

## Salting-out of methane in single-salt solutions at 25°C and below 800 psia

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**Abstract**—Aqueous solubilities of methane at 25°C have been determined in single-salt solutions equilibrated with a CH<sub>4</sub> gas phase at 350, 550, and 750 psia. Measurements were made over a range of ionic strengths in NaCl, KCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, and KHCO<sub>3</sub> aqueous solutions.

At 25°C and constant pressure and methane fugacity, methane solubilities were largely controlled by the stoichiometric ionic strength, I, and the cation of the salt. Except for an increased salting-out due to HCO<sub>3</sub><sup>-</sup>, the anion effect was relatively insignificant. Different but consistent solubility trends were followed in monovalent and divalent cation salt solutions as a function of I. Solubilities increased in salt solutions having a common anion in the following cation sequence: Na<sup>+</sup> < K<sup>+</sup> ≪ Ca<sup>2+</sup> < Mg<sup>2+</sup>.

The molal salting coefficient,  $k_m$ , for each salt was constant under the experimental conditions of the study.  $k_m$  is defined by  $\log \gamma_{\text{CH}_4}/I$  where  $\gamma_{\text{CH}_4}$ , the molal activity coefficient, is the methane solubility ratio ( $m_{\text{H}_2\text{O}}/m_{\text{salt solution}}$ ) measured at constant temperature, pressure, and CH<sub>4</sub> fugacity. Single-salt  $k_m$  values are as follows: 0.121, NaCl (4*m*); 0.121, Na<sub>2</sub>SO<sub>4</sub> (1*m*); 0.118, Na<sub>2</sub>CO<sub>3</sub> (1.5*m*); 0.146, NaHCO<sub>3</sub> (0.5*m*); 0.101, KCl (4*m*); 0.108, K<sub>2</sub>SO<sub>4</sub> (0.5*m*); 0.111, K<sub>2</sub>CO<sub>3</sub> (2*m*); 0.145, KHCO<sub>3</sub> (0.5*m*); 0.071, CaCl<sub>2</sub> (2*m*); 0.063, MgCl<sub>2</sub> (2*m*); and 0.066, MgSO<sub>4</sub> (1.5*m*) where the molalities in parentheses refer to the maximum salt concentrations used in this study.

### INTRODUCTION

METHANE is an important gas component in geologic systems: produced biogenically at low temperatures (Claypool and Kaplan, 1974) and by thermal cracking of organic matter with increasing temperature (Tissot and Welte, 1978). The factors controlling methane solubility in aqueous fluids include temperature, pressure, the composition of the equilibrated gas phase and the dissolved salt content of the solution. Previous reliable measurements of methane solubility have usually utilized mixtures of seawater and distilled water (e.g. Yamamoto *et al.*, 1976; Claussen and Polyglase, 1952) or concentrated on the temperature and pressure effects in distilled water and sodium chloride solutions (e.g. Culberson and McKetta, 1951; O'Sullivan and Smith, 1970; Price, 1979). With few exceptions (Morrison, 1952; Morrison and Billett, 1952), studies are lacking in the literature which examine the effects of different cations and anions on the salting-out of methane.

The goal of this research was to examine systematically the effects on methane solubility of the different major cations and anions found in natural waters. These are Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, and HCO<sub>3</sub><sup>-</sup>. The salts used were of the A<sub>x</sub>B<sub>y</sub> type, having a cation A<sup>z+</sup> and an anion B<sup>w-</sup>. Of the 16 possible salts, five were excluded due to low solubilities. These were CaSO<sub>4</sub>, CaCO<sub>3</sub>, Ca(HCO<sub>3</sub>)<sub>2</sub>,

MgCO<sub>3</sub>, and Mg(HCO<sub>3</sub>)<sub>2</sub>. Temperature was not a variable, because all measurements were made at 25°C. Solubilities were determined over a range of ionic strengths at 3 pressures: 350, 550, and 750 psia. The different pressure data served as a check for data consistency, because the salting coefficient for a given salt is not expected to vary over such a low pressure range.

We hope that this research and other studies will lead to a fundamental understanding of the salting-out of gases. This will allow gas solubility predictions to be made in complex fluids of geochemical interest, such as the Na-Ca-Cl brines characteristic of most reservoir fluids (Dickey, 1966) or the Na-K-SO<sub>4</sub>-CO<sub>3</sub>-Cl brines associated with playa sediments (Jones *et al.*, 1969).

### EXPERIMENTAL SYSTEM

The equilibration and sampling systems have previously been described in detail (Stoessel and Byrne, 1982). Briefly, the equilibration system consists of a titanium-lined saturation chamber within a stainless steel reaction vessel which is jacketed by a water bath for temperature control. System pressure is set by controlling the input and output of gas (methane) within the chamber's headspace. Gas pressure was read using a Heise CM 32507 gauge, having a dead weight accuracy within 1 psia. Saturation of a salt solution in the chamber with methane was achieved by rocking the vessel for 3 hours at system temperature (25°C) and pressure.

Salt solutions used in the experiments were made up gravimetrically using analytical reagent grade chemicals.<sup>1</sup> Generally, salt concentrations of 0.5, 1, and 2 molal were used in the experiments. Lower concentrations were used for the more insoluble salts and for KHCO<sub>3</sub> (for reasons discussed below). Methane gas used in this study was Matheson ultra high purity (manufacturer reports a minimum content of 99.97 mole % methane).

The sampling system consists primarily of a sample loop,

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<sup>1</sup> At the suggestion of a journal reviewer, the HCO<sub>3</sub><sup>-</sup> solutions were later analyzed to check for HCO<sub>3</sub><sup>-</sup> to CO<sub>3</sub><sup>2-</sup> transformation in the solid reagents. Consistent inorganic carbon and alkalinity values indicated the solution molalities were correct.

Table 1. 25°C methane solubilities in single-salt solutions, distilled water and seawater

Salt Molality*	CH <sub>4</sub> Molalities		
	350 psia	550 psia	750 psia
NaCl			
0.5	0.0284	0.0412	0.0539
1.0	0.0244	0.0352	0.0464
2.0	0.0180	0.0272	0.0347
4.0	0.0106	0.0157	0.0206
KCl			
0.5	0.0282	0.0416	0.0545
1.0	0.0247	0.0359	0.0475
2.0	0.0194	0.0289	0.0370
4.0	0.0126	0.0186	0.0245
CaCl <sub>2</sub>			
0.5	0.0250	0.0375	0.0485
1.0	0.0191	0.0295	0.0379
2.0	0.0120	0.0179	0.0236
MgCl <sub>2</sub>			
0.5	0.0257	0.0376	0.0485
1.0	0.0199	0.0300	0.0390
2.16	0.0128	0.0185	0.0237
Na <sub>2</sub> SO <sub>4</sub>			
0.5	0.0211	0.0311	0.0407
1.0	0.0135	0.0208	0.0277
K <sub>2</sub> SO <sub>4</sub>			
0.25	0.0261	0.0393	0.0515
0.5	0.0223	0.0325	0.0431
MgSO <sub>4</sub>			
0.5	0.0233	0.0352	0.0472
1.0	0.0174	0.0261	0.0342
1.5	0.0128	0.0192	0.0253
Na <sub>2</sub> CO <sub>3</sub>			
0.5	0.0211	0.0311	0.0400
1.0	0.0135	0.0204	0.0260
1.5	0.0091	0.0149	0.0182
K <sub>2</sub> CO <sub>3</sub>			
0.5	0.0219	0.0324	0.0427
1.0	0.0142	0.0217	0.0290
2.0	0.0073	0.0103	0.0128
NaHCO <sub>3</sub>			
0.25	0.0296	0.0450	0.0572
0.5	0.0270	0.0400	0.0532
KHCO <sub>3</sub>			
0.25	0.0296	0.0457	0.0574
0.5	0.0268	0.0406	0.0530
Seawater**			
34.84 ‰	0.0263	0.0400	0.0514
Distilled water			
	0.0319	0.0483	0.0617

\*Unless otherwise indicated.

\*\*Stoessel and Byrne (1982).

expansion loop, and a Meriam 10A25WM manometer which could be read within 0.05 cm of Hg. Prior to sampling, the entire system was evacuated, the manometer equilibrated with water vapor from an unsaturated sample of the salt solution, and the sample loop filled with distilled water. During sampling, solution from the chamber flushed the water out of the sample loop, at system pressure and room temperature, through a back pressure regulator. Room temperatures were a few degrees below 25°C, preventing fractionation due to increased CH<sub>4</sub> solubilities below 25°C at system pressure. Once a representative sample filled the sample loop, it was flashed and the pressure of the released gas measured on the manometer. The manometer reading stabilized within five minutes for nonbicarbonate salt solutions and within twenty minutes for distilled water. Problems associated with bicarbonate solutions are discussed below. The total gas volume and pressure change were used with the ideal gas law to compute the moles of

released gas. A small correction was made in the computed solubility for the dissolved CH<sub>4</sub> not released during flashing, using an approximate CH<sub>4</sub> solubility in the solution at the final manometer pressure. Densities, used to convert molar to molal units, were interpolated from the densities at 20°C listed by Weast (1977-1978) for the salt solutions. The molalities were not 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. The measured values in distilled water differ by +0.0002 to +0.0014 molal units from estimated saturations, computed from Eqn. (3) and listed in Table 1 of Stoessel and Byrne (1982). The agreement with solubilities interpolated from the 25°C smoothed values of Culberson and McKetta (1951) is between -0.0002 and +0.0006 molal units.

Gas chromatography was used to measure CO<sub>2</sub> mole fractions in the headspace gas within the saturation chamber and in the flashed sample gas from CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> solutions. Amounts of CO<sub>2</sub> were insignificant except in the flashed sample gas from the HCO<sub>3</sub><sup>-</sup> solutions. Mole fractions of CO<sub>2</sub> in these gases exhibited a time dependency and averaged 5, 10, 25, and 50%, respectively, for 0.25, 0.5, 1 and 2 molar HCO<sub>3</sub><sup>-</sup> solutions. The accuracy of the CH<sub>4</sub> solubility measurements decreases with an increase in the necessary CO<sub>2</sub> corrections. For this reason the maximum molality of HCO<sub>3</sub><sup>-</sup> solutions used in this study was 0.5 molal.

## RESULTS AND DISCUSSION

Methane solubility data for the single-salt solutions and distilled water are listed in Table 1 together with data for seawater from an earlier study (Stoessel and Byrne, 1982). Solubilities reported here for distilled water are the average of several measurements and are considered more accurate than those reported in the earlier study. The single-salt data are shown on Figs. 1-7 as a function of *I*, the stoichiometric ionic strength, at the 3 experimental pressures. The curves on these figures represent solubility trends, drawn to facilitate comparison between salts.

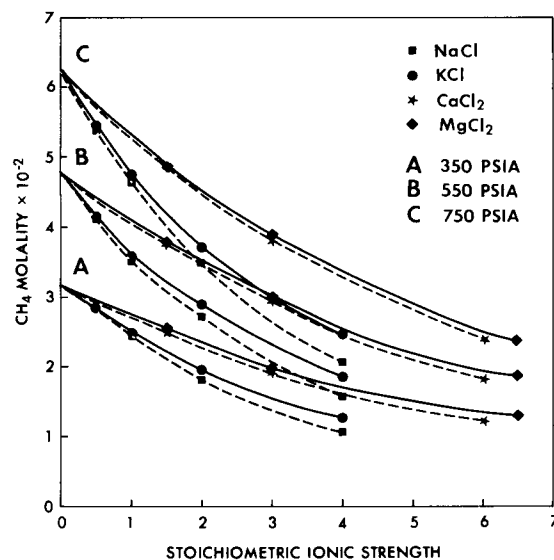


FIG. 1. Methane saturations and solubility trends in aqueous Cl<sup>-</sup> solutions at 25°C.

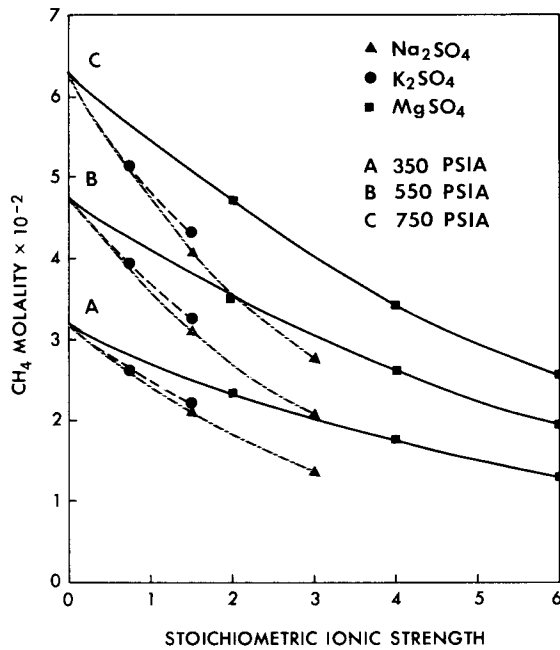


FIG. 2. Methane saturations and solubility trends in aqueous  $\text{SO}_4^{2-}$  solutions at  $25^\circ\text{C}$ .

The data for  $\text{Cl}^-$  salt solutions, shown on Fig. 1, are the most complete for illustrating the solubility effects due to different cations with the same anion. Different but consistent solubility trends are followed in the monovalent and divalent cation salt solutions. Solubilities increase in  $\text{Cl}^-$  solutions, at constant  $I$  and pressure  $P$ , in the following cation sequence:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ . A similar cation sequence is given by Randall and Failey (1927) for a general decreasing salting-out effect on non-electrolytes. Note the large solubility increase in the divalent cation solutions relative to the monovalent cation solutions. Similar trends are shown in the less complete data on Figs. 2, 3, and 4 for  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , and  $\text{HCO}_3^-$  solutions, respectively.

Solubility effects due to different anions with the same cation are displayed in Figs. 5, 6, and 7 for  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$  salt solutions, respectively. At constant  $I$  and  $P$ , changing the anion has a nearly insignificant effect on methane solubility for three of the four anions used in this study. The exception is  $\text{HCO}_3^-$ . There is a significant solubility decrease in  $\text{HCO}_3^-$  solutions relative to  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{CO}_3^{2-}$  solutions having a common cation. This solubility decrease is tenuous because of the low ionic strength of the  $\text{HCO}_3^-$  solutions and the necessary  $\text{CO}_2$  corrections.  $\text{HCO}_3^-$  is not included in the anion sequence given by Randall and Failey (1927) for a general decreasing salting-out effect on non-electrolytes; however,  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$  are listed as equivalent and having a greater effect than  $\text{Cl}^-$ .

A molal salting coefficient,  $k_m$ , for each salt is defined by Eqn. (1), consistent with the usage of Garrels

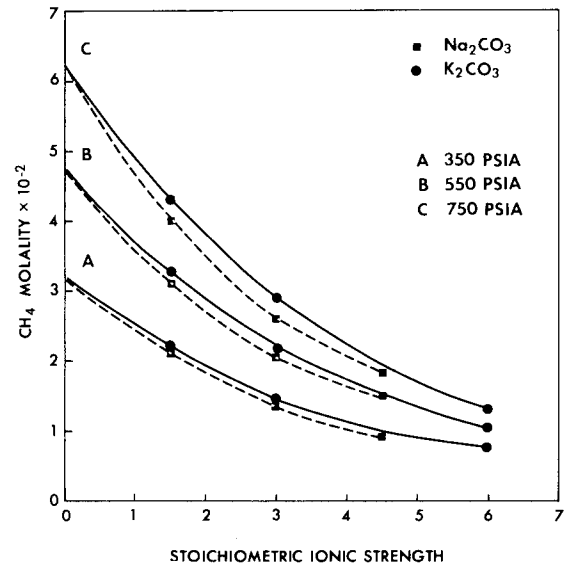


FIG. 3. Methane saturations and solubility trends in aqueous  $\text{CO}_3^{2-}$  solutions at  $25^\circ\text{C}$ .

and Christ (1965, p. 69) and Randall and Failey (1927):

$$k_m = \log \gamma_{\text{CH}_4} / I \quad (1)$$

where  $\gamma_{\text{CH}_4}$  is the molal activity coefficient. In aqueous salt solutions,  $\gamma_{\text{CH}_4}$  is given by Eqn. (2):

$$\gamma_{\text{CH}_4} = \left( \frac{m_{\text{CH}_4}^* f_{\text{CH}_4}}{m_{\text{CH}_4} f_{\text{CH}_4}^*} \right)_{P,T} \quad (2)$$

where  $m_{\text{CH}_4}$  and  $f_{\text{CH}_4}$  are the solubility in molal units and fugacity, respectively, of methane at  $P$  and tem-

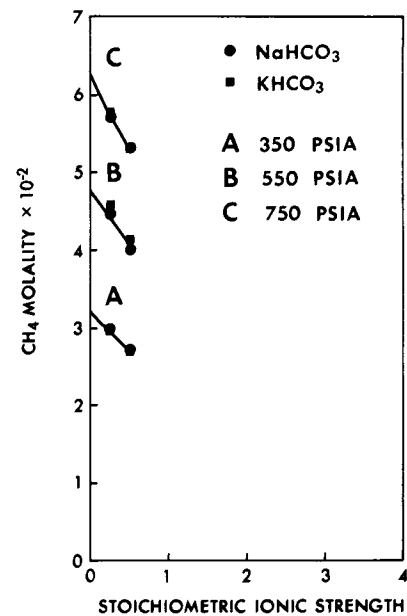


FIG. 4. Methane saturations and solubility trends in aqueous  $\text{HCO}_3^-$  solutions at  $25^\circ\text{C}$ .

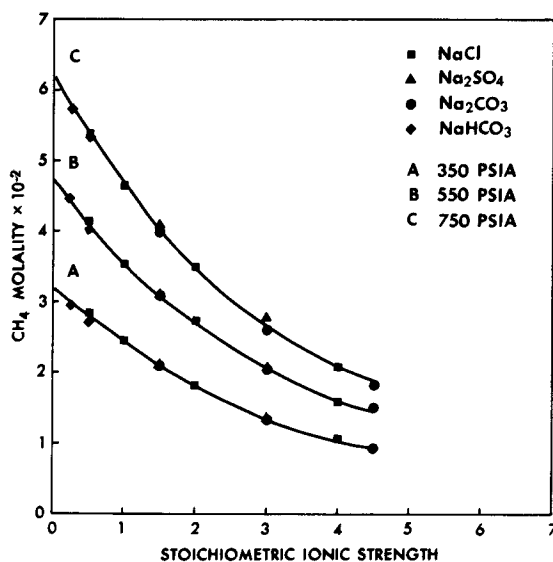


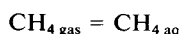
FIG. 5. Methane saturations and solubility trends in aqueous  $\text{Na}^+$  solutions at  $25^\circ\text{C}$ .

perature  $T$ . The superscript \* refers to saturation in distilled water. The fugacity ratios,  $f_{\text{CH}_4}/f_{\text{CH}_4}^*$ , were unity at constant  $P$  for the experimental conditions of the data in Table 1.

The variation in  $\gamma_{\text{CH}_4}$  with  $P$  for each salt solution was generally insignificant relative to the experimental uncertainties of the data. This was expected because the change in  $\log \gamma_{\text{CH}_4}$  at constant  $T$  and salt composition can be shown to be

$$\log \left[ \left( \frac{m_{\text{CH}_4}}{f_{\text{CH}_4}} \right)_{P_1} \left( \frac{f_{\text{CH}_4}}{m_{\text{CH}_4}} \right)_{P_2} \right] + \frac{\bar{V}_{\text{CH}_4}^0 (P_1 - P_2)}{2.303RT}$$

for the equilibrium



where the pressure has changed from  $P_1$  to  $P_2$ , and

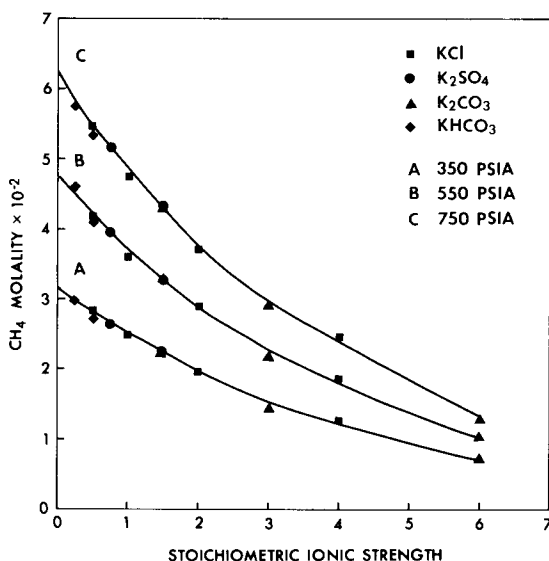


FIG. 6. Methane saturations and solubility trends in aqueous  $\text{K}^+$  solutions at  $25^\circ\text{C}$ .

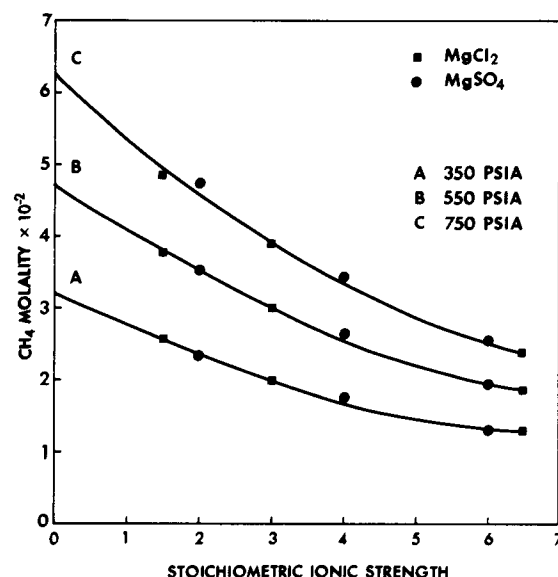


FIG. 7. Methane saturations and solubility trends in aqueous  $\text{Mg}^{2+}$  solutions at  $25^\circ\text{C}$ .

$\bar{V}_{\text{CH}_4}^0$  is the standard state partial molal volume of methane, and  $R$  is the gas constant. The standard state of aqueous methane is taken to be a function of  $P$ , but  $\bar{V}_{\text{CH}_4}^0$  is assumed constant between  $P_1$  and  $P_2$ . The two terms cancel over the pressure range used in this study. This can be verified using the data from Table 1, fugacity coefficients from Tester (1961, p. 65) and  $35.5 \text{ cm}^3/\text{mole}$  for  $\bar{V}_{\text{CH}_4}^0$  (value explained below).

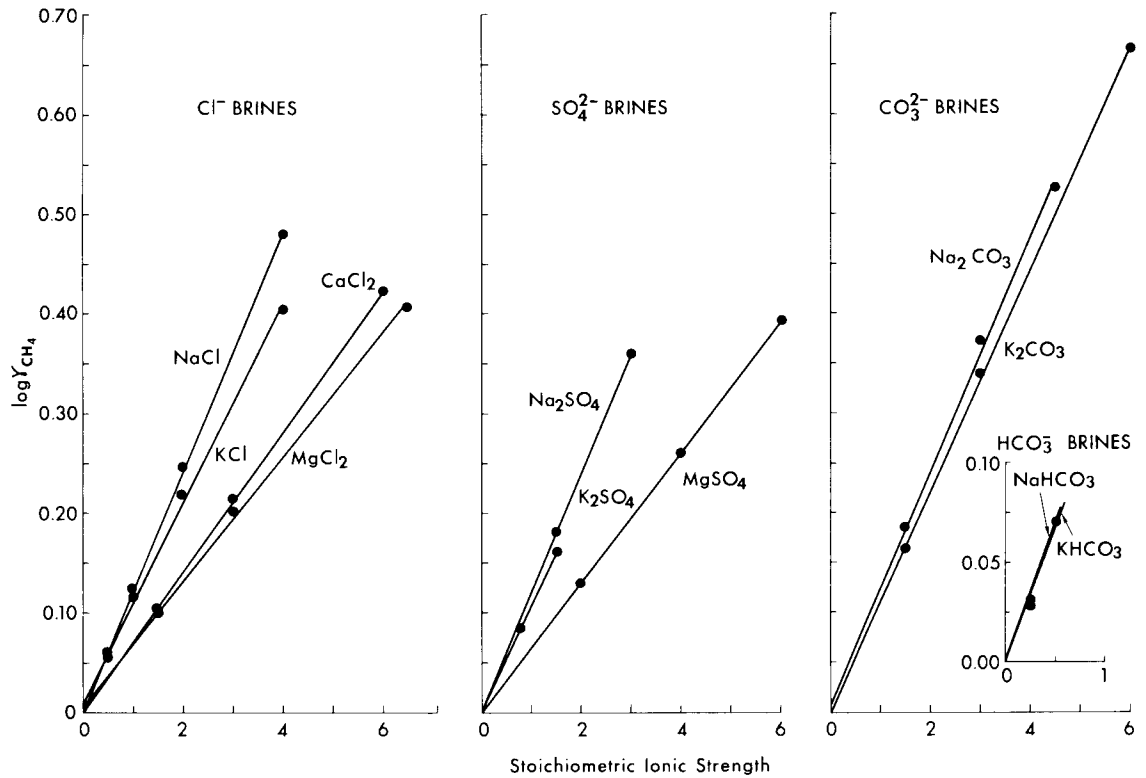
$\log \gamma_{\text{CH}_4}$  values are plotted on Fig. 8 as a function of  $I$ . These points are the arithmetic means for the three experimental pressures. Each straight line is a least squares fit to Eqn. (1) for a given salt using the mean values and  $\log \gamma_{\text{CH}_4} = 0$  at  $I = 0$ . The slope of the line is  $k_m$ . The molal salting coefficients for the salts and for seawater are tabulated in Table 2, together with their respective correlation coefficients. There is a good linear fit of  $\log \gamma_{\text{CH}_4}$  to Eqn. (1) for each of the 11 salts over the concentration ranges of the measurements. The correlation coefficients for  $\text{KHCO}_3$  and  $\text{NaHCO}_3$  reflect the sensitivity of  $k_m$  to experimental error in  $\gamma_{\text{CH}_4}$  as  $\gamma_{\text{CH}_4}$  approaches unity, *i.e.* as  $I$  approaches zero.

We have used  $k_m$  rather than the more commonly used Setschenow constant,  $k_s$ , as the salting coefficient.  $k_s$  is defined by

$$\log \gamma_{\text{CH}_4} / \text{salt concentration.}$$

$k_m$  is a more useful parameter in the multisalt solutions of geochemical interest. In these solutions use of  $k_m$  normalizes salting contributions from the individual salts on the basis of individual contributions to  $I$ . For ion-solvent interactions this is a better procedure than normalization on the basis of concentrations.

Eqn. (3) is a general relation that can be used to estimate  $m_{\text{CH}_4}$  at  $25^\circ\text{C}$  and at pressures below gas

FIG. 8. Log  $\gamma_{\text{CH}_4}$  in single-salt solutions at 25°C.

hydrate formation in solutions equilibrated with a multicomponent gas phase.

$$(m_{\text{CH}_4})_P = \chi_{\text{CH}_4} X_{\text{CH}_4} P \left( \frac{m_{\text{CH}_4}}{f_{\text{CH}_4}} \right)_{1 \text{ atm}} e^{\bar{V}_{\text{CH}_4}(1-P)/RT} \quad (3)$$

where  $\chi_{\text{CH}_4}$  and  $X_{\text{CH}_4}$  are the methane fugacity coefficient and mole fraction, respectively, in the gas phase at  $P$  and  $\bar{V}_{\text{CH}_4}$  is the partial molal volume of methane. Eqn. (3) depends upon Henry's law (molal basis) and the assumption of a constant  $\bar{V}_{\text{CH}_4}$  with changes in  $P$ . The derivation is made at constant  $T$  and dissolved salt content, following the general procedure of O'Sullivan and Smith (1970).

The  $f_{\text{CH}_4}/m_{\text{CH}_4}$  ratio in the salt solution at 1 atm and 25°C is computed from the value in distilled water, 708 molal<sup>-1</sup> (Yamamoto *et al.*, 1976), and  $k_m$  for the salt solution.  $\chi_{\text{CH}_4}$  values are estimated using procedures described by Prausnitz (1969) and data listed by Tester (1961, p. 65).  $\bar{V}_{\text{CH}_4}$  is approximately 35.5 cm<sup>3</sup>/mole, based on fitting Eqn. (3) to the high pressure and low temperature solubilities reported by Culberson and McKetta (1951) and O'Sullivan and Smith (1970). This partial molal volume is consistent with the low pressure data reported in Table 1, within the experimental uncertainties of the measurements.  $\bar{V}_{\text{CH}_4}$  is insensitive to temperature and salt content below 60°C.

Use of Eqn. (3) for the multisalt fluids of geochemical interest requires knowing  $k_m$  as a function of dissolved salt content. The salting theories of Debye, Kirkwood, and McDevit and Long do not predict

accurate values of  $k_m$  (Long and McDevit, 1952; Morrison, 1952). Solubility measurements at 25°C are needed in multisalt solutions to fit an empirical equation for  $k_m$  as a function of the salting coefficients of single salts presented here.

As a first approximation, we might assume this empirical equation to be simply the sum of single-salt coefficients normalized on the basis of the  $I$  contribution of each salt in the solution. This approach for seawater predicts  $k_m$  to be about 7.5% lower than

Table 2. Molal salting-out constants of  $\text{CH}_4$  in single-salt solutions and seawater

Salt	$k_m$	Maximum salt Molality	$r^*$
NaCl	0.121	4.0	0.9998
Na <sub>2</sub> SO <sub>4</sub>	0.121	1.0	0.9999
Na <sub>2</sub> CO <sub>3</sub>	0.118	1.5	0.9989
NaHCO <sub>3</sub>	0.146	0.5	0.9976
KCl	0.101	4.0	0.9986
K <sub>2</sub> SO <sub>4</sub>	0.108	0.5	0.9994
K <sub>2</sub> CO <sub>3</sub>	0.111	2.0	0.9998
KHCO <sub>3</sub>	0.145	0.5	0.9942
CaCl <sub>2</sub>	0.071	2.0	0.9999
MgCl <sub>2</sub>	0.063	2.0	0.9992
MgSO <sub>4</sub>	0.066	1.5	0.9999
Seawater	0.113	**	

\*Correlation coefficient for the fit of  $\gamma_{\text{CH}_4}$  data to eqn (1).

\*\*Based on measurements at 34.84 ‰ salinity.

the observed value listed in Table 2. The predicted value varies slightly, depending on the cation assigned with  $\text{SO}_4^{2-}$ . The agreement between observed and predicted methane solubilities is much closer, within 2%, reflecting the sensitivity of  $k_m$  to small changes in  $m_{\text{CH}_4}$ . Byrne and Stoessel (in preparation) will report measured solubilities in multisalt solutions and discuss the agreement with predicted values based on the sum of single-salt coefficients.

#### SUMMARY

Aqueous methane solubilities were presented as a function of dissolved salt concentration at 25°C and below 800 psia for 11 single salts. At constant pressure and stoichiometric ionic strength, (1) solubilities were significantly higher in solutions containing divalent cations as compared to those containing monovalent cations; (2) solubilities increased in solutions having a common anion in the following cation sequence:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ; and (3) with the exception of the increased salting-out effect of the  $\text{HCO}_3^-$  anion, solubilities varied almost insignificantly between solutions having a common cation but different anions.

Molal salting coefficients were derived from the experimental data for the salts. The use of salting coefficients was discussed in predicting methane solubilities in multisalt fluids equilibrated with a multicomponent gas phase. Solubility data at 25°C are needed in multisalt solutions of geochemical interest to fit an empirical equation for  $k_m$  as a function of the single-salt molal salting coefficients presented in this study.

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