Linear Solvation Energy Relationships. Part 19.† Correlation of the Free Energies of Solution of 41 Solutes in Select Solvents with Hildebrand's Solubility Parameter, δ_H, and with the Solvatochromic Parameter, π^*

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The effect of a series of select solvents on the standard free energies of solution of 34 volatile solutes and on the standard free energies of transfer of 7 involatile solutes has been correlated with δ_H, with π^*, and with a linear combination of δ_H and π^*. For nonpolar solutes, only the regression with δ_H is significant, but for polar solutes the multiple regression with δ_H and π^* is generally much more satisfactory than either single regression. It is suggested that the term in δ_H represents the solvent–solvent interaction that has to be overcome in order to create a suitably sized cavity in the solvent. Indeed, the value of the coefficient in δ_H is directly proportional to the size of the (nonpolar) solute. It is also suggested that the term in π^* represents the mainly dipolar–dipolar solute–solvent interaction; thus the coefficient in π^* is related, though not linearly, to the solute dipole moment or charge separation. Use of the combination of δ_H and π^* thus enables the solvent effect on the free energies of a very wide range of solutes to be correlated and interpreted in a conceptually simple manner.

THE effect of solvents on the standard free energies of solutes has for many years been of considerable interest. On the one hand, Hildebrand's solubility parameter theory[1,2] has been used to correlate and to predict values for relatively nonpolar solutes in the less polar aprotic solvents,[3] whilst in the other hand values for ionic species have been related to more or less empirical solvent parameters such as Gutmann's donor number[4] or the E_T function,[5] or more recently have been calculated by continuum theories.[6] There has been, however, less work on solutes of moderate polarity: reaction field theory has proved especially useful in certain cases,[7,8] particularly those involving equilibria between solutes of like molar volume, such as conformational isomers,[9] and in principle it would be possible to apply some extended multiparameter equation on the lines of the work of Palm.[10] To date, however, there has been no general approach that would include solutes ranging from nonpolar non-electrolytes to highly polar species such as ion pairs, and the present work seeks to provide a framework that would embrace this wide range of solute character.

We first consider the process of dissolution of a solute into a solvent in terms of cavity theories of solution. The required energy terms are then[6] (1) the energy needed to make a suitably sized cavity in the bulk solvent, (2) the energy of reorganisation of the solvent round the cavity, and (3) the energy of interaction of the solute with the reorganised solvent. Thus in order to deal with the solvent effect on the free energy of a solute, at least two parameters will be required: firstly, since the origin of the cavity term lies in the solvent–solvent interaction energy, a parameter that reflects these energies is needed to take care of the cavity term; secondly, a parameter that reflects the solute–solvent interaction energy is required to deal with process (3). There is then left the energy of solvent reorganisation, but in terms of free energy (though not of enthalpy or entropy) this energy is expected to be relatively small.[11] In principle, it is possible to calculate the cavity term by, for example, Pierotti's version of the scaled-particle theory,[12] or to eliminate this term by referencing the observed ΔG^0 values for a given solute to the corresponding ΔG^0 values for a nonpolar solute of similar volume to the given solute.[13] Although we have in the past used both these methods,[11,13] neither is very convenient to use in a simple correlative and predictive procedure. We therefore decided to use the solubility parameter, δ_H, as a reflection of the solvent–solvent interaction energy. One advantage of this parameter is that values are known[14,15] for almost all the common solvents. In order to account for the solute–solvent interaction energy, we used the solvatochromic parameter, π^*, which is related to the ability of a bulk solvent to stabilise a charge or a dipole through charge–dipole or dipole–dipole interactions.[16–18] For a group of ' select solvents,' namely nonchlorinated aliphatic aprotic solvents, with single dominant bond dipoles, values of π^* have been shown[19] to be nearly proportional to the molecular dipole moments. Abboud and Taft[20] have also shown there to be a good linear relationship between π^* values of select solvents and the dielectric θ function of Block and Walker,[21] so that if we consider only these ' select ' solvents, we expect that solute dipole–solvent dipole interactions will be proportional to π^* values. Thus a combination of δ_H and π^* parameters could account for both the solvent–solvent cavity term and the solute–solvent interaction term. Our method is thus to set up linear regression equations (1)—(3), where

$$\Delta G^0 = g + h\delta_H + s\pi^* \qquad (1)$$

$$\Delta G^0 = g + h\delta_H \qquad (2)$$

$$\Delta G^0 = g + s\pi^* \qquad (3)$$

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† Part 18, J. L. M. Abboud, R. W. Taft, and M. J. Kamlet, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 603.

g, h, and s will be constants that characterise a given solute, and δ_H and π^* are parameters characteristic of given solvents. In order to assess whether the multiple regression equation (1) is to be preferred over the simple equations (2) or (3), we applied the t-test or F-statistic to calculate the percentage confidence level (CL) of the constants h and s in equations (1)—(3), as well as calculating the simple or multiple correlation coefficient, ρ. In general, only if CL is greater than 95% can the given constant be taken to be significant in the regression equation. There are also chemical considerations that must be taken into account. If the ΔG^0 term in equations (1)—(3) is a free energy of solution or a free energy of transfer from one solvent to another, then because a large solvent–solvent interaction (large δ_H value) will inhibit the solution process, the value of the constant h in equations (1) and (2) should be positive, whereas because a large solute–solvent interaction (large π^* value) will aid solution, the constant s in equations (1) and (3) should be negative in value.

In Table 1 are the δ_H and π^* values that we have used.

TABLE 1

Values of δ_H and π^* used in the regression equations

No.	Solvent	δ_H	π^*
1	Hexane	7.27	−0.08
2	Cyclohexane	8.20	0.00
3	Triethylamine	7.45	0.14
4	Di-n-butyl ether	7.62	0.24
5	Di-isopropyl ether	7.46	0.27
6	Diethyl ether	7.50	0.27
7	Ethyl acetate	8.90	0.55
8	Methyl acetate	9.50	0.56
9	Tetrahydrofuran	9.30	0.58
10	Methyl formate	10.20	0.61
11	Butanone	9.21	0.67
12	Butyronitrile	10.01	0.71
13	Propiononitrile	10.63	0.73
14	Acetone	9.60	0.73
15	Cyclohexanone	9.90	0.76
16	Nitromethane	12.61	0.85
17	Acetonitrile	11.74	0.85
18	Butyrolactone	12.60	0.87
19	Dimethylacetamide	10.80	0.88
20	Dimethylformamide	11.76	0.88
21	*N*-Methylpyrrolidone	11.30	0.92
22	Dimethyl sulphoxide	13.00	1.00

For the most part, the former are based on calorimetrically determined enthalpies of vaporisation at 298 K, supplemented by literature values.[14,15] The π^* values are from a recent review.[18] The ΔG^0 values to be used in equations (1)—(3) mostly refer to process (4); values for the rare gases, the inorganic gases, the alkanes, and

$$\text{Solute (gas, 1 atm)} \longrightarrow \text{Solute (ideal solution, unit mol-fraction)} \qquad (4)$$

the hydrocarbon-like compounds Me_4Sn and Et_4Sn are from recent compilations,[22—24] those for ethene[25] are from Wilhelm and Battino's review supplemented by data in Seidell, those for pent-1-ene are from literature data[26,27] on vapour–liquid equilibria, as are also those for benzene.[27,28] Values for toluene, butanone, ethanol, nitrobenzene, and dioxan were calculated from data given by Rohrschneider,[29] those for ethyl iodide are from Abraham and Grellier,[30] and those for t-butyl chloride from literature values,[31] supplemented by more recent data.[32] Vapour–liquid equilibrium measurements are also available for trimethylamine[33] and triethylamine.[34] The remaining solutes are solids, and in these cases the ΔG^0 values in equations (1)—(3) refer to standard free energies of transfer from one solvent to another, on the mol fraction scale; the relevant ΔG^0 values have been recorded.[15,31,33] In the case of the gaseous and liquid solutes, where ΔG^0 refers to process (4), the intercept g of equations (1)—(3) may be interpreted as the standard free energy of solution of the gaseous solute in a solvent for which δ_H or π^* is zero. For the solid solutes, that is p-nitrobenzyl chloride and the various R_4NX ion pairs, no such meaning can be attached to the values of g in corresponding correlations of free energies of transfer. However, the slopes h and s are entirely equivalent for the ΔG^0_s and ΔG^0_t values. It should be noted that the ΔG^0 values in equation (4) are identical to values of $RT\ln K^H$ where K^H is the limiting Henry's law constant, or gas–liquid partition coefficient, of the solute in a solvent, provided that due consideration is given to the standard states used. All the ΔG^0 values we have used refer to a temperature of 298 K.

The regression equations (1)—(3) for the 41 solutes studied are detailed in Table 2, together with the simple or multiple correlation coefficient and the percentage confidence level for the constants h and s that refer to δ_H and π^* in the regressions. It is quite clear that for the first 22 solutes listed (up to and including Et_4Sn) the π^* term in the multiple regression is not significant, and that for these nonpolar solutes the free energy of solution is largely determined by the solvent–solvent interactions, as assessed by the δ_H term. Thus for these nonpolar solutes, the ΔG^0 values are well correlated through the simple equation (2). As expected, all give rise to positive values of h, and it is evident that as the solute size increases so does the value of h. As the solute increases in size, so will the work required to create a suitable cavity also increase, and therefore so will the magnitude of the cavity term, as reflected in the constant h. There are several ways of expressing the size of a solute, such as molar volume, hard-sphere diameter, *etc.*, but quite recently it has been shown that ΔG^0_s values for nonpolar solutes may be correlated with a size parameter, R, closely related to the hard-sphere diameter.[22] We find that for the 22 nonpolar solutes we have considered, values of g and h in equation (2) are correlated with R through the equations (5) and (6). The intercept

$$h = -0.0103 + 0.1440R \quad \rho\ 0.9639 \qquad (5)$$

$$g = 9.681 - 4.472R \quad \rho\ 0.9962 \qquad (6)$$

in equation (5) is very nearly zero, merely reflecting the fact that for a solute of zero size, there should be no dependence of ΔG^0 on the solvent–solvent interaction. However, the intercept in equation (6) is quite large, 9.681 kcal mol^{-1}, being the standard free energy of solution of a hypothetical solute of zero size in a hypo-

TABLE 2

Results of correlations of ΔG^0 through equations (1)—(3)

Solute	No.[a]	Equation	ρ[b]	CL[c]	
				δ_H	π^*
H_2	7	$2.841 + 0.211\,\delta_H$	0.9954	99.999	
		$4.382 + 0.890\,\pi^*$	0.8504		98
		$2.712 + 0.230\,\delta_H - 0.108\,\pi^*$	0.9966	99.9	<80
N_2	7	$2.079 + 0.251\,\delta_H$	0.9748	99.9	
		$3.924 + 1.229\,\pi^*$	0.8643		98
		$1.958 + 0.269\,\delta_H - 0.110\,\pi^*$	0.9754	98.0	<50
O_2	7	$1.756 + 0.260\,\delta_H$	0.9929	99.999	
		$3.683 + 1.023\,\pi^*$	0.8093		95
		$1.422 + 0.310\,\delta_H - 0.278\,\pi^*$	0.9988	99.99	98
CO	8	$2.167 + 0.219\,\delta_H$	0.9667	99·99	
		$3.822 + 0.774\,\pi^*$	0.7885		98
		$1.679 + 0.289\,\delta_H - 0.342\,\pi^*$	0.9797	99.8	80
He	5	$3.513 + 0.203\,\delta_H$	0.9806	99.5	
		$5.105 + 0.934\,\pi^*$	0.8799		95
		$3.225 + 0.242\,\delta_H - 0.216\,\pi^*$	0.9835	90	<50
Ne	5	$3.225 + 0.212\,\delta_H$	0.9786	99.5	
		$4.887 + 0.971\,\pi^*$	0.8752		90
		$2.893 + 0.257\,\delta_H - 0.249\,\pi^*$	0.9822	90	<50
Ar	6	$1.788 + 0.244\,\delta_H$	0.9636	99.8	
		$3.684 + 1.142\,\pi^*$	0.8898		98
		$1.675 + 0.259\,\delta_H - 0.084\,\pi^*$	0.9638	90	<20
Kr	5	$1.012 + 0.264\,\delta_H$	0.9904	99.8	
		$3.056 + 1.257\,\pi^*$	0.9214		98
		$1.060 + 0.257\,\delta_H + 0.036\,\pi^*$	0.9904	90	<20
Xe	5	$0.051 + 0.282\,\delta_H$	0.9965	99.9	
		$2.235 + 1.346\,\pi^*$	0.9286		95
		$0.121 + 0.272\,\delta_H + 0.053\,\pi^*$	0.9966	95	<20
Rn	4	$-0.987 + 0.354\,\delta_H$	0.9967	99.5	
		$1.558 + 1.088\,\pi^*$	0.9681		95
CH_4	8	$1.375 + 0.244\,\delta_H$	0.9953	99.9999	
		$3.167 + 1.103\,\pi^*$	0.9107		99.8
		$1.322 + 0.252\,\delta_H - 0.042\,\pi^*$	0.9954	99.9	<50
C_2H_6	8	$0.337 + 0.243\,\delta_H$	0.9846	99·999	
		$2.075 + 1.113\,\pi^*$	0.9292		99.9
		$0.685 + 0.192\,\delta_H + 0.279\,\pi^*$	0.9940	99.5	80
C_3H_8	6	$-1.069 + 0.315\,\delta_H$	0.9914	99.9	
		$1.360 + 1.363\,\pi^*$	0.9400		99
		$-0.865 + 0.288\,\delta_H + 0.135\,\pi^*$	0.9919	95	<50
iso-C_4H_{10}	4	$-2.161 + 0.384\,\delta_H$	0.9925	99	
		$0.875 + 1.713\,\pi^*$	0.9594		95
n-C_4H_{10}	5	$-2.210 + 0.359\,\delta_H$	0.9873	99.8	
		$0.617 + 1.615\,\pi^*$	0.9646		99
n-C_5H_{12}	14	$-3.689 + 0.444\,\delta_H$	0.9714	99.9999	
		$-0.330 + 1.846\,\pi^*$	0.8006		99.9
		$-4.060 + 0.502\,\delta_H - 0.338\,\pi^*$	0.9742	99.999	<80
n-C_6H_{14}	12	$-4.398 + 0.452\,\delta_H$	0.9799	99.9999	
		$-1.005 + 1.973\,\pi^*$	0.8496		99.9
		$-4.426 + 0.456\,\delta_H - 0.024\,\pi^*$	0.9799	99.99	<20
n-C_7H_{16}	8	$-5.562 + 0.509\,\delta_H$	0.9904	99.999	
		$-1.685 + 2.169\,\pi^*$	0.9136		99.8
		$-5.493 + 0.500\,\delta_H + 0.049\,\pi^*$	0.9904	99.8	<20
n-C_8H_{18}	20	$-6.492 + 0.542\,\delta_H$	0.9787	99.9999	
		$-2.851 + 0.286\,\pi^*$	0.8963		99.999
		$-6.225 + 0.497\,\delta_H + 0.283\,\pi^*$	0.9794	99.9999	<30
cyclo-C_6H_{12}	9	$-4.641 + 0.435\,\delta_H$	0.9690	99.99	
		$-1.308 + 1.757\,\pi^*$	0.8676		99.5
		$-4.821 + 0.460\,\delta_H - 0.126\,\pi^*$	0.9693	99.5	<20
Me_4Sn	11	$-3.925 + 0.389\,\delta_H$	0.9593	99.999	
		$-1.213 + 1.924\,\pi^*$	0.9029		99.9
		$-3.548 + 0.331\,\delta_H + 0.331\,\pi^*$	0.9613	99.0	<50
Et_4Sn	7	$-8.172 + 0.559\,\delta_H$	0.9716	99.9	
		$-3.915 + 2.751\,\pi^*$	0.9533		99.9
		$-6.766 + 0.367\,\delta_H + 1.025\,\pi^*$	0.9797	90	50
Ethene	6	$1.683 + 0.082\,\delta_H$	0.2448	20	
		$2.244 + 0.435\,\pi^*$	0.2546		20
		$2.102 + 0.020\,\delta_H + 0.341\,\pi^*$	0.2556	<20	<20
Pent-1-ene	10	$-3.349 + 0.391\,\delta_H$	0.9515	99.99	
		$-1.867 + 3.456\,\pi^*$	0.8080		99.5
		$-3.329 + 0.366\,\delta_H + 0.312\,\pi^*$	0.9524	99.5	20
Benzene	11	$-1.668 + 0.071\,\delta_H$	0.4663	80	
		$-0.975 + 0.079\,\pi^*$	0.1035		20
		$-2.833 + 0.246\,\delta_H - 1.004\,\pi^*$	0.7852	99	95

TABLE 2 (*continued*)

				CL[c]	
Solute	No.[a]	Equation	ρ[b]	δ_H	π^*
Toluene	20	$-3.052 + 0.146\ \delta_H$	0.8193	99.999	
		$-1.980 + 0.612\ \pi^*$	0.5967		99
		$-3.751 + 0.261\ \delta_H\ -0.741\ \pi^*$	0.8786	99.99	98
EtI	12	$-1.061 + 0.103\ \delta_H$	0.6807	98	
		$-0.803 + 0.383\ \pi^*$	0.4657		80
		$-2.038 + 0.173\ \delta_H\ -0.435\ \pi^*$	0.7285	95	50
Bu^{t}Cl	9	$-1.626 + 0.177\ \delta_H$	0.9352	99.9	
		$-0.359 + 0.843\ \pi^*$	0.7552		98
		$-2.141 + 0.263\ \delta_H\ -0.560\ \pi^*$	0.9593	99.5	80
p-Nitrobenzyl chloride	6	$2.795 - 0.232\ \delta_H$	0.6061	50	
		$1.632 - 2.010\ \pi^*$	0.8890		98
		$-0.656 + 0.335\ \delta_H\ -3.773\ \pi^*$	0.9756	90	99
Me_3N	6	$-0.174 + 0.111\ \delta_H$	0.8739	95	
		$0.575 + 0.597\ \pi^*$	0.7957		90
		$-0.112 + 0.101\ \delta_H\ +0.067\ \pi^*$	0.8749	50	<20
Et_3N	12	$-3.370 + 0.313\ \delta_H$	0.9696	99.9999	
		$-1.576 + 1.675\ \pi^*$	0.9282		99.99
		$-3.722 + 0.312\ \delta_H\ +0.156\ \pi^*$	0.9999	99.9999	99.999
MeCOEt	17	$-0.323 - 0.065\ \delta_H$	0.4625	90	
		$-0.608 - 0.619\ \pi^*$	0.7617		99.9
		$-1.781 + 0.173\ \delta_H\ -1.510\ \pi^*$	0.9239	99.9	99.999
EtOH	17	$0.834 - 0.188\ \delta_H$	0.5156	95	
		$-0.084 - 1.623\ \pi^*$	0.7657		99.9
		$-2.601 + 0.370\ \delta_H\ -3.577\ \pi^*$	0.8767	99.5	99.99
$MeNO_2$	18	$1.705 - 0.326\ \delta_H$	0.7736	99.9	
		$-0.126 - 2.354\ \pi^*$	0.9665		99.999
		$-1.543 + 0.209\ \delta_H\ -3.440\ \pi^*$	0.9905	99.99	99.999
Dioxan	18	$-0.839 - 0.072\ \delta_H$	0.5613	98	
		$-1.200 - 0.589\ \pi^*$	0.7987		99.99
		$-1.909 + 0.104\ \delta_H\ -1.132\ \pi^*$	0.8753	98	99.99
Me_4NI	11	$25.778 - 2.208\ \delta_H$	0.8491	99.9	
		$11.968 - 13.744\ \pi^*$	0.9949		99.999
		$9.875 + 0.291\ \delta_H\ -15.103\ \pi^*$	0.9964	80	99.999
Me_4NBr	11	$33.880 - 2.714\ \delta_H$	0.8540	99.9	
		$16.812 - 16.736\ \pi^*$	0.9914		99.999
		$15.058 + 0.244\ \delta_H\ -17.87\ \pi^*$	0.9921	50	99.999
Me_4NCl	10	$39.786 - 3.039\ \delta_H$	0.8856	99.9	
		$19.843 - 17.962\ \pi^*$	0.9925		99.999
		$19.346 + 0.068\ \delta_H\ -18.29\ \pi^*$	0.9926	<20	99.99
Et_4NI	13	$24.700 - 2.065\ \delta_H$	0.8359	99.9	
		$11.848 - 12.948\ \pi^*$	0.9873		99.9999
		$9.264 + 0.359\ \delta_H\ -14.62\ \pi^*$	0.9897	80	99.9999
Et_4NBr	10	$36.167 - 2.90\ \delta_H$	0.8604	99.8	
		$16.995 - 16.314\ \pi^*$	0.9943		99.9999
		$15.566 + 0.193\ \delta_H\ -17.14\ \pi^*$	0.9946	50	99.999
Et_4NCl	8	$41.747 - 3.170\ \delta_H$	0.8883	99.5	
		$19.978 - 17.267\ \pi^*$	0.9964		99.9999
		$19.089 + 0.119\ \delta_H\ -17.79\ \pi^*$	0.9965	20	99.99

[a] Number of solvents used (see Table 4). [b] Simple or multiple correlation constant [c] Percentage confidence level for the terms in δ_H or π^* calculated using the *t*-test or *F*-test

thetical solvent of zero δ_H. There is no reason why this term should be zero, since it will include, for example, the loss of translational entropy on transferring a solute from the gas phase (1 mol per 24.46 l) to a solution of unit mol fraction solute.

The solutes ethyl iodide and t-butyl chloride also behave superficially like the nonpolar solutes, in that the dependency on δ_H is much more pronounced than that on π^*. However, both the sign and magnitude of the π^* term in the multiple regression (1) are consistent with a slight polar character in each case.

The final six solutes in Table 2 are all highly polar ion pairs that are expected to undergo very large solute–solvent interactions. Thus for these six solutes, the ΔG^0_t values are now very well correlated with π^*, the term in δ_H being relatively insignificant. As expected, the values of *s* are all very large negative numbers, and again, as expected, they become more negative along the series $R_4NI < R_4NBr < R_4NCl$. In between the 22 nonpolar solutes and the six highly polar ion pairs are a number of solutes of intermediate polarity, and it is just these solutes for which both the δ_H and the π^* term might be important. The best examples are the four solutes examined by Rohrschneider, *viz.* butanone, ethanol, nitromethane, and dioxan. In all four cases, the multiple regression equation (1) is a significant improvement over either of the single regressions (2) or (3), and in all four cases the signs of the constants *h* and *s* in the multiple regression are chemically reasonable, as outlined previously. Even though these solutes are by no means very polar (for butanone μ 2.9 D and for nitromethane μ 3.5 D) the π^* term still dominates in the multiple regression. Dioxan is a very interesting solute because, although the gas-phase dipole moment is zero, it behaves as a solute only slightly less polar than butanone (*s* -1.132 for dioxan and -1.510 for butanone).

It is known that as a *solvent* dioxan resembles tetrahydrofuran (μ 1.6 D) in many ways; thus π^* for dioxan is 0.55 compared to 0.58 for tetrahydrofuran, and in terms of solvent effects on reaction rates the effective dielectric constant of dioxan (ε 2.21) seems to be close to that of tetrahydrofuran (ε 7.39). We have discussed this before,[13] and have suggested that when a dioxan molecule is near a given molecule, the latter ' sees ' only part of the dioxan molecule and hence regards dioxan as having a dipole. Alternatively, although the dominant conformer of dioxan in the gas phase and in the pure liquid is the chair form, which has no dipole moment, it is possible that the solute dioxan surrounded by solvent molecules, especially if polar, may assume the boat conformation which has an appreciable dipole moment. In any case, it is clear that for solutes of intermediate polarity both the cavity solvent–solvent interactions and the solute–solvent interactions are important factors that determine the magnitude of the standard free energy of the solute in the select solvents. It might be noted that for the solutes butanone, ethanol, nitromethane, and dioxan, the method of referencing the K^H values to those for solutes of like molar volume [13] leads to rather better correlations than does the present method. However, the correlations with δ_H and π^* are more convenient, and have the advantage that the division into solvent–solvent and solute–solvent contributions is clearly seen.

The correlation coefficients for ethanol are not very good, but this solute can interact with solvents not only by dipole–dipole forces but also by hydrogen bonding. A more detailed analysis should therefore include a parameter that reflects the ability of a solvent to act as a hydrogen bond acceptor. The solvatochromic β-parameter is such a quantity, and inclusion of β into the correlation as well as δ_H and π^* raises the multiple correlation coefficient from 0.8767 (δ_H and π^*) to 0.9719 (δ_H, π^*, and β).

There remain a number of solutes that do not fall into the simple division of solutes, above. Firstly, there are the solutes ethene, pent-1-ene, benzene, and toluene, that contain polarisable π-electrons. In the case of ethene, there is no correlation with any of the parameters δ_H, π^*, or δ_H plus π^*, although the number of solvents is limited. Pent-1-ene, as might be expected, behaves more like a simple nonpolar solute and the correlation equation in δ_H is very similar to those for n-butane or n-pentane. Neither benzene nor toluene are well correlated through equations (1)—(3), although the values of h and s in the multiple regression are chemically reasonable (h being positive and s being negative in each case). However, the standard deviations between calculated and observed ΔG^0 values are even smaller than those for nitromethane, butanone, and dioxan, and the low ρ values reflect the small range of values of ΔG^0 for benzene and toluene. Secondly, there are the two tertiary amines trimethylamine and triethylamine, that both behave rather like nonpolar solutes in that correlations are much better with δ_H than with π^*. Triethylamine has been studied in some detail by Abraham and Nasehzadeh [34] who have calculated the magnitude of the specific triethylamine–solvent interaction terms, and have shown that for the select solvents these terms are very small, in agreement with the results of our correlation analysis. Finally, the solute p-nitrobenzyl chloride is of some interest in that, like the solutes such as butanone and nitromethane, both the δ_H and the π^* terms contribute significantly to the overall regression.

We have already outlined the significance of the magnitude and sign of the constant h in equations (1) and (2) for nonpolar solutes, where h becomes more positive with increasing solute size [equation (5)]. For the more polar solutes, the sign of h in the multiple regression equation (1) is always positive, as required, although the magnitude of h is not always in accord with the solute size, and hence the size of the cavity to be formed in the solvent.

For some of these more polar solutes the sign of h in the simple regression equation (2) is negative. This (physically meaningless) sign probably arises because of a certain amount of collinearity between δ_H and π^*; in all cases where the sign of h in equation (2) is negative, the sign of s in equations (1) and (3) is also negative. In any case, if h is negative in the simple regression equation (2), this equation is invariably inferior to the multiple regression equation (1), in which the sign of h is always positive, as pointed out above.

Since the π^* term in equations (1) and (3) refers to solute–solvent interactions of the dipole–dipole type, there should be some connection between the magnitude of the constant s and the dipole moment of the corresponding solute. In Table 3 are collected values of s and μ for a number of solutes, including the ion pairs, and it can be seen that indeed there is a clear correlation: the larger the solute dipole moment, the more negative is the value of s. However, a plot of μ against s (not shown) is definitely non-linear; this may be due, at least in part, to the ion pair solutes interacting with solvents more by ion–dipole than by dipole–dipole forces. We

TABLE 3

Values of multiple regression constant, s, and solute dipole moments and charge separations

Solute	s	μ/D [a]	Z [b]
CH_4 [c]	−0.04	0	0
EtI	−0.44	1.8	0.18
Bu^tCl	−0.56	2.2	0.25
Dioxan	−1.13	0.0 [d]	
MeCOEt	−1.51	2.9	0.50
$MeNO_2$	−3.44	3.5	
EtOH	−3.58	1.7	
p-$NO_2C_6H_4CH_2Cl$	−3.77	3.7	
$Me_4N^+Cl^-$	−18.3	8.5 [e]	(1) [f]
$Et_4N^+I^-$	−14.6	9.2 [g]	(1) [f]

[a] Gas-phase dipole moments from A. L. McClellan, ' Tables of Experimental Dipole Moments,' Freeman, San Francisco, 1963. [b] Calculated as described in the text. [c] Taken as an example of a nonpolar solute for which $s \simeq 0$. [d] The value for tetrahydrofuran is 1.6 D. [e] Calculated in ref. 7. [f] Nominal Z value. [g] Unpublished calculations by M. H. Abraham and R. J. Abraham.

also explored the possibility that the actual charge separation, Z, in the solute dipole might be better correlated with s, and in Table 3 are given values of Z for solutes whose dipole moment results mainly from a given bond dipole (C=O in the case of butanone, C–Cl for t-butyl chloride, and C–I for ethyl iodide), as well as the ion pairs for which we have taken nominal Z values of unity. As for the solute dipole moments, there is clearly a connection between values of Z and values of s, although the correlation is non-linear. Unfortunately, there is a rather large gap in the spread of s values between the moderately polar volatile solutes such as butanone and nitromethane and the highly polar ion pairs. However, it does seem possible, at least in principle, to obtain information about the polarity (Z and μ) of species that cannot be investigated directly, through analyses in terms of multiple regression equation (1).

Finally, we list in Table 4 details of the actual solvents used in the simple and multiple regression equations.

TABLE 4

Solvents used in the regression equations

Solute	Solvents studied
H_2	1, 2, 6, 7, 8, 14, 22
N_2	1, 2, 6, 8, 14, 16, 22
O_2	1, 2, 6, 8, 11, 14, 22
CO	1, 2, 6, 7, 8, 13, 14, 20
He	1, 2, 14, 16, 22
Ne	1, 2, 14, 16, 22
Ar	1, 2, 14, 16, 17, 22
Kr	1, 2, 14, 16, 22
Xe	1, 2, 14, 16, 22
Rn	1, 6, 7, 14
CH_4	1, 2, 6, 8, 14, 20, 21, 22
C_2H_6	1, 2, 6, 7, 8, 14, 21, 22
C_3H_8	1, 2, 14, 20, 21, 22
iso-C_4H_{10}	1, 2, 21, 22
n-C_4H_{10}	1, 2, 17, 21, 22
n-C_5H_{12}	1, 2, 9, 11—17, 19—22
n-C_6H_{14}	1, 2, 11—17, 20, 21, 22
n-C_7H_{16}	1, 2, 11, 12, 13, 17, 21, 22
n-C_8H_{18}	1, 7, 9, 11—22
cyclo-C_6H_{12}	1, 2, 12—15, 17, 21, 22
Me_4Sn	1, 2, 4, 6, 7, 9, 14, 17, 20, 21, 22
Et_4Sn	1, 2, 14, 16, 17, 20, 22
Ethene	1, 8, 14, 20, 21, 22
Pent-1-ene	9, 11—14, 16, 17, 19, 20, 21
Benzene	1, 2, 11, 13—17, 20, 21, 22
Toluene	1—7, 9, 11—22
Ethyl iodide	1, 2, 6, 7, 9, 11, 13, 14, 16, 17, 20, 22
t-Butyl chloride	1, 6, 7, 14, 16, 17, 20—22
p-Nitrobenzyl chloride	1, 6, 7, 14, 16, 17
Trimethylamine	1, 6, 7, 14, 16, 17
Triethylamine	1—3, 6, 7, 9, 11, 14, 16, 17, 20—22
Butanone	1—6, 9, 11, 14—22
Ethanol	1—7, 9, 11, 15—22
Nitromethane	1—7, 9, 11, 14—22
Dioxan	1—7, 9, 11, 14—22
Me_4NI	1, 2, 6, 7, 11, 14, 16, 17, 20—22
Me_4NBr	1, 2, 6, 7, 11, 14, 16, 17, 20—22
Me_4NCl	1, 2, 6, 7, 14, 16, 17, 20—22
Et_4NI	1, 2, 6, 7, 10, 11, 13, 14, 16, 17, 20—22
Et_4NBr	1, 2, 6, 11, 13, 14, 16, 17, 20, 21
Et_4NCl	1, 2, 6, 14, 16, 17, 20, 21

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