

kali metal and ammonium halide solubilities decreasing with solvent in the order: ethylenediamine (4) > DMF (6) > 3Me2Ox > 3tBu2Ox > acetonitrile (4).

These data show that 3Me2Ox and tBu2Ox may be suitable media for conductance (2), spectroscopy, and acid-base equilibrium studies. Due to their relatively high dielectric constants and large polarities, these cyclic urethanes have promise as electrolytic solvents for a wide variety of applications.

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## Solubility of Methane in Distilled Water and Seawater

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**Bunsen solubility coefficients for methane in distilled water and in seawater at three salinities were determined with an estimated accuracy of 0.5%. The experimental data were fit by the least-squares method to an equation established by Weiss. A table of Bunsen solubility coefficients covering the temperature range -2° to 30°C and the salinity range 0-40 parts per thousand was calculated from the fitted equation. For seawater of salinity 34‰, the Bunsen coefficients ranged from 0.04489 at 0°C to 0.02368 at 30°C. Solubility values for distilled water were in agreement with those reported by Bunsen and Claussen and Polglase but were 3-5% higher than those of Winkler and Morrison and Billet.**

During the past several years, there has been increasing interest in the oceanic distribution of methane (1, 11, 12, 15). Concentrations of methane in the atmosphere and seawater were measured by Swinnerton and his coworkers (11), but they were unable to conclude from their observations whether the ocean is acting as a source or sink for this gas. More recently, Swinnerton and Lamontagne (12) proposed an empirical relationship involving the ratio of the measured methane concentration and its baseline concentration in seawater and similar ratios for ethane and propane as an index of contamination for hydrocarbon pollution. Proper interpretation and use of such information require accurate values for the solubility of methane in seawater. This paper reports the measurement of Bunsen solubility coefficients of methane in distilled water and in seawater at three salinities.

Methane solubilities in distilled water have been reported by a number of workers (2, 3, 9, 18). The results of Bunsen (2) and Claussen and Polglase (3) are about 3-5% higher than those of Winkler (18) and Morrison and Billet (9). Measurements were made in NaCl solutions by Morrison and Billet (9) and by Mishnina et al. (7, 8). The latter workers made measurements in NaCl solutions ranging from 1.00 to 5.31M which is considerably higher than the range of salinities encountered in seawater. Measured solubilities of methane in

seawater have not been reported previously. Calculated solubilities were reported by Atkinson and Richards (1), and Weiss (14) made measurements at one salinity and one temperature.

#### Experimental

Research grade methane gas (Linde Specialty Gas, 99.99% purity) was used for all measurements. The gas was passed through a tube of Ascarite to remove CO<sub>2</sub> prior to use. Seawater was collected, prepared, and degassed as described by Crozier and Yamamoto (4).

Solubility measurements were made by the Scholander microgasometric technique (10) as modified by Douglas (5), using the procedure described previously (4). Measurements were made at several temperatures for waters of a given salinity. Saturation halftimes for distilled water at 11°C was 2.5 min, and for seawater (27.8‰) at 30°C, 4 min. The solution was allowed to equilibrate at least 45 min to ensure complete mixing.

The volumes of absorbed gas and of the water were measured. Bunsen solubility coefficients,  $\beta$ , were calculated from the observed volumes (5).  $\beta$  is defined as the volume of gas (corrected to standard temperature and pressure) absorbed in a unit volume of water at the measurement temperature when the partial pressure of the gas is 760 mm. The calculated solubilities were corrected for the effect of dissolved gas on the volume of the aqueous phase by using a value of 37 cm<sup>3</sup> for the partial molal volume of methane (6). The corrections increased the solubility coefficients by about 0.16%.

#### Results and Discussion

The experimental Bunsen solubility coefficients for methane in distilled water and seawater at three salinities are given in Table I.

The Bunsen solubility coefficient can be expressed as a function of temperature and salinity as follows (13):

$$\ln \beta = A_1 + A_2(100/T) + A_3 \ln (T/100) + S[B_1 + B_2(T/100) + B_3(T/100)^2] \quad (1)$$

where  $A$  and  $B$  are constants,  $T$  is temperature in degrees Kelvin, and  $S$  is salinity in parts per thousand. The constants

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were calculated by fitting the experimental data to Equation 1 by the method of least squares (4). Values of the constants obtained from the fit are shown in Table II. These constants were substituted back into Equation 1, and Bunsen solubility

coefficients for the temperature range  $-2^{\circ}$  to  $30^{\circ}\text{C}$  and salinity range 0–40 parts per thousand were calculated (Table III).

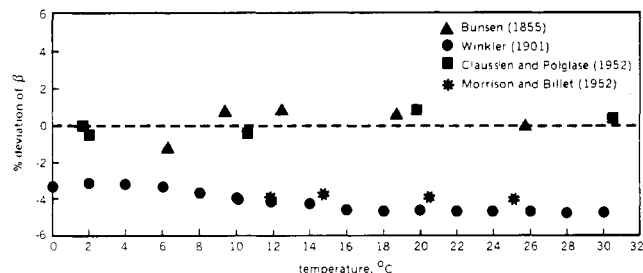
Percent deviations of Bunsen solubility coefficients ob-

Table I. Experimental Bunsen Solubility Coefficients for Methane in Distilled Water and Seawater

Salinity	Temp, °C	$\beta$	Temp, °C	$\beta$	Temp, °C	$\beta$	
0.0	0.76	0.05592	10.93	0.04216	18.02	0.03606	
	0.78	0.05612	10.93	0.04242	24.10	0.03196	
	0.79	0.05613	10.94	0.04224	24.11	0.03192	
	0.80	0.05600	10.94	0.04220	24.15	0.03189	
	0.80	0.05591	10.94	0.04238	24.16	0.03211	
	0.81	0.05604	10.95	0.04224	24.17	0.03200	
	4.92	0.04957	10.95	0.04226	29.52	0.02915	
	4.94	0.04963	10.96	0.04252	29.54	0.02913	
	4.95	0.04973	17.99	0.03606	29.54	0.02915	
	4.96	0.04963	18.00	0.03603	29.54	0.02911	
	4.97	0.04968	18.01	0.03619	29.55	0.02901	
	10.90	0.04235	18.02	0.03607			
	27.738	2.07	0.04431	9.54	0.03611	20.05	0.02901
		2.08	0.04433	9.55	0.03640	20.20	0.02905
2.08		0.04418	9.55	0.03667	20.21	0.02919	
2.09		0.04412	9.55	0.03649	21.40	0.02902	
2.09		0.04410	9.56	0.03653	21.40	0.02895	
2.09		0.04410	9.75	0.03620	21.70	0.02902	
2.15		0.04420	15.00	0.03238	25.15	0.02664	
2.40		0.04385	15.00	0.03213	25.17	0.02645	
2.48		0.04394	15.00	0.03212	25.20	0.02641	
9.45		0.03650	15.00	0.03204	25.20	0.02632	
9.45		0.03657	15.10	0.03218	25.25	0.02644	
9.45		0.03637	15.10	0.03213	25.25	0.02621	
9.45		0.03626	15.10	0.03236	25.30	0.02640	
9.45		0.03659	15.10	0.03200	25.30	0.02646	
9.45		0.03660	15.10	0.03205	25.35	0.02659	
9.45		0.03648	20.00	0.02918	25.40	0.02658	
9.45		0.03669	20.00	0.02916	25.50	0.02609	
9.46		0.03670	20.00	0.02918	25.60	0.02636	
9.53	0.03631						
33.461	1.60	0.04305	1.65	0.04282	1.73	0.04291	
	1.60	0.04299	1.70	0.04301	1.79	0.04312	
	1.60	0.04294	1.70	0.04302	1.79	0.04278	
	1.60	0.04304	1.70	0.04298	1.80	0.04287	
33.515	6.85	0.03706	7.42	0.03681	13.48	0.03218	
	7.25	0.03705	7.42	0.03707	13.48	0.03214	
	7.33	0.03687	7.45	0.03680	13.48	0.03208	
	7.35	0.03712	7.45	0.03693	13.53	0.03214	
	7.35	0.03680	7.47	0.03677	13.53	0.03207	
	7.35	0.03682	7.50	0.03698	13.53	0.03210	
	7.40	0.03692	7.60	0.03687	13.53	0.03216	
	7.42	0.03682	7.64	0.03704	13.54	0.03210	
	7.42	0.03690					
33.629	0.73	0.04409	18.65	0.02889	24.85	0.02578	
	0.78	0.04388	18.65	0.02898	24.85	0.02585	
	0.79	0.04396	18.66	0.02886	24.85	0.02573	
	0.81	0.04396	18.70	0.02897	24.85	0.02579	
	0.81	0.04389	18.70	0.02895	24.88	0.02583	
	6.65	0.03742	18.70	0.02880	29.46	0.02420	
	6.65	0.03771	18.70	0.02893	29.46	0.02412	
	6.66	0.03767	24.80	0.02584	29.47	0.02402	
	6.74	0.03700	24.80	0.02582	29.49	0.02406	
	6.75	0.03739	24.83	0.02580	29.51	0.02409	
	18.60	0.02902	24.85	0.02578	29.54	0.02405	
	18.60	0.02893	24.85	0.02563	29.56	0.02418	
	18.62	0.02899					
	39.379	10.30	0.03287	15.09	0.02981	24.90	0.02479
10.35		0.03306	15.09	0.02934	24.95	0.02477	
10.35		0.03261	15.09	0.02973	24.95	0.02459	
10.35		0.03307	20.00	0.02684	24.95	0.02472	
10.35		0.03310	20.00	0.02698	29.96	0.02248	
10.35		0.03271	20.05	0.02696	29.96	0.02292	
10.35		0.03291	20.09	0.02673	29.96	0.02288	
10.35		0.03315	20.10	0.02699	29.96	0.02285	
14.81		0.02987	20.80	0.02685	29.96	0.02266	
14.85		0.02992	24.70	0.02489	29.99	0.02292	
14.99		0.02953	24.90	0.02478	30.01	0.02260	
15.09		0.02996	24.90	0.02475	30.01	0.02286	
15.09		0.02974					

**Table II. Constants for Calculation of Bunsen Solubility Coefficients of Methane by Equation 1**

$$\begin{aligned}
 A_1 &= -67.1962 \\
 A_2 &= 99.1624 \\
 A_3 &= 27.9015 \\
 B_1 &= -0.072909 \\
 B_2 &= 0.041674 \\
 B_3 &= -0.0064603
 \end{aligned}$$



**Figure 1. Percent difference of previous Bunsen solubility coefficients,  $\beta$ , for methane in distilled water from those of present work**

**Table III. Bunsen Solubility Coefficients for Methane Where  $\beta$  Is Expressed as ml  $\text{CH}_4$  (STP) Dissolved in 1 ml  $\text{H}_2\text{O}$**

Temp, °C	Salinity, parts per thousand								
	0	10	20	30	32	34	36	38	40
-2	...	...	0.05278	0.04902	0.04830	0.04759	0.04689	0.04620	0.04552
-1	...	...	0.05121	0.04758	0.04689	0.04621	0.04553	0.04487	0.04422
0	0.05749	0.05346	0.04970	0.04622	0.04555	0.04489	0.04424	0.04360	0.04297
1	0.05577	0.05188	0.04827	0.04492	0.04427	0.04364	0.04301	0.04240	0.04179
2	0.05412	0.05039	0.04691	0.04367	0.04305	0.04244	0.04184	0.04125	0.04066
3	0.05256	0.04896	0.04561	0.04249	0.04189	0.04130	0.04072	0.04015	0.03958
4	0.05108	0.04761	0.04438	0.04136	0.04078	0.04022	0.03965	0.03910	0.03855
5	0.04966	0.04631	0.04319	0.04028	0.03973	0.03918	0.03863	0.03810	0.03757
6	0.04831	0.04508	0.04207	0.03926	0.03872	0.03818	0.03766	0.03714	0.03663
8	0.04579	0.04278	0.03996	0.03733	0.03683	0.03633	0.03584	0.03535	0.03488
10	0.04350	0.04068	0.03804	0.03558	0.03510	0.03463	0.03417	0.03372	0.03327
12	0.04141	0.03876	0.03628	0.03397	0.03352	0.03308	0.03265	0.03222	0.03180
14	0.03950	0.03701	0.03468	0.03249	0.03207	0.03166	0.03125	0.03084	0.03044
16	0.03775	0.03540	0.03320	0.03114	0.03074	0.03035	0.02996	0.02958	0.02920
18	0.03616	0.03394	0.03185	0.02990	0.02952	0.02915	0.02878	0.02842	0.02806
20	0.03469	0.03259	0.03061	0.02875	0.02840	0.02804	0.02769	0.02735	0.02701
22	0.03335	0.03135	0.02947	0.02770	0.02736	0.02702	0.02669	0.02636	0.02604
24	0.03211	0.03021	0.02842	0.02673	0.02640	0.02608	0.02577	0.02545	0.02514
26	0.03098	0.02916	0.02745	0.02583	0.02552	0.02522	0.02491	0.02461	0.02432
28	0.02994	0.02819	0.02655	0.02501	0.02471	0.02442	0.02412	0.02384	0.02355
30	0.02898	0.02731	0.02573	0.02425	0.02396	0.02368	0.02340	0.02312	0.02285

tained by other workers for distilled water from values reported here are shown in Figure 1. Our results are in good agreement with those reported by Bunsen (2) and Claussen and Polglase (3), but are higher by 3–5% than those reported by Winkler (18) and Morrison and Billet (9). Reasons for the discrepancy between our results and those of Winkler's, which are the most widely quoted, are not clear. It is not attributable to differences in experimental methods and procedures since hydrogen solubility values reported by us (4) and by Winkler (16) were measured by the same respective procedures, and agreement between the two sets of data was good. In addition, Bunsen solubility coefficients for oxygen and nitrogen were measured by Douglas by the method used in this work and agreed well with those obtained by Winkler (17). Standard deviations for a single measurement at constant temperature and pressure ranged from 0.09 to 0.53% (see Table I). Sources of errors in the method used in this work were evaluated in detail by Douglas (5), who estimated the accuracy of the determination to be  $\pm 0.26\%$ . Impurities in the gas are potential sources of error. Of particular importance is  $\text{CO}_2$  since its solubility in water is 500–600 times greater than that of methane. The gas used in this work was analyzed by mass spectrometry, and the  $\text{CO}_2$  content was 1 ppm (on a mole basis). The error in the Bunsen solubility coefficient from this level of  $\text{CO}_2$  would be less than 0.01%.

Atkinson and Richards (1) reported methane solubilities for seawater of salinity 36‰ in the temperature range 0–30°C. These values were obtained by interpolation of values for distilled water and for seawater having a salinity of 40‰ and dif-

fered from our values by as much as 6.3%. By the Scholander method, Weiss (14) obtained a solubility coefficient of 0.03023 at 15.09°C and salinity 36.425‰ which agrees well with the value 0.03044 obtained by us.

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