Solubility of CCl_2F_2, $CClF_3$, CF_4, and CH_4 in Water and Seawater at 288.15–303.15 K and 101.325 kPa†

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The Ostwald coefficients $L_{2,1}$ of dichlorodifluoromethane (CCl_2F_2) (Freon-12), chlorotrifluoromethane ($CClF_3$) (Freon-13), tetrafluoromethane (CF_4) (Freon-14), and methane (CH_4) dissolved in seawater were measured at four temperatures in the range 288–303 K and at a partial pressure of gas of 101.325 kPa. A computer-controlled version of the Ben-Naim/Baer apparatus was used, and the precision of the measurements was on the order of 1.0% or better.

Introduction

During the past 30 years there has been an increasing interest in the study of the distribution of various anthropogenic gases in the oceans and fresh waters, and also the study of the exchange of these gases between the atmosphere and natural waters. The literature survey of the early studies is given in refs 1 and 2. In recent years much attention has been directed to the distribution of chlorofluorocarbons in natural waters (*3–6*). Freons are extremely stable: the estimated lifetime in the atmosphere ranging from 60 to 400 years for the most commonly used chlorofluorocarbons (*7–9*). In a recent study (*10*) the lifetime of $CClF_3$ has been estimated to be 640 years, and the perfluorocarbons last for thousands of years. CF_4, for example, persists in the atmosphere about 5×10^4 years (*10*). Therefore, a large reservoir of freons already exists in the atmosphere, and the emission of freons and other anthropogenic gases still continues despite the predicted decrease in the growth rates during the next decades (*11–16*). There has been an increasing concern for the effect of chlorofluorocarbons on the destruction of atmospheric ozone (*17*), and freons have become the subject of extensive laboratory investigations, especially after the discovery of the Antarctic ozone hole (*18*). Studies have recently been initiated to develop methods to mitigate or destroy freons (*19, 20*). Nevertheless, freons have several useful features. Due to their chemical stability and known atmospheric history some of the halocarbons have, for instance, become valuable to oceanographers as chemical tracers of ocean mixing and circulation pathways (*3, 21–28*). To interpret the distribution of gases in the oceans, and to study the exchange of gases between natural waters and the atmosphere, it is necessary to know accurately their aqueous solubilities as a function of temperature. Reliable solubility values also need to be known for appropriate modeling and the calculation of the long-term fate of freons in the environment. However, few accurate data exist concerning the solubility of freons in water and seawater. The aim of this work was to produce a reliable and consistent set of data on the solubility of various substituted methanes in distilled water and seawater in the range 288–303 K and at 1 atm of pressure.

Experimental Section

Materials. All gases were used as received. CCl_2F_2 and $CClF_3$ were from Liquid Carbonic Specialty Gases Corp.; CF_4 and CH_4 were from Airco. The gases had the following minimum mole percentage purities: CCl_2F_2, 99; $CClF_3$, 99; CF_4, 99.7; CH_4, 99.99.

The seawater used in the measurements was obtained through the courtesy of the Scripps Institution of Oceanography. The preparation of the seawater was as follows: surface seawater was collected at the Scripps pier in La Jolla. This water was poisoned with 100 μL of saturated mercuric chloride per liter, and was allowed to evaporate approximately 3% to increase its salinity. It was then filtered through a 1 μm filter, mixed in a glass carboy, and subsampled for determination of its salinity by conductivity. The measured salinity was reported to be 35.086‰ (in practical salinity units).

Apparatus and Operation. The apparatus used for all solubility measurements was based on a design of Ben-Naim and Baer (*29*) which had been improved by the modifications described in detail in ref 30. The solubility apparatus was housed in a large air thermostat, the temperature of which was controlled to ±0.03 K with a Yellow Springs Instrument Co. Model 72 proportional controller. Temperatures were determined with a Leeds and Northrup knife blade platinum resistance thermometer calibrated on the IPTS-68 scale (negligibly different for this work from ITS-90). The equipment and the experimental technique have been described in detail in refs 30 and 31. Depending on the solubility of the gas, two mixing chambers with volumes of approximately 65 and 380 cm^3 were used in the measurements. The chambers were calibrated with double-distilled water, and the volume of seawater in the measurements was known to better than ± 0.01 cm^3. Gas volumes were determined by a computer counting steps for the stepping motor used to drive a close-fitting stainless steel or Teflon piston with two O-ring seals through a Fisher and Porter precision bore tube. Depending on the magnitude of the Ostwald coefficient, the diameter of the tube used in the measurements was either 15.875 ± 0.008 or 4.7625 ± 0.005 mm. The combination of tube diameter, the pitch of the drive screw, and the number of steps per revolution of the stepping motor allowed gas volumes to be determined to a few parts per thousand.

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† Communicated in part by P. Scharlin at the IUPAC 5th International Symposium on Solubility Phenomena, Moscow, Russia, July 8–10, 1992.

0021-9568/95/1740-0167$09.00/0

Table 1. Ostwald Coefficients, $L_{2,1}$, for Substituted Methanes Dissolved in Seawater at 288–303 K and in Distilled Water at 288–318 K and 101.325 kPa Partial Pressure of Gas

gas	T/K	$10^2L_{2,1}$	gas	T/K	$10^2L_{2,1}$
Seawater (S = 35.086‰)			H_2O[d]		
CH_4	288.19	3.216	CH_4[a]	288.15	4.095
	293.20	3.002		293.15	3.740
	298.13	2.866		298.15	3.456
	303.19	2.830		303.15	3.227
CCl_2F_2	288.19	7.839	CCl_2F_2[b]	288.19	9.828
	293.18	6.834		298.14	7.110
	298.15	6.216		308.12	5.613
	303.25	5.758		318.25	4.397
$CClF_3$	288.18	2.323	$CClF_3$[b]	288.22	2.812
	293.19	2.103		298.06	2.253
	298.15	1.970		308.02	1.871
	303.20	1.882		318.02	1.683
CF_4	288.20	0.5159	CF_4[c]	288.19	0.6399
	293.19	0.4528		298.17	0.5083
	298.15	0.4021		308.15	0.4592
	303.20	0.3633		318.20	0.4391

[a] Recommended data from ref 34. [b] Reference 35. [c] Reference 31. [d] These water values are reproduced here for convenience.

The solubilities of CCl_2F_2, $CClF_3$, CF_4, and CH_4 in seawater were determined at four temperatures in the range of 288–303 K. The salinity S of the "fresh" seawater was 35.086‰. The conductivity measurements with a YSI Model 34 conductance–resistance meter before and after solubility experiments showed that, within the experimental error, the salinity of seawater remained unchanged during the degassing and dissolution processes.

Results

The Ostwald coefficient $L_{2,1}(T,P)$ *(32)* is defined by eq 1 *(33)*, where V^g is the volume of dissolved gas (determined via the microprocessor), and V^l is the volume of the liquid solution after equilibrium is reached.

$$L_{2,1}(T,P) = V^g/V^l \qquad (1)$$

The primary solubilities in seawater, expressed as the Ostwald coefficients, at different temperatures are shown in Table 1. The Ostwald coefficients for the $CH_4 + H_2O$ system presented in the same table are values recommended in ref 34. The solubilities of CF_4, CCl_2F_2, and $CClF_3$ in distilled water are from our previous works *(31, 35)* and are reproduced here for convenience.

The primary experimental data in the range 288–303 K were fitted to a Clarke/Glew/Weiss equation *(36–38)*:

$$\ln L_{2,1} = A_0 + A_1/(T/100\ \mathrm{K}) + A_2 \ln(T/100\ \mathrm{K}) \qquad (2)$$

The coefficients A_i of eq 2 and the standard deviation in ln $L_{2,1}$ are listed in Table 2.

Table 2. Coefficients A_i of Eq 2 for Smoothed Results for Solubilities of Substituted Methanes in Seawater and Distilled Water

gas	$-A_0$	A_1	A_2	% SE[a]
		Seawater (S = 35.086‰)		
CH_4	200.828	283.771	93.4621	0.18
CCl_2F_2	210.718	304.282	96.9221	0.26
$CClF_3$	188.072	267.580	86.4104	0.15
CF_4	93.8568	136.046	39.0983	0.12
		H_2O		
CCl_2F_2	59.0763	93.6487	22.9172	1.2
$CClF_3$	102.686	150.260	44.3843	0.63
CF_4	174.133	248.381	78.3141	0.78

[a] The average percentage deviation in $L_{2,1}$. % SE = 100(SE/$L_{2,1}$).

Table 3. Smoothed Values for Ostwald Coefficients, $L_{2,1}$, and Solubilities, m_2, of Substituted Methanes Dissolved in Seawater and Distilled Water at 288.15–303.15 K and 101.325 kPa Partial Pressure of Gas

T/K	$10^2L_{2,1}$	10^3m_2/(mol·kg^{-1})	T/K	$10^2L_{2,1}$	10^3m_2/(mol·kg^{-1})
Seawater (S = 35.086‰)				H_2O	
	CH_4			CH_4[a]	
288.15	3.220	1.327	288.15	4.095	1.733
293.15	2.997	1.216	293.15	3.740	1.558
298.15	2.872	1.147	298.15	3.456	1.417
303.15	2.828	1.113	303.15	3.227	1.303
	CCl_2F_2			CCl_2F_2	
288.15	7.842	3.232	288.15	9.800	4.148
293.15	6.860	2.783	293.15	8.351	3.478
298.15	6.198	2.475	298.15	7.201	2.952
303.15	5.771	2.271	303.15	6.279	2.535
	$CClF_3$			$CClF_3$	
288.15	2.324	0.9581	288.15	2.823	1.195
293.15	2.109	0.8554	293.15	2.489	1.037
298.15	1.968	0.7858	298.15	2.232	0.9151
303.15	1.885	0.7414	303.15	2.034	0.8212
	CF_4			CF_4	
288.15	0.5169	0.2130	288.15	0.6385	0.2703
293.15	0.4527	0.1836	293.15	0.5647	0.2352
298.15	0.4027	0.1608	298.15	0.5128	0.2102
303.15	0.3635	0.1430	303.15	0.4773	0.1927

[a] $L_{2,1}$ values for the $CH_4 + H_2O$ system are values recommended in ref 34.

Assuming ideal gas behavior, the solubilities on the molality basis, m_2, were calculated from the equation

$$m_2 = n_2/w_1 = (P_2V_2)/(RT\varrho_1V_1) = (P_2L_{2,1})/(RT\varrho_1) \qquad (3)$$

where n_2 is the amount of the dissolved gas, w_1 is the mass of solvent, P_2 is the partial pressure of the gas, V_2 is the volume of dissolved gas, V_1 is the volume of solvent, ϱ_1 is the density of the solvent, R is the gas constant (8.315 41 J K^{-1} mol^{-1}), and T is the thermodynamic temperature. The density for seawater with S = 35.086‰ at different temperatures was calculated using the equation given in ref 39. The density of water at different temperatures was taken from ref 40. Smoothed values for Ostwald coefficients and solubilities on the molality basis at temperatures of 288.15, 293.15, 298.15, and 303.15 K are presented in Table 3.

The solubility values found in the literature for substituted methanes in seawater and distilled water have usually been given as either Bunsen or Ostwald coefficients. They were converted to correspond to solubilities on the molality basis according to eq 3. The relation between the Bunsen coefficient α and the Ostwald coefficient $L_{2,1}$, assuming ideal gas behavior and Henry's law, is *(33)*

$$\alpha = L_{2,1}(273.15\ \mathrm{K}/T) \qquad (4)$$

The Bunsen coefficient α is defined as the volume of gas, reduced to 273.15 K and 1 atm of pressure, which is absorbed by a unit volume of solvent at the temperature of measurement under a partial pressure of 1 atm. The literature values are listed in Table 4 for comparison.

The smoothing equation given in ref 41 for the calculation of the solubility of CH_4 in seawater is reported to be valid from 273.15 to 303.15 K and in a salinity range S of 0–40‰. The solubility values calculated for methane at the salinity S = 35.086‰ (Table 4) are in good agreement

Table 4. Literature Values for Solubilities, m_2, of Substituted Methanes Dissolved in Seawater and Distilled Water at 288.15−303.15 K

gas	T/K	$10^3 m_2$/(mol·kg^{-1})
	Seawater (S = 35.086‰)	
CH_4	288.15	1.335[a]
	293.15	1.211[a]
	298.15	1.109[a]
	303.15	1.027[a]
CCl_2F_2	288.15	3.074[b]
	293.15	2.501[b]
	298.15	2.073[b]
	303.15	1.750[b]
		H_2O
CCl_2F_2	288.15	4.347[b]
	293.15	3.526[b]
	298.15	2.924,[b] 2.941,[c] 2.135[d]
	303.15	2.474,[b] 1.937[d]
$CClF_3$	288.15	
	293.15	
	298.15	0.7925,[c] 0.9495[d]
	303.15	0.8685[d]
CF_4	288.15	0.2638[e] 0.2690[g]
	293.15	0.2316[e] 0.2317,[f] 0.2368[g]
	298.15	0.2126,[c] 0.2075,[e] 0.2082,[f] 0.2121[g]
	303.15	0.1895,[e] 0.1938,[f] 0.1931[g]

[a] Calculated using the smoothing equation given in ref 41. [b] From the smoothing equation given in ref 42. [c] Reference 43. [d] Reference 44; smoothing equation by Wilhelm et al. in ref 45. [e] Reference 46. [f] Reference 47. [g] Reference 48; smoothing equation by Wilhelm et al. in ref 45.

with our values (Table 3), except the value at 303.15 K which is about 8% lower than that of ours.

The values for the solubility of CCl_2F_2 in seawater measured in this work (Table 3) differ considerably from the values calculated from the smoothing equation in ref 42 (Table 4). Our values are 5−30% higher. On the other hand, the values for the solubility of CCl_2F_2 in H_2O calculated from our data in ref 35 (Table 3) and the values calculated from the data in ref 42 (Table 4) are consistent with each other within the experimental error. The value reported in ref 43 for the solubility of CCl_2F_2 in H_2O at 298.15 K agrees well with our value. The results of Parmelee (*44*) are considered to be of poor precision (*43*, *45*).

We found no literature data for the solubility of $CClF_3$ and CF_4 in seawater. The literature values found for the solubility of $CClF_3$ in H_2O (*43*, *44*) differ considerably from our values.

Acknowledgment

We thank Professor R. F. Weiss and R. Van Woy (Scripps Institution of Oceanography) for preparing and donating the seawater. We are also grateful to W. Jasper (YSI, Inc.) for assistance with the conductivity measurements.

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Received for review April 29, 1994. Accepted August 17, 1994.® P.S. gratefully acknowledges a grant from the Maj and Tor Nessling Foundation, Helsinki, Finland.

JE9400825

® Abstract published in *Advance ACS Abstracts,* November 15, 1994.