

NOTE

Methane solubilities in multisalt solutions

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Abstract—Solubilities of methane in multisalt solutions at 550 psia and 25°C can be predicted from single-salt salting coefficients. The ionic strength contribution of the *i*th salt, I_i , is multiplied by its molal salting coefficient, k_{m_i} , in the following summation over all salts:

$$\log \frac{m_o}{m_s} = \sum_i k_{m_i} I_i$$

where m_o and m_s are molal methane solubilities in distilled water and the salt solution, respectively, at the T, P, and methane fugacity of interest.

This equation predicts methane solubility in multisalt brines containing Na^+ , K^+ , Mg^{+2} , Ca^{+2} , Cl^- , SO_4^{-2} , and CO_3^{-2} ions. k_{m_i} values reported by Stoessel and Byrne (1982b) can be used in solubility predictions in brines at earth surface conditions. Prediction in reservoir brines would require determination of k_{m_i} for the different salts at reservoir temperatures and pressures.

INTRODUCTION

THIS PAPER is the third in a series on methane solubility at 25°C and below 800 psia. The first paper (Stoessel and Byrne, 1982a) dealt with the solubility of methane in sediment slurries up to 11 weight percent. The second paper (Stoessel and Byrne, 1982b) investigated the solubility of methane in single-salt solutions, and this paper deals with the extension of those results to predictions of methane solubility in multisalt brines.

EXPERIMENTAL

The equilibration and sampling systems have previously been described in detail by Stoessel and Byrne (1982a). The method for determination of methane salting coefficients for single-salt solutions was described by Stoessel and Byrne (1982b). Experimental procedures for this study were the same as reported in those studies, with several minor modifications. Gas pressure was read using a Heise CM 31542 gauge having a dead weight accuracy within 1 psia. Saturation measurements were made at a single pressure of 550 psia and 25°C. Stoessel and Byrne (1982b) showed salting coefficients to be independent of pressure below 800 psia, eliminating the necessity of multiple pressure measurements. Sample withdrawal, isolation of sample, and determination of system volumes to obtain methane molarity remained unchanged.

Salt solutions used in the experiments were made up gravimetrically using analytical reagent grade chemicals. The solution compositions are listed in Table 1. Equal molalities of salts were used in multisalt mixtures at levels close to the maximum solubility of the least soluble salt. Binary salt solutions made up all but one of the solutions studied. One solution contained a four-salt mixture, and one binary

salt solution was studied at two ionic strengths. Methane gas used in this study was Matheson ultra-high purity (manufacturer reports a minimum content of 99.97 mole % methane).

Densities, used to convert molar to molal units, were determined gravimetrically with pycnometers at 25°C for the salt solutions studied. The molalities were corrected for the volume of dissolved gas, the correction generally being less than 0.0001 molal units. Precision of the measurements in molal units was within 0.0005, averaging 0.0003. Each saturation value reported in this study is the average of at least two measurements.

RESULTS AND DISCUSSION

Measured and predicted methane solubility data and the corresponding salting coefficients for the multisalt solutions are shown in Table 1. Measured molal salting coefficients at 25°C and below 800 psia for single-salt solutions were reported by Stoessel and Byrne (1982b). The empirical equation by which the molal salting coefficients were computed is

$$\log \frac{m_o}{m_s} = k_m I \quad (1)$$

where

- m_o = methane molality in distilled water;
- m_s = methane molality in the single-salt solution;
- k_m = molal salting coefficient;
- I = stoichiometric ionic strength of salt solution.

Eqn. (1) differs from the Setchénow equation in the use of I instead of salt concentration. We have followed the convention of Garrels and Christ (1965) and Randall and Failey (1927).

Our predictive equation, which we tested for use on multisalt solutions, has the following form for k_m :

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Table 1. Measured and predicted solubilities and salting coefficients at 25°C and 550 psia*

Salt Solution Salt (Molality)	CH ₄ Solubility**		Salting Coefficient***	
	Measured	Predicted	Measured	Predicted
1. NaCl (1.0), KCl(1.0)	0.0286	0.0290	0.114	0.111
2. NaCl (1.0), CaCl ₂ (1.0)	0.0219	0.0225	0.086	0.083
3. NaCl (1.0), MgCl ₂ (1.0)	0.0264	0.0236	0.066	0.078
4. CaCl ₂ (1.0), MgCl ₂ (1.0)	0.0173	0.0191	0.074	0.067
5. NaCl (0.5), KCl (0.5) MgCl ₂ (0.5), CaCl ₂ (0.5)	0.0245	0.0236	0.074	0.078
6. Na ₂ SO ₄ (0.25), K ₂ SO ₄ (0.25)	0.0322	0.0327	0.119	0.115
7. Na ₂ SO ₄ (0.5), MgSO ₄ (0.5)	0.0221	0.0234	0.097	0.090
8. K ₂ SO ₄ (0.25), MgSO ₄ (0.25)	0.0345	0.0345	0.084	0.084
9. NaCl (1.0), Na ₂ SO ₄ (1.0)	0.0173	0.0159	0.111	0.121
10. MgCl ₂ (0.5), MgSO ₄ (0.5)	0.0275	0.0286	0.070	0.065
11. MgCl ₂ (0.25), MgSO ₄ (0.25)	0.0358	0.0371	0.076	0.066
12. NaCl (1.0), Na ₂ CO ₃ (1.0)	0.0171	0.0161	0.113	0.119
13. KCl (1.0), K ₂ CO ₃ (1.0)	0.0177	0.0177	0.109	0.109
14. Na ₂ SO ₄ (0.5) Na ₂ CO ₃ (0.5)	0.0211	0.0212	0.120	0.121

*Used m_o and k_{m_i} values from Stoessell and Byrne (1982b)

**Molality

*** k_m

$$k_m = (\sum_i k_{m_i} I_i) / I \quad (2)$$

where k_{m_i} and k_m represent salting coefficients for the i th salt and multisalt mixture, respectively, and I_i/I is the ionic strength fraction of the i th salt in the mixture. Substitution of Eqn. (2) into Eqn. (1) yields

$$\log \frac{m_o}{m_s} = \sum_i k_{m_i} I_i \quad (3)$$

and

$$m_s = m_o 10^{-\sum_i k_{m_i} I_i} \quad (4)$$

where m_s = methane molality in the multisalt solution.

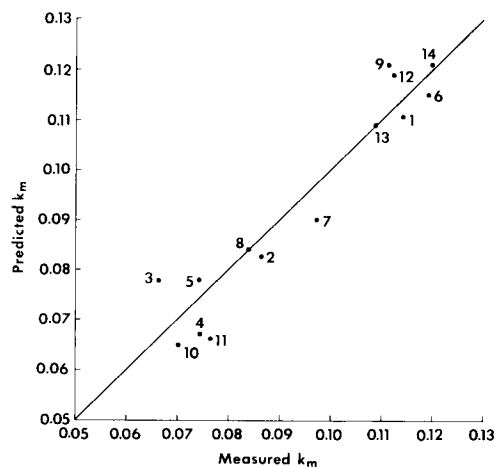


FIG. 1. Predicted and measured CH₄ salting coefficients in multisalt solutions. See Table 1 for solution compositions.

Eqn. (3) is similar to that used by Marshall and Chen (1982) to predict amorphous silica solubilities in multisalt solutions. The only difference is our single-salt constants are based on I and their constants are based on salt molality.

The relationships between predicted methane salting coefficients and measured methane salting coefficients are shown on Fig. 1. Similar relationships are shown in Fig. 2 for methane solubilities. A line has been drawn in with a slope equal to 1 to facilitate comparison on both figures. Even with the spread of the salting coefficients, the molalities predicted from these data show good agreement with measured data.

The increased spread in Fig. 1, as compared to Fig. 2, reflects the sensitivity of k_m to small changes in methane molality. Good agreement is shown in Table 2 between measured and predicted solubilities. The maximum deviation is 0.0028 molal units for the NaCl-MgCl₂ solution. The average difference between measured methane molalities and predicted methane molalities is less than -0.0001. The average absolute difference is 0.0010 molal units, or only twice the precision range of a single measurement. The solutions that deviated less than average are KCl-K₂CO₃ and K₂SO₄-MgSO₄ with deviations of zero; Na₂SO₄-Na₂CO₃, NaCl-KCl, and Na₂SO₄-K₂SO₄ with deviations less than 0.0005 molal units; NaCl-CaCl₂, NaCl-Na₂CO₃, and NaCl-KCl-MgCl₂-CaCl₂ with deviations less than 0.0010 molal units. Solutions that deviated between 0.0010 and 0.0020 molal units are MgSO₄-MgCl₂; Na₂SO₄-MgSO₄; MgSO₄-MgCl₂; and NaCl-Na₂SO₄ and CaCl₂-MgCl₂. Predictions were not randomly distributed but tended (10 out of 14) to be slightly on the higher side of the perfect correlation line.

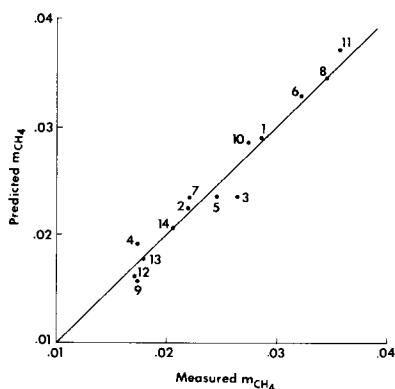


FIG. 2. Predicted and measured CH_4 solubilities in multivalent solutions. See Table 1 for solution compositions.

Use of Eqn. (4) to estimate methane solubilities necessitates knowing m_o at P, T, and the CH_4 fugacity of interest. For geochemical conditions below metamorphism, m_o can be estimated using empirical equations based on fitting measured solubilities in distilled water (e.g., Haas, 1978; Price *et al.*, 1981), combined with Henry's law. The values of k_{m_i} reported by Stoessel and Byrne (1982b) at 25°C and below 800 psia can be used in Eqn. (4) at T and P corresponding to earth surface and early diagenetic conditions. Values of k_{m_i} for use with reservoir fluids, need to be measured for $CaCl_2$ at reservoir T and P. Reservoir fluids are primarily mixtures of NaCl and $CaCl_2$ (Dickey, 1969). The empirical equation by Haas (1978), mentioned above, has also been fit to

experimental solubilities in NaCl solutions, allowing the computation of $k_{m_{NaCl}}$ at reservoir T and P. Experimental data on solubilities in $CaCl_2$ solutions, needed to compute $k_{m_{CaCl_2}}$, are lacking at elevated temperatures and pressures.

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