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Hydrogen bonding

XVI. A new solute solvation parameter, π_2^H, from gas chromatographic data

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ABSTRACT

The general solvation equation,

$$\log V_G^0 \text{ (or } \log L) = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l \log L^{16}$$

has been used to set up a new π_2^H parameter of solute dipolarity–polarisability, mainly through the extensive data of McReynolds and Patte *et al.* Values of π_2^H are tabulated for several hundred solutes, and two simple rules have been formulated to enable π_2^H to be estimated for many types of aliphatic functionally substituted compounds. A coherent set of effective solvation parameters, $\Sigma\pi_2^H$, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$, and also R_2 and log L^{16}, allows the application of the general solvation equation to the characterisation of any gas–liquid chromatographic stationary phase.

INTRODUCTION

Previously, we have shown [1–3] that processes in which a solute is distributed between the gas phase and some condensed phase can usefully be described through the general solvation equation

$$\log SP = c + rR_2 + s\pi_2^* + a\alpha_2^H + b\beta_2^H + l \log L^{16} \qquad (1)$$

Such processes include the solubility of a series of gaseous solutes in a given solvent [2], and chromatographic processes in which retention data are obtained for a series of compounds on a given stationary phase, at some constant temperature [3].

As regards gas–liquid chromatography (GLC), the dependent variable in eqn. 1 can be log *L* (or log *K*), where *L* (or *K*) is the Ostwald solubility coefficient or gas–liquid partition coefficient, log V_G, where V_G is either the specific retention volume referred to 273 *K* or the specific retention volume at the column temperature, or even log τ, where τ is the adjusted relative retention time [3]. All these dependent variables will give rise to the same values of

r, s, a, b and l in eqn. 1, but will yield different values of the constant term. The explanatory variables in eqn. 1 are R_2, an excess molar refraction that can be determined experimentally [1], π_2^*, the solute dipolarity–polarisability, to which we shall refer later, α_2^H, an experimentally determined solute hydrogen-bond acidity [4], β_2^H, an experimentally determined solute hydrogen-bond basicity [5], and log L^{16}, where L^{16} is the solute Ostwald solubility coefficient on hexadecane at 298 K [6].

Of course, values of R_2, α_2^H, β_2^H and log L^{16} can be obtained through various approximations and estimations, all based on the original experimentally determined values. There are, however, difficulties with the solute parameter π_2^*. Originally [7,8] π_2^* was taken as identical with the Kamlet–Taft solvatochromic solvent parameter π_1^* for non-associated liquids only. As π_1^* is experimentally accessible only for compounds that are liquid at 298 K, values of π_2^* had then to be estimated not only for all associated compounds (including acids, alcohols, phenols and amides), but also for all compounds that are solid (or gaseous) at 298 K. In addition, there is present the inherent assumption that π_1^* is identical with π_2^* for non-associated liquids. We know that the Kamlet–Taft solvatochromic solvent basicity parameter β_1 is not exactly equivalent to the solute parameter β_2^H even for non-associated liquids [9], and it is possible that although π_2^* can be taken as equal to π_1^* for non-associated liquids as a generality, there may be a number of exceptions to this rule.

It seems necessary to set up a scale of solute dipolarity–polarisability based on some experimental procedure that will include, at least in principle, all types of solute molecule. The main purpose of this paper is to use the extensive sets of GLC data of McReynolds [10] and Patte *et al.* [11] to construct a new solute dipolarity–polarisability scale π_2^H for use in eqn. 1. At the same time, we shall set out an updated list of solute parameters that can be used in eqn. 1 to characterise GLC stationary phases and to interpret GLC retention data.

Since this work was started, Li *et al.* [12] have also concluded that the π_2^* scale derived from π_1^* is not very suitable for use in solvation equations such as eqn. 1, and have constructed an alternative π_2^c scale of solute dipolarity. We shall refer to this scale later.

RESULTS

McReynolds [10] determined V_G^0 values for up to 376 solutes on up to 77 stationary phases. Nearly all the phases were examined at a common temperature of 120°C. Of these 77 phases, 75 were found [3] to have no hydrogen-bond acidity at all, hence the $b\beta_2^H$ term in eqn. 1 drops out, and the log V_G^0 values can be correlated by the equation

$$\log V_G^0 = c + rR_2 + s\pi_2^* + a\alpha_2^H + l\log L^{16} \qquad (2)$$

We thus have a series of equations (n = 1–75), one for each stationary phase, where the constants c, r, s, a and l have been determined by multiple linear regression analysis (MLRA), using known values of the solute parameters R_2, π_2^*, α_2^H and log L^{16} for as many solutes as possible. Typically, around 150 solutes were included in each regression eqn. 2, generalised as

$$\log V_{G(n)}^0 = c_n + r_nR_2 + s_n\pi_2^* + a_n\alpha_2^H + l_n \log L^{16} \quad (3)$$

It is convenient to subsume the constant c_n into the dependent variable to give 75 equations:

$$\begin{aligned} V_{n-1} &= r_{n-1}R_2 + s_{n-1}\pi_2^* + a_{n-1}\alpha_2^H + l_{n-1}\log L^{16} \\ &\vdots \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (4) \\ V_{n-75} &= r_{n-75}R_2 + s_{n-75}\pi_2^* + a_{n-75}\alpha_2^H + \\ &\qquad\qquad\qquad\qquad\qquad l_{n-75}\log L^{16} \end{aligned}$$

where

$$V_n = \log V_{G(n)}^0 - c_n \qquad (5)$$

We can now use the matrix defined by eqn. 4 in a vertical format, by regarding V_n for a given solute as the dependent variable and the constants r_n, s_n, a_n and l_n as four explanatory variables. In this new (vertical) MLR equation, R_2, π_2^*, α_2^H and log L^{16} for the particular solute now become the unknown coefficients to be evaluated by MLRA. As all the input data are now related purely to properties of the solute, we can replace π_2^* with an experimentally determined parameter, π_2^H:

$$V(\text{solute}) = V_n = R_2r_n + \pi_2^Hs_n + \alpha_2^Ha_n + \log L^{16}\, l_n \qquad (6)$$

We carried out an analysis using eqn. 6, where the regression equation was forced through the origin, and obtained reasonable values of R_2, π_2^H, α_2^H and log L^{16} for the various solutes studied. However, as R_2

TABLE I

SOME CALCULATED PARAMETERS USING EQN. 7

Solute	π_2^H	α_2^H	Log L^{16}	n	S.D.
Pent-1-ene	0.09 ± 0.004 0.08[a]	0.00 ± 0.007 0.00[a]	2.040 ± 0.007 2.013[a]	36	0.014
Toluene	0.47 ± 0.004 0.55[a]	−0.01 ± 0.007 0.00[a]	3.327 ± 0.008 3.344[a]	73	0.017
Diethyl ether	0.27 ± 0.004 0.27[a]	−0.02 ± 0.007 0.00[a]	1.975 ± 0.008 2.061[a]	71	0.017
Butanone	0.69 ± 0.004 0.67[a]	0.00 ± 0.007 0.00[a]	2.282 ± 0.007 2.287[a]	71	0.016
n-Propyl acetate	0.61 ± 0.004 0.55[a]	0.00 ± 0.007 0.00[a]	2.847 ± 0.007 2.878[a]	73	0.016
Propan-1-ol	0.41 ± 0.009 0.40[a]	0.37 ± 0.006 0.33[a]	2.060 ± 0.006 2.097[a]	72	0.016

[a] Previous values, see ref. 1.

is either known or can easily be calculated for any solute[a], we can reduce the number of explanatory variables by incorporating R_2 into the dependent variable:

$$\log V^0_{G(n)} - c_n - r_n R_2 = V' = \pi_2^H s_n + \alpha_2^H a_n + \log L^{16} l_n \quad (7)$$

Again, the regression eqn. 7 is constrained to pass through the origin; we found that the results were much more self-consistent than when a constant term was allowed to float. We can check results using our preferred eqn. 7 by comparison of calculated solute parameters with known values, where available. Some typical results are given in Table I together with the standard deviation (S.D.) of the parameter, the number of stationary phases in the set (always less than 75, because not all solutes were examined on all phases by McReynolds), and the overall S.D. of the dependent variable V'. We do not give correlation coefficients because these have little meaning for a regression equation forced through the origin.

There are a number of deficiencies in McReynolds' data, especially those connected with interfacial adsorption, and it is clear that for certain combinations of solute and stationary phase, the retention data are inexact owing to sorption at the liquid interface. Hydrocarbons in very polar phases are a particularly well known example. We point out, however, that our vertical or "inverse" MLRA procedure yields solvation parameters that are effectively averages for a given solute over 30–70 stationary phases (see Table I). In the event, hydrocarbons such as alkanes and alkenes behave normally in our inverse MLRA (see Table II).

We list in Table II the π_2^H values that we obtained through eqn. 7. We note that the π_2^H values in Table II are effective π_2^H values for a situation in which a solute molecule is surrounded by an excess of solvent molecules, and so may be more correctly denoted as $\Sigma\pi_2^H$. Before discussing these π_2^H values, we first analyse the extensive GLC data of Patte *et al.* [11].

Patte *et al.* [11] obtained retention data for 240 solutes on five stationary phases. All these phases are non-acidic, and so we obtained [1] five regression equations of the following type, one for each phase:

$$\log L' = c + rR_2 + s\pi_2^* + a\alpha_2^H + l \log L^{16} \quad (8)$$

In eqn. 8, log L' = log L − log L(decane), but this affects only the constant in the regression equations. We cannot apply the "reverse" MLRA we used for the McReynolds data set, because we would have

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[a] Like the molar refraction itself, R_2, an excess molar refraction, is almost an additive quantity.

TABLE II

CALCULATED VALUES OF π_2^H AND LOG L^{16} VALUES

Compound	π_2^H			Log L^{16}
	Eqn. 7	Eqn. 16	Eqn. 8	
Alkanes				
Ethane		0.03	0.11	0.492
Propane		0.03	0.08	1.050
Butane		0.03	0.05	1.615
2-Methylpropane		0.07	0.07	1.409
Pentane		0.03	0.03	2.162
Hexane	0.02	0.03	0.02	2.688
2,3-Dimethylbutane	−0.01			2.495
Heptane		0.03	0.01	3.173
2,4-Dimethylpentane		−0.04	−0.02	2.809
Octane	0.01	0.03	0.00	3.677
2-Methylheptane		0.08	0.01	3.480
3-Methylheptane		0.07	0.03	3.510
Nonane		0.03	0.00	4.182
2,2,5-Trimethylhexane		0.16		3.530
Decane	0.03	0.03	−0.01	4.686
Undecane		0.03	−0.02	5.191
Dodecane	0.03	0.03	0.03	5.696
Tridecane		0.03	−0.04	6.200
Tetradecane	0.05	0.03	−0.03	6.705
Hexadecane	0.07			7.714
Octadecane	0.05			8.722
Cyclohexane		0.08	0.14	3.007
Hydrindane		0.19	0.22	4.530
Decalin		0.23	0.27	5.077
Alkenes				
Ethene		−0.13	0.32	0.289
Propene		−0.09	0.25	0.946
But-1-ene		−0.05	0.21	1.491
Pent-1-ene	0.09	−0.05	0.19	2.047
Hex-1-ene		0.00	0.11	2.572
Hept-1-ene		0.06	0.11	3.063
Oct-1-ene		0.08	0.09	3.568
cis-Oct-2-ene		0.11	0.12	3.683
2-Ethylhex-1-ene		0.16	0.13	3.510
α-Pinene		0.30	0.18	4.200
Ethers (contined)				
Dibutyl ether	0.24	0.16	0.18	3.924
Dipentyl ether	0.27			4.875
Di-3-methylbutyl ether	0.21			4.538
Dihexyl ether	0.27			5.938
Di-2-ethyl-1-butyl ether	0.17			5.421
Methyl propyl ether	0.30			2.090
Methyl butyl ether	0.30			2.630
Methyl 2-methylpropyl ether	0.25			2.442
Methyl *tert.*-butyl ether	0.29			2.378
Ethyl butyl ether	0.26			2.989
Ethyl *tert.*-butyl ether	0.20			2.611
Propyl isopropyl ether	0.19			2.771
Isopropyl *tert.*-butyl ether	0.16			2.896
Bis(2-ethoxyethyl)ether	0.79			4.592
Ethyl vinyl ether	0.37			1.910
Butyl vinyl ether	0.34			2.970
2-Methylpropyl vinyl ether	0.29			2.746
2-Ethyl-1-hexyl vinyl ether	0.32			4.682
2-Methoxyethyl vinyl ether	0.68			2.932
Diallyl ether	0.38			2.430
Ethylene oxide	0.59			1.371
1,2-Propylene oxide	0.57			1.775
1,2-Butylene oxide	0.55			2.350
2-Methyl-1,2-propylene oxide	0.52			2.050
trans-2,3-Butylene oxide	0.52			2.140
cis-2,3-Butylene oxide	0.55			2.290
1,3-Propylene oxide	0.61			2.086
1,3-Butylene oxide	0.52			2.360
Furan	0.54	0.39	0.51	2.140
2-Methylfuran	0.50			2.430
2-Acetyl-3-methylfuran		1.17		
2-Acetyl-5-methylfuran		1.19		
2-Propanoyl-3-methylfuran		0.91		
Tetrahydrofuran	0.55			2.636
2-Methyltetrahydrofuran	0.47			2.820
2,5-Dimethyltetrahydrofuran	0.38			2.980
1,4-Dioxane	0.75	0.69	0.74	2.892

Alkynes				
But-2-yne		0.17	0.37	1.856
Oct-1-yne		0.19	0.23	3.480
Oct-2-yne		0.16	0.31	3.850
Haloaliphatics				
1-Fluorooctane		0.30		3.850
Dichloromethane	0.66			2.019
Trichloromethane	0.65	0.25	0.36	2.480
Tetrachloromethane	0.35	0.28	0.35	2.823
1,2-Dichloroethane	0.74	0.35	0.55	2.573
1,1,2,2-Tetrachloroethane		0.32	0.65	3.803
1-Chlorohexane		0.27	0.36	3.710
Trichloroethene		0.34	0.33	2.997
Hexachlorobutadiene		0.62		
Bromoethane		0.30	0.42	2.120
1-Bromopentane		0.30	0.39	3.611
2-Bromooctane		0.33	0.28	5.110
Iodomethane		0.35	0.44	2.106
1-Iodobutane		0.38	0.39	3.628
2-Iodobutane		0.40	0.39	3.390
1,1-Difluorotetrachloroethane		0.41		2.970
1,2-Difluorotetrachloroethane		0.41	0.33	3.000
Aromatic hydrocarbons				
Benzene	0.48	0.53	0.47	2.803
Toluene	0.47	0.57	0.46	3.344
Ethylbenzene	0.47	0.56	0.46	3.789
o-Xylene	0.50	0.63	0.43	3.942
m-Xylene	0.47	0.60	0.46	3.864
p-Xylene	0.46	0.61	0.46	3.836
1,3,5-Trimethylbenzene		0.64	0.46	4.316
1,2-Diethylbenzene	0.50			4.690
1,3-Diethylbenzene	0.48			4.680
1,4-Diethylbenzene	0.47			4.680
Styrene		0.70	0.55	3.863
Phenylethyne		0.55	0.68	3.715
Haloaromatics				
1,2-Dichlorobenzene		0.65	0.70	4.489
Benzylchloride		0.69	0.78	4.320
Ethers				
Dimethyl ether	0.36			1.285
Diethyl ether	0.27	0.19	0.27	2.015
Dipropyl ether	0.23			2.954
Diisopropyl ether	0.16			2.482
Tetrahydropyran	0.49			3.057
3,4-Dihydropyran	0.51			2.910
Trioxane	1.02			2.650
Trimethyltrioxane (paraldehyde)	0.68			3.169
2-Methyl-2-ethyl-1,3-dioxolane	0.58			3.337
Anethole		1.02		
Dimethoxymethane	0.52			1.894
Methoxyethoxymethane	0.49			2.371
Methoxyisopropoxymethane	0.45			2.697
Diethoxymethane	0.45			2.789
Ethoxypropoxymethane	0.44			3.280
Ethoxyisopropoxymethane	0.41			3.093
Ethoxy-*sec.*-butyloxymethane	0.41			3.609
Dipropyloxymethane	0.42			3.762
Propoxy-*sec.*-butyloxymethane	0.40			4.037
Diisopropoxymethane	0.37			3.376
Dibutyloxymethane	0.43			4.726
Diisobutyloxymethane	0.37			4.331
Di-*sec.*-butyloxymethane	0.37			4.380
1,1-Dimethoxyethane	0.49			2.334
1,1-Diethoxyethane	0.41			3.066
1,1-Dipropoxyethane	0.37			3.964
1,1-Diisobutyloxyethane	0.26			4.491
1,1-Dimethoxypropane	0.46			2.841
1,1-Diethoxypropane	0.38			3.498
1,1-Dimethoxybutane	0.47			3.313
1,1-Dimethoxy-2-methylpropane	0.42			3.148
2,2-Dimethoxypropane	0.43			2.699
2,2-Diethoxypropane	0.32			3.304
1,1,3-Trimethoxybutane	0.69			3.962
Methyl phenyl ether		0.73	0.70	3.859
1,8-Cineole		0.47		4.290
Aldehydes				
Formaldehyde	0.73			0.730
Acetaldehyde	0.70	0.63	0.65	1.230
Propanal	0.65	0.59	0.62	1.815
Butanal	0.63	0.61	0.61	2.270
2-Methylpropanal	0.58	0.59	0.59	2.120
Pentanal	0.63			2.851
2-Methylbutanal	0.58			2.733
3-Methylbutanal	0.60	0.62	0.58	2.620
2,2-Dimethylpropanal	0.49			2.406
Hexanal	0.64	0.59	0.59	3.370
Heptanal	0.65	0.58	0.59	3.860
Octanal		0.57	0.57	4.380

(*Continued on p. 218*)

TABLE II (*continued*)

Compound	π_2^H			Log L^{16}
	Eqn. 7	Eqn. 16	Eqn. 8	
Aldehydes (*continued*)				
2-Ethylhexanal	0.56			4.179
Prop-2-ene-1-al (acrolein)	0.74	0.68	0.58	1.656
trans-But-2-ene-1-al	0.81	0.85	0.75	2.570
2-Methylprop-2-ene-1-al (methacrolein)	0.62			2.180
trans-Hex-2-ene-1-al		0.88	0.85	
2-Ethylbut-2-ene-1-al	0.68			3.436
trans-Hept-2-ene-1-al		0.85	0.84	
trans-Oct-2-ene-1-al		0.55		
2-Ethylhex-2-ene-1-al	0.62			4.371
Hexa-2,4-dienal	0.90			3.800
Furfural		0.97	1.05	3.262
Benzaldehyde		0.99	0.94	3.985
3-Methoxybutanal	0.85			
Ketones				
Propanone	0.73	0.77	0.66	1.696
Butanone	0.69	0.72	0.66	2.287
Pentan-2-one	0.66	0.70	0.66	2.755
Pentan-3-one	0.64			3.271
3-Methylbutan-2-one	0.63			2.692
Hexan-2-one	0.67	0.71	0.65	3.262
Hexan-3-one	0.62	0.65	0.58	3.271
3-Methylpentan-2-one	0.62			3.163
4-Methylpentan-2-one	0.62			3.089
3,3-Dimethylbutan-2-one	0.58			2.928
Heptan-2-one	0.67	0.69	0.64	3.760
Heptan-3-one	0.62			3.776
Heptan-4-one	0.61			3.705
4,4-Dimethylpentan-2-one	0.57			3.344
2,4-Dimethylpentan-3-one	0.52			3.403
Octan-2-one	0.68	0.68	0.65	4.257
Nonan-2-one	0.68	0.69	0.64	4.735
Nonan-5-one	0.61			4.698
Decan-2-one		0.67	0.65	5.245
Undecan-2-one		0.67	0.64	5.732
Dodecan-2-one		0.67	0.64	6.167
Cyclopentanone	0.84	0.83	0.86	3.221
Cyclohexanone	0.84	0.87	0.87	3.792
Cycloheptanone		0.84	0.86	4.376
Esters (*continued*)				
2-Ethyl-1-hexyl acetate	0.60			5.025
Cyclohexyl acetate	0.69			4.454
Methyl propanoate	0.62	0.56	0.58	2.431
Ethyl propanoate	0.58			2.807
Propyl propanoate	0.57			3.338
Isopropyl propanoate	0.52			3.028
Butyl propanoate	0.57			3.883
Isobutyl propanoate	0.54			3.635
Pentyl propanoate	0.58			4.331
3-Methylbutyl propanoate	0.56			4.153
2-Pentyl propanoate	0.52			4.024
2-Ethyl-1-hexylpropanoate	0.55			5.486
Methyl butanoate	0.61			2.893
Ethyl butanoate	0.56			3.271
Propyl butanoate	0.56	0.54	0.51	3.783
Isopropyl butanoate	0.51			3.482
Butyl butanoate	0.56			4.275
Isobutyl butanoate	0.54			4.097
Pentyl butanoate	0.57			4.764
3-Methylbutyl butanoate	0.55			4.597
2-Pentyl butanoate	0.51			4.472
2-Ethyl-1-hexyl butanoate	0.57			5.856
Methyl isobutanoate	0.56			2.636
Butyl isobutanoate	0.51			4.068
Isobutyl isobutanoate	0.49	0.56	0.46	3.885
3-Methylbutyl isopentanoate		0.55	0.55	4.371
Allyl formate	0.76			2.256
Allyl acetate	0.72			2.723
Allyl propanoate	0.67			3.241
Vinyl acetate	0.66			2.152
Vinyl butanoate	0.56			3.191
1-Propenyl acetate	0.67			2.741
Isopropenyl acetate	0.68			2.611
Methyl acrylate	0.68			2.360
Ethyl acrylate	0.64			2.758
2-Ethyl-1-hexyl acrylate	0.61			5.445
Propyl acrylate	0.62			3.260
Butyl acrylate	0.62			3.790
Methyl methacrylate	0.62			2.880

Cyclo-octanone		0.83	0.85	4.981
Cyclononanone		0.83	0.84	5.537
Cyclodecanone		0.83	0.84	6.063
Cycloundecanone		0.83	0.83	6.621
Cyclododecanone		0.83	0.83	7.222
Cyclotridecanone		0.82	0.82	7.783
Cyclotetradecanone		0.82	0.82	8.334
Carvone		0.86	0.98	5.330
But-3-ene-2-one	0.76			2.330
3-Methylbut-3-ene-2-one	0.68			2.691
Hex-5-ene-2-one	0.75			3.181
4-Methylpent-3-ene-2-one	0.70			3.300
Butane-2,3-dione	0.52	0.71	0.74	1.639
Pentane-2,3-dione	0.47			2.209
Pentane-2,4-dione	0.56			2.772
Acetophenone		1.09	0.99	4.483
Esters				
Methyl formate	0.72			1.285
Ethyl formate	0.67			1.845
Propyl formate	0.65	0.56	0.60	2.443
Isopropyl formate	0.62			2.230
Butyl formate	0.66			2.958
Isobutyl formate	0.62			2.789
sec.-Butyl formate	0.61			2.730
Pentyl formate	0.66			3.448
2-Pentyl formate	0.60			3.250
3-Pentyl formate	0.60			3.226
Hexyl formate	0.67			3.970
Methyl acetate	0.67	0.63	0.61	1.911
Ethyl acetate	0.62	0.60	0.59	2.314
Propyl acetate	0.61	0.60	0.57	2.819
Isopropyl acetate	0.57			2.546
Butyl acetate	0.61	0.59	0.58	3.353
Isobutyl acetate	0.58			3.161
sec.-Butyl acetate	0.56			3.054
tert.-Butyl acetate	0.50			2.802
Pentyl acetate	0.62	0.58	0.59	3.844
3-Methylbutyl acetate	0.60	0.59	0.53	3.740
2-Pentyl acetate	0.56			3.568
3-Pentyl acetate	0.56			3.679
2-Methyl-2-butyl acetate	0.51			3.340
Hexyl acetate	0.63			4.351
4-Methyl-2-pentyl acetate	0.55			3.822
2-Ethyl-1-butyl acetate	0.60			4.178
Heptyl acetate	0.63			4.865
Allyl acrylate	0.72			3.160
2-Methoxyethyl acetate	0.93			3.290
2-Ethoxyethyl acetate	0.87	0.68	0.79	3.747
3-Methoxy-1-butyl acetate	0.83			4.048
3-Methoxy-1-butyl acrylate	0.83			4.048
Methylene diacetate	1.16			3.419
Ethylene diacetate	1.20			3.937
Ethylene dipropanoate	1.05			4.914
Propylene diacrylate	1.10			4.979
Benzyl acetate		1.19	0.95	4.991
Methyl benzoate		0.77	1.11	4.634
Methyl salicylate		0.82		
Nitro compounds				
Nitromethane		0.73	0.86	1.892
Nitroethane		0.74	0.87	2.414
1-Nitropropane		0.71	0.86	2.894
2-Methyl-2-nitropropane		0.82	0.82	2.710
3-Nitrotoluene		1.08	1.05	5.062
Nitriles				
Acetonitrile		0.80	0.85	1.739
1-Cyanopropane		0.78	0.84	2.604
1-Cyanobutane		0.80	0.83	3.108
Benzonitrile		1.05	1.04	4.004
Amines				
sec.-Butylamine		0.21	0.47	2.410
Allylamine		0.29		2.268
Trimethylamine		0.47		1.620
Heterocyclics				
Pyridine		0.80	0.80	3.003
2,3,6-Trimethylpyridine		0.71		4.200
Pyrrole		0.61	0.65	2.865
Trimethylpyrazine		0.77		
2-Methyl-3-ethylpyrazine		0.73		
2-Methoxy-3-isobutylpyrazine		0.56		
2,4,5-Trimethyloxazole		0.68		
Carboxylic acids				
Acetic acid		0.68		1.750
Propanoic acid		0.60		2.290
Butanoic acid		0.56		2.830
2-Methylpropanoic acid		0.58		2.670
Pentanoic acid		0.58		3.380
2-Methylbutanoic acid		0.55		3.260
3-Methylbutanoic acid		0.56		3.140

(*Continued on p. 220*)

TABLE II *(continued)*

Compound	π_2^H			Log L^{16}
	Eqn. 7	Eqn. 16	Eqn. 8	
Carboxylic acids (continued)				
Hexanoic acid		0.62		3.920
2-Methylpentanoic acid		0.68		3.680
Heptanoic acid		0.58		4.460
Octanoic acid		0.56		5.000
Nonanoic acid		0.53		5.550
Decanoic acid		0.50		6.090
Undecanoic acid		0.46		6.640
Dodecanoic acid		0.43		7.180
3-Butenoic acid		0.62		
Phenyls				
2-Chlorophenol		0.66		4.937
Salicylaldehyde		0.98		4.750
Hydroxylic compounds				
Water	0.40			0.260
Methanol	0.39	0.46		0.970
Ethanol	0.40	0.41		1.485
Propan-1-ol	0.41	0.42		2.031
Butan-1-ol	0.42	0.41		2.601
2-Methylpropan-1-ol	0.38	0.42		2.413
Pentan-1-ol		0.41		3.106
2-Methylbutan-1-ol	0.39	0.41		3.011
3-Methylbutan-1-ol	0.39	0.42		3.011
2,2-Dimethylpropan-1-ol	0.33			2.650
Hexan-1-ol	0.42	0.40		3.610
2-Methylpentan-1-ol	0.40			3.530
3-Methylpentan-1-ol	0.44			3.500
4-Methylpentan-1-ol	0.43			3.500
2-Ethylbutan-1-ol	0.40			3.523
2,2-Dimethylbutan-1-ol	0.37			3.320
Heptan-1-ol	0.43	0.39		4.115
2,2-Dimethylpentan-1-ol	0.37			3.780
Octan-1-ol	0.43	0.39		4.619
2-Ethylhexan-1-ol	0.41			4.433
2-Ethyl-4-methylpentan-1-ol	0.39			4.266
Nonan-1-ol	0.39	0.39		5.124
Decan-1-ol		0.39		5.628
Undecan-1-ol		0.39		6.130
Dodecan-1-ol		0.38		6.640
Propan-2-ol	0.39	0.42		1.764

Compound	π_2^H			Log L^{16}
	Eqn. 7	Eqn. 16	Eqn. 8	
Hydroxylic componds (contined)				
Prop-2-en-1-ol (allyl alcohol)	0.44	0.46		1.951
But-2-en-1-ol	0.49			2.618
But-3-en-1-ol	0.47			2.442
But-3-en-2-ol	0.43			2.206
2-Methylprop-2-en-1-ol	0.45			2.509
Pent-3-en-1-ol	0.50			3.064
Pent-4-en-1-ol	0.46			2.715
Pent-1-en-3-ol	0.43			2.752
2-Methylbut-3-en-2-ol	0.41			2.376
trans-Hex-2-en-1-ol		0.43		3.510
trans-Hept-2-en-1-ol		0.40		4.010
trans-Oct-2-en-1-ol		0.41		4.520
Prop-2-yn-1-ol	0.46			2.050
2-Methylbut-3-yn-2-ol	0.47			2.209
2-Chloroethanol	0.54			2.630
2-Methoxyethanol	0.59			2.490
2-Ethoxyethanol	0.56			2.815
2-Butoxyethanol	0.57			3.806
2-Allyloxyethanol	0.64			3.283
2-Methoxypropan-1-ol	0.58			2.793
2-Ethoxypropan-1-ol	0.56			3.115
3-Ethoxypropan-1-ol	0.57			3.426
1-Methoxypropan-2-ol	0.61			2.655
1-Propoxypropan-2-ol	0.57			3.495
3-Methoxybutan-1-ol	0.66			3.398
1-Ethoxypentan-3-ol	0.60			4.102
4-Methyl-4-methoxypentan-2-ol	0.65			3.963
3-Hydroxybutan-2-one	0.78			3.573
4-Hydroxybutan-2-one	0.85			3.160
3-Methyl-4-hydroxybutan-2-one	0.81			3.573
3-Methyl-3-hydroxybutan-2-one	0.75			2.951
4-Methyl-4-hydroxypentan-2-one	0.83			3.475
Thiols				
Ethanethiol		0.26	0.34	2.173
1-Propanethiol		0.25	0.34	2.685
2-Propanethiol		0.30	0.32	2.406
1-Butanethiol		0.28	0.33	3.243
2-Methyl-1-propanethiol		0.30	0.37	3.091
2-Methyl-2-propanethiol		0.28	0.29	2.558

Butan-2-ol	0.41	0.44	2.338
Pentan-2-ol	0.40		2.840
Pentan-3-ol	0.40		2.860
3-Methylbutan-2-ol	0.39		2.793
Hexan-2-ol	0.40	0.44	3.340
Hexan-3-ol	0.39	0.41	3.343
3-Methylpentan-2-ol	0.40		3.371
4-Methylpentan-2-ol	0.38		3.179
2-Methylpentan-3-ol	0.39		3.240
2,3-Dimethylbutan-2-ol	0.41		3.167
3,3-Dimethylbutan-2-ol	0.37		3.090
Heptan-2-ol	0.40		3.842
Heptan-3-ol	0.40		3.860
Heptan-4-ol	0.39		3.850
2,4-Dimethylpentan-3-ol	0.40		3.603
Octan-2-ol	0.41		4.343
2-Methylpropan-2-ol	0.38	0.50	1.963
2-Methylbutan-2-ol	0.41	0.47	2.630
2-Methylpentan-2-ol	0.40	0.48	3.081
3-Methylpentan-3-ol	0.45	0.47	3.277
2-Methylheptan-2-ol		0.47	3.990
3-Methylheptan-3-ol		0.46	4.000
3-Ethylpentan-3-ol	0.47		3.785
Cyclopropylcarbinol	0.57		2.675
Cyclopentanol	0.55	0.47	3.241
Cyclohexanol	0.57		3.758
2-Methylcyclohexanol	0.52		4.110
cis,cis-2,6-Dimethylcyclohexanol		0.43	
cis,trans-2,6-Dimethylcyclohexanol		0.45	
trans,trans-2,6-Dimethylcyclohexanol		0.51	
dl-α-Terpineol		0.57	
exo-Ethylfenchol		0.52	
1,2-Ethanediol	0.50		2.661
1,2-Propanediol	0.49		2.918
1,2-Butanediol	0.63		3.525
2-Methyl-1,2-propanediol	0.60		3.190
dl-2,3-Butanediol	0.62		3.250
meso-2,3-Butanediol	0.65		3.291
1,3-Propanediol	0.46		3.263
1,3-Butanediol	0.68		3.642
1,4-Butanediol	0.46		3.795
1-Pentanethiol	0.27	0.34	3.720
3-Methyl-1-butanethiol	0.27	0.18	3.360
1-Hexanethiol	0.26	0.35	4.220
1-Heptanethiol	0.27	0.33	4.720
1-Octanethiol	0.26	0.33	5.270
1-Nonanethiol	0.26	0.33	5.790
1-Decanethiol	0.25	0.33	6.318
Thiophenol	0.70	0.84	4.118
1,2-Ethanedithiol	0.43		
Benzylthiol	0.71		
Allylthiol	0.35	0.44	2.654
Sulphides			
Dithiapentane	0.68		
Dimethyl sulphide	0.40	0.37	2.238
Diethyl sulphide	0.37	0.34	3.104
Dipropyl sulphide	0.36	0.31	4.120
Methyl ethyl sulphide	0.28		2.730
Methyl propyl sulphide	0.38	0.34	3.240
Diisopentyl sulphide	0.44	0.28	5.540
Dibutyl sulphide	0.38	0.33	4.950
Diallyl sulphide	0.49		3.750
Propylene sulphide	0.39		2.870
Tetrahydrothiophene	0.47	0.50	3.660
Thiophene	0.50	0.50	2.943
2-Methylthiophene	0.55	0.53	3.302
2,5-Dimethylthiophene	0.60	0.49	3.806
Dimethyl disulphide	0.47	0.41	3.550
Diethyl disulphide	0.49	0.44	4.210
Dimethyl trisulphide	0.53		
Methyl thioacetate	0.65		
Methyl thiopropanoate	0.61		
Methyl thiobutanoate	0.59		
Methyl thiopentanoate	0.61		
Thiocyanates and isothiocyanates			
Phenyl isothiocyanate	1.00		
Allyl isothiocyanate	0.60		
Ethyl isothiocyanate	0.61		
Methyl thiocyanate	0.76		

only five data points in each regression, and no less than four explanatory variables. In principle, since we have five equations and (for each solute) four unknowns, *viz.*, R_2, π_2^*, β_2^H and log L^{16}, we could determine these unknowns through a set of simultaneous equations. This procedure proved to be useless, probably because there is not a wide enough range of constants in the five equations of the type of eqn. 8. However, Patte *et al.* [11] did manage to analyse the 240 × 5 data matrix to yield five characteristic solute parameters, denoted α, w, ε, π and β. In order to avoid confusion with our own parameters, we refer to Patte *et al.*'s set as αL, wL, εL, πL and βL. Each of these parameters for the 240 solute set can be examined via eqn. 1, where log $SP = \alpha L$, wL, etc. We found that αL was mainly a size factor and that βL was a general combination of factors. For the other three solute parameters of Patte *et al.* we obtained the following regressions:

$$\pi L = -0.040 + 0.342R_2 - 0.265\pi_2^* + 2.540\alpha_2^H \quad (9)$$

$$\varepsilon L = 0.165 + 2.796R_2 - 0.602\pi_2^* - 1.426{}_2^H \quad (10)$$

$$wL = -0.081 - 1.700R_2 + 2.490\pi_2^* + 0.561\alpha_2^H \quad (11)$$

Eqns. 9–11 can be rearranged to yield

$$\alpha_2^H = 0.0218 + 0.0335wL - 0.0251\varepsilon L + 0.3722\pi L \quad (12)$$

$$\tau_2^*(\pi_2^H) = -0.0060 + 0.4755wL + 0.2826\varepsilon L + 0.0536\pi L \quad (13)$$

$$R_2 = 0.0492 + 0.1195wL + 0.4057\varepsilon L + 0.2014\pi L \quad (14)$$

If R_2 is known, as it usually is, then any two equations out of eqns. 9–11 will yield α_2^H and π_2^*. However, the best pair of equations to use is clearly eqns. 9 and 11, which yield

$$\alpha_2^H = 0.0187 - 0.0620R_2 + 0.0409wL + 0.3847\pi L \quad (15)$$

$$\pi_2^*(\pi_2^H) \mathrel{\hat{=}} 0.0287 + 0.6954R_2 + 0.3932wL - 0.0789\pi L \quad (16)$$

Values of π_2^H calculated via eqn. 16 are listed in Table II. We can also simply take the set of five equations, eqn. 8, and, knowing R_2, log L^{16} and where necessary α_2^H, back-calculate values of π_2^H. For each solute the five back-calculated π_2^H values can be averaged, and this average is also given in Table II. The error in π_2^H between the five equations is *ca.* 0.03 unit. There are a few omissions in this set of π_2^H values; these arise through the lack of one or another of the remaining solute parameters.

Although the combination of solutes in the McReynolds and Patte *et al.* sets numbers several hundred, there are some notable omissions. First, most of the solutes are aliphatic, so that some of the simplest functionally substituted aromatic solutes are missing. Second, many of the polyhalogenated aliphatic solutes are either missing, or have π_2^H values that are discordant when calculated from the McReynolds or Patte *et al.* set. Finally, a number of important solutes such as nitroalkanes and nitriles need to be studied further.

Fellous *et al.* [13] listed GLC data for seventeen aromatic solutes on a number of stationary phases. In order to back-calculate π_2^H using the general solvation equation (eqn. 1), it is essential that the s coefficient be as large as possible, *i.e.*, that the stationary phase be polar. Results from the seven most polar phases used by Fellous *et al.* are given in Table III. There is generally good agreement with values listed in Table II.

Several workers have examined sets of halogenated or polyhalogenated solutes on various stationary phases [14–18]. In Table IV we give π_2^H values back-calculated from the general solvation regression equation (eqn. 1) and also from our own results on a variety of polar stationary phases.

McReynolds [10] did not examine any aliphatic nitro compounds or nitriles, but in Table II we give values of π_2^H for a few such compounds, obtained from Patte *et al.*'s data set. We examined both series of solutes on a number of stationary phases, and conclude that π_2^H is even larger than the values given in Table II. Our results suggest that for 1-nitroalkanes π_2^H is 0.95 and that for *n*-alkyl cyanides π_2^H is *ca.* 0.90 unit (see Table IV).

We have not detailed the α_2^H values calculated from eqn. 7 or 15 because these follow closely the original hydrogen-bond α_2^H values described before [4]. Only with the carboxylic acids do the new effective or $\Sigma\alpha_2^H$ values (0.60 unit) differ markedly from α_2^H (0.54 unit). In Table IV we collect all the $\Sigma\alpha_2^H$ values that correspond to the π_2^H values we have set out.

Although it was not our intention to construct a new $\Sigma\beta_2^H$ scale, we thought it prudent to check that

TABLE III

VALUES OF π_2^H FOR SOME AROMATIC COMPOUNDS CALCULATED FROM RESULTS OF FELLOUS *ET AL.* [13]

X in PhX	π_2^H	S.D.[a]	π_2^H (Table II)		
			Eqn. 7	Eqn. 16	Eqn. 8
H	0.53	0.02	0.48	0.53	0.47
CF_3	0.45	0.02			
CH_3	0.52	0.01	0.47	0.57	0.46
OCH_3	0.73	0.02		0.73	0.70
F	0.57	0.02			
Cl	0.67	0.01			
Br	0.73	0.01			
I	0.79	0.01			
CHO	0.99	0.01		0.99	0.94
SH	0.78	0.01		0.70	0.84
CO_2CH_3	0.85	0.01		0.77	1.11
CN	1.07	0.01		1.05	1.04
$COCH_3$	0.98	0.01		1.09	0.99
NH_2	0.96	0.02			
NO_2	1.10	0.01		1.08[b]	1.05[b]
CH_2OH	0.85	0.01			
OH	0.88	0.01			

[a] Average deviation from 7 results.

[b] For 3-nitrotoluene.

the combined solvation parameters do yield reasonable results in systems where solute basicity is important. We therefore give in Table IV preliminary $\Sigma\beta_2^H$ values, again based on our original β_2^H values [5]. We hope in the near future to report on a much more comprehensive list of effective or $\Sigma\beta_2^H$ values.

Finally, we include in Table II the log L^{16} values that we have used. Where these differ from previous values, the new set is to be preferred.

DISCUSSION

The "inverse matrix" method we have used to analyse the data of McReynolds is a novel approach to the extraction of solvation parameters from data on a large number of stationary phases. The method works very well, but is limited in scope to results for a given set of solutes on at least fifteen phases. Our back-calculation of parameters from regression equations based on Patte *et al.*'s data set, eqn. 8, is likely to be the most common procedure. In principle, as pointed out above, if three solvation parameters are unknown (*e.g.*, π_2^H, α_2^H and log L^{16} in eqn. 8), it is possible to calculate all three using three simultaneous equations derived from retention data on three phases. In practice, this method can hardly ever be used unless the three phases are specifically chosen to give rise to solvation equations with very different coefficients. In the event, all of our new π_2^H values have been obtained by either the inverse matrix method or simple back-calculation and averaging. Overall we think that the π_2^H values listed in Table IV are accurate to *ca* 0.02 unit, but not more.

As can be seen from the data collected in Table II, there is a compelling need to correlate and interpret π_2^H values in order to codify existing data and to help in the estimation of further values. An analysis of all of our results has led us to two very simple rules governing π_2^H values for aliphatic solutes:

Rule 1. In any homologous series of functionally substituted aliphatic compounds, π_2^H is constant except for the first one or two members of the series.

Rule 2. In any given series of functionally substituted aliphatic compounds, π_2^H decreases by 0.03 unit for each branch in a carbon chain.

We now examine these rules in turn. Rule 1 would be extremely valuable in the estimation of π_2^H values, because if π_2^H was known for a few members of a homologous series, then the same value could be applied to all other members. Unfortunately, Li *et al.* [12] apparently find that their own π_2^C parameter varies markedly along homologous series. Thus along the homologous series of *n*-alkylcarboxylic acids, π_2^C increases from 0.50 (acetic acid) to 0.72 (nonanoic acid) (see Table V), whereas our π_2^H value is constant at 0.60 unit after the first few members of the series. We note that π_2^C and π_2^H are "scaled" differently, so that for the present discussion only trends in these parameters are important. How the two sets of π_2 values in Table V both result in good fits to experimental data can be seen by inspection of the corresponding $\Sigma\alpha_2^H$ values, also given in Table V. Our constant π_2^H value is accompanied by a constant $\Sigma\alpha_2^H$ value, whereas Li *et al.*'s increase in π_2^C is counteracted by a decrease in $\Sigma\alpha_2^H$, so that both combinations of $\pi_2/\Sigma\alpha_2^H$ fit the experimental data with respect to the solvation eqn. 1. We suggest, however, that other experimental evidence supports the constancy of π_2^H and $\Sigma\alpha_2^H$. Thus, the dipole moment of the *n*-alkylcarboxylic acids (except for formic acid) remains constant [19], the gas-phase proton transfer acidities of acetic acid, propanoic

TABLE IV

RECOMMENDED SOLVATION PARAMETERS FOR USE IN EQN. 1[a]

Values in parentheses are approximate values.

Solute	$\Sigma\pi_2^H$	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$
Rare gas	0.00	0.00	0.00
Hydrogen	0.00	0.00	0.00
Oxygen	0.00	0.00	0.00
Nitrogen	0.00	0.00	0.00
Nitrous oxide	0.35	0.00	0.10
Carbon monoxide	0.00	0.00	0.04
Carbon dioxide	0.42	0.00	0.10
Alkane	0.00	0.00	0.00
Cycloalkane	0.10	0.00	0.00
Decalin	0.25	0.00	0.00
Hydrindane	0.20	0.00	0.00
Ethene	0.10	0.00	0.07
Other alkene	0.08	0.00	0.07
Cycloalkene	0.20	0.00	0.10
α-Pinene	0.24	0.00	0.10
Diene	0.23	0.00	0.10
Ethyne	0.25	0.15	0.15
Propyne	0.25	0.13	0.15
But-1-yne	0.25	0.13	0.15
Other alk-1-yne	0.23	0.13	0.10
Alk-2-yne	0.30	0.00	0.10
Benzene	0.52	0.00	0.14
Toluene	0.52	0.00	0.14
o-Xylene	0.54	0.00	0.17
m-Xylene	0.52	0.00	0.17
p-Xylene	0.52	0.00	0.17
Ethylbenzene	0.52	0.00	0.15
n-Propylbenzene	0.52	0.00	0.15
Isopropylbenzene	(0.51)	0.00	0.15
1,2,3-Trimethylbenzene	0.54	0.00	0.20
1,2,4-Trimethylbenzene	0.52	0.00	0.20
1,3,5-Trimethylbenzene	0.52	0.00	0.20
n-Alkylbenzene	0.52	0.00	0.15
Styrene	0.63	0.00	0.18
Phenylethyne	0.58	0.12	0.21
Naphthalene	0.90	0.00	0.21
Fluoroalkane	0.35	0.00	0.10
Chloromethane	0.43[b]	0.00	0.08
Chloroalkane	0.40	0.00	0.10
Bromomethane	0.43[b]	0.00	0.10
Bromoalkane	0.40	0.00	0.12
Iodomethane	0.43[b]	0.00	0.13
Iodoalkane	0.40	0.00	0.15
sec.-Chloroalkane	0.35[b]	0.00	0.12
sec.-Bromoalkane	0.35[b]	0.00	0.14
sec.-Iodoalkane	0.35[b]	0.00	0.17
tert.-Chloroalkane	0.25[b]	0.00	0.12
tert.-Bromoalkane	0.25[b]	0.00	0.12
tert.-Iodoalkane	0.25[b]	0.00	0.10
Dichloromethane	0.57[b]	0.10	0.05
Trichloromethane	0.49	0.15	0.02
Tetrachloromethane	0.38	0.00	0.00
1,1-Dichloroethane	0.49	0.10	0.10
1,2-Dichloroethane	0.64	0.10	0.11
1,1,1-Trichloroethane	0.41	0.00	0.09
1,1,2-Trichloroethane	0.68	0.13	0.08
1,1,1,2-Tetrachloroethane	0.63	0.10	0.08
1,1,2,2-Tetrachloroethane	0.76	0.16	0.12
Dibromomethane	0.67	0.10	0.10
Tribromomethane	0.68	0.15	0.09
Fluorobenzene	0.57	0.00	0.10
Chlorobenzene	0.67	0.00	0.09
1,2-Dichlorobenzene	0.79	0.00	0.03
1,3-Dichlorobenzene	0.74	0.00	0.03
1,4-Dichlorobenzene	0.69	0.00	0.03
2-Chlorotoluene	0.66	0.00	0.09
3-Chlorotoluene	0.67	0.00	0.09
4-Chlorotoluene	0.67	0.00	0.09
2,4-Dichlorotoluene	0.73	0.00	0.03
2,6-Dichlorotoluene	0.73	0.00	0.03
3,4-Dichlorotoluene	0.79	0.00	0.03
Bromobenzene	0.73	0.00	0.09
1,2-Dibromobenzene	0.89	0.00	0.03
1,3-Dibromobenzene	0.84	0.00	0.03
1,4-Dibromobenzene	0.79	0.00	0.03
Iodobenzene	0.79	0.00	0.09
Dimethyl ether	0.27	0.00	0.41
Di-*n*-alkyl ether	0.25[b]	0.00	0.45
Furan	0.53	0.00	0.15
2-Methylfuran	0.50	0.00	(0.15)
Tetrahydrofuran	0.52	0.00	0.48
2-Methyltetrahydrofuran	0.48	0.00	0.55
3,5-Dimethyltetrahydrofuran	0.38	0.00	0.55
Tetrahydropyran	0.47	0.00	0.55
1,4-Dioxane	0.75	0.00	0.64
Paraldehyde	0.68	0.00	
Methyl phenyl ether	0.73	0.00	(0.33)
Ethyl phenyl ether	0.72	0.00	(0.33)
Benzodioxane	1.01	0.00	
Formaldehyde	0.70	0.00	(0.33)
Acetaldehyde	0.67	0.00	0.45
n-Alkanal	0.65[b]	0.00	0.45
Prop-2-en-1-al	0.74	0.00	0.45
trans-Alk-2-en-1-al	0.80	0.00	0.45
Benzaldehyde	0.99	0.00	(0.42)
2-, 3- or 4-methylbenzaldehyde	0.95	0.00	(0.44)
Propanone	0.70	0.04	0.51
Butanone	0.70	0.00	0.51
Alkan-2-one	0.68[b]	0.00	0.51

TABLE IV *(continued)*

Solute	$\Sigma\pi_2^H$	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$
Alkan-(3,4,5)-one	0.66[b]	0.00	0.51
Cycloalkanone	0.86[b]	0.00	0.52
Acetophenone	0.98	0.00	(0.51)
Methyl formate	0.68	0.00	0.38
Ethyl formate	0.66	0.00	0.38
n-Alkyl formate	0.63[b]	0.00	0.38
Methyl acetate	0.64	0.00	0.45
Ethyl acetate	0.62	0.00	0.45
n-Alkyl acetate	0.60[b]	0.00	0.45
Methyl propanoate	0.60	0.00	0.45
Ethyl propanoate	0.58	0.00	0.45
n-Alkyl propanoate	0.56[b]	0.00	0.45
Vinyl acetate	0.64	0.00	0.42
Methyl acrylate	0.66	0.00	0.42
Ethyl acrylate	0.64	0.00	0.42
n-Alkyl acrylate	0.62[b]	0.00	0.42
Methyl benzoate	0.85	0.00	0.50
n-Alkyl benzoates	0.80	0.00	0.50
Nitromethane	0.95	0.12	0.27
Nitroethane	0.95	0.05	0.27
1-Nitropropane	0.95	0.02	0.27
1-Nitroalkane	0.95[b]	0.00	0.27
Nitrobenzene	1.10	0.00	0.27
2-, 3- or 4-nitrotoluene	1.10	0.00	0.27
Acetonitrile	0.90	0.09	0.30
Propionitrile	0.90	0.02	0.35
n-Alkyl cyanide	0.90	0.00	0.36
Benzonitrile	1.07[b]	0.00	(0.30)
Ammonia	0.35[c]	0.10	0.62
Primary *n*-alkylamines	0.35[c]	0.10	0.64
Dimethylamine	0.30[c]	0.08	0.67
sec.-dialkylamines	0.30[c]	0.08	0.70
Triethylamine	0.15[c]	0.00	0.81
Aniline	0.96[c]	0.26	(0.53)
o-Toluidine	0.94	0.23	(0.57)
m-Toluidine	0.94	0.23	(0.55)
p-Toluidine	0.94	0.23	(0.57)
2,6-Dimethylaniline	0.93	0.20	(0.60)
N-Methylaniline	0.94	0.17	(0.47)
N,N-Dimethylaniline	0.82	0.00	(0.48)
Pyridine	0.82	0.00	
2-Methylpyridine	0.80	0.00	
3-Methylpyridine	0.80	0.00	
4-Methylpyridine	0.80	0.00	
2,4,6-Trimethylpyridine	0.72	0.00	
Acetic acid	0.65	0.61	0.41
Propanoic acid	0.65	0.60	0.43
Butanoic acid	0.62	0.60	0.43
n-Alkanoic acids	0.60[b]	0.60	0.43
Water	0.45	0.82	0.35
Methanol	0.44	0.43	0.47
Ethanol	0.42	0.37	0.48
Primary alcohols	0.42[b]	0.37	0.48
Secondary alcohols	0.36[b]	0.33	0.56
Tertiary alcohols	0.30[b]	0.31	0.60
Trifluoroethanol	0.60	0.57	(0.15)
Hexafluoropropan-2-ol	0.55	0.77	(0.03)
Decafluoroheptan-1-ol	0.55	0.60	0.22
Phenol	0.88	0.60	
o-Cresol	0.86	0.52	
m-Cresol	0.87	0.57	
p-Cresol	0.87	0.57	
2,3-Dimethylphenol	0.82	0.53	
2,4-Dimethylphenol	0.82	0.53	
2,5-Dimethylphenol	0.82	0.54	
2,6-Dimethylphenol	0.82	0.39	
3,4-Dimethylphenol	0.87	0.56	
3,5-Dimethylphenol	0.87	0.57	
2,4,6-Trimethylphenol	0.83	0.37	
Benzyl alcohol	0.85	0.39	
Carbon disulphide	0.21	0.00	0.07
Methanethiol	(0.35)	0.00	
1-Alkanethiol	0.35[b]	0.00	0.24
3-Methyl-1-butanethiol	0.18[d]	0.00	
Thiophenol	0.78	0.12	(0.15)
Di-*n*-alkyl sulphide	0.38[b]	0.00	0.32
Tetraalkyltin	0.00	0.00	0.00

[a] Values of π_2^H (this work) derived from those in Tables II and III plus other values we have calculated. Values of $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ are based on those given in refs. 4 and 5.

[b] Subtract 0.03 from π_2^H for each additional branch.

[c] Provisional values.

[d] See text.

acid and butanoic acid are almost the same (if anything, there is a slight increase in acidity along this series) [20] and the gas-phase hydrogen-bond acidity of propanoic acid is slightly less than that of acetic acid [21], not larger. As retention data can be accommodated as well by our constant π_2^H and $\Sigma\alpha_2^H$ values as by the variable parameters of Li *et al.*, we feel that Rule 1 is operative here.

There are other homologous series for which Li *et al.* found π_2^C to be a variable quantity, but for which $\Sigma\alpha_2^H = 0$, *e.g.*, the alkan-2-ones or the cycloalkanones where π_2^C increases sharply along the series. In

TABLE V

COMPARISON OF π_2^H WITH π_2^c FOR CARBOXYLIC ACIDS

R in ROC_2H	This work		Li *et al.* [12]	
	π_2^H	α_2^H	π_2^c	α_2^H
Methyl	0.65	0.61	0.50	0.72
Ethyl	0.65	0.60	0.61	0.67
n-Propyl	0.62	0.60	0.57	0.62
n-Butyl	0.60	0.60	0.56	0.62
n-Pentyl	0.60	0.60	0.60	0.52
n-Hexyl	0.60	0.60	0.64	0.47
n-Heptyl	0.60	0.60	0.68	0.41
n-Octyl	0.60	0.60	0.72	0.35

some other series, however, π_2^c decreases slightly (the alk-1-ene series), or remains approximately constant (the alkanal or the alkylbenzene series). For the cycloalkanone series, as an example, we feel that the difference between Li *et al.*'s result and our findings is not fundamental at all, but is probably due to small but systematic differences in the log L^{16} values. As the sign of the $s\pi_2$ and l log L^{16} coefficients is always positive, a systematic trend in π_2^c increasing, together with a trend in log L^{16} becoming slightly smaller than expected, would tend to cancel out. This can be seen by comparison of the figures in Table VI. Just as for the carboxylic acid results, the combination of π_2^c with Li *et al.*'s calculated log L^{16} values will lead to very nearly the same goodness-of-fit as our combination of π_2^H and log L^{16}. As it is always found that solute dipolarity, as the dipole moment, is constant along any homologous series, we again feel that Rule 1 applies to the various homologous series we have considered.

TABLE VI

COMPARISON OF π_2^H WITH π_2^c FOR CYCLOALKANONES

n in $(CH_2)_nCO$	This work		Li *et al.* [12]	
	π_2^H	Log L^{16}	π_2^c	Log L^{16}
4	0.86	3.221	0.58	3.120
5	0.86	3.792	0.59	3.616
6	0.86	4.376	0.66	4.110
7	0.86	4.981	0.69	4.610
8	0.86	5.537	0.72	5.110
9	0.86	6.063	0.75	5.610
10	0.86	6.621	0.78	6.110
11	0.86	7.226	0.81	6.600

Rule 2 is not so well founded, and we think it possible that there will be exceptions or amendments to the rule. However, at the moment, we feel that application of Rule 2 does allow a very large number of π_2^H values to be estimated for aliphatic compounds. We note that the starting point for application of the rule is not always the simplest member of any series.

According to our results in Table II, the alkanols are a significant exception to Rule 2, as π_2^H seems roughly constant over non-branched and branched members. However, because the coefficients of π_2^H and α_2^H are both positive, and indeed follow each other for most stationary phases, there will be various combinations of π_2^H and α_2^H that give rise to the same (or very similar) goodness-of-fit in any given solvation equation. We have checked that π_2^H values for alkanols calculated using Rules 1 and 2, together with the α_2^H values listed in Table IV, yield regression eqations that are just as good as if π_2^H and α_2^H are allowed to "float". We give in Table IV our suggested π_2^H and α_2^H values for alkanols, noting that we have deliberately amended the first-calculated values in Table II.

We also find a few minor anomalies, with respect to Rule 2. Thus, π_2^H for isopentanethiol is 0.18 (using Patte *et al.*,'s set) rather than 0.32 as calculated by Rule 2. Whether or not this is the result of a systematic experimental error, or even of an incorrectly named compound, we cannot say. Interestingly, Li *et al.* [12] also found an anomalously low π_2^c value for isopentylthiol.

Finally, we can compare our π_2^H scale, as summarised in Table IV, with the π_2^c scale of Li *et al.*. We agree completely with Li *et al.* in that a new π_2 scale is needed in place of π_2^*. Apart from the difference in treatment of homologous series, the two scales are in approximate agreement. For 198 of the 203 compounds listed by Li *et al.* [12], we have π_2^H values, and find that

$$\pi_2^c = -0.103 + 0.845\pi_2^H \qquad (17)$$

with $r = 0.944$ and S.D. $= 0.083$ units. The intercept of -0.103 arises because Li *et al.* took cyclohexane as the zero ($\pi_2^c = 0.00$), but we take alkanes as zero. On the π_2^H scale, cyclohexane has $\pi_2^H = 0.10$ units.

As mentioned above, we include in Table IV a provisional set of $\Sigma\beta_2^H$ values to use with our new π_2^H and our $\Sigma\alpha_2^H$ scale. In our view, it is most important that these three scales are constructed more or less simultaneously in order that they all be compatible. How well the scales listed in Table IV deal with various processes remains to be seen, but at the moment we can compare regressions of Patte *et al.*'s data using the Table IV values with our original regression equations. Details are given in Table VII and show that the new equations are much better than the old ones in terms of the correlation constant and standard deviation. However, the characteristic constants, *r, s, a* and *l*, are almost unchanged. Similarly, regression equations using McReynolds' data are much better than the original ones, whilst still giving very similar characteristic constants. Hence our analysis of the McReynolds' phases into clusters or groups remains unchanged, and it is not necessary to repeat the 75 regressions. We give in Table VII a few comparisons to show exactly the connection between the old and the new equations.

In conclusion, we have constructed a comprehensive π_2^H scale, based only on solute properties, for use in solvation equations. As the dependent variable, log L' or log V_G, in the equations used to calculate π_2^H is a free energy-related term, then π_2^H also will be related to Gibbs energy. We are now in a position where the main terms in eqn. 1, *viz.*, π_2^H, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$ and log L^{16}, are all related to Gibbs energy and hence form a thermodynamically consistent set of explanatory variables. The new π_2^H scale has an advantage in that the characteristic constants in all our previous equations remain the same, within any reasonable experimental error, so that our previous analyses and conclusions are unchanged.

TABLE VII

COMPARISON OF NEW AND OLD REGRESSIONS[a]

Phase	*c*	*r*	*s*	*a*	*l*	S.D.	*R*	No.
Patte *et al.*'s set								
Carbowax	−2.01	0.25	1.26	2.07	0.429	0.07	0.997	199
	−2.07	0.26	1.37	2.11	0.442	0.13	0.986	168
DEGS[b]	−1.77	0.35	1.58	1.84	0.383	0.07	0.997	199
	−1.83	0.35	1.70	1.92	0.396	0.15	0.981	168
PPE (6 rings)[b]	−2.51	0.14	0.89	0.67	0.547	0.06	0.997	199
	−2.55	0.19	0.98	0.59	0.552	0.11	0.991	168
TCEP[b]	−1.69	0.26	1.93	1.88	0.365	0.06	0.998	199
	−1.75	0.23	2.12	1.94	0.379	0.16	0.982	168
ZE7[b]	−1.99	−0.41	1.46	0.77	0.432	0.07	0.995	199
	−2.07	−0.38	1.61	0.70	0.442	0.13	0.983	168
The McReynolds' set at 120°C								
Apiezon J	−0.48	0.24	0.15	0.13	0.596	0.02	0.999	165
	−0.48	0.27	0.13	0.13	0.594	0.03	0.998	148
PPE (5 rings)	−0.69	0.14	0.92	0.61	0.560	0.02	0.999	168
	−0.70	0.21	0.88	0.54	0.564	0.06	0.994	155
Pluronic L72	−0.54	0.09	0.93	1.42	0.529	0.03	0.998	163
	−0.54	0.17	0.89	1.41	0.531	0.08	0.992	153
Carbowax 1540	−0.75	0.22	1.37	1.92	0.456	0.04	0.998	169
	−0.75	0.31	1.34	1.87	0.457	0.09	0.987	151
DEGS[b]	−0.97	0.26	1.76	1.80	0.375	0.05	0.995	158
	−0.99	0.43	1.74	1.68	0.379	0.11	0.975	145
ZE7[b]	−0.76	−0.42	1.55	0.78	0.448	0.07	0.991	170
	−0.82	−0.28	1.63	0.69	0.449	0.07	0.990	150

[a] The new constants in eqn. 1 are on the top lines and the old constants on the bottom lines; in all instances $b = 0$.

[b] Abbreviations: DEGS = diethylene glycol succinate; PPE = polyphenyl ether; TCEP = tricyanoethoxypropane; ZE7 = zonyl E-7.

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