Clays and Clay Minerals, Vol. 30, No. 1, 67–72, 1982.

METHANE SOLUBILITIES IN CLAY SLURRIES

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Abstract—Methane solubilities at 25°C were measured at 350, 550, and 750 psia in dilute (<11 wt. %) clay slurries of Na-montmorillonites and argillaceous sediment. Methane solubilities were not significantly affected by the presence of clay. Water hydrated onto the external clay surfaces did not appear to exclude methane. In addition there was no detectable sorption of methane onto the clays. The measured solubilities are consistent with an open structure of the water hydrated onto the clay surface for which the partial molal volume is larger than that of normal water. The results imply that aqueous methane solubilities measured in the laboratory can be used to determine degrees of methane saturation in interstitial solutions in unconsolidated sediments.

Key Words—Adsorption, Interlayer water, Interstitial water, Methane, Montmorillonite, Solubility, Water.

INTRODUCTION

Methane forms biogenetically in sediments at surface temperatures (Claypool and Kaplan, 1974) and by thermal cracking of organic matter with increasing temperatures (Tissot and Welte, 1978). Degrees of methane saturation in interstitial waters are usually determined by comparison of field measurements with laboratory solubility measurements made in similar aqueous solutions at the same pressure and temperature.

Hinch (1978) suggested that hydrocarbons are excluded from the water hydrated to the surface of clays. If significant amounts of such water in sediments are unavailable as a solvent for dissolving methane, the apparent solubility would be lowered, introducing errors in the interpretation of degrees of saturation. In addition, water occupying interlayer space within clay-mineral particles may not be available as a solvent for methane in slurries. Methane is a nonpolar molecule and is not expected to enter this space. The purpose of this study was to measure methane solubilities in aqueous clay slurries and to compare these values with solubilities measured in similar aqueous solutions. The measurements were made at 25°C at 350, 550, and 750 psia. Unless otherwise noted, the solubilities of methane in this study are reported relative to the amounts of bulk water in the slurries. The bulk water includes the surface-hydrated water on the external surfaces of particles but not the interlayer water within particles.

EXPERIMENTAL APPARATUS AND PROCEDURE

Methane gas used in this study was Matheson ultra high purity. The manufacturer reports the methane content to be 99.97 mole %. The equilibration system is shown schematically in Figure 1. The Tem-Pres stainless steel saturation vessel contains a 500-cm^3 titanium-lined chamber with 3 ports at the top. Port A was used to introduce pressurized methane, and port C was used to purge the solution or slurry prior to an experiment and to sample the saturation chamber after equilibration. Pressure input into the saturation chamber was controlled by a Grove 16L regulator. Pressure within the saturation chamber was measured via port B by a Heise CM 32507 gauge. This gauge has a dead weight accuracy within 1 psia over the pressure range used in this study. Pressure within the saturation vessel was controlled by periodic venting through port B. Equilibrium pressures were maintained within 1 psia of the reported gauge values, and the estimated accuracy of the reported equilibrium pressures was within 2 psia. Temperature in the water jacket surrounding the bottom and sides of the saturation chamber was controlled to within 0.1°C by a Lauda K-2/R constant-temperature-bath circulator.

A schematic drawing of the stainless steel sampling system is shown in Figure 2. The sampling system connects to the saturation vessel at valve 8 during sampling. Each sample was taken isobarically in the 13.22-cm^3 sample loop and then flashed into the evacuated expansion loop. The change in pressure was measured manometrically by a 30-inch Meriam 10A25WM manometer which could be read to within 0.5 mm of Hg. A Grove 155 back pressure regulator at c was used to flush fluids through the sample loop under isobaric conditions. The evacuated glass flask at a contained 5 ml of the slurry or solution in the reaction vessel. Prior to sampling, this fluid was used to equilibrate the manometer and the previously evacuated system with water vapor at room temperature (22–24°C). The evacuated glass flask at b was used to flash a sample for observation purposes.

An experimental run began with 400 ml of slurry or solution in the vessel. The fluid and headspace were purged with methane to remove residual air. Pressure

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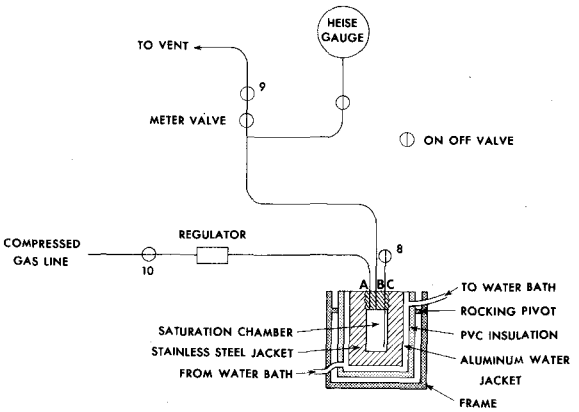


Figure 1. Equilibration system.

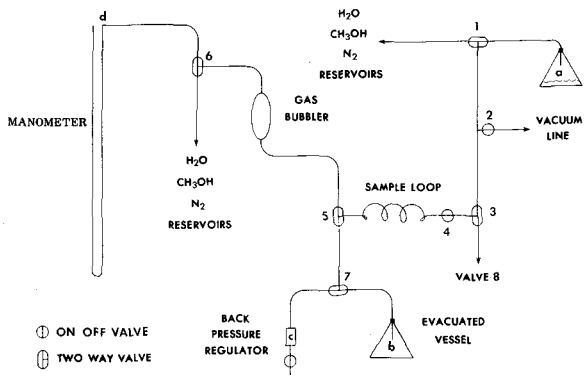


Figure 2. Sampling system.

within the vessel was then allowed to reach the desired equilibration value. The vessel was rocked 30° from the vertical at 60 oscillations/min for 3 hr to insure that equilibration had occurred. Equilibration actually occurred within 2 hr as determined by reproducible measurements of dissolved gas content. The pressure was maintained within 3 psia of the desired gauge value during the first 2 hr and within 1 psia during the final hour.

The sampling system was connected at valve 8 to the vessel, evacuated, and then equilibrated with water vapor. Distilled water under pressure filled the lines from valve 8 through the back pressure regulator (c). The solution from the chamber was then passed under near isobaric conditions through the sample loop and out c. After flushing 45 ml of fluid (a 5-min operation) through c, the sample loop was isolated and valve 5 opened to flash the sample into the expansion loop. The sampling procedure took less than 15 min from the time the vessel stopped rocking.

A half-hour equilibration time was allowed for the expanded gas to warm to room temperature before the manometer was read. Residual dissolved gas at manometer pressure was estimated and included in calculating the original gas molality of the sample. The mass of water in each slurry sample was needed for expressing methane solubility in molal units. In the absence of flocculation of the solids in the vessel, the water mass could be computed using the sample loop volume and the water content and density of the original slurry. Flocculation in the vessel resulted in a lower solids content in the sample. To check for flocculation, the measured mass of sample solids was compared with that predicted using the original slurry. Generally, there was no significant difference. If flocculation occurred, the correct density and wt. % solids in the sample were obtained by matching the mass of solids in the sample with those predicted using successive dilutions of the original slurry.

Following the completion of sampling, the entire sample system was disconnected from the vessel, flushed with distilled water and methanol, and then dried with N_2. The pressure in the vessel was then raised to a higher equilibration value and the entire procedure was repeated. It was possible to take samples until the fluid volume in the vessel dropped to less than 80 cm^3. For a viscous slurry, a presample was flashed to b (a glass flask) to check for bubbles contained in the liquid. A presample was also flashed to b prior to taking the first sample in an experimental run. Undissolved bubbles that may have collected in the sample tube (in the vessel) during purging and that resisted flushing from the sample loop were removed by taking this presample.

The precision of the measurements is within 0.0005 molal units of CH_4. The estimated accuracy, taking into account experimental uncertainties, is within 0.001 molal units, corresponding to a possible 3.2% error at 350 psia and a possible 1.6% error at 750 psia for CH_4 saturation in distilled water at 25°C. The corresponding possible errors using sea water are 3.9% and 2.0%, respectively. The experimental apparatus is adequate for ungelled clay slurries having less than 10 wt. % clay (110°C dried weight). Extrapolation of data obtained with this apparatus to the higher clay:fluid ratios characteristic of purely argillaceous sediments is tenuous; however, some conclusions can be inferred. In addition, the data apply directly to sediment having minor clay content and provide indirect evidence on the nature of water hydrated onto clay surfaces.

CLAY AND SEDIMENT PREPARATION

Two CMS Source Clay montmorillonites and one argillaceous sediment from the Mississippi delta were used in the slurries. The two montmorillonites were the Cheto montmorillonite from Arizona (SAz-1) and a bentonite from Wyoming (SWy-1) obtained from The Clay Minerals Society. Data on these clays are reported by Van Olphen and Fripiat (1979). The marine sediment was supplied by Thomas Whelan of Carbon Systems

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Table 1. Measured and predicted 25°C CH_4 solubilities in distilled water and in sea water of 34.84‰ salinity.

Solution	Molal solubilities[1]		
	350 psia	550 psia	750 psia
Distilled water			
Measured	0.0318	0.0473	0.0623
Predicted	0.0313	0.0469	0.0615
Sea water			
Measured	0.0263	0.0400	0.0514
Predicted	0.0255	0.0384	0.0502

[1] Precision and estimated error limits are within 0.0005 and 0.001 molal units, respectively.

Table 2. Measured 25°C CH_4 solubilities in Na-saturated SAz-1 dispersed into distilled water.

Clay concentration (wt. %)	Molal solubilities		
	350 psia	550 psia	750 psia
1.09	0.0300	0.0457	0.0596
1.99	0.0298	0.0457	0.0610
5.52	0.0299	0.0466	0.0620
10.32	0.0296	0.0472	0.0608

Inc. from a core off the present Mississippi delta in 60 m of water and 10 m below the bottom.

Samples of SAz-1 and SWy-1 were each treated with H_2O_2 to remove organic material. Following settling to remove nonclay minerals, the clays were centrifuged and washed to remove soluble salts. Crystalline impurities were undetected on X-ray powder diffraction (XRD) patterns of sample SAz-1; however, patterns of sample SWy-1 showed the presence of minor quartz.

Predominant Na occupancy of exchange sites was achieved by mixing 10 g of clay (110°C wt.) with 1 liter of a 1-M NaCl solution. The slurries were allowed to sit for one week with occasional shaking and were then washed and centrifuged until Cl^- could not be detected by silver nitrate titration. The washed clay was then dispersed in distilled water to make the slurries.

Sample SWy-1 dispersed easily into gels in which the particles are the fundamental 10-Å silicate sheets (Norrish and Quirk, 1954). There is no interlayer water "within" particles in these gels. SAz-1 did not form gels, apparently due to its large negative structural charge (Grim, 1962, p. 222) as shown by its large CEC of 120 meq/100 g (Van Olphen and Fripiat, 1979). Coulter counter measurements of the unflocculated particles indicated an average particle diameter between 0.5 and 0.8 μm. During the experiments, the rocking mechanism was sufficient to keep the slurries of sample SAz-1 unflocculated.

Hydration measurements on Na-saturated SAz-1 samples at 100% humidity indicated that 16 water molecules were present per unit cell. XRD patterns of wet, oriented slides showed 2 water layers in the interlayer space. For the purpose of computing interlayer water contents, the unit cell of the clay in the SAz-1 slurries was assumed to contain 2 water layers with 8 water molecules per layer.

The argillaceous sediment was stored for 2 months in a brine containing 150,000 ppm NaCl. It was then centrifuged and washed until Cl^- could not be detected. The organic C content was 1.2 ± 0.2 wt. %. XRD patterns of the sediment showed the following major components: quartz, feldspar, dioctahedral smectite, and well-crystallized mica and kaolinite. One portion of the washed sediment was dispersed in distilled water. A second portion was washed twice with sea water and then dispersed in sea water.

All slurries were used in the experiments within one week of their preparation. Analyses of the dissolved salt content in the slurries showed insignificant hydrolysis of the solids during this period.

RESULTS

The experimental procedure was checked by measuring CH_4 solubilities in distilled water and in sea water of 34.84‰ salinity. These solubilities are compared with predicted solubilities in Table 1. The predicted values are from the following equation derived (in terms of mole fractions) by O'Sullivan and Smith (1970):

$$m = (XP)\exp(\ln m^* - \bar{V}(P - 1)/RT)$$

where m is the predicted molality, X is the fugacity coefficient at pressure P, R is the gas constant, T is the absolute temperature, and $\bar{V}$ is the partial molal volume of CH_4. The symbol m* is the molality of methane measured in the solution which was equilibrated with a methane gas phase at 1 atm and temperature T.

The equation depends on Henry's law and the assumption of a constant $\bar{V}$ with changes in P. X values can be interpolated from data listed by Din (1961), and m* values can be computed from the Bunsen solubility coefficients of Yamamoto *et al.* (1976). $\bar{V}$ was taken to be 35.5 cm^3/mole on the basis of the high pressure low temperature (below 60°C) solubilities of Culberson and McKetta (1951) and O'Sullivan and Smith (1970). $\bar{V}$ is insensitive to temperature and salt content below 60°C.

The agreement between the measured and predicted values for distilled water is within the experimental uncertainty. The reason for the discrepancy between predicted and measured sea-water solubilities is unknown; however, a 2% increase in the sea-water Bunsen coefficient of Yamamoto *et al.* (1976) would produce good agreement.

Solubilities measured in SAz-1 slurries, SWy-1 slurries, and sediment slurries are listed in Tables 2, 3, and 4, respectively. Solubilities in clay slurries are reported relative to the bulk water content, which (as discussed

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Table 3. Measured 25°C CH_4 solubilities in Na-saturated SWy-1 dispersed into distilled water.

Clay concentration (wt.%)	Molal solubilities		
	350 psia	550 psia	750 psia
1.01	0.0306	0.0467	0.0621
2.01	[1]	0.0465	0.0613

[1] The pressure drop on flashing was not sufficient to release bubbles from the gel due to its high viscosity. The increasing viscosity limited the maximum clay content to 2%.

Table 4. Measured 25°C CH_4 solubilities in Mississippi delta sediment dispersed in distilled water and in sea water of 34.84‰ salinity.

Sediment concentration (wt. %)	Molal solubilities		
	350 psia	550 psia	750 psia
Distilled water			
7.1	0.0312	0.0468	0.0616
Sea water			
9.7	0.0250	0.0396	0.0517

above) does not include interlayer water within particles. Clay wt. % values in clay slurries include the 110°C clay mass plus the estimated interlayer water mass. Solubilities and sediment wt. % values in sediment slurries are reported relative to the total water content and the 110°C sediment mass, respectively, because interlayer water contents could not be reliably estimated.

The SWy-1 data in Table 3 are for slurries having only 1 and 2 wt. % of clay. The increased viscosity of the more concentrated gels resulted in bubbles (observed) remaining in flashed samples and not being released to the manometer. Observed bubbles remained in the 2 wt. % slurry at 350 psia where the pressure drop was not sufficient to release the bubbles. Surface areas of clays and sediment in the slurries are not accurately known. Surface areas determined from gas adsorption techniques on the CMS source clays (Van Olphen and Fripiat, 1979) do not necessarily correspond to the reactive surface areas in solution (Lerman, 1979, p. 389).

The CH_4 solubilities in Tables 2, 3, and 4 show no significant differences compared to the solubilities in Table 1, measured in the pure aqueous solutions. Minor decreases were noted in the distilled water slurries and, with one exception, are less than 0.002 molal units, which is the combined estimated error of 2 measurements. The decreases do not show a consistent correlation with increasing clay content in the slurries. These decreases cannot be explained; however, they are relatively insignificant.

DISCUSSION

The measurements do not show a "definitive" change of methane solubilities between the slurries and the pure aqueous solutions. Solubility increases in the slurries would have indicated sorption of methane into the interlayer space or onto particle surfaces. The lack of an increase is thought to be due to the nonpolar nature of methane. The lack of a decrease must be related to the nature of hydrated water on the clay surfaces. Because salt solutions show a reduction in solubility, a comparison of properties may help explain the results and their application to sediments.

Water hydrated onto clay surfaces has a different structure from water hydrated around salt ions. The data of Low and Anderson (1958) indicate a continuous increase in the partial molal volume of water approaching the clay surfaces. This increase extends over a 60-Å distance. Salt solutions produce the opposite effect. Partial molal volumes of water in NaCl solutions, computed from data in the Handbook of Chemistry and Physics (Weast, 1977–1978), decrease with increasing salt content. Salt ions constrict or compress hydrated water molecules, effectively removing them as a solvent for methane. On the other hand, water hydrated onto clay surfaces has a more open structure which is somewhat similar to that of ice (Grim, 1968, p. 246). Methane should be soluble in this water because it readily forms ice-like gas hydrates (clathrates) at higher pressures (Miller, 1974). Indeed, the open structure of the hydrated water may alter the PT conditions of the formation of these gas hydrates in interstitial waters of clay-rich sediments.

The effect of increasing temperature on changes in CH_4 solubilities in slurries, relative to the pure aqueous solvent, is debatable. Intuitively, one might expect hydrated water bound to clay surfaces or to dissolved ions to become more like normal water with increasing temperature. This is not necessarily the case for salt solutions. The low temperature (<25°C) study of Eucker and Hertzberg (1950) shows that with increasing temperature the percentage of salting-out in NaCl solutions decreases for CH_4 solubilities relative to distilled water; however, the intermediate temperature (50°–125°C) data of O'Sullivan and Smith (1970) are inconclusive. The high temperature (100°–240°C) study of Blount *et al.* (1979) indicates a substantial increase.

Extrapolation of solubility data obtained in slurries to unconsolidated argillaceous sediments is tenuous. The sediments will have a larger clay surface area relative to the bulk water content. However, assuming that the above conclusion regarding the solubility of methane in clay-surface hydrated water is valid, the solubility of methane should be the same in the sediment as in the pure aqueous solution.

Consolidated argillaceous sediments represent a different situation. A limiting pore size must exist such that the nonpolar nature of methane excludes it from the pore. This follows from the apparent lack of ab-

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sorption of methane into the interlayer space. Hinch (1978) postulated hydrocarbon expulsion from shales due to molecular interactions between mineral surfaces and pore fluids. Such methane expulsion is likely, resulting from its inability to form hydrogen bonds with the clay surfaces.

CONCLUSIONS

Methane solubilities were not significantly affected by sorption of methane onto clays or by clay surface hydration in the slurries used in this study. Methane solubilities in unconsolidated argillaceous sediments should be similar to those measured in interstitial waters in the absence of mineral surfaces. This follows from the open structure of the hydrated water.

ACKNOWLEDGMENTS

We thank Dr. R. V. Nauman of the Chemistry Department of Louisiana State University for his advice on the experimental design, Dr. T. Whelan of Carbon Systems, Inc. for a discussion of the results, and Drs. L. Price of the U.S. Geological Survey and H. Hinch of the Amoco Production Company Research Center for informal constructive reviews. This research was funded by the U.S. Geological Survey (Geopressured Zones and Mississippi Delta Studies) and by the Louisiana Geological Survey.

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(Received 30 October 1980; accepted 10 March 1981)

Резюме—Измерялись растворяемости метана при температуре 25°C и давлениях 350, 550, и 750 psi (фунт силы/дюйм²) в разбавленных (<11 весовых %) Na-монтмориллонитовых глинистых илах и в глинистых осадках. Присутствие глины не влияло значительно на растворяемости метана. Вода, гидратированная на внешних поверхностях глины, не исключала присутствия метана. Дополнительно не наблюдалось сорбции метана на глинах. Измеренные растворяемости соответствуют откурытой структуре воды, гидратированной на поверхности глины, парциальный молярный обьем которой больше, чем для нормальной воды. Результаты указывают на то, что растворяемости метана в воде, измеренные в лаборатории, могут быть использованы для определения степеней насыщения метаном промежуточных растворов в неконсолидированных осадках. [E.C.]

Resümee—Es wurden die Methan-Löslichkeiten bei 25°C und 350, 550, und 750 psi in verdünnten (<11 Gew.-%) Tonschlämmen von Na-Montmorillonit und tonigen Sedimenten gemessen. Die Methan-Löslichkeiten wurden kaum durch die Gegenwart von Ton beeinflußt. Das Wasser, das auf den äußeren Tonoberflächen hydratisiert war, schien das Methan kaum auszuschließen. Außerdem wurde keine Adsorption von Methan an die Tone beobachtet. Die gemessenen Löslichkeiten sind in Übereinstimmung mit einer offenen Struktur des Wassers, das an den Tonoberflächen hydratisiert ist und dessen partielles Molvolumen größer ist als das des normalen Wassers. Die Resultate bedeuten, daß die Löslichkeiten von wasserhaltigem Methan im Labor benutzt werden können, um den Grad der Methan-Sättigung in Zwischenschichtlösungen von nichtverfestigten Sedimenten zu bestimmen. [U.W.]

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Résumé—On a mesuré les solubilités du méthane à 25°C, à 350, 550, et 750 psia dans des coulées argileuses diluées (<11% poids) de montmorillonite-Na et de sédiment argileux. Les solubilités du méthane n'étaient pas affectées de manière significative par la présence d'argile. L'eau hydratée sur les surfaces externes de l'argile n'avait pas l'air d'exclure le méthane. De plus, il n'y avait pas de sorption détectible de méthane sur les argiles. Les solubilités mesurées sont compatibles avec une lattice ouverte de l'eau hydratée sur la surface de l'argile dont le volume molal partiel est plus grand que celui de l'eau normale. Les résultats impliquent que les solubilités aqueuses de méthane mesurées dans le laboratoire peuvent être utilisées pour déterminer les degrés de saturation du méthane dans les solutions interstitiales dans des sédiments non-consolidés. [D.J.]

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