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CORRELATION

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Correlations Involving the Solubility of Gases in Water at 298.15 K and 101325 Pa

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ABSTRACT: Factors influencing the solubilities of a large number of gases in water at 298.15 K and 101325 Pa partial pressure of gas have been examined. (For purposes of this article gases are considered to be compounds having normal boiling points below 298.15 K.) Since the solubility of these solutes in water range over 7 orders of magnitude and the gases examined include both gases that are chemically inert and gases that react with water, it was not possible to find a single correlation to adequately cover all of them. Accordingly, the gases were grouped into compatible classes, such as chemically reactive, inert, permanent, hydrocarbons, halogen-containing gases, etc. Reasonable correlations with gas solute properties were generally found within each class of compounds.

INTRODUCTION

In a previous study, we examined the solubilities of gases in several representative solvents (benzene, hexane, 1-octanol, ethanol, and water).[1] That study disclosed that in most cases the solute polarizability by itself proved to be a remarkably good descriptor, accounting for 88 to 93 % of the variance in the solubility data when used as a single descriptor and 95 to 97 % of the variance when coupled with its quadratic form. The solubilities of the gases in water, however, were a notable exception, displaying only minimal dependencies on the polarizabilities of the gas solutes. In this report we attempt to assess the factors responsible for the solubilities of gases in water.

Water is undoubtedly the most important solvent in our lives. Knowledge about the solubility of gases in water is significant in many areas such as physiology, limnology, environmental science, sewage treatment, oceanography, and industrial processes among many others. For example, when you take in a breath of air the gases in the air go through a series of dissolutions and transfers in a variety of aqueous solutions. The solubility of pharmaceuticals in water has been the subject of many studies (see, e.g., Abraham et al.[2]); a subset of these has been the solubility of gases in water. (Of course, the solubility of gases in aqueous biological fluids has also been extensively studied.) In this paper we present a number of correlations of the solubility of gases in pure water at 298.15 K and 101325 Pa partial pressure of gas. Wilhelm et al.[3] in a review article on the solubility of gases in water explored a number of correlations. Battino and Clever[4] reviewed the solubility of gases in water and seawater, and Battino[5] reviewed the high precision solubility of a number of gases in water.

METHODS

Strictly speaking, a gas is a fluid substance that is above its critical point. Below the critical point and at temperatures where two fluid phases can be in equilibrium, the less dense phase is called the vapor and the more dense phase the liquid. For purposes of this paper we are considering any substance to be a gas if its normal boiling point is below 298.15 K. (This working definition has also been used by Fogg and Gerrard.[6])

Data have been collected for the solubility of 65 gases in water in terms of the mole fraction solubility at 101325 Pa partial pressure and 298.15 K (x_2). For these gases we have been able to locate four physical properties for all of the gases. Table 1 gives ln x_2 for these gases along with the physical properties. To connect with the sections which follow, the gases have been arranged in seven groupings, and within each group in order of increasing solubility. (There is an eighth grouping of perfluorinated gases which was not tabulated separately.) Note that for some of the correlations other physical properties have been tested, but only for those gases for which we could locate reliable data. Also note that we are not providing sources for the data we use since this would make this paper overly cumbersome. Many sources were consulted (a principal one was the IUPAC Solubility Data Series[7]) and in some cases the data used were averages or estimates. In addition, Table 2 just gives the decreasing mole fraction solubility for all of the gases to give the reader some perspective, and to relate to the discussion section.

The solubility of gases in water covers an enormous range extending over 7 magnitudes from that of $C_2H_5NH_2$ where there are roughly six molecules of $C_2H_5NH_2$ per four molecules of water to C_3F_8 where two molecules are dissolved in ten million water molecules. The gases include those that chemically react with water, those which are inert, and those which are polar and nonpolar. The common convention for chemically reactive gases is that the reported solubilities are bulk ones, i.e., calculated as if the gas did not react with water and thus includes all solute species in solution. The goal of finding one fitting equation to cover all of these gases is simply not practical. This is illustrated in Figure 1 where we have chosen to plot ln x_2 vs P_c, the critical

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Table 1. Data for the Solubility of 65 Gases in Water at 298.15 K and 101325 Pa Partial Pressure of Gas[a]

gas	$\ln x_2$	MM $g \cdot mol^{-1}$	NBP K	T_c K	P_c 101325 Pa
Chem Reactive					
NO	−10.2668	30.01	121.45	180.15	64.85
AsH_3	−8.7316	77.93	210.65	373.00	64.13
NO_2	−7.7179	46.01	294.20	431.20	99.68
CO_2	−7.4002	44.01	194.67	304.19	73.82
H_2Se	−6.5118	80.98	228.25	411.10	83.44
Cl_2	−6.4082	70.91	239.04	417.15	77.11
H_2S	−6.3034	34.08	212.88	373.53	89.63
CH_3NH_2	−4.4748	31.06	266.70	430.10	73.60
SO_2	−3.705	64.07	263.15	430.75	78.84
NH_3	−1.6734	17.03	239.80	405.65	112.78
$(CH_3)_2NH$	−0.59431	45.09	280.00	437.60	52.40
$C_2H_5NH_2$	−0.4527	45.09	289.70	456.40	55.50
Rare Gases					
He	−11.872	4.00	4.23	5.20	2.28
Ne	−11.7196	27.25	27.25	44.40	26.53
Ar	−10.5903	39.95	87.29	150.86	48.98
Kr	−10.0102	83.80	119.90	209.35	55.02
Xe	−9.4638	131.29	165.15	289.74	58.4
Rn	−8.6945	222.00	211.15	377.40	63.00
Spherical Gases					
CF_4	−12.4726	88.01	145.15	227.50	37.39
SF_6	−12.3481	146.06	209.25	318.69	37.60
C_5H_{12} neopentane	−11.4387	72.15	282.65	433.78	31.99
CH_4	−10.5938	16.04	111.54	190.564	45.39
Permanent Gases					
N_2	−11.3534	28.01	77.34	126.10	33.94
H_2	−11.1672	2.02	20.37	33.18	13.13
CO	−10.9683	28.01	81.65	132.92	34.99
O_2	−10.6809	32.00	90.18	154.58	50.43
Hydrocarbons					
C_5H_{12} neopentane	−11.4387	72.15	282.65	433.78	31.99
C_4H_{10} isobutane	−11.1324	58.12	261.40	408.20	36.02
C_4H_{10}	−10.7258	58.12	272.65	425.12	37.46
CH_4	−10.5938	16.04	111.54	190.564	45.39
C_3H_8	−10.5182	44.10	231.08	369.83	41.92
C_2H_6	−10.3055	30.07	184.55	305.32	48.08
C_4H_8 1-butene	−9.5489	56.11	266.90	419.60	39.67
C_2H_4	−9.3634	28.05	169.45	282.36	50.32
$CH_2{=}C(CH_3)_2$	−9.1818	56.11	266.25	419.59	40.20
C_3H_6	−8.9207	42.08	225.45	364.76	46.13
c-C_3H_6	−8.4809	42.08	240.29	397.91	55.75
C_4H_6 1,3-butadiene	−8.3151	54.09	268.74	425.37	43.30
C_2H_2	−7.1982	26.04	189.15	308.32	61.39
C_3H_4 propyne	−6.6983	40.07	249.90	402.40	55.56
Halogenated HCs					
C_3F_8	−15.3339	188.02	236.60	345.10	26.45
C_2F_6	−13.8155	138.02	194.90	293.00	30.20
c-C_4F_8	−13.0408	200.03	267.17	388.37	27.42
CF_4	−12.4726	88.01	145.15	227.50	37.39
$C_2Cl_2F_4$	−11.4213	170.92	276.58	418.90	31.95
$CClF_3$	−10.9764	104.47	193.20	302.00	38.19
C_3F_6	−10.6888	150.02	244.15	368.00	29.00
C_2F_4	−10.467	100.02	197.20	306.45	39.44
CCl_2F_2	−9.8454	120.93	245.20	385.00	40.86
CCl_3F	−8.5132	137.38	296.90	471.20	43.52
CHF_3	−8.356	70.02	191.00	299.30	47.96
CH_2F_2	−7.5144	52.02	221.43	351.26	57.29
C_2HF_5	−7.4697	120.02	225.06	339.15	35.68
$CHClF_2$	−7.3798	86.47	232.35	369.30	49.71
$CHCl_2F$	−7.3798	102.93	282.10	451.60	51.12
CH_3CH_2F	−7.1197	48.06	235.50	375.30	49.54
$CH_2{=}CHCl$	−7.0931	62.50	259.80	425.00	50.83
CH_3F	−6.8429	34.03	194.80	317.70	58.77
$CH_2{=}CHBr$	−6.698	106.96	288.95	471.15	
CH_3Cl	−6.2775	50.49	248.93	416.25	66.79
CH_3Br	−5.8331	94.94	276.61	467.00	80.00
CH_2Cl_2	−5.5894	84.94	313.00	510.00	62.18
Miscellaneous					
SF_6	−12.3481	146.06	209.25	318.69	37.60
NF_3	−11.1574	71.00	144.12	233.85	45.30
N_2F_4	−11.076	104.02	203.15	309.15	37.01
C_2N_2	−8.921	52.04	252.00	400.00	59.02
COS	−7.8662	60.08	222.95	378.80	63.49
N_2O		−7.7326	44.01	184.20	309.57
ClO_2	−4.0047	67.45	283.05	465.00	108

[a] 101323 Pa = 1 atm.

pressure of the gases. There is obviously a great deal of scatter, particularly with the very high and very low solubility gases. The adjusted R^2 value of 0.4930 is reasonable for the fitting equation which follows:

$$\ln x_2 = -13.928(\pm 0.704) + 0.10012 (\pm 0.0126) P_c / 101325 \text{ Pa} \tag{1}$$

(In this paper the adjusted R^2 value, which is less than R^2, is used since it is adjusted for the number of independent variables used in the regression fits.) However, there are two gases whose residuals are greater than two standard deviations, and ten gases where the residual is greater than one standard deviation. It therefore appears that the best way to correlate the solubility of gases in water is to group the gases in reasonable ways, and then to fit those groupings separately. It is noted in passing that fitting $\ln x_2$ vs the molar mass (MM), the normal boiling point (NBP), and T_c resulted in an R^2 of 0.5797 but with 17 gases having residuals greater than one standard deviation. With a sufficient number of parameters it would presumably be possible to correlate the solubility of all 65 gases reasonably well, but a goal of this paper is to find correlations using a minimum number of parameters.

Table 2. Gases Tabulated in Decreasing Solubility

gas	x_2	gas	x_2
CH_3NH_2	0.6392	C_2N_2	$1.336 \cdot 10^{-4}$
$C_2H_5NH_2$	0.6359	$CH_2{=}C(CH_3)_2$	$1.029 \cdot 10^{-4}$
$(CH_3)_2NH$	0.5519	C_2H_4	$8.851 \cdot 10^{-5}$
NH_3	0.1876	Xe	$7.761 \cdot 10^{-5}$
SO_2	$2.460 \cdot 10^{-2}$	C_4H_8 1-butene	$7.128 \cdot 10^{-5}$
ClO_2	$1.823 \cdot 10^{-2}$	CCl_2F_2	$5.299 \cdot 10^{-5}$
CH_2Cl_2	$3.737 \cdot 10^{-3}$	Kr	$4.494 \cdot 10^{-5}$
CH_3Br	$2.929 \cdot 10^{-3}$	NO	$3.477 \cdot 10^{-5}$
CH_3Cl	$1.878 \cdot 10^{-3}$	C_2H_6	$3.345 \cdot 10^{-5}$
H_2S	$1.830 \cdot 10^{-3}$	C_2F_4	$2.846 \cdot 10^{-5}$
Cl_2	$1.648 \cdot 10^{-3}$	C_3H_8	$2.704 \cdot 10^{-5}$
$CH_2{=}CHBr$	$1.233 \cdot 10^{-3}$	Ar	$2.526 \cdot 10^{-5}$
C_3H_4 propyne	$1.233 \cdot 10^{-3}$	CH_4	$2.507 \cdot 10^{-5}$
H_2Se	$1.149 \cdot 10^{-3}$	O_2	$2.298 \cdot 10^{-5}$
CH_3F	$1.067 \cdot 10^{-3}$	C_3F_6	$2.280 \cdot 10^{-5}$
$CH_2{=}CHCl$	$8.308 \cdot 10^{-4}$	C_4H_{10}	$2.197 \cdot 10^{-5}$
CH_3CH_2F	$8.090 \cdot 10^{-4}$	CO	$1.724 \cdot 10^{-5}$
C_2H_2	$7.479 \cdot 10^{-4}$	$CClF_3$	$1.710 \cdot 10^{-5}$
$CHClF_2$	$6.237 \cdot 10^{-4}$	N_2F_4	$1.548 \cdot 10^{-5}$
$CHCl_2F$	$6.237 \cdot 10^{-4}$	C_4H_{10} isobutane	$1.463 \cdot 10^{-5}$
CO_2	$6.111 \cdot 10^{-4}$	NF_3	$1.427 \cdot 10^{-5}$
C_2HF_5	$5.701 \cdot 10^{-4}$	H_2	$1.413 \cdot 10^{-5}$
CH_2F_2	$5.452 \cdot 10^{-4}$	N_2	$1.173 \cdot 10^{-5}$
NO_2	$4.448 \cdot 10^{-4}$	$(CClF_2)_2$	$1.096 \cdot 10^{-5}$
N_2O	$4.383 \cdot 10^{-4}$	C_5H_{12} neopentane	$1.077 \cdot 10^{-5}$
COS	$3.835 \cdot 10^{-4}$	Ne	$8.133 \cdot 10^{-6}$
C_4H_6 1,3-butadiene	$2.448 \cdot 10^{-4}$	He	$6.983 \cdot 10^{-6}$
CHF_3	$2.350 \cdot 10^{-4}$	SF_6	$4.338 \cdot 10^{-6}$
c-C_3H_6	$2.074 \cdot 10^{-4}$	CF_4	$3.830 \cdot 10^{-6}$
CCl_3F	$2.008 \cdot 10^{-4}$	c-C_4F_8	$2.170 \cdot 10^{-6}$
Rn	$1.675 \cdot 10^{-4}$	C_2F_6	$1.000 \cdot 10^{-6}$
AsH_3	$1.614 \cdot 10^{-4}$	C_3F_8	$2.190 \cdot 10^{-7}$
C_3H_6	$1.336 \cdot 10^{-4}$		

■ RESULTS

To begin, it is possible to draw some general conclusions based on the data shown in Table 2, where the gases are arranged in order of decreasing solubility. First, it is clear that the most soluble gases in water are those able to (1) hydrogen-bond with water and (2) dissolve to form additional species. Next we find a broad class of gaseous compounds which lack hydrogen-bonding capability, but are capable of other interactions, presumably dispersion and possibly induction interactions, with the aqueous solvent. Finally, forming the least soluble gases, one finds a group of perfluorinated gases we label as "Teflon" gases.

Solubility of Chemically Reactive Gases in Water. A number of judgments had to be made about which gases are chemically reactive with water; that is, for some gases the choice was obvious, but for others it was not clear even after consulting references on inorganic chemistry. The 12 gases chosen are (in order of increasing solubility) as follows: NO, AsH_3, NO_2, CO_2, H_2Se, Cl_2, H_2S, CH_3NH_2, SO_2, NH_3, $(CH_3)_2NH$, and $C_2H_5NH_2$. Acid and base dissociation constants were found for all of these gases, except for NO_2 (HNO_3 is completely dissociated in water). Complete sets of physical parameters were available for MM, NBP, $\Delta H_{\mathrm{vap}}^{\mathrm{NBP}}$, dipole moment (DM), T_c, and P_c. Although one would consider that the dipole moment would be especially significant for solubilities in polar water, note that the dipole moments for CO_2 and Cl_2 are zero. The polarizability of the gas molecule would also appear to be of special significance, but values for AsH_3 and H_2Se were not found.

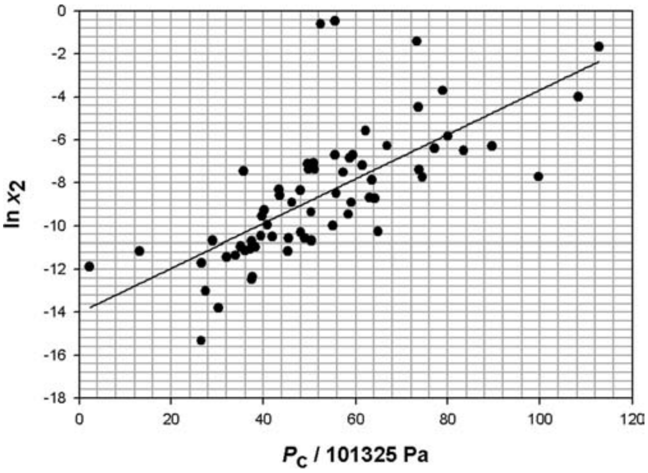

Figure 1. ln x_2 vs P_c/101325 Pa for 65 gases.

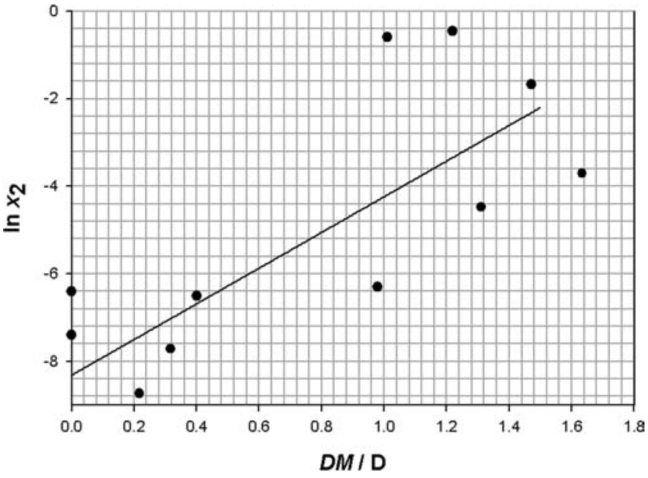

Figure 2. ln x_2 vs DM/D for 12 chemically reactive gases.

For these 12 chemically reactive solutes the first fitting test was to use all six of the parameters cited above with an R^2 value of 0.6083 and a standard deviation of 2.00 in ln x_2. The t values for the coefficients for these parameters were all about 1.0 or less. (A coefficient is considered to be statistically significant if its t value is greater than 4.) The data were fit for all solutes vs lone pairs, for 11 vs K_a or K_b, and for 10 vs the polarizability, with R^2 values less than 0.6 in all cases. The single parameter fit with the best t value (3.83) was for the dipole moment and this is shown in Figure 2. The best overall fit was for ln x_2 vs NBP and DM with an R^2 of 0.6550 and a standard deviation (sd) of 1.88 in ln x_2. The equation for that follows:

$$\ln x_2 = -13.847(\pm 2.93) + 0.02669(\pm 0.0135)\mathrm{NBP/K} + 2.998(\pm 1.08)\mathrm{DM/D} \qquad (2)$$

The scatter in Figure 2 and the modest value of R^2 illustrate the difficulty of fitting solubilities of gases in water, especially for the highly soluble chemically reactive solutes.

Solubility of the Rare Gases in Water. Almost any physical property will work in correlating the solubility of the rare gases in water. Data were available for all six of the rare gases as follows: MM, NBP, α (polarizability), vdw *a*, vdw *b*, T_c, P_c, $V_c^{2/3}$, Z_c, FP, ΔH_{fus}, and calculated values[7] of the Lennard-Jones parameters ε/k and the hard sphere diameter σ. The latter were chosen to get a complete and consistent set of data.

Initially, the data were fit against three groups of four parameters [(1) MM + NBP + vdw *a* + vdw *b*; (2) $T_c + P_c + Z_c + V_c^{2/3}$; (3) ε/k, σ, *FP*, ΔH_{fus}) to obtain a sense of the contribution of each of these parameters. The R^2 and standard deviations for these three groupings in that order are 0.9999, 0.105; 0.9997, 0.0493; and 0.9972, 0.0662. Although the R^2 values were excellent, the *t* values for the individual parameters were all less than 4 for (2) and (3), and above 4 for (1). Nevertheless, the results indicated that it would make sense to test the "best" parameters singly and also some as pairs.

For the properties T_c, NBP, MM, α, ε/k, and σ the R^2 values ranged from 0.8654 to 0.9945 and sd from 0.461 to 0.0934. The best single parameter fit is with R^2 = 0.9945 and sd =0.0934

$$\ln x_2 = -11.969(\pm 0.065) + 0.009083 (\pm 0.000303)(\varepsilon/k)/\mathrm{K} \tag{3}$$

The best two-parameter fit with R^2 = 0.9954 and sd =0.0850 is

$$\ln x_2 = -11.971(\pm 0.059) - 03276(\pm 0.0243)T_c/\mathrm{K} + 0.04295(\pm 0.0251)(\varepsilon/k)/\mathrm{K} \tag{4}$$

Of course, solubility data for the rare gases in water are readily available in the literature. These correlations are presented here as a prelude for the other groupings which follow.

Solubility of Spherical Nonpolar Gases in Water. In addition to the six rare gases, in this section are added four spherical nonpolar gases: CH_4, 2,2-dimethylpropane (neopentane, C_5H_{12}), CF_4, and SF_6. The physical parameters that would appear to be best for this group of gases would be those characteristic of van der Waals forces such as polarizability and related properties such as the NBP and T_c. The data available for all gases are MM, NBP, α, vdw *a*, vdw *b*, T_c, P_c, $V_c^{2/3}$, Z_c, FP, and ΔH_{fus}. Recall that $V_c^{2/3}$ is effectively the surface area of the molecule. The best single parameter was MM with an R^2 of 0.1360 and sd of 1.17. Several combinations of 2, 3, and 4 parameters were tested. Of these the best was the following two-parameter equation using NBP and T_c with an R^2 of 0.8877 and sd of 0.42 with excellent *t* values (−43.9, −8.07, and +8.37, respectively)

$$\ln x_2 = -11.907(\pm 0.271) - 0.10018(\pm 0.0124)\mathrm{NBP/K} + 0.06517(\pm 0.00778)T_c/\mathrm{K} \tag{5}$$

Solubility of Spherical Nonpolar Gases plus Four "Permanent" Gases in Water. In addition to the gases and vapors listed in the previous section, in this part are added four gases that are frequently called the "permanent" gases, i.e., H_2, N_2, O_2, and CO. CO_2 is generally added to this latter grouping, but it is chemically reactive with water and has been included in that group earlier. Note that of the 14 gases treated in this section only CO has a dipole moment; it is relatively small: 0.110 D. Twelve parameters were available for the complete data set of 14 solutes. Four groups of four parameters each were fit linearly to obtain a sense of which parameters worked best. Of these eight were fit individually but with no decent R^2 values. Then nine pairs of parameters were used with the best fit being NBP + T_c. One gas (CF_4) showed a residual greater than 2 sd, and two solutes showed residuals a bit greater than 1sd. Deciding not to omit any of the solutes resulted in

$$\ln x_2 = -11.683(\pm 0.195) - 0.09873(\pm 0.0113)\mathrm{NBP/K} + 0.06362(\pm 0.00703)T_c/\mathrm{K} \tag{6}$$

with R^2 = 0.8658 and sd =0.389.

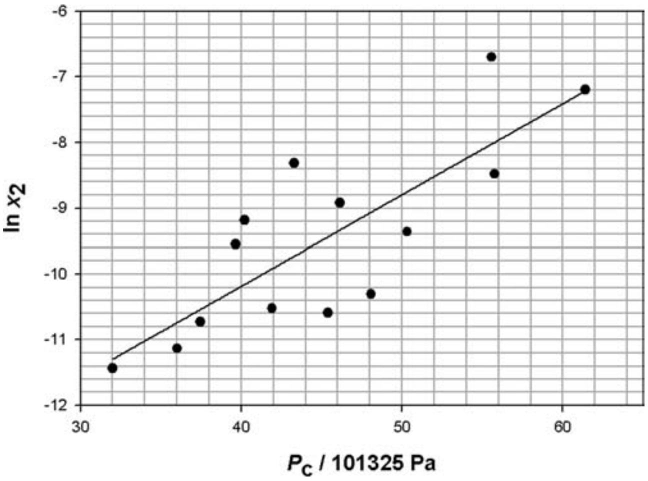

Figure 3. ln x_2 vs P_c/101325 Pa for 15 hydrocarbon gases.

Solubility of Hydrocarbon Gases in Water. The data set includes 14 hydrocarbon gases and these are *n*-alkanes, isomeric alkanes, alkenes, and alkynes. The mole fraction solubilities range from $1.2 \cdot 10^{-3}$ for propyne to $1.1 \cdot 10^{-5}$ for neopentane or a range of 100-fold. There were 11 sets of physical property data for all of the solutes: MM, NBP, α, ΔH_{vap}^{BP}, ω (acentric factor), T_c, P_c, $V_c^{2/3}$, Z_c, *FP*, and B_{22} (second virial coefficient). Several three- and four-parameter groups were tested with marginal results and poor *t* values. The best of the individual parameters was P_c with an R^2 of 0.6205, sd of 0.89, and good *t* values. Equation 7 is for this fit.

$$\ln x_2 = -15.737(\pm 1.35) + 0.1388(\pm 0.0294) P_c/101325\ \mathrm{Pa} \tag{7}$$

This is illustrated in Figure 3. There is, or course, some scatter about the best straight line with moderate residuals greater than one sd for five solutes.

A better fit of the data was obtained by using two parameters (P_c and α) as shown in eq 8 with R^2 = 0.8327, sd of 0.588, and good *t* values.

$$\ln x_2 = -22.418(\pm 1.89) + 0.02238(\pm 0.0288) P_c/101325\ \mathrm{Pa} + 0.4362(\pm 0.108)\alpha/\mathrm{A}^3 \tag{8}$$

Both P_c and α can be taken as measures of van der Waals forces.

Another two-parameter fit which is of some significance is the one where ln x_2 was fit against P_c and the number of Pi bonds in each hydrocarbon (Pi). The R^2 was 0.9067 and sd = 0.439 with all three *t* values greater than 4. Only four residuals were >1 sd. The fitting equation is

$$\ln x_2 = -14.156(\pm 0.718) + 0.08734(\pm 0.0168) P_c/101325\ \mathrm{Pa} + 1.0453(\pm 0.170)\mathrm{Pi} \tag{9}$$

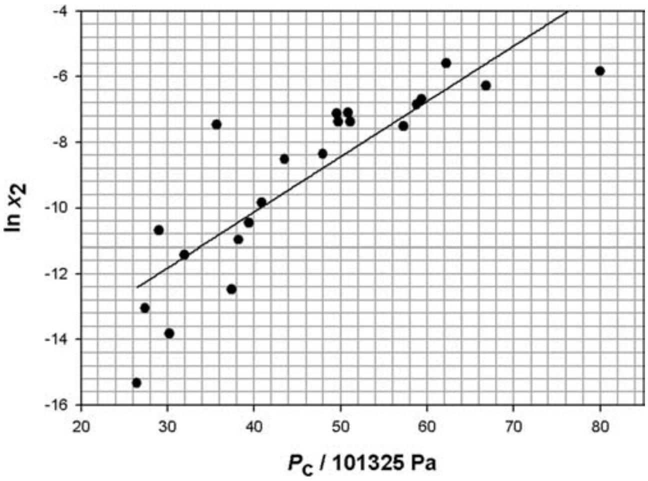

Figure 4. ln x_2 vs P_c/101325 Pa for 22 halogenated hydrocarbons.

This is better than the fit just against P_c and incorporates a parameter relevant for hydrocarbons.

Solubility of Halogenated Hydrocarbon Gases in Water. The halogenated hydrocarbon solutes include some that have double bonds as well as some perfluorinated compounds. The range in the mole fraction solubility is from $1.1 \cdot 10^{-3}$ for CH_3F to $2.2 \cdot 10^{-7}$ for C_3F_8 for 4 orders of magnitude. Six of the 22 solutes are nonpolar, and the dipole moments of the remaining 16 gases range up to 2.0 D. (Fitting the solubility for only 16 of the solutes was not done.) There was a complete set of data for only the properties of MM, NBP, T_c, P_c, and FP. Solubilities were fit for a number of groupings of parameters, for all of the mentioned single parameters, and for several pairs. The best single parameter was P_c with an R^2 of 0.7157 and sd of 1.49. This is given in the following equation:

$$\ln x_2 = -16.882(\pm 1.11) + 0.1690 (\pm 0.0230) P_c/101325\ \text{Pa} \tag{10}$$

and illustrated in Figure 4.

Solubility of Miscellaneous Gases in Water. The next correlations are for 7 "miscellaneous" gases: N_2O, C_2N_2, COS, ClO_2, NF_3, N_2F_4, and SF_6. (Although SF_6 was included in spherical nonpolar gases, it made sense to include it here.) The range of solubilities was $1.8 \cdot 10^{-2}$ (ClO_2) to $4.3 \cdot 10^{-6}$ (SF_6) which is about 4 orders of magnitude. There were 7 properties for all of these gases: MM, NBP, DM, T_c, P_c, FP, and ω. Combinations of the parameters were not productive in groups of two or more. The best single parameter was again P_c with $R^2 = 0.9497$ and sd = 0.635. Figure 5 illustrates this. The equation for this fit is

$$\ln x_2 = -15.702(\pm 0.670) + 0.11010 (\pm 0.0103) P_c/101325\ \text{Pa} \tag{11}$$

■ DISCUSSION

In this paper are presented the results of correlating the solubility of gases in water as ln x_2 at 298.15 K and 101325 Pa partial pressure of gas in seven groupings. Figure 1 is an illustration of an attempt to fit all 65 gases. It is obvious that with the enormous range of solubility and variety of solutes that the "dream" of finding one equation with just a few physical properties of the gases was hopeless. So, the gases were divided into groupings reflecting similar characteristics. (The last "miscellaneous" group was somewhat arbitrary.)

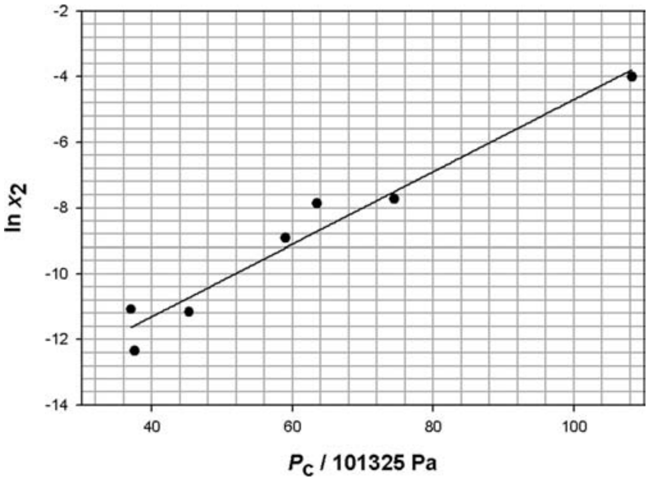

Figure 5. ln x_2 vs P_c/101325 Pa for 7 miscellaneous gases.

Table 3. Solubility Interaction Factors[a]

type	comment	example
strong H-bonds	positive hydrogens and/or electron lone pairs	CH_3NH_2
weak H-bonds	less positive hydrogens and/or lone electron pairs	CCl_2H_2
induction and dispersion forces	depend on polarizabilities of gas molecules	
more polarizable gas molecule		Xe
less polarizable gas molecule		He
"teflon" molecules	perfluorinated compounds	$CF_3CF_2CF_3$

Considering R^2, sd, and t values for the coefficients for the chosen fitting equations for each grouping showed some success. Studies by researchers (like Abraham, et al.[1]) had significant success with many more solutes, but at the cost of using a great many parameters. Ideally, the utilization of parameters calculatable from just the structure of the solute molecule would be preferred since the correlations could then be readily extended to additional gases. Two structural parameters used in this paper are the molar mass (MM) and ATNO, the total number of electrons in a molecule. However, the three other parameters given in Table 1 (NBP, T_c, and P_c) are generally available for other solutes.

As noted earlier, parameters which can be directly related to intermolecular forces, such as the polarizability and dipole moment and potential hydrogen bonds, would be the ones of choice with solubility in highly polar hydrogen-bonded water. Instead, it was found that parameters strongly indicative of intermolecular forces (such as NBP, T_c, and P_c) yielded good correlations. A separate study was done of the 34 gases that have dipole moments. The R^2 value of 0.3068 and sd of 2.37 were not impressive since there were 7 points with residuals > 1 sd, although both *t* values were greater than or about 4. So, the dipole moment alone did not give a good fit for polar gases. Molecular mass is related to the number of electrons in a molecule, and hence to polarizability. Initially, it was thought that $V_c^{2/3}$ (which is a measure of the surface area of a molecule) would prove to be a useful parameter. Unfortunately, it was not, and in addition V_c data were not available for many of the gases in this study.

Solubility depends on the strength of the interaction between gas and water molecules. Table 3 is a summary of the strength of the interaction by type, indicating that as the strength of the interaction increases so does the solubility. In general, the chemically reactive gases are the most soluble. What characterizes the least soluble gases? These are the seven perfluorinated hydrocarbons which might be considered to be "Teflon" molecules. Dalvi and Rossky[9] consider that these perfluorinated molecules show enhanced hydrophobicity (decreased solubility) due to their "fatness"; that is, they pack less densely on surfaces leading to weaker van der Waals interactions with water. This led to fitting the seven gases (in order of decreasing solubility: C_2F_4, C_3F_6, SF_6, CF_4, c-C_4F_8, C_2F_6, and C_3F_8) in several ways. The single parameters tested had poor *t* values, but MM (7.0) and ATNO (7.0) combined (*t* values in parens) yielded an R^2 of 0.9185 with sd = 0.49, and

$$\ln x_2 = -7.2782(\pm 0.780) - 5.6106(\pm 0.803)\mathrm{MM}/(\mathrm{g \cdot mol^{-1}}) + 11.632(\pm 1.672)\mathrm{ATNO} \qquad (12)$$

where ATNO is the total number of electrons in the molecule.

The paper by Wilhelm et al.[3] gave a number of correlations involving changes in thermodynamic properties upon solution, such as the enthalpy and entropy. The necessary temperature-dependent data to calculate these properties were only available for a small number of gases. This would be a good area for future studies.

The authors hope that this paper will be of use to researchers in the field and also inspire more work.

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DEDICATION

We are pleased to make this small contribution in honor of Professor John M. Prausnitz who has contributed so much to both the practical and theoretical aspects of thermodynamics as applied to pure substances and mixtures. Indeed, we had reference to his book with Poling and O'Connell[10] (and all of the prior editions) for much of our work, including this paper. Thank you, John.

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