions.

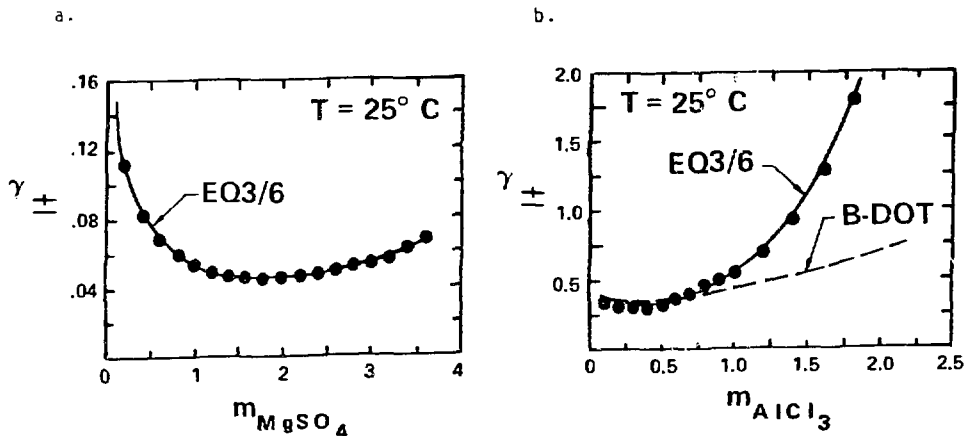


Figure 1. Mean molal activity coefficients (γ_{\pm}) of MgSO_4 (a) and AlCl_3 (b) at 25°C as functions of molality. The solid curves represent values calculated by EQ3/6, and the symbols represent experimental data [21,26]. The dashed curve represents values calculated by EQ3/6 using the B-dot equation (see text).

Pitzer's equations can also be used to accurately predict activity coefficients in more complicated compositional systems. For example, mean molal activity coefficients of HCl ($\gamma_{\pm, \text{HCl}}$) in the quaternary system $\text{HCl}-\text{NaCl}-\text{KCl}-\text{H}_2\text{O}$ have been measured using the electromotive force method [24]. Representative data from this work together with values calculated by EQ3NR are listed in Table 1. As shown in this table, the maximum difference between the experimental and calculated $\log \gamma_{\pm}$ values is 7.2×10^{-4} , which represents less than about 0.5%

of the associated experimental value. In most cases the agreement is considerably better than this limit. Similarly accurate approximations of γ_{\pm} for HCl can be demonstrated for the system HCl-NH₄Cl-KCl-H₂O [3], and are implicitly illustrated for other solutes by the fit of calculated solubility limits to experimental data discussed below.

Table 1. Mean molal activity coefficients of HCl at 25°C in the quaternary system HCl-NaCl-KCl-H₂O. Values of $\log \gamma_{\pm}$, HCl in this table are separated into two columns which represent experimental data [24] and values calculated using EQ3/6. The column labeled $\Delta \log \gamma_{\pm}$ represents the absolute value of the differences between the experimental and calculated values [3].

mHCl	mNaCl	mKCl	$\log \gamma_{\pm}$, HCl		$\Delta \log \gamma_{\pm}$
			experimental	calculated	
0.79956	0.05011	0.15033	-0.10145	-0.10114	0.00031
0.59972	0.10007	0.30021	-0.11245	-0.11192	0.00053
0.29979	0.17505	0.52516	-0.12819	-0.12792	0.00027
0.09977	0.22506	0.67517	-0.13865	-0.13846	0.00019
0.05000	0.23750	0.71250	-0.14135	-0.14106	0.00029
0.01000	0.24750	0.74520	-0.14314	-0.14315	0.00001
0.79992	0.10004	0.10004	-0.09969	-0.09957	0.00012
0.59913	0.20043	0.20043	-0.10894	-0.10887	0.00007
0.30035	0.34983	0.34983	-0.12279	-0.12254	0.00025
0.10062	0.44969	0.44969	-0.13229	-0.13157	0.00072
0.05000	0.47500	0.47500	-0.13443	-0.13384	0.00062
0.01000	0.49500	0.49500	-0.13604	-0.13553	0.00041

The capability of EQ3/6 to calculate the thermodynamic properties of a brine at elevated temperatures and to model the interaction of such a solution with evaporite minerals is demonstrated by the following example. Results of EQ6 runs defining the solubility limits as a function of composition in the ternary system NaCl-KCl-H₂O at 40°C are shown in figure 2. The solid curves in this figure represent the computed equilibrium solubility limits of halite and sylvite as indicated, whereas the dashed portions of the curves represent metastable extensions.

Recently [13] Pitzer's equations have been used to quantitatively describe equilibrium solubilities of evaporite minerals in concentrated solutions in an eight component system (Na₂O, K₂O, MgO, CaO, CO₂, H₂SO₄, HCl, H₂O). Harvie et al. [13] also include a compilation of thermodynamic data for mineral phases in this system and a set of interaction parameters for Pitzer's equations which explicitly includes several ion pairs and aqueous complexes (i.e. MgOH⁺, HCO₃⁻, HSO₄⁻, CaCO₃, and MgCO₃). When these parameters are inserted into the appropriate EQ3/6 data files, resulting solubility calculations parallel the impressively accurate results of Harvie et al. [13]. An example of EQ3/6 calculations using this data set is shown in figure 3 where the computed and measured solubility of gypsum (CaSO₄·2H₂O) is plotted as a function of dissolved NaCl. As can be seen from this figure,

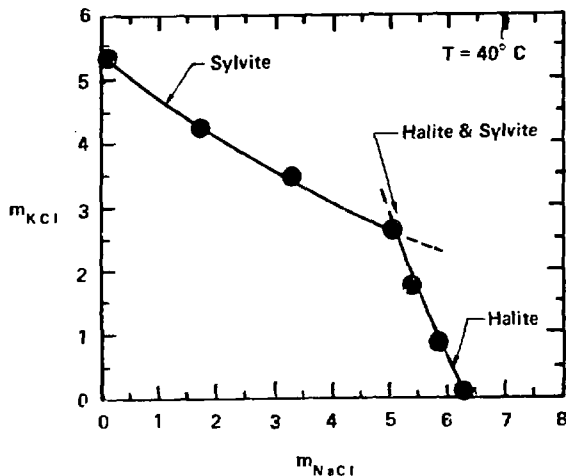


Figure 2. Solubility limits of halite and sylvite in the system NaCl-KCl-H₂O at 40°C. Experimentally determined solubilities [23] are represented by filled circles. Values calculated by EQ6 are represented by the solid curves.

the calculated values (represented by the curve) closely approximate the experimental determinations (designated by the symbols) over a wide range of solution compositions. Even at concentrations of NaCl approaching halite (NaCl) saturation, the deviation of the curve from the data is relatively minor.

Examples of EQ3/6 applications for which the brine modifications described above are necessary include modeling the composition of aqueous solutions which might be anticipated in the near-field environment of a nuclear waste canister in a salt repository or the formation of both marine and non-marine evaporite deposits.

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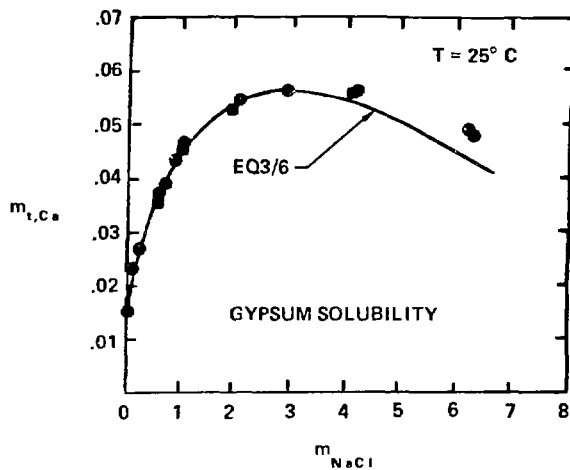


Figure 3. Calculated and experimental solubility of gypsum at 25°C as a function of NaCl concentration. The filled squares [25] and circles [26] represent selected experimental values. The curve designates values calculated by EQ3/6.

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REFERENCES

1. Wolery, T. J., EQ3/6 Modifications for Geochemical Modeling of Brines, UCRL report in preparation, Lawrence Livermore National Laboratory, Livermore, CA, (1984).
2. Wolery, T. J., EQ6, A Computer Program for Reaction Path Modeling of Aqueous Geochemical Systems: User's Guide and Documentation, UCRL report in preparation, Lawrence Livermore National Laboratory, Livermore, CA, (1984).
3. Jackson, K. J., Verification and Validation Studies of the EQ3/6 Brine Model, UCRL report in preparation, Lawrence Livermore National Laboratory, Livermore, CA, (1984).
4. Pitzer, K. S. "Thermodynamics of electrolytes, I. Theoretical basis and general equations," J. Phys. Chem., 77, pp. 268-277, (1973).
5. Helgeson, H. C., "Thermodynamics of hydrothermal systems at elevated temperatures and pressures," Amer. J. Sci., 267, pp. 729-804, (1969).
6. Wolery, T. J., EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: Users Guide and Documentation, UCRL-53414, Lawrence Livermore National Laboratory, Livermore, CA, 191 pp., (1983).
7. Pitzer, K. S., "Theory: Ion Interaction Approach," Activity Coefficients in Electrolyte Solutions, R. M. Pytkowicz, ed., CRC Press, Boca Raton, FL, (1979), pp. 157-208.
8. Pitzer, K. S., "Thermodynamics of electrolytes, V. Effects of higher-order electrostatic terms," J. Soln. Chem., 4, pp. 249-265, (1975).
9. Pitzer, K. S., "Electrolyte theory--Improvements since Debye and Hückel," Accounts of Chem. Res., 10, pp. 371-377, (1977).
10. Pitzer, K. S. and Kim, J. J., "Thermodynamics of electrolytes. IV. Activity and osmotic coefficients for mixed electrolytes," J. Amer. Chem. Soc., 96, pp. 5701-5707, (1974).
11. Pitzer, K. S. and Mayorga, G., "Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent," J. Phys. Chem., 77, pp. 2300-2308, (1973).
12. Pitzer, K. S. and Mayorga, G., "Thermodynamics of electrolytes. III. Activity and osmotic coefficients for 2-2 electrolytes," J. Soln. Chem., 3, pp. 539-546, (1974).
13. Harvie, C. E., Moller, N. and Weare, J. H., "The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₂-CO₂-H₂O system to high ionic strengths at 25°C," Geochim. Cosmochim. Acta, 48, pp. 723-751, (1984).
14. Harvie, C. E. Theoretical investigations in geochemistry and atom surface scattering, Ph.D. Dissertation, University Microfilm, Int., Ann Arbor, MI #AAD82-03026, (1981).
15. Harvie, C. E. and Weare, J. H., "The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-Cl-SO₄-H₂O systems from zero to high concentration at 25°C," Geochim. Cosmochim. Acta, 44, pp. 981-997, (1980).

14. Harvie, C. E. Theoretical investigations in geochemistry and atom surface scattering, Ph.D. Dissertation, University Microfilm, Int., Ann Arbor, MI #AAD82-03026, (1981).
15. Harvie, C. E. and Weare, J. H., "The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-Cl-SO₄-H₂O systems from zero to high concentration at 25°C, Geochim. Cosmochim. Acta 44, pp. 981-997, (1980).
16. Harvie C. E., Eugster, H. P. and Weare, J. H., "Mineral equilibria in the six-component seawater systems, Na-K-Mg-Ca-SO₄-Cl-H₂O at 25°C. II. Compositions of the saturated solutions," Geochim. Cosmochim. Acta 46, p. 1603, (1982).
17. Stewart, F. H., "Marine evaporites," U.S.G.S. Prof. Paper, 440-Y, 52 pp., (1963).
18. Hardie, L. A., "Evaporites: Marine or Non-marine," Amer. J. Sci., 284, pp. 193-240, (1984).
19. Eugster, H. P., Harvie, C. E., and Weare, J. H., "Mineral equilibria in a six-component seawater system, Na-K-Mg-Ca-SO₄-Cl-H₂O, at 25°C," Geochim. Cosmochim. Acta, 44, pp. 1335-1347, (1980).
20. Helgeson, H. C., Kirkham, D. H., and Flowers, G. C., "Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressure and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal properties to 600°C and 5kb," Amer. J. Sci., 281, pp. 1249-1516, (1981).
21. Rard, J. A. and Miller, D. G., "Isopiestic determination of the osmotic coefficients of aqueous Na₂SO₄, MgSO₄, and Na₂SO₄-MgSO₄ at 25°C," J. Chem. Eng. Data, 26, pp. 33-38, (1981).
22. Robinson, R. A. and Stokes, R. H., Electrolyte Solutions, 2nd edition, Butterworths, London, 571 pp., (1965).
23. Linke, W. F., Solubilities of Inorganic and Metal Organic Compounds, 4th edition, Amer. Chem. Soc., Washington, (1965).
24. Chan, C. Y., Khoo, K. H., and Lim, T. K., "Specific ionic interactions in the quaternary systems HCl-NaCl-KCl-Water and HCl-H₄Cl-KCl-water at 25°C," J. Soln. Chem., 8, pp. 41-52, (1979).
25. Block, J. and Waters, O. B., Jr., "The Ca-SO₄-Na₂SO₄-NaCl-H₂O system at 25° to 100°C," J. Chem. Eng. Data, 13, pp. 336-344, (1968).
26. Marshall, W. L. and Slusher, R., "Thermodynamics of calcium sulfate dihydrate in aqueous sodium chloride solutions, 0-110°," J. Phys. Chem., 6, pp. 4015-4027, (1966).