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Solubility Properties in Polymers and Biological Media. 1. Correlations in Various Media of the Solubilities of Gaseous Anesthetics and Other Solutes with a Number of Solute Parameters

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Abstract: Stern and Shiah have suggested that the solubility of a series of gaseous solutes in a given solvent system may be correlated with the solute critical pressure and temperature through the equation $\log (LP_c) = a + b(T_c/T)$, where L is the Ostwald solubility coefficient. It is now shown that when applied to the solution of 28 gaseous inert solutes in benzene solvent, the term in P_c is not important and that there is a better linear correlation between $\log L$ itself and (T_c/T). It is further shown for the same system that $\log L$ is even better correlated with Abraham's solute parameter R_G than with (T_c/T) or $(T_c/T)^2$ or the solute interaction energy (ϵ/k). Good linear regressions are also observed between $\log L$ for the solution of inhalation anesthetics in various media and R_G, and between $\log L$ for the solution of a number of gaseous solutes in polyethylene and hydropol. A theoretical explanation for these linear regressions is given, and the possible extent of the regressions with respect to solute type and solvent type is explored.

The solubility of gases and vapors in media such as lipid phases and polymers is of considerable technical interest, and there have been numerous attempts to correlate and to predict such solubilities. The starting point has often been Hildebrand's solubility parameter approach, but all expressions based on the solubility parameter include a term $(\delta_1 - \delta_2)^2$, where δ_1 and δ_2 are the solubility parameters of solvent and solute, respectively. The solubility parameter is defined as $\delta = [(\Delta H^\circ_v - RT)/\bar{V}]^{1/2}$, where ΔH°_v and $\bar{V}$ are the molar enthalpy of vaporisation and molar volume (both at 298 K) of the compound, respectively. Since for "solvents" such as lipid phases and polymers it is possible to obtain δ_1 only through indirect methods, this method then reduces to empirical relationships between the solubility of gases and vapors and $\delta_2{}^2$ (or even δ_2). [The term "solvent" is used to mean lipid phases and polymers as well as conventional solvents. The indirect methods include, for example, studies on the swelling of polymers by solvents.]

A similar difficulty arises with other correlations, in that many of the "solvents" studied cannot be characterized physicochemically and therefore the correlations can only include physicochemical parameters characteristic of the solutes, and not of the "solvents". A number of correlations of this type have been suggested, one of the first by Michaels and Bixler[1] who put forward eq 1. In

$$\log L = a + b(\epsilon/k) \tag{1}$$

this equation, L is the solubility of a solute expressed as the Ostwald coefficient; L = volume of gaseous solute, at the experimental temperature T and partial pressure P_2, dissolved in a unit volume of solvent. The term (ϵ/k) is the Lennard-Jones interaction parameter of the solute,[2] and a and b are constants. Equation 1 is designed to apply to a series of solutes in a given solvent at some specified temperature. Later on, Stern et al.[3] showed that the solubility of gases in polythene could be described by eq 2, in which α' and b' are constants, T_c is the solute critical temperature, and T is the experimental temperature. Equation 2 is rather more general than eq 1 because the former will cover the solubilities of a series of solutes at different temperatures in a given solvent. Stern et al.[3] pointed out that since (ϵ/k) was

$$\log L = a' + b'(T_c/T)^2 \tag{2}$$

proportional to T_c for a series of solutes, it would be expected from Michaels and Bixler's work that $\log L$ should be proportional to T_c/T rather than to $(T_c/T)^2$. Equation 2, however, was still used by Suwandi and Stern[4] to correlate solubilities in silicone rubber as well as in polyethylene. Stern and Shiah[5] then showed that there was a correlation to be expected between $\log (LP_c)$ and a function of (T_c/T), where P_c is the solute critical pressure, and confirmed a linear correlation, eq 3, for the solubilities of solutes in a variety of lipid phases and rubbers. Some time before the

$$\log (LP_c) = a'' + b''(T_c/T) \tag{3}$$

work of Suwandi and Stern, a solubility correlation involving the solute constants P_c and T_c had also been suggested by Maloney and Prausnitz.[6]

A different approach altogether was adopted by Abraham,[7,8] who showed that the solubility of gaseous solutes, expressed in terms of the Henry's law constant, K^H, could be correlated through a series of equations:

$$\Delta G^\circ_s = -RT \ln K^H = d + lR_G \tag{4}$$

In these equations, R_G is an empirical parameter characteristic of the solute, and d and l then characterize the solvent. R_G was determined by normalizing and averaging the solubility of solutes in a range of solvents; typically about 10–20 solvents were used for the determinations.[8,9] As with eq 1–3, eq 4 was applied to the solution of a series of solutes in a given solvent. Abraham also showed that analogous equations to eq 4 could be used to correlate the enthalpy and entropy of solution of solutes in solvents.[8,9] The application of eq 4 to the solubility of gaseous solutes was much wider than attempted previously through eq 1–3. No less than 489 ΔG°_s (or $\ln K^H$) values were correlated through eq 4 with an average deviation of 0.08 kcal mol^{-1} in ΔG°_s (0.06 units in $\log K^H$).[8] The solutes were all nonpolar, inert compounds, but the correlations covered all nonaqueous solvents (32) for which

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[1] Michaels, A. S.; Bixler, H. J. *J. Polym. Sci.* **1961**, *50*, 393.
[2] Pierotti, R. A. *Chem. Rev.* **1976**, *76*, 717.
[3] Stern, S. A.; Mullhaupt, J. T.; Gareis, P. J. *AIChE J.*, **1969**, *15*, 64.
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[5] Stern, S. A.; Shiah, S.-P. *Mol. Pharmacol.* **1981**, *19*, 56.
[6] Maloney, D. P.; Prausnitz, J. M. *AIChE J.* **1976**, *22*, 75.
[7] Abraham, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5477.
[8] Abraham, M. H. *J. Am. Chem. Soc.* **1982**, *104*, 2085.
[9] Abraham, M. H. *J. Am. Chem. Soc.* **1980**, *102*, 5910.

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Table **I**. Solute Parameters and Values of log L in Benzene at 298.15 K

no.	solute	log L^a	$R_G{}^a$	$(\epsilon/k)^b$	$T_c{}^c$	P_c/atm^c
1	He	−1.68	1.32	6.03	5.1	2.3
2	Ne	−1.50	1.39	34.9	44.3	25.9
3	Ar	−0.62	1.75	122	151.1	48.1
4	Kr	−0.12	1.95	158	209.3	54.3
5	Xe	0.50	2.19	229	289.7	58.2
6	Rn	1.04	2.39	290	377.2	62
7	H_2	−1.15	1.54	29.2	33.2	12.8
8	N_2	−0.91	1.64	95.0	126.0	33.5
9	CO	−0.74	1.71	100	134.0	34.6
10	O_2	−0.65	1.74	118	154.3	49.7
11	CH_4	−0.25	1.90	157	191.9	45.4
12	C_2H_6	0.61	2.26	236	305.2	48.3
13	C_3H_8	1.18	2.47	350	369.8	41.9
14	*i*-C_4H_{10}	1.53	2.61	400	408.1	36
15	*n*-C_4H_{10}	1.76	2.70	400	425.2	37.5
16	*n*-C_5H_{12}	2.29	2.89	450	469.6	33.3
17	*n*-C_6H_{14}	2.82	3.11	500	507.2	29.9
18	*n*-C_7H_{16}	3.29	3.32	550	540.0	27
19	*n*-C_8H_{18}	3.92	3.52	580	569.0	24.8
20	CF_4	−0.80	1.70	134	227.5	41.4
21	SF_6	−0.14	1.98	201	318.7	37.1
22	Me_4C	1.84	2.73	350	433.6	31.6
23	c-C_5H_{10}	2.59	3.02	500	511.8	44.5
24	Me_4Sn	2.92	3.14	400	521.8^d	29.4^d
25	c-C_6H_{12}	3.10	3.24	550	553.4	40.2
26	Et_4C	4.27	3.68	450	590	22
27	Et_4Sn	5.14	4.02	500	630^e	20^e
28	Et_4Pb	5.55	4.17	510^e	650^e	21^e

[a] From ref 8. [b] Wilhelm, E.; Battino, R. *J. Chem. Phys.* 1971, *55*, 4012. Abraham, M. H.; Naschzadeh, A. *J. Chem. Soc., Faraday Trans. 1*, 1981, *77*, 321. [c] References 1 and 5, and, "Handbook of Chemistry and Physics", 55th ed., CRC Press: Cleveland, Ohio, 1974–75, except where shown. [d] Hugill, J. A.; McGlashan, M. L. *J. Chem. Thermodyn.* 1978, *10*, 85. [e] Estimated values, see text.

Table **II**. Correlations between the Solubilities of Gases in Benzene (log L and log (LP_c)) and Solute Parameters[a]

	R_G	ϵ/k	T_c/T	$(T_c/T)^2$	δ_H	$\delta_H{}^2$
		A. All 28 Solutes in Table I				
log L	1.000	0.938	0.970	0.991	0.804	0.841
log (LP_c)	0.992	0.945	0.980	0.976	0.837	0.866
R_G		0.940	0.972	0.992	0.807	0.843
ϵ/k	0.940		0.969	0.939	0.864	0.894
T_c	0.972	0.969			0.885	0.905
$T_c{}^2$	0.992	0.939			0.803	0.846
δ_H	0.807	0.864	0.885	0.803		
$\delta_H{}^2$	0.843	0.994	0.905	0.846		
		B. The First 26 Solutes in Table I				
log L	1.000	0.967	0.975	0.988	0.833	0.870
log (LP_c)	0.990	0.966	0.982	0.967	0.862	0.891
R_G		0.968	0.977	0.988	0.836	0.873
ϵ/k	0.968		0.972	0.962	0.860	0.894
T_c	0.977	0.972			0.894	0.915
$T_c{}^2$	0.988	0.962			0.826	0.871
δ_H	0.836	0.860	0.894	0.826		
$\delta_H{}^2$	0.873	0.894	0.915	0.871		

[a] Values taken from Table **I**. Correlation coefficients given for linear regressions between the various parameters.

Table **III**. Correlations of log L and log (LP_c) for Solution of Gases in Benzene with Solute Parameters[a]

correlation equation	r^b	s^c	% CL^d
A. All 28 Solutes in Table I			
$\log L = -5.078 + 2.540R_G$	0.99985	0.036	>99.9999
$\log L = -1.884 + 0.01054(\epsilon/k)$	0.93761	0.732	>99.9999
$\log L = -2.313 + 3.076(T_c/T)$	0.96952	0.516	>99.9999
$\log L = -1.161 + 1.376(T_c/T)^2$	0.99146	0.275	>99.9999
$\log (LP_c) = -3.604 + 2.549R_G$	0.99206	0.267	>99.9999
$\log (LP_c) = -0.449 + 0.01748(\epsilon/k)$	0.94530	0.694	>99.9999
$\log (LP_c) = -0.896 + 3.144(T_c/T)$	0.97961	0.428	>99.9999
$\log (LP_c) = 0.346 + 1.371(T_c/T)^2$	0.97635	0.460	>99.9999
B. The First 26 Solutes in Table I			
$\log L = -5.064 + 2.533R_G$	0.99980	0.037	>99.9999
$\log L = -1.738 + 0.00951(\epsilon/k)$	0.96683	0.465	>99.9999
$\log L = -2.134 + 2.838(T_c/T)$	0.97475	0.406	>99.9999
$\log L = -1.137 + 1.353(T_c/T)^2$	0.98810	0.280	>99.9999
$\log (LP_c) = -3.707 + 2.597R_G$	0.98959	0.271	>99.9999
$\log (LP_c) = -0.321 + 0.00984(\epsilon/k)$	0.96573	0.489	>99.9999
$\log (LP_c) = -0.759 + 2.962(T_c/T)$	0.98208	0.355	>99.9999
$\log (LP_c) = 0.345 + 1.372(T_c/T)$	0.96718	0.479	>99.9999

[a] All values of log L and log (LP_c) (at 298.15 K) and solute parameters from Table I. [b] Correlation coefficient. [c] Standard deviation defined as $s = [(y - \hat{y})^2/(n-2)]^{1/2}$, where n is the number of solutes. [d] Percentage confidence level for the correlation.

extensive results were available.

The Henry's law constant in eq 4, in units of atm/mol fraction, may be converted into the Ostwald solubility coefficient for solvents that have a definite molecular weight through eq 5, where ρ_1 and

$$K^H L = 82.05T\rho_1/M_1 = 24463\rho_1/M_1 \text{ (at 298.15 K)} \quad (5)$$

M_1 are the solvent density and molecular weight. Substitution of eq 5 into eq 4 leads to an equation of similar form to eq 1–3 (in comparing eq 6 to eq 4, note that $d' = \log (82.05T\rho_1/M_1) - d/1.36425$, $l' = -l/1.36425$, and that any set of solutes correlated through eq 4 will yield a regression equation with the same correlation constant when eq 6 is used.)

$$\log L = d' + l'R_G \quad (6)$$

Since eq 1–3 and 6 all purport to correlate the solubility of a series of solutes in a given solvent, it follows that the various explanatory variables, ϵ/k, $(T_c/T)^2$, (T_c/T), and R_G, should all be linearly related. It is the purpose of this paper to probe the connection between these explanatory variables and other possible properties characteristic of solutes and to show how the solubility of gases in the systems studied by Stern and Shiah[5] may best be correlated.

Solubility in Benzene

Before comparing any correlations on the solubility of gases in polymers and lipid phases, we thought it would be useful to study correlations on solvent systems for which there are more data available. Abraham[8] has tabulated the Gibbs energy of solution of a large number of solutes in a number of solvents. Since all these Gibbs energies of solution in any one nonaqueous solvent are linearly correlated with the corresponding Gibbs energies of solution in any other nonaqueous solvent,[8] it is sufficient just to study one particular solvent; any deductions thus made are directly transferable to all the other solvents listed by Abraham. We chose benzene as a suitable test solvent, since solubilities of no less than 28 inert solutes are available. In Table I are log L values at 298.15 K obtained from the $\Delta G^\circ{}_s(RT \ln K^H)$ values listed,[8] together with a set of solute parameters R_G, ϵ/k, T_c, and P_c. In order that the various correlations should be comparable, it is useful to have all the solute parameters for all the solutes. We estimated ϵ/k for Et_4Pb and also T_c and P_c for Et_4Sn and Et_4Pb, the latter two quantitites by standard estimation methods.[10] We also investigated correlations with use of the solute Hildebrand solubility parameter, δ_H or $\delta_H{}^2$, but found that these correlations were not at all good. Although we shall give brief details of correlations involving δ_H or $\delta_H{}^2$, we do not tabulate the δ_H values used.

In Table II are listed the correlation coefficients, *r*, for various linear regressions between the parameters given in Table I. Since the parameters for solutes number 27 and 28 are estimated, we repeated the correlations for the first 26 solutes only. The first very important observation is that the solute critical pressure, P_c, can be omitted without any decrease in goodness of fit. Indeed, values of *r* for correlations of log L are just as good as for correlations of log $(LP)_c$; we shall find that this is also the case for the systems studied by Stern and Shiah[5] (see below). Second,

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(10) Hāla, E.; Pick, J.; Fried, V.; Vilim, O. "Vapour-liquid Equilibrium"; 2nd ed.; Pergmamon Press: London, 1967.

Table IV. Solute Parameters and Values of log L at 310.1 K[a]

	log L							
solute	oil	human fat	silicone rubber	rubber[b]	olive oil[c]	R_G[d]	T_c[e]	P_c/atm[e]
1. Ar					−0.830 (297.9)	1.75	151.1	48
2. CO					−1.041 (297.6)	1.71	134.0	35
3. CO_2					0.150 (298.0)	(2.06/2.16)[f−h]	304.0	73
4. $CHCl_3$	2.602	2.595	2.243	2.477	2.585	(3.23)[h,i] ((3.28))	534.1	52.4
5. c-C_3H_6	1.061	1.114	1.064[j]	0.820		(2.57)[f]	394.9	52.9
6. Et_2O	1.813	1.866	1.861	1.763	1.841	(2.89)[f,h]	466.8	36.0
7. $(CH_2{=}CH)_2O$	1.778	1.773		1.653		(2.87)[h,i] ((2.85))	463.1	41.9
8. $CHClFCF_2OCHF_2$	1.991		1.760		1.943	(2.97)[h,i] ((2.89))	470.0	33.1
9. C_2H_4	0.239					2.17[f,h]	282.8	50.5
10. $CF_3CH_2OCH{=}CH_2$	1.681	1.731		1.301		(2.83)[f,h]	463.8	31.4
11. $CHF_2CF_2CH_2Br$	2.505			2.134		(3.18)[f,h]	519.7	34.3
12. $CH_3CHClBr$	2.342	2.260	1.989	2.079	2.293	(3.10)[h,i] ((3.04))	496.4	52.1
13. Kr	−0.347					1.95	209.3	54.3
14. $CHCl_2CF_2OCH_3$	2.978	2.914	2.724	2.799	2.969	(3.38)[f,h]	559.8	40.2
15. Ne					−1.670 (297.6)	1.39	44.3	25.9
16. N_2	−1.155				−1.137 (297.6)	1.64	126.0	33.5
17. N_2O	0.146			0.079		2.22	309.6	71.7
18. O_2					−0.896 (298.2)	1.74	154.3	49.7
19. CF_3CHFBr	1.462			0.903		(2.74)[f,h]	431.1	38.9
20. $CCl_2{=}CHCl$	2.954	2.802	2.594	2.919		(3.35)[h,i] ((3.53))	570.9	45.7
21. Xe	0.255					2.19	289.7	58.2

[a] All log L values from ref 5. [b] At 296.1 K. [c] At 310.1 K except where indicated. [d] The primary R_G values are those averaged from several solubility determinations,[8] and are shown unparenthesized. Secondary R_G values are in parentheses and have been obtained from solubility data using only a limited number of solvents. Tertiary R_G values are doubly parenthesized and have been calculated via eq 7. [e] Reference 5. [f] Reference 11. [g] This value is not certain. [h] Obtained only from data in nonpolar solvents.

there are good correlations between log L (or log (LP_c)) and the previously used parameters ϵ/k, T_c/T, and $(T_c/T)^2$, with values of r being 0.938, 0.970, and 0.991, respectively. (Note that for experiments carried out at a given temperature, as is usually the case, correlations with T_c/T are exactly equivalent to correlations with T_c.) However, the standard deviation, s, defined as $s = [(y_i - \hat{y}_i)^2/(n-2)]^{1/2}$, for these correlations is quite high. (Note also that the term "SD" given by Stern and Shiah[5] appears to be equivalent to s^2, thus the "SD" values are much smaller than our s values. If $s = 0.275$ then $s^2 = 0.0756$.) Even for the best correlations, against $(T_c/T)^2$, $s = 0.27$–0.28 (see Table III), which corresponds to a deviation in the estimated value of L of around 90%. On the other hand, for the correlations of log L with R_G, s is only 0.036–0.037 (see Table III), corresponding to a deviation in the estimated value of L of about 10%. As we pointed out, above, there are such good linear relationships between log L in benzene and log L in all the other nonaqueous solvents previously studied that we can firmly conclude that the R_G parameter will lead to substantially better correlations for solutes in these other solvents than will ϵ/k, T_c, or $(T_c)^2$.

It is useful to be able to estimate values of R_G for solutes not studied before. From the general survey of correlation coefficients given in Table I, it seems that there is a reasonable correlation between R_G and $(T_c/T)^2$, i.e., a correlation between R_G and T_c^2. The correlation equations for the 28 and 26 solutes studied are given in eq 7 and 8, respectively. We suggest that eq 7 could

$$R_G = 1.542 + [6.0978 \times 10^{-6}](T_c)^2 \qquad r = 0.99174$$
$$s = 0.106 \qquad n = 28 \tag{7}$$

$$R_G = 1.550 + [6.0099 \times 10^{-6}](T_c)^2 \qquad r = 0.98843$$
$$s = 0.109 \qquad n = 26 \tag{8}$$

be used to obtain at least preliminary values of R_G. However, all the solutes included in this correlation are rare gases and alkanes, or alkane-like compounds, and whether the correlation can be extended to other solute types remains to be determined.

Solubility of Anesthetics in Various Media

We now turn to the solvent systems discussed by Stern and Shiah,[5] and in Table IV we list the relevant log L values, as well as values of T_c and P_c for the solutes. In Table V are results of regressions of log L and log (LP_c) against T_c or (T_c/T). For solution in human fat and in rubber, the log L correlations are significantly better than those of log (LP_c) as judged by both the increase in correlation coefficient and decrease in the standard deviation, s, while in the other three solvent systems there is little difference between the two types of correlation. From an empirical point of view, it is therefore better to omit the term in P_c altogether. Although the log L against (T_c/T) correlations given in Table V are reasonably good, with percentage confidence levels of the order of 99.999, the standard deviations in log L range from 0.09 (human fat) to 0.19 (rubber). These amount to deviations in the predicted and observed L values from about 20% to 50%; although these percentage deviations seem large, it is probable that this is the order of experimental uncertainty in the observed L values.

Correlations of the solubility of the solutes in Table IV against the R_G parameter were then attempted. A number of "primary" R_G values are available, determined by using solubility data in a large number of solvents,[8,9] and we have also obtained some "secondary" values from solubility data in a limited number of solvents.[11] There remain five solutes in Table IV for which no R_G values are presently available. We obtained these first by averaging all the solubility results available and second from the R_G against $(T_c)^2$ regression given in eq 7. Correlations of the log L values in Table IV against these two sets of R_G values are in Table V. For solution in oil, human fat, and rubber, the correlations against the "solubility-determined" R_G values are appreciably better than the correlations against (T_c/T), while for silicone rubber there is not much difference. We conclude that if a larger set of R_G values can be determined, this would provide the best available method for prediction and correlation of a set of solutes in rather nonpolar phases. The latter rider is important, because it is clear from available data on polar solvent phases that to predict and correlate the solubility of polar solutes in any other than a nonpolar phase must require some additional parameter to deal with dipole–dipole interactions. Furthermore, even for nonpolar solutes, simple linear regressions against R_G (or against T_c or ϵ/k) must break down for solvent systems that are aqueous or partially aqueous, as has been demonstrated already.[7,8]

Also in Table V are regressions of log L against the alternative set of R_G values that includes data obtained through the R_G against $(T_c)^2$ correlation. These regressions are not at all as good as those for the solubility-determined R_G regressions. We conclude that

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(11) Abraham, M. H.; Kamlet, M. J.; Taft, R. W.; Weathersby, P., unpublished work.

Table V. Correlations of log L Values in Table IV[a]

correlation equation	r	% CL	s	n
Oil				
$\log (LP_c) = -0.786 + 0.009271T_c$	0.991	>99.9999	0.17	16
$\log (LP_c) = -0.786 + 2.875(T_c/T)$	0.991	>99.9999	0.17	16
$\log L = -2.514 + 0.009470T_c$	0.993	>99.9999	0.15	16
$\log L = -2.514 + 2.937(T_c/T)$	0.993	>99.9999	0.15	16
$\log L^b = -4.959 + 2.349R_G$	0.999	>99.9999	0.05	16
$\log L^c = -4.774 + 2.276R_G$	0.995	>99.9999	0.13	16
Human Fat				
$\log (LP_c) = -1.408 + 0.01049T_c$	0.976	99.99	0.15	8
$\log (LP_c) = -1.408 + 3.252(T_c/T)$	0.976	99.99	0.15	8
$\log L = -3.016 + 0.01043T_c$	0.991	99.999	0.09	8
$\log L = -3.016 + 3.234(T_c/T)$	0.991	99.999	0.09	8
$\log L^b = -4.456 + 2.176R_G$	0.999	>99.9999	0.03	8
$\log L^c = -3.559 + 1.868R_G$	0.978	99.99	0.14	8
Silicone Rubber				
$\log (LP_c) = -0.773 + 0.008918T_c$	0.989	99.99	0.09	7
$\log (LP_c) = -0.773 + 2.765(T_c/T)$	0.989	99.99	0.09	7
$\log L = -2.431 + 0.008947T_c$	0.985	99.99	0.10	7
$\log L = -2.431 + 2.774(T_c/T)$	0.985	99.99	0.10	7
$\log L^b = -3.855 + 1.918R_G$	0.982	99.99	0.11	7
$\log L^c = -2.973 + 1.624R_G$	0.967	99.9	0.16	7
Rubber				
$\log (LP_c) = -1.708 + 0.01071T_c$	0.955	99.999	0.27	11
$\log (LP_c) = -1.708 + 3.171(T_c/T)$	0.955	99.999	0.27	11
$\log L = -3.653 + 0.01134T_c$	0.979	>99.9999	0.19	11
$\log L = -3.653 + 3.360(T_c/T)$	0.979	>99.9999	0.19	11
$\log L^b = -5.539 + 2.468R_G$	0.984	>99.9999	0.17	11
$\log L^c = -5.056 + 2.293R_G$	0.984	>99.9999	0.17	11
Olive Oil				
$\log (LP_c) = -0.743 + 2.865(T_c/T)$	0.998	>99.9999	0.13	11
$\log L = -2.300 + 2.803(T_c/T)$	0.995	>99.9999	0.17	11
$(T/310.1) \log L^{b,d} = -4.870 + 2.311R_G$	1.000	>99.9999	0.04	11
$(T/310.1) \log L^{b,e} = -4.820 + 2.299R_G$	0.999	>99.9999	0.09	11
$(T/310.1) \log L^{c,d} = -4.840 + 2.315R_G$	0.998	>99.9999	0.11	11
$(T/310.1) \log L^{c,e} = -4.889 + 2.327R_G$	0.999	>99.9999	0.08	11

[a] The terms r, s, and % CL as defined in Table II. Note that for data at a given temperature correlations in T_c and T_c/T are identical. [b] Using the first set of R_G values in Table IV. [c] Using the alternative parenthesized R_G values in Table IV. [d] With R_G for CO_2 as 2.16. [e] With R_G for CO_2 as 2.06.

Table VI. Values of log L in Polyethylene and Hydropol[a] at 298.15 K

solute	log L poly-ethylene	log L hydropol	R_G	(ϵ/k)	T_c
He	-1.921	-1.921	1.32	6.03	5.1
Ne	-1.385	-1.237	1.39	34.9	44.3
Ar	-0.987	-0.943	1.75	122	151.1
CO	-1.194	-1.167	1.71	100	134.0
O_2	-1.114	-0.987	1.74	118	154.3
CO_2	-0.346	-0.239	2.06	189	304.0
CH_4	-0.693	-0.585	1.90	157	191.9
C_2H_6	0.107	0.176	2.26	236	305.2
C_3H_8	0.599	0.675	2.47	350	369.8
SF_6	-0.752	-0.688	1.98	201	318.7
propene	0.549	0.636	2.45[b]	281	364.9

[a] log L values from ref 1; solute parameters from ref 1 or Table I except where shown. Hydropol is a hydrogenated polybutadiene. [b] From solubilities in five nonpolar solvents: M. H. Abraham, unpublished work.

Table VII. Correlations of the log L Values in Table VI[a]

correlation equation	r	% CL	s
Polyethylene			
$\log L = -4.587 + 2.060R_G$	0.982	>99.9999	0.16
$\log L = -1.887 + 0.007585(\epsilon/k)$	0.968	99.999	0.21
$\log L = -1.897 + 0.005859T_c$	0.926	99.99	0.32
$\log L = -1.505 + [1.427 \times 10^{-5}](T_c)^2$	0.924	99.99	0.32
Hydropol			
$\log L = -4.536 + 2.074R_G$	0.976	>99.9999	0.18
$\log L = -1.818 + 0.007640(\epsilon/k)$	0.962	99.999	0.23
$\log L = -1.830 + 0.005911T_c$	0.922	99.99	0.33
$\log L = -1.432 + [1.434 \times 10^{-5}](T_c)^2$	0.917	99.99	0.34

[a] The terms r, s, and % CL as defined in Table II, n = 11 for all the regressions.

for a wider range of solutes than that listed in Table I, it is much better to rely on solubility-determined R_G values. However, if only one or two R_G values are missing in a given solute set, then a rough estimate may be obtained through eq 7.

It might be felt that correlations of log L against (T_c/T) have an advantage over those against R_G in that the latter sets are restricted to results obtained isothermally. However, the factor $1/T$ is only a correction to the log L values, and can equally well be incorporated into R_G correlations through eq 9. In this

$$(T/T_m) \log L = d' + l'R_G \qquad (9)$$

equation, T_m is either the mean experimental temperature of the data or the temperature at which most of the results were obtained and T is the temperature of the individual experiments. Thus for results in olive oil, Table IV, we took T_m as 310 K (5 results) and corrected the remaining six results through eq 9. As seen in Table V, the resulting regression is excellent, and illustrates the use of the modified R_G equation in dealing with gas solubility data obtained at different temperatures.

Results for a rather different set of solutes to those studied by Stern and Shiah[5] were earlier obtained by Michaels and Bixler[1] and are given in Table VI, together with R_G and T_c values and the values of (ϵ/k) used by Michaels and Bixler[1] in their correlation through eq 1. We correlated the log L values in polyethylene and hydropol against R_G, (ϵ/k), T_c, and $(T_c)^2$; results are in Table VII. As for the previous correlations, the R_G parameter clearly yields the best fit, with regard to both the correlation coefficients

(0.982 and 0.976) and the standard deviation (0.16 and 0.18).

General Discussion

Thus taking all the solvent systems together—the 32 pure nonaqueous solvents studied by Abraham[8] and the various solvent systems investigated in this work—a single solute parameter, R_G, will yield very acceptable correlations of all the log L values for the solutes listed in Table I, IV, and VI. The success, and possible limitations, of this approach can be discussed in terms of cavity theories of solution, the overall energy of solution being broken down into the following terms:[2,12,13] (1) the energy needed to make a cavity in the bulk solvent, (2) the energy of reorganization of the solvent around the cavity, and (3) the energy of interaction of the solute with the reorganized solvent. Term 2 is normally expected to be very small, at least with regard to the Gibbs energy function. Term 1 will be some function of solute size, and it was pointed out originally[7,8] that the R_G parameter was related to the size of the solute. In the case of a nonpolar solute, term 3 is simply the solute–solvent dispersion energy, often approximated by a Lennard-Jones (6–12) potential involving the expression (ϵ/k) for the solute and solvent.[2] Hence, see Table II, there must be some connection between log L and (ϵ/k) for the solute. Furthermore, since R_G and solute (ϵ/k) are related, the R_G solute function will take care of both term 1 and term 3 for the case of a nonpolar solute, and thus we can explain the success of the R_G correlations.

But if the solute is polar, then there must be included in term 3 not only a dispersion energy expression but also expressions for the inductive energy and the dipole–dipole energy,[2] not to mention expressions for possible hydrogen bonding between solute and solvent. For some polar solutes in nonpolar solvents, these additional energy terms might be quite small, so that the R_G correlation is still maintained. In general, though, as the solute and solvent become more polar, so these additional energy terms will become larger, and we therefore predict that the simple R_G correlations will become less successful. One modification of the R_G approach would be to include additional parameters that would deal with the extra energy terms, and plans to investigate this modification are already in hand. A further complication arises with hydrophobic solutes in aqueous or partially aqueous solvent systems, but we have already proposed[11] suitable methods for dealing with this complication, at least for rather nonpolar solutes.

Although there are very poor correlations of log L for a series of solutes in a given solvent with the solute solubility parameter, see Table II, yet for the solution of a given gaseous nonpolar solute in a series of aprotic solvents there are very good correlations with solvent solubility parameter.[13] Therefore in order to predict the solubility of a given gaseous solute in a given solvent system there are two possible methods, viz., (a) through correlations of a set of solute solubilities in the given solvent system, as outlined in this work, or (b) through correlations of the solubility of the given solute in a set of solvents.

We are currently exploring the merits of these two methods, as well as attempting to contruct new correlations that will allow the R_G parameter to be predicted from solute molecular properties.

Registry No. Benzene, 71-43-2; polyethylene, 9002-88-4; hydropol, 39316-18-2.

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Charge Reversal of the Conjugate Bases of Acetonitrile and Nitromethane

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Abstract: The mass spectra of CH_2CN^+ generated by charge reversal of the conjugate base of acetonitrile and CH_2CN^+ generated by loss of H from the molecular ion of acetonitrile differ; the latter is dominated by the loss of C, the former by loss of CH_2. Labeling and semiempirical MO theory are used to examine the rearrangement of the ion that must precede the loss of C. The spectra of $CH_2NO_2^+$ generated by charge reversal of $CH_2NO_2^-$ and H loss from $CH_3NO_2^{+\cdot}$ also differ. In this case the fragmentations cannot be interpreted in terms of unique structures or unique mixtures of structures.

Following collision-induced charge reversal of an even-electron anion (by stripping two electrons from it, eq 1) its fragmentation often differs from that of any stable isomer.[1-4] In our first studies

$$A^- + N \rightarrow A^+ + N + 2e^- \qquad (1)$$

we assumed that fragmentation of a charge-reversed species would resemble collision-induced fragmentation of a cation of the same structure formed in the source and took the difference between the spectra of the charge-reversed anion and its stable isomer to demonstrate the production of a new, unstable structure by charge reversal, for example, the formation of CH_3O^+,[1] CH_3COO^+,[2] or cyclopentadienyl cation.[3] The discovery of two stable anions, $C_3H_5^-$ and CH_3Se^-, whose charge reversal spectra are the same as the collisional activation (CA) spectra of stable $C_3H_5^+$ and CH_3Se^+ formed in the source has supported our assumption.[5] Having demonstrated this identity in these two cases for even-electron anions and cations, we now return to problems of

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