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Correlations

On the Role of Solute Polarizability in Determining the Solubilities of Gases in Liquids

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Understanding the factors determining the solubilities of gases in liquids is important from both practical and theoretical standpoints. Gas solute polarizability can be expected to be a significant influence on solubility in many cases. The importance of gas solute polarizability in determining solubility in several solvents has been assessed using regression analysis. Two measures of gas solute polarizability have been employed: (1) a carefully compiled collection of experimental values from the literature; and (2) values calculated using an additive method proposed by Bosque and Sales. Whereas solute polarizability plays very little role in determining solubility in water, it plays a dominant role in other solvents, including benzene, hexane, 1-octanol, and ethanol. The results are interpreted in terms of the dominant intermolecular interactions prevailing in each solvent.

Introduction

Knowledge of the solubility of gases in liquids is important for both practical and theoretical reasons. There have been a number of reviews,[1−3] and critically evaluated experimental data have been published in the *IUPAC Solubility Data Series* volumes[4] (a list of these volumes prior to 2004 is in a history of that project[5]). This paper is part of a larger project involving the development of useful correlations for the solubilities of gases in liquids. For that purpose we have examined a large number of experimental and calculated descriptors. Among these descriptors the polarizability of the solute molecule has the potential to be especially useful. In this paper we provide a set of polarizability data for gases that has been critically evaluated, which may be useful for a variety of purposes.

Polarizability has been used as one of the factors affecting solubility in water in studies related to pharmaceuticals. For example, Abraham et al.[6] used five factors to fit the solubilities of 408 gaseous compounds in water at 298 K. One of these factors was the "dipolarity/polarizability" of the compounds. Duchowicz and Castro[7] calculated molecular polarizabilities of alkanes and alcohols and used these values to correlate water solubilities of those solutes with an R^2 of 0.988 for alcohols ($n = 51$) and 0.895 for alkanes ($n = 18$). They used molecular polarizabilities from three earlier papers.[8−10] Yan and Gasteiger[11] used 18 topological descriptors to fit the aqueous solubilities of 1293 organic compounds; among these descriptors was the "mean molecular polarizability" calculated from the Petra program. Sadus[12] has carried out simulations on 12 different single solute plus solvent systems calculating Henry's constants at temperatures between the triple point and the critical point of the solvent. He found that the magnitude of the interactional Lennard−Jones energy parameters and the polarity of the solvent were the dominant influences on solubility.

Perhaps the most useful calculated polarizabilities (discussion following eq 1 in the next section) are those proposed by Bosque and Sales[13] who used an additive scheme based on derived atomic polarizabilities of 10 elements, C, H, N, S, P, F, Cl, Br, and I, and the experimental polarizabilities of 426 compounds.

Data Sources Reviewed. A number of different polarizability (α) data sets can be found in the literature. To determine which of these is most useful for the study of gas solubilities, these data sets were collected and subjected to regression analysis against our solubility data.

The compilation (COMP) set is a carefully compiled list of polarizabilities obtained from several sources of experimental values. This is the most complete of the lists, with 58 values for different gases. The units used in this paper are $\mathrm{cm^3 \cdot 10^{-24}}$ or $\mathrm{Å^3}$. Polarizability data were taken directly from the 2008−2009 CRC Handbook of Chemistry and Physics.[14] Since the COMP and CRC data sets were essentially identical, we use only the COMP set in Table 1. The range of the COMP values is 0.21 to 10.2.

The additive (ADD) set is composed of polarizabilities obtained from adding values for the number and types of atoms in a molecule and is a *calculated* set of polarizabilities. The fitting equation was chosen to best approximate literature values. Many kinds of additive polarizability methods have been reported in the recent literature. The additive method used here is taken directly from the work of Bosque and Sales.[13] This additive method is useful because it is said to be a better approximation of polarizabilities than most other additive methods.[15,16] The Bosque and Sales equation is:

$$\alpha/Å^3 = 0.32 + 1.51N_\mathrm{C} + 0.57N_\mathrm{O} + 0.17N_\mathrm{H} + 2.99N_\mathrm{S} + 3.29N_\mathrm{Br} + 1.03N_\mathrm{N} + 0.22N_\mathrm{F} + 2.16N_\mathrm{Cl} + 2.48N_\mathrm{P} \quad (1)$$

Here N_C is the number of carbon atoms, N_O the number of oxygen atoms, and so forth. For example, for methane (CH_4): $\alpha = 0.32 + 1.51 \cdot 1 + 0.17 \cdot 4 = 2.51\ Å^3$. There are 52 ADD

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Table 1. Polarizability and ln x_2 Water Values

		COMP	ADD	
	gas	Å^3	Å^3	ln x_2
1	He	0.2050		−11.8720
2	Ne	0.3956		−11.7196
3	Ar	1.6411		−10.5903
4	Kr	2.4844		−10.0102
5	Xe	4.044		−9.4638
6	Rn	5.3		−8.6945
7	O_2	1.5812	1.46	−10.6809
8	N_2	1.7403	2.42	−11.3534
9	H_2	0.804	0.66	−11.1672
10	H_2S	3.782	3.65	−6.2920
11	C_2H_2	3.63^a	3.68	−7.1982
12	C_2H_4	4.252	4.02	−9.3634
13	C_2N_2	7.99	5.44	−8.921
14	CH_4	2.593	2.51	−10.5938
15	C_2H_6	4.45^a	4.36	−10.3055
16	C_3H_4, propyne	6.18	5.53	−6.6983
17	C_3H_6	6.26	5.87	−8.9207
18	C_3H_8	6.33^a	6.21	−10.5182
19	C_4H_6, 1,3-butadiene	8.64	7.38	−8.3151
20	C_4H_8, 2-mepropene	8.29	7.72	−9.3796
21	C_4H_8, 1-butene	8.25^a	7.72	−9.5489
22	C_4H_{10}	8.20	8.06	−10.7258
23	C_4H_{10}, isobutane	8.14	8.06	−11.1324
24	neopentane	10.20	9.91	−11.4387
25	*c*-C_3H_6	5.66	5.87	−8.4809
26	CCl_2F_2	7.87^a	6.59	−9.965
27	CCl_3F	9.47	8.21	
28	$CClF_3$	5.66^a	4.65	
29	$CH_2{=}C(CH_3)_2$	8.29	7.56	−9.1818
30	$CH_2{=}CF_2$	5.01	4.12	
31	$CH_2{=}CHBr$	7.59	7.14	−6.698
32	$CH_2{=}CHCl$	6.41	4.07	
33	CH_3Br	5.95^a	5.63	−5.8331
34	CH_3CClF_2	8.05	6.02	
35	CH_3CH_2F	4.96	7.43	−7.1197
36	CH_3Cl	5.04^a	2.56	−6.2775
37	CH_2Cl_2	7.21^a	4.98	
38	CH_3F	2.97	2.56	−6.8476
39	CF_4	3.838	2.71	−12.4755
40	C_2F_4	4.22	4.22	−10.4670
41	C_2F_6	6.82	4.66	
42	C_3F_6	6.17	6.17	−12.1482
43	CH_3NH_2	4.36^a	3.39	−1.4118
44	$CH_3OCH{=}CH_2$	6.35	6.44	
45	$CHCl_2F$	6.82	2.65	
46	$CHClF_2$	6.15^a	2.66	−7.3798
47	CHF_3	3.55^a	2.66	−8.356
48	CO	1.95	2.4	−10.9683
49	CO_2	2.911	2.97	−7.4002
50	COS	5.45^a	5.39	−7.8662
51	Cl_2	4.61	4.32	−6.4082
52	ClO_2	3.62	3.30	−4.0041
53	N_2O	3.03	2.99	−7.7326
54	NF_3	3.62	2.03	−11.1490
55	NH_3	2.18^a	1.37	−1.6734
56	NO	1.70	1.92	−10.2668
57	SF_6	6.54	4.63	−12.3353
58	SO_2	4.00^a	4.45	−3.6773

[a] Average value from CRC.[14]

values with a range of 0.66 to 9.91. The correlation between COMP and ADD was 0.850.

There are several quantum chemical methods for generating values for polarizabilities, and they are not reviewed here. The semiempirical AM1, PM3, and MNDO methods all include methods for calculating polarizabilities. These methods all require an appropriate program to generate polarizability values. No substantial lists of polarizability values for gases were found on the basis of these methods. We tested the polarizabilities generated by the QsarIS program[16] in the present context but did not find them to be useful.

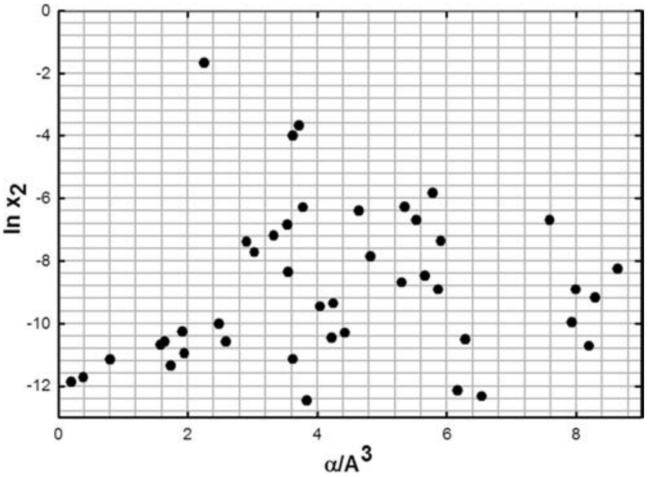

Figure 1. Experimental ln x_2 values for gases in water ($n = 49$).

Table 1 gives polarizability values for all of the gases for COMP and ADD and also the natural logarithm of the mole fraction solubility in water at 1 atm partial pressure of gas at 298.15 K.

Strengths and Weaknesses of Each Data Set

The ease of use and the degree of usefulness of the COMP and ADD polarizabilities are reviewed here. The COMP method yields the most accurate polarizability data. Data for a large number of gases can be found in the literature. All data points were carefully reviewed. The data points are *experimentally* determined. COMP is by far the most time-consuming way to assemble a data set. In ref 13 more than one value is occasionally given at one temperature—in those cases we used the average. Polarizabilities for many gases are simply not reported in the experimental literature.

ADD is a versatile and simple method to use. ADD is purely calculational and based on experimental values, and additional experimental descriptors are not needed to generate the polarizabilities. However, ADD applies only to molecules containing the atoms listed earlier (note: most additive methods have fewer atoms than the cited method.) Furthermore, it does not exactly fit the experimental values. The halogenated hydrocarbons, C_2N_2, NF_3, and 1,3-butadiene show the largest differences (> 1.0) between the COMP and the ADD data sets.

The solubility values used were primarily taken from the *IUPAC Data Solubility Series*.[4] The solubility data points were used as the natural log of the mole fraction at one atm partial gas pressure at 298.15 K as found in this source. The polarizabilities from COMP and ADD were regressed against the mole fraction solubilities (ln x_2) of the gases in the different liquids. The regressions and graphs were obtained using the SigmaPlot[17] program.

Gas Polarizability as a Single Solubility Descriptor

Water. None of the polarizabilities obtained from any of the sources gave good single descriptor results for gas solubility in water. The best results ($R^2 = 0.272$) were obtained from COMP polarizabilities. ADD gave R^2 values below 0.1 for water. Figure 1 shows a plot of calculated ln x_2 versus the experimental ln x_2 for the COMP data set for water. Further analysis of the usefulness of the polarizability as one of several descriptors of the solubility of gases in water was performed using SAS. Twenty-seven physical descriptors were reviewed using the SAS program. The polarizability was never the largest contributor for any of the combinations reviewed with R^2 larger than 0.5.

The best quadratic fit equation for the solubilities in water is:

$$\ln x_2 = -11.96(\pm 1.25) + 1.68(\pm 0.55)\alpha/\text{Å}^3 - 0.169(\pm 0.054)(\alpha/\text{Å}^3)^2$$
$$n = 49 \qquad R^2 = 0.177 \qquad s = 2.41 \qquad F = 4.96 \qquad P = 0.0112 \qquad (2)$$

where n is the number of solute compounds, R^2 is the coefficient of determination (gives the fraction of the variance in the data explained by the model), s is the standard error, F is the Fisher statistic, and P is the probability that the correlation arises by chance.

The reason for the poor performance of polarizability in describing solubilities in water is most likely due to the fact that in water the strong hydrogen bonding is far more important than the solute polarizability for this solvent. Secondly, the very large range of solubilities in water (six orders of magnitude) make it difficult for any single descriptor to account for these solubilities.

Other Solvents. In contrast to the water results, solute polarizability alone was able to account for a sizable fraction of the variation in the solubilities of gases in several other liquids examined. It is important to note that the number and range of solubility points used is severely reduced for the other solvents (as compared to water). The COMP polarizabilities provided a good R^2 value of 0.954 for the polarizability as a single solubility descriptor for benzene for a quadratic fit (vs 0.878 for the linear fit). Figure 2 plots ln x_2 of gases in benzene versus the calculated ln x_2 of benzene using the COMP polarizabilities. Figure 3 shows for benzene a plot of ln x_2 vs α. Since the graphs for the other three solvents are similar to those for benzene, only the benzene figures are shown. The COMP polarizabilities provided R^2 values that were better than the ADD ones for these four solvents. Table 2 gives ln x_2 at 298.15 K and the polarizability of each gas in the four solvents treated in this section. Both linear and quadratic fits are given for solubilities in each solvent.

The equations for solubilities in benzene are:

$$\ln x_2 = -8.74(\pm 0.35) + 1.000(\pm 0.093)\alpha/\text{Å}^3$$
$$n = 18 \qquad R^2 = 0.878 \qquad s = 0.806 \qquad F = 115 \qquad P < 0.0001 \qquad (3)$$

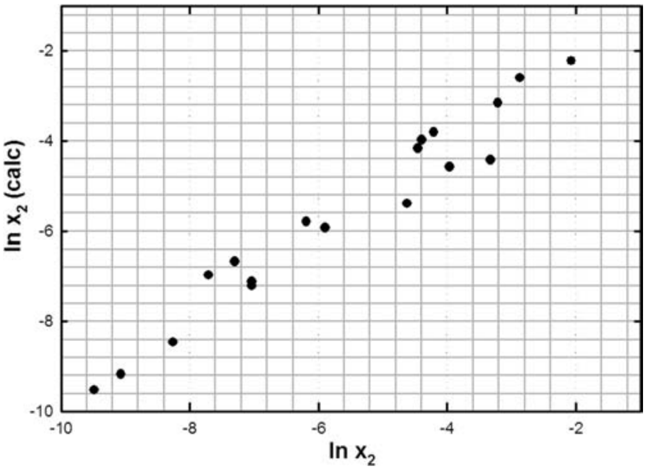

Figure 2. Calculated ln x_2 (calc) solubility versus experimental ln x_2 solubility values in benzene (eq 4, $n = 18$).

$$\ln x_2 = -9.90(\pm 0.32) + 1.888(\pm 0.187)\alpha/\text{Å}^3 - 0.1159(\pm 0.0232)(\alpha/\text{Å}^3)^2$$
$$n = 18 \qquad R^2 = 0.954 \qquad s = 0.510 \qquad F = 156 \qquad P < 0.0001 \qquad (4)$$

The equations for solubilities in hexane are:

$$\ln x_2 = -7.62(\pm 0.23) + 0.880(\pm 0.058)\alpha/\text{Å}^3$$
$$n = 20 \qquad R^2 = 0.929 \qquad s = 0.573 \qquad F = 235 \qquad P < 0.0001 \qquad (5)$$

$$\ln x_2 = -8.50(\pm 0.23) + 1.493(\pm 0.129)\alpha/\text{Å}^3 - 0.0733(\pm 0.0148)(\alpha/\text{Å}^3)^2$$
$$n = 20 \qquad R_2 = 0.971 \qquad s = 0.377 \qquad F = 284 \qquad P < 0.0001 \qquad (6)$$

The equations for solubilities in 1-octanol are:

$$\ln x_2 = -8.47(\pm 0.27) + 0.955(\pm 0.076)\alpha/\text{Å}^3$$
$$n = 15 \qquad R^2 = 0.924 \qquad s = 0.628 \qquad F = 157 \qquad P < 0.0001 \qquad (7)$$

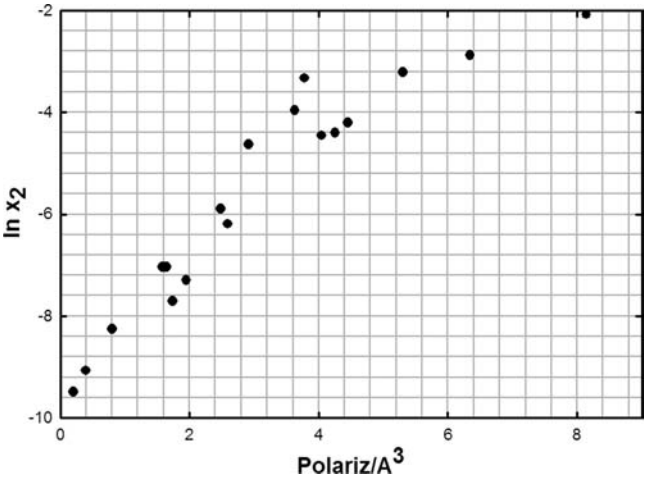

Figure 3. ln x_2 solubility in benzene versus polarizability (eq 4, $n = 18$).

Table 2. Polarizability and ln x_2 for Gases in Ethanol, 1-Octanol, *n*-Hexane, and Benzene at 298.15 K[a]

gas	α/Å^3	ethanol	1-octanol	*n*-hexane	benzene
He	0.2050	−9.4450	−9.0220	−8.2548	−9.4861
Ne	0.3956	−9.1240	−8.6840	−7.8993	−9.0706
H_2	0.804	−8.4880	−7.8440	−7.3370	−8.2587
O_2	1.5812	−7.4630	−6.7840	−6.2247	−7.0390
Ar	1.6411	−7.3780	−6.6670	−5.9835	−7.0333
N_2	1.7403	−7.9320	−7.4020	−6.5642	−7.7107
CO	1.95	−7.7310	−7.0710	−6.3368	−7.0038
Kr	2.4844		−5.5800	−4.9690	−5.8998
CH_4	2.593	−6.6610	−5.8920	−5.2963	−6.1899
CO_2	2.911	−5.0440	−4.6690	−4.4170	−4.6284
N_2O	3.03	−4.9340	−4.2860	−3.9992	
C_2H_2	3.63			−4.3428	−3.9633
H_2S	3.782			−3.1489	−3.3298
Xe	4.044			−3.6535	−4.4568
C_2H_4	4.252	−5.0930	−4.3510	−4.1402	−4.3390
C_2H_6	4.45	−5.0150	−4.0750	−3.5200	−4.2098
Rn	5.3	−4.3200		−2.6078	−3.2139
C_3H_8	6.34	−3.7900	−2.1800	−2.1884	−2.8753
i-C_4H_{10}	8.14	−2.9780		−1.2809	−2.0754
n-C_4H_{10}	8.20	−2.5070	−1.2520	−0.9258	

[a] Arranged in order of increasing polarizability.

$$\ln x_2 = -9.22(\pm 0.31) + 1.551(\pm 0.196)\alpha/\text{Å}^3 - 0.0746(\pm 0.0233)(\alpha/\text{Å}^3)^2$$
$$n = 15 \qquad R^2 = 0.959 \qquad s = 0.480 \qquad F = 140 \qquad P < 0.0001 \qquad (8)$$

The equations for solubilities in ethanol are:

$$\ln x_2 = -8.85(\pm 0.29) + 0.816(\pm 0.069)\alpha/\text{Å}^3$$
$$n = 16 \qquad R^2 = 0.909 \qquad s = 0.684 \qquad F = 139 \qquad P < 0.0001 \qquad (9)$$

$$\ln x_2 = -9.70(\pm 0.32) + 1.474(\pm 0.192)\alpha/\text{Å}^3 - 0.0780(\pm 0.0219)(\alpha/\text{Å}^3)^2$$
$$n = 16 \qquad R^2 = 0.954 \qquad s = 0.506 \qquad F = 134 \qquad P < 0.0001 \qquad (10)$$

The success of polarizability in correlating the solubilities of gases in these latter solvents is not surprising and reflects the dominant role of intermolecular London dispersion interactions, which depend on local polarizabilities, in these liquids. This role was demonstrated experimentally four decades ago by Meyer and co-workers,[18,19] who showed that the properties of nonpolar liquids—and even many relatively polar liquids—are dominated by dispersion forces. This interpretation has also been employed by subsequent theoretical analyses, which are consistent with the present results.[20,21]

Summary

The polarizability of a gas is easily calculated or available and is a fairly accurate descriptor for the solubility of gases in liquids *other than water*. The ADD method is easy to use and is recommended for use in any further research when the COMP list does not have the needed polarizability data. The lack of success in using polarizability to describe the solubilities of gases in water reflects the dominant role of hydrogen bonds and related Coulombic interactions in this liquid. In contrast, the strong dependence of the gas solubilities in benzene, hexane, octanol, and ethanol on polarizability can be most readily interpreted as arising from the dominance of dispersion forces in these solvents.

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