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Solvatochromic Linear Solvation Energy Relationships for Solubility of O_2 in Various Solvents

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Linear solvation energy relationships for solution of O_2 in 27 solvents have been examined. Multiple linear regression equations for mole fraction solubility of O_2 are developed based on Hildebrand's solubility parameter δ_H^2 as well as the π^*, α, and β solvatochromic parameters describing the solvent polarizability/dipolarity, hydrogen bond acidity and hydrogen bond basicity, respectively. Use of the combination of these parameters enables the medium effect on solution of O_2 to be correlated and interpreted in a conceptually simple manner.

A knowledge of the thermodynamic parameters (e.g., solubility) for solution of dioxygen (O_2) in a liquid is necessary for an essential understanding of its roles in a variety of physicochemical phenomena. For example, O_2 is seven-to-eight times more soluble in organic solvents than in water, a point worth bearing in mind when considering its oxidative damage to the hydrophobic interior of biological membranes.[1,2] In this study, the correlationships between mole fraction solubility of O_2 (f_{O2}) and the so-called solvent parameters will be examined to model solution processes of O_2 gas in various media and further to make solvent effects on f_{O2} clear. Because of its nonpolar and hydrophobic character, O_2 gas is much more soluble in hydrophobic solvents than in hydrophilic ones (e.g., in H_2O).[3,4] However, contrary to our expectations, there have been only a few papers concerning the solvent dependence of f_{O2}.[3—8] In their study on the correlation of the free energies (ΔG°) of solution of 41 solutes in a series of solvents with Hildebrand's solubility parameter (δ_H) and with solvatochromic parameter (π^*), Abraham et al.[7] have pointed out that the ΔG° values for solution of O_2 in 7 solvents (hexane, cyclohexane, diethyl ether, methyl acetate, butanone, acetone, and dimethyl sulfoxide) show better linear correlation with δ_H than with π^*. Here, the solution of O_2 in 27 solvents including those employed by Abraham et al.[7] will be examined by conveniently classifying them into three groups of solvents based on their polarity, acidity and basicity[9] i.e., (A) so-called "select solvents", namely nonchlorinated aliphatic aprotic solvents, (B) solvents with amphiprotic hydrogen bond acceptor–donor (HBA–D) property, and (C) aromatic solvents other than (A) and (B). On the basis of the linear solvation energy relationship (LSER) analysis,[7,12—14,17—20] which has been known as the Kamlet–Taft concept and successfully applied to unravel, quantify, correlate and rationalize multiple interacting solvent effects on many types of physicochemical properties and reactivity parameters, we will propose reasonable correlationships between f_{O2} and solvent parameters such as δ_H^2, π^*, α, and β.[11—13]

Experimental

All the data employed in this study are summarized in Table 1. The ΔG° values for solution of O_2 in various solvents were taken from Ref. 10, and the f_{O2} values could be calculated by the equation $\Delta G^\circ = -2.303\, RT \log f_{O2}$, where R is the gas constant and T is the absolute temperature. The Hildebrand solubility parameter δ_H,[11] the solvatochromic parameters π^*, α, and β,[12,13] and the polarizability correction factor δ_P were taken from the cited literature. These data were used in the calculation of the coefficients for the solvatochromic regression equations.

All multiple linear regression results were obtained by using a least-square fitting method and by applying the *F*-statistic analysis to calculate the percentage confidence level of the regression equations. The linear fitting program was written in C++ language and run on an IBM PC compatible computer (Gateway 2000).

Results and Discussion

The data in Table 1 demonstrate that the solubility of O_2 is highly influenced by the solvent. It can be observed, for instance, that the solubility of O_2 in hexane and diethyl ether is ca. 88 times its value in H_2O. The effect of solvents on the solubility may be rationalized by correlating it to parameters characteristic of the solvents. According to a scaled particle theory,[16] the process of dissolution of a gas in a liquid is taken to consist of two hypothetical stages: The first stage consists of the creation of a cavity suitably sized to accommodate a gas in the solvent and the second stage consists of the filling of the cavity with the gas molecules. Although theoretical calculations of the separate terms of the Gibbs energy of solution (ΔG°) are very difficult and not accurate, experimental solubility data can be fitted to multiparameter linear Gibbs energy relationships which take into account the cohesive energy (i.e., the solvent–solvent forces) of a solvent and its solvation effects. Taft and coworkers[7,17] have suc-

Table 1. Mole Fraction Solubility of Dioxygen in Various Solvents and the Corresponding Solvatochromic Parameters

No.	Solvent[a]	Type of Solvent[b]	$10^4 f_{O2}$/log (f_{O2})[c]	π^*[d]	α[d]	β[d]	δ_P[e]	$10^{-3}\cdot\delta_H^2$/J cm^{-3} [f]
1	H_2O	B	0.22/−4.657	1.09	1.17	0.18	0.0	2.294
2	$(CH_2OH)_2$	B	0.69/−4.061	0.92	0.90	0.52	0.0	0.888
3	DMSO	A	1.77/−3.752	1.00	0.00	0.76	0.0	0.600
4	Nitromethane	A	2.82/−3.549	0.85	0.22	0.25	0.0	0.676
5	DMF	A	3.65/−3.437	0.88	0.00	0.69	0.0	0.615
6	Methanol	B	4.18/−3.378	0.60	0.93	0.62	0.0	0.876
7	AN	A	4.32/−3.365	0.75	0.19	0.31	0.0	0.590
8	PC		4.85/−3.314	0.83	0.00	0.40	0.0	0.740
9	Nitrobenzene	C	4.94/−3.306	1.01	0.00	0.39	1.0	0.416
10	PhI	C	5.12/−3.290	0.81	0.00	0.06	1.0	0.416
11	Ethanol	B	5.85/−3.232	0.54	0.83	0.77	0.0	0.676
12	1-Propanol	B	6.93/−3.159	0.52	0.78	0.93	0.0	0.590
13	PhBr	C	7.54/−3.122	0.79	0.00	0.06	1.0	0.408
14	2-Propanol	B	7.80/−3.108	0.48	0.76	0.95	0.0	0.552
15	1-Butanol	B	7.93/−3.100	0.47	0.79	0.88	0.0	0.543
16	PhCl	C	7.93/−3.100	0.71	0.00	0.07	1.0	0.376
17	Benzene	C	8.20/−3.086	0.59	0.00	0.10	1.0	0.353
18	AC	A	8.34/−3.078	0.71	0.08	0.48	0.0	0.412
19	Isobuthyl alcohol	B	8.35/−3.078	0.41	0.68	1.01	0.0	0.488
20	Methyl acetate	A	8.93/−3.049	0.60	0.00	0.42	0.0	0.384
21	Toluene	C	9.08/−3.041	0.54	0.00	0.11	1.0	0.331
22	Ethylacetate	A	9.75/−3.011	0.55	0.00	0.45	0.0	0.346
23	2-Butanone	A	10.0/−3.000	0.67	0.06	0.46	0.0	0.361
24	CCl_4		12.1/−2.917	0.28	0.00	0.00	0.5	0.309
25	Cyclohexane	A	12.5/−2.903	0.00	0.00	0.00	0.0	0.282
26	Diethyl ether	A	19.4/−2.712	0.27	0.00	0.47	0.0	0.228
27	Hexane	A	19.4/−2.712	−0.08	0.00	0.00	0.0	0.222

a) DMSO: dimethyl sulfoxide, DMF: *N*,*N*-dimethylformamide, AN: acetonitrile, PC: propylene carbonate, AC: acetone, PhI: iodobenzene, PhBr: bromobenzene, PhCl: chlorobenzene, CCl_4: carbon tetrachloride. b) A: nonchlorinated aliphatic aprotic solvents ("select solvents"[13]) B: solvents with amphiprotic hydrogen bond acceptor–donor property, C: aromatic solvents other than A and B. c) The values of f_{O2} were calculated from the ΔG° values for solution of O_2 in each solvent[9] using the equation $\Delta G^\circ = -2.303RT \log f_{O2}$, where R is the gas constant and T is the absolute temperature. d) From Ref. 12. e) From Ref. 14. f) From Ref. 11.

cessfully employed a simple two-parameter equation, which relates ΔG° of solution to the Hildebrand solubility parameter δ_H[10] and the dipolarity parameter π^*,[12,13] to interpret the solvent effect on the free energies of solution of a very wide range of solutes in a conceptually simple manner. According to the LSER proposed by Taft, Kamlet and their coworkers,[7,12,14,17—20] f_{O2} can be given by the following linear regression equations:

$$\log f_{O2} = f_{O2}^\circ + h\delta_H^2 \tag{1}$$

$$\log f_{O2} = f_{O2}^\circ + s\pi^* \tag{2}$$

$$\log f_{O2} = f_{O2}^\circ + h\delta_H^2 + s\pi^* \tag{3}$$

where f_{O2}°, h, and s are constants that characterize O_2 solute. The term δ_H^2 (the square of the Hildebrand solubility parameter) reflects the solvent–solvent interaction energy required for the formation of the cavity, while the solvatochromic parameter π^*, which is related to the ability of a bulk solvent to stabilize a charge or a dipole through charge–dipole or dipole–dipole interaction (and in turn may be associated with so-called hydrophobic effect), accounts for the solute–solvent interaction energy. Here it is noted that the linear regressions of $\log f_{O2}$ with the first power of δ_H are often used,[4,7] but regular solutions theory requires that the linear regressions be with δ_H^2 as in Equations 1 and 2.[11,14,17]

Abraham et al.[7] have shown that for seven "select solvents" (hexane, cyclohexane, diethyl ether, methyl acetate, butanone, acetone, and dimethyl sulfoxide), the ΔG° values for solution of O_2 are much better correlated with δ_H than with π^*. Similar results were also obtained for 11 select solvents of group A (including those used by Abraham et al.) in the present study (see Fig. 1). That is, the correlation coefficients (γ) are 0.855 and 0.955 for $\log f_{O2}$ vs. π^* plot and $\log f_{O2}$ vs. δ_H^2 plot, respectively. f_{O2} tends to decrease with an increase in π^* and δ_H^2 (i.e., the sign of h and s in Eqs. 2 and 3 is negative), indicating that the solubility of O_2 is lower in a more polar/polarizable solvent with a larger solvent–solvent interaction, as expected.[10,18] In other words, O_2 is more soluble in a more hydrophobic solvent with a smaller solvent–solvent interaction. From the results of a simple or multiple linear regression analysis (Table 2), we can see that the multiple regression gives no significant further improvement of the correlation and γ is just raised from 0.955 (for Eq. 2) to 0.958 (for Eq. 1). This indicates that, for the select solvents examined here, f_{O2} is largely determined by solvent–solvent interactions.

We also have examined the correlationship between $\log f_{O2}$ and δ_H^2 and/or π^* for solvents of groups B and C. In Figs. 2 and 3, plots of $\log f_{O2}$ vs. π^* and $\log f_{O2}$ vs. δ_H^2 are given, and the results of a simple or multiple linear regression

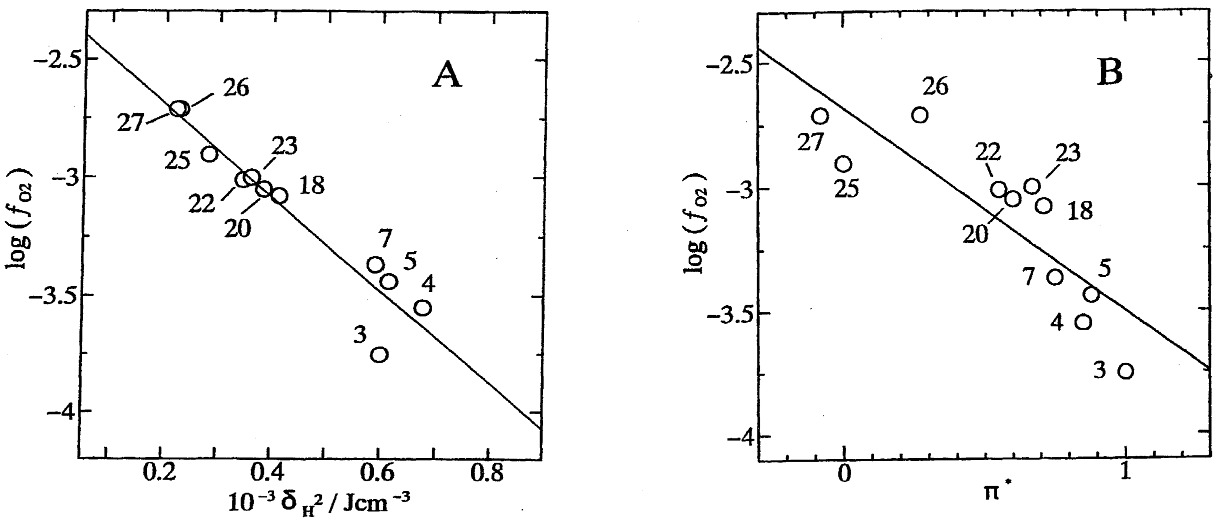

Fig. 1. Plots of (A) log f_{O2} vs. δ_H^2 and (B) log f_{O2} vs. π^* at 25 °C for 11 select solvents (group A). Each number indicates solvent numbering in Table 1.

Table 2. Multiple Linear Regression Results

LSER equations[a)]	Solvents[b)]	Regression coefficients[c)]						γ[d)]
		f°_{O2}	$10^3 \cdot h$	s	a	b	d	
1	A(11)	−2.296	−1.974					0.955
		(0.088)	(0.200)					
2	A(11)	−2.682		−0.817				0.855
		(0.093)		(0.165)				
3	A(11)	−2.326	−1.731	−0.131				0.958
		(0.100)	(0.407)	(0.188)				
1	B(8)	−2.704	−0.888					0.918
		(0.136)	(0.162)					
2	B(8)	−1.987		−2.360				0.992
		(0.079)		(0.125)				
3	B(8)	−2.085	−0.204	−1.933				0.996
		(0.067)	(0.082)	(0.186)				
1	C(6)	−2.145	−2.640					0.844
		(0.322)	(0.841)					
2	C(6)	−2.727		−0.580				0.877
		(0.118)		(0.159)				
3	C(6)	−2.518	−0.865	−0.415				0.885
		(0.497)	(1.984)	(0.419)				
1	(27)[e)]	−2.731	−0.918					0.889
		(0.052)	(0.095)					
2	(27)[e)]	−2.581		−1.061				0.746
		(0.118)		(0.189)				
3	(27)[e)]	−2.506	−0.707	−0.549				0.948
		(0.058)	(0.079)	(0.108)				
4	(27)[e)]	−2.610	−0.431	−0.786	−0.244	0.299	0.159	0.956
		(0.081)	(0.173)	(0.164)	(0.155)	(0.164)	(0.097)	

a) The percentage confidence level of the LSER equations (according to the *F*-statistic analysis) was more than 99%, except for the LSER equation (Eq. 3) obtained for 6 solvents of group C (the confidence level >90%). b) A, B, and C represent types of solvents (see Table 1). The number of solvents used for linear regression is given in parentheses. c) Standard errors of the coefficients are given in parentheses. d) (Multiple) correlation coefficients. e) All the solvents in Table 1 were used for linear regression.

analysis are detailed in Table 2. For eight amphiprotic HBA-D solvents, log f_{O2} is very well correlated both with π^* (γ= 0.992) and with δ_H^2 (γ=0.918). Especially, the γ value for the single parameter (π^*) equation in almost comparable to that for the two-parameter equation, and thus the very good linear correlationship of log f_{O2} with the single parameter π^* can be satisfactorily used to predict the solubility of O_2 in another amphiprotic HBA-D solvent from its π^* parameter. On the

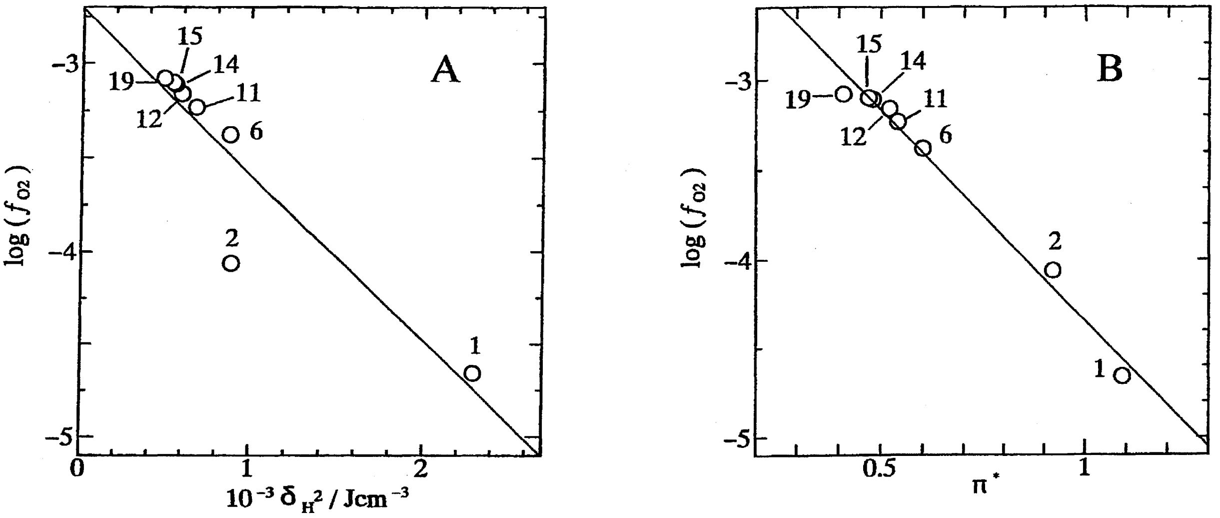

Fig. 2. Plots of (A) log f_{O2} vs. δ_H^2 and (B) log f_{O2} vs. π^* at 25 °C for 8 amphiprotic HBA-D solvents (group B). Each number indicates solvent numbering in Table 1.

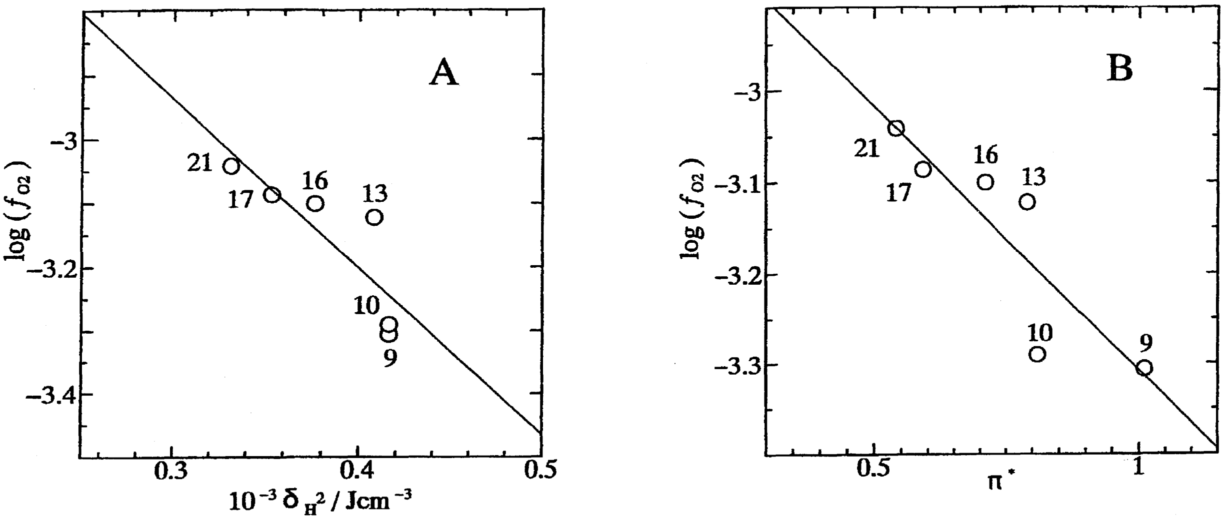

Fig. 3. Plots of (A) log f_{O2} vs. δ_H^2 and (B) log f_{O2} vs. π^* at 25 °C for 6 aromatic solvents (group C). Each number indicates solvent numbering in Table 1.

other hand, for aromatic solvents of group C, the correlation of log f_{O2} with the single parameter π^* or δ_H^2 is almost the same (γ=0.877 and 0.844), and the correlation is slightly improved using the two-parameter equation (Table 2). The low confidence level in this case is probably because the number of data (6 in this case) is not so many compared with that of parameters used in multiple linear regression.

Figure 4 shows plots of log f_{O2} vs. π^* and log f_{O2} vs. δ_H^2 for *all* the available data in Table 1. The results of a simple or multiple linear regression analysis are also given in Table 2. The linearity with a single parameter π^* or δ_H^2 is worse, as expected, compared with those in each group of solvents (mentioned above). However, the two-parameter regression equation has a reasonably high multiple correlation coefficient (γ=0.948) compared with the single-parameter correlations.

Recently, a more complicated five-parameter linear equation involving parameters of both specific and nonspecific solvation has been developed by Rutan et al.,[14)]

$$\log f_{O2} = f_{O2}^{\circ} + h\delta_H^2 + s\pi^* + a\alpha + b\beta + d\delta_P \qquad (4)$$

where α is a measure of the ability of the solvent to donate a proton (accept an electron pair) in a solvent-to-solute hydrogen bond,[18)] β is a measure of the ability of the solvent to accept a proton (donate an electron pair) in a solute-to-solvent hydrogen bond[18)] and δ_P is a polarizability correction factor. The δ_P parameter is equal to 0.0 for nonchlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents.[12,14)] The δ_P values reflect the fact that, as a general rule, differences in solvent polarizability (expressed in terms of the refractive index function) are significantly greater between these classes of solvents than within the classes.[21)] Inclusion of α, β, and δ_P into the correlation as well as δ_H^2 and π^* raises the multiple correlation coefficient from 0.948 (δ_H^2 and π^*) to 0.956 (δ_H^2, π^*, α, β, and

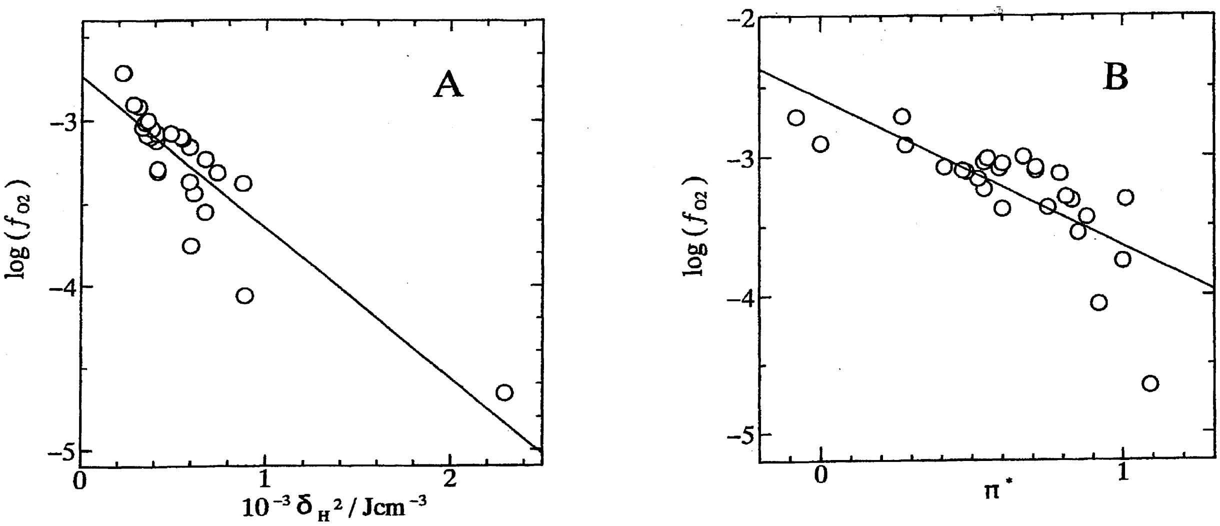

Fig. 4. Plots of (A) log f_{O2} vs. δ_H^2 and (B) log f_{O2} vs. π^* at 25 °C for *all* the available data in Table 1.

δ_P). In this case, the coefficients of correlation between the (assumed) independent variable of the five-parameter equation (Eq. 4), i.e., π^* vs. δ_H^2 (γ=0.524), π^* vs. α (0.123), π^* vs. β (0.108), π^* vs. δ_P (0.175), δ_H^2 vs. α (0.674), δ_H^2 vs. β (0.098), δ_H^2 vs. δ_P (0.266), α vs. β (0.545), α vs. δ_P (0.407) and β vs. δ_P (0.548), are insignificant compared to the overall γ value (0.956). That is, the variables are independent ones to all intents and purposes. In addition, the percentage confidence level of this five-parameter equation (according to the F-static analysis)[15] was higher than 99%. Thus, the solution of O_2 in the solvents examined is satisfactorily rationalized by the multiple regression equation using δ_H^2, π^*, α, β, and δ_P. The fact that the signs of the constants a and b referring to α and β are negative and positive, respectively, may suggest that O_2 molecule functions as a Lewis acid and thus the solution of O_2 is more favored in solvents with higher ability to donate an electron pair to a hydrogen bond donor or Lewis acid solute. Thus, it is thought that in addition to the solvent–solvent and solute–solvent interactions reflected as solvent parameters δ_H^2 and π^*, respectively, donor–acceptor interactions of the acid-base type also play a significant role in the process of O_2 solution.

Conclusions

For solvents with common properties f_{O2} is very well correlated with the single solvent parameter with $\gamma > 0.95$, i.e., with δ_H^2 for nonchlorinated aliphatic aprotic solvents and with π^* for amphiprotic HBA-D solvents. In addition for *all* the available data (27 solvents) the two-parameter regression equation using δ_H^2 and π^* was obtained with γ=0.948, and the five-parameter regression equation based on δ_H^2, π^*, α, β, and δ_P with γ=0.956. Use of the combination of δ_H^2 and π^* (or including α, β, and δ_P) thus enables the medium effect on solution of O_2 to be correlated and interpreted in a conceptually simple manner. The present results support previous observations concerning in vitro and in vivo solution of O_2[1—7] and may explain them from viewpoints of multiple solvation interactions. Further, the obtained LSER equations may serve to predict the solubility of O_2 that can not be directly obtained experimentally, e.g., in various biological environments.

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