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Hydrogen Bonding. Part 14.† The Characterisation of Some *N*-Substituted Amides as Solvents: Comparison with Gas–Liquid Chromatography Stationary Phases

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Equations previously used for the characterisation of GLC stationary phases have been found to be equally suitable for the characterisation of common solvents. Thus equation (a) has been applied to solubility data for series of solutes on *N*-formylmorpholine (NFM), *N*-methylpyrrolidinone (NMP), *N*,*N*-dimethylformamide (DMF), and *N*,*N*-dimethylacetamide (DMA).

$$SP = c + r \cdot R_2 + s \cdot \pi_2^* + a \cdot \alpha_2^H + b \cdot \beta_2^H + l \cdot \log L^{16} \qquad (a)$$

In equation (a), SP can be log V_G° or log L for a series of solutes on a given solvent where V_G° is the specific retention volume and L is the Ostwald solubility coefficient. The solute parameters are R_2, a polarisability parameter; π_2^*, the solute dipolarity; α_2^H, the solute hydrogen-bond acidity; β_2^H, the solute hydrogen-bond basicity; and log L^{16} where L^{16} is the solute Ostwald solubility coefficient on n-hexadecane at 298 K.

It is shown that at 298 K all four amides have about the same dipolarity, as judged by the *s*-constant, and have nearly the same hydrogen-bond basicity, as judged by the $a \cdot \alpha_2^H$ term: all have zero hydrogen-bond acidity so that $b = 0$ in equation (a). Comparison can be made between results for NFM and NMP at 393 K and results for some GLC stationary phases. The two amides are less dipolar than tricyano(ethoxy)propane and diethyleneglycol succinate, about the same as Zonyl E-7® and Carbowax®, and more dipolar than poly(phenyl ether). The amides, however, have rather more hydrogen-bond basicity than any of the above five GLC phases. It is suggested that equation (a) can be used as the basis of method for characterising condensed phases, such that common solvents as well as GLC stationary phases can be included within the scope of the method.

A number of amides are industrially important solvents, and there are several reports dealing with vapour–liquid equilibria (VLE) of *N*-substituted amides, especially.[1–6] A particularly convenient method of obtaining VLE data for a series of solutes in a given amide is the gas-chromatographic procedure in which the amide acts as the stationary phase.[1,3–6] The obtained specific retention volumes, either at the column temperature (V_G) or corrected to 273 K (V_G°), can be converted into infinite dilution activity coefficients of the solute in the amide solvent, γ_2^∞, at the column temperature, through well established equations.[1,3–5] Alternatively, values of V_G can be transformed into Ostwald solubility coefficents, L_2, defined by equation (1), through the very simple equation (2) in which ρ_1 is the density

$$L_2 = \frac{\text{concentration of solute in solution}}{\text{concentration of solute in the gas phase}} \qquad (1)$$

$$L_2 = V_{G \cdot \rho 1} \qquad (2)$$

of the amide at the column temperature. For measurements at essentially zero solute concentration, L_2 is effectively L_2°, and the concentration of solute in solution becomes identical with the concentration of solute in the pure solvent.

Medina and co-workers[3] used both their own gas–liquid chromatographic (GLC) measurements and literature data to obtain γ^∞-values for hydrocarbons in *N*-methylpyrrolidinone (NMP) and were able to account rather well for these γ^∞-values using the group contribution method, UNIFAC. A much more extensive set of solutes was studied by Gmehling and co-workers[4,6] with both the amides NMP and *N*-formylmorpholine (NFM). They obtained V_G°-values for a set of hydrocarbons, esters, aldehydes, ketones, and alcohols at various temperatures, and listed both V_G°- and γ^∞-values.

Now although the calculation of γ^∞-values using methods such as UNIFAC, UNIQUAT, and ASOG is well established, there is always an over-riding difficulty in the interpretation of parameters that refer to γ^∞: since γ^∞ is an equilibrium constant (or partition coefficient) between the bulk liquid solute and the solute at infinite dilution in the solvent, γ^∞ will contain not only contributions from solute–solvent interactions, but also those from solute–solute interactions. As has been pointed out before,[7] gas–liquid partition coefficients contain only the solute–solvent interaction terms, and hence are inherently easier to interpret than quantitites that refer to partition between the bulk liquid and the solvent. Since gas–liquid partition coefficients, either as values of L or as Henry's constants K^H, are convertible into γ^∞-values through the solute vapour pressure, P°, and since, in any case, P°-values are needed to obtain γ^∞

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† Part 13 is ref. 10.

Table 1. Solutes used in the correlations with V_G°, Tables 2–5.

NFM	NMP
n-Pentane	n-Pentane
n-Hexane	n-Hexane
n-Heptane	n-Heptane
n-Octane	n-Octane
2,2,4-Trimethylpentane	2,2,4-Trimethylpentane
n-Decane	Cyclopentane
Cyclopentane	Cyclohexane
Methylcyclopentane	Methylcyclopentane
Cyclohexane	Methylcyclohexane
Methylcyclohexane	Benzene
Ethylcyclohexane	Toluene
1,4-*trans*-Dimethylcyclohexane	Hex-1-ene
1,4-*cis*-Dimethylcyclohexane	Oct-1-ene
1,2-*trans*-Dimethylcyclohexane	Methanol
1,2-*cis*-Dimethylcyclohexane	Ethanol
Benzene	Propan-2-ol
Toluene	t-Butyl alcohol
2-Xylene	Methyl acetate
3-Xylene	n-Propyl acetate
4-Xylene	Ethyl propanoate
Ethylbenzene	Ethyl butanoate
Isopropylbenzene	Vinyl acetate
Hex-1-ene	Acetone
Oct-1-ene	Butan-2-one
Methanol	Pentan-2-one
Ethanol	Pentan-3-one
Propan-2-ol	Butanal
Propan-1-ol	2-Methylpropanal
t-Butyl alcohol	Pentanal
Methyl acetate	(*E*)-But-2-enal
Ethyl acetate	Thiophene
n-Propyl acetate	
Ethyl propanoate	
Ethyl butanoate	
Vinyl acetate	
Acetone	
Butan-2-one	
Pentan-2-one	
Pentan-3-one	
4-Methylpentan-2-one	
Butanal	
2-Methylpropanal	
Pentanal	
(*E*)-But-2-enal	
Thiophene	

Table 2. Correlations of log V_G° for 45 solutes in NFM[4] by using equations (3) and (4).

T/K	*c*	*s*	*a*	*l*	*SD*[a]	*R*[b]
298.2	−0.313	2.311	4.335	0.708	0.122	0.985
	0.107[c]	0.069	0.216	0.031		
313.3	−0.349	2.153	3.916	0.656	0.114	0.985
	0.101	0.065	0.204	0.029		
332.7	−0.386	1.966	3.430	0.594	0.104	0.985
	0.091	0.059	0.184	0.026		
352.5	−0.425	1.811	2.998	0.536	0.099	0.983
	0.088	0.056	0.177	0.025		
373.4	−0.459	1.645	2.582	0.487	0.094	0.982
	0.083	0.053	0.167	0.024		

[a] Overall standard deviation in log V_G°. [b] Overall correlation coefficient. [c] These are the standard deviations in the various constants.

Table 3. Correlations of log V_G° for 45 solutes in NFM[4] by using equation (5).

T/K	*c*	*r*	*q*	*a*	*l*	*SD*	*R*
298.2	−0.040	1.756	0.159	4.156	0.621	0.330	0.890
313.3	−0.095	1.659	0.149	3.742	0.572	0.302	0.892
332.7	−0.155	1.534	0.136	3.266	0.516	0.271	0.895
352.5	−0.215	1.432	0.126	2.843	0.464	0.245	0.897
373.4	−0.264	1.337	0.114	2.425	0.417	0.217	0.902

Table 4. Correlations of log V_G° for 31 solutes in NMP[4] by using equations (3) and (4).

T/K	*c*	*s*	*a*	*l*	*SD*	*R*
298.2	−0.159[a]	2.103	5.049	0.779	0.107	0.988
	0.141	0.073	0.241	0.046		
323.4	−0.212	1.883	4.298	0.680	0.096	0.987
	0.126	0.066	0.216	0.041		
333.2	−0.220	1.803	4.016	0.644	0.093	0.986
	0.121	0.063	0.208	0.040		
343.4	−0.246	1.730	3.777	0.612	0.092	0.986
	0.120	0.063	0.206	0.039		

[a] For log L_{NMP}, this constant takes the value −0.110.

Table 5. Correlations of log V_G° for 31 solutes in NMP[4] by using equation (5).

T/K	*c*	*r*	*q*	*a*	*l*	*SD*	*R*
298.2	−0.094[a]	1.422	0.142	5.172	0.785	0.300	0.902
323.4	−0.151	1.300	0.127	4.397	0.683	0.268	0.900
333.2	−0.164	1.254	0.121	4.109	0.647	0.255	0.900
343.4	−0.189	1.215	0.116	3.860	0.613	0.246	0.898

[a] For log L_{NMP}, this constant takes the value −0.045.

from V_G, it seems a theoretically simpler matter to deal with gas–liquid parameters (such as L, K^H, or V_G) than with γ^∞.

A number of equations have already been derived for the correlation of gas–liquid partition coefficients, as log L or log V_G, for a series of solutes in a given liquid phase.[8–10]

$$\mathrm{SP} = c + d\cdot\delta_2 + s\cdot\pi_2^* + a\cdot\alpha_2^H + b\cdot\beta_2^H + l\cdot\log L^{16} \quad (3)$$

$$\mathrm{SP} = c + r\cdot R_2 + s\cdot\pi_2^* + a\cdot\alpha_2^H + b\cdot\beta_2^H + l\cdot\log L^{16} \quad (4)$$

$$\mathrm{SP} = c + r\cdot R_2 + q\cdot\mu_2^2 + a\cdot\alpha_2^H + b\cdot\beta_2^H + l\cdot\log L^{16} \quad (5)$$

In these equations SP can be log L or log V_G, *etc.*,† and the various explanatory variables are as follows: δ_2 is an empirical solute polarisability correction term taken as zero except for aromatic solutes ($\delta_2 = 1$) and polyhalogenated solutes ($\delta_2 = 0.5$), π_2^* is the solute dipolarity/polarisability, α_2^H and β_2^H are respectively the solute hydrogen-bond acidity and hydrogen-bond basicity, L^{16} is the solute Ostwald solubility coefficient on n-hexadecane at 298.15 K, R_2 is the solute molar refraction less that of an alkane of the same characteristic volume, and μ_2 is the solute dipole moment.[10] Equations (3) and (4) have usually given better correlations than has equation (5).

We start with the results of Gmehling and co-workers on NFM,[4] where V_G°-values were obtained for 45 solutes at various temperatures, ranging from 303.4 to 373.4 K. Not all solutes were studied at all temperatures, and so we have interpolated values, and have also extrapolated values from either 303.4 K or 313.3 K down to 298.15 K to obtain a

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† Note that log L and log V_G give rise to exactly the same constants in equations (3), (4), and (5) except for the *c*-constant which will differ by log ρ_1.

Table 6. Values of log L at 298 K for solutes in NMP, DMF, and DMA.

Solute	NMP	DMF	DMA
Argon	−0.98[19,‡]	−0.86[19]	
Hydrogen	−1.46[27]	−1.35[26,27]	
Nitrogen	−1.25[15]		
Ammonia	1.34[14]		
Carbon monoxide		−1.06[28]	
Methane	−0.61[16–19]	−0.52[19]	
Ethane	0.19[16,17,19]	0.22[14,19]	0.35[29]
Propane	0.65[14,16,17,19]	0.64[14]	0.81[29]
n-Butane	1.14[16,17,19]	1.08[14]	1.28[29]
Isobutane	0.88[14,16,17,19]		
n-Pentane	1.56[3,16,19]	1.51[19]	1.70[29]
2-Methylbutane	1.32[3]	1.39‡	1.45‡
n-Hexane	2.03[3,16,19]	1.99[19]	2.10[29]
n-Heptane	2.34[3,16,19]	2.36[19]	
n-Octane	2.77[3,16,19,20]	2.81[19,20]	2.90[20]
2,2,4-Trimethylpentane	2.29[3,21]	2.22[30]	
n-Nonane	3.05[3]		
Cyclopentane	1.92[3]		
Methylcyclopentane	2.20[3]		
Cyclohexane	2.33[3,16,21,22]	2.31[2,19]	
Methylcyclohexane	2.64[3,16]	2.58[19,30]	
Ethylcyclohexane	3.02[3]		
n-Propylcyclohexane	3.35[3]		
n-Butylcyclohexane	3.73[3]		
Ethene	0.29[16,18]		
Propene	0.91[18]		
But-1-ene		1.30[25]	
Pent-1-ene	1.65[1]	1.70[1,2,30]	1.72[1]
3-Methylbut-1-ene	1.50[1]	1.53[1]	1.56[1]
2-Methylbut-2-ene	1.86[1,22]	1.88[1]	1.89[1]
Hex-1-ene	2.06[4]	2.21[2]	
Oct-1-ene	2.91[4]		
Cyclopentene		2.22[2]	
Cyclohexene		2.68[2]	
Buta-1,3-diene	1.73[18]	1.68[24]	
2-Methylbuta-1,3-diene	2.14[1,22]	2.11[1,2]	2.12[1]
2,3-Dimethylbuta-1,3-diene		2.63[2]	
(*E*)-Penta-1,3-diene	2.24[1]	2.23[1]	2.25[1]
(*Z*)-Penta-1,3-diene	2.29[1]	2.27[1]	2.29[1]
Cyclopenta-1,3-diene		2.50[2]	
Pent-1-yne		2.54[2]	
Benzene	3.30[21,22]	3.26[31]	
Toluene	3.71[20]	3.64[20]	3.64[20]
Chloromethane		1.74[32]	
Chloroethane		2.01[29]	2.16[29]
Trichloromethane	3.84[24]		
Bromoethane		2.45[29,30]	2.53[29]
Iodomethane	2.76[23]	2.56[30]	2.66[23]
Iodoethane		2.86[29,30,33]	2.91[29]
Dimethyl ether		1.56[32]	
1,4-Dioxane	3.66[20]	3.72[20]	3.66[20]
Butanal	3.05[4]		
2-Methylpropanal	2.78[4]		
Pentanal	3.42[4]		
(*Z*)-But-2-enal	3.66[4]		
Acetone	2.77[4]		
Butan-2-one	3.42[20]	3.36[20]	3.28[20]
Pentan-2-one	3.47[4]		
Pentan-3-one	3.49[4]		
Methyl acetate	2.72[4]		
n-Propyl acetate	3.39[4]		
Ethyl propanoate	3.29[4]		
Ethyl butanoate	3.59[4]		
Vinyl acetate	3.05[4]		
Acetonitrile		3.41[34]	
Propanonitrile		3.67[29]	3.66[29]
Nitromethane		4.07[20]	4.02[20]
Methylamine		1.95[14]	
Dimethylamine		2.11[14]	
Trimethylamine		1.77[14]	
Triethylamine		2.62[33]	
Thiophene	3.43[4]		
Tetramethyltin	2.19[19]	2.15[19]	
Water		4.07[34]	
Methanol	3.43[4]		
Ethanol	3.78[20]	3.73[20]	3.82[20]
Propan-1-ol		4.08[a]	
Propan-2-ol	3.73[4]		
Butan-1-ol			4.84[a]
Butan-2-ol		4.16[a]	4.32[a]
t-Butyl alcohol	3.75[4]		
2,2,2-Trifluoroethanol		5.08[a]	4.99[a]
NMP	5.63§		
DMF		4.72§	
DMA			4.69§

[a] This work, see the text. ‡,§ — see footnotes in the text.

coherent set of log V°_{G}-values at five given temperatures. Explanatory variables are available for all 45 solutes,[9–13] and so we can apply equations (3), (4), and (5) at each temperature. Preliminary results suggested that the solute hydrogen-bond basicity, β^{H}_{2} was not important, as expected on general chemical grounds,[†] and so we can reduce the equations to four explanatory variables.

In the event, neither δ_2 in equation (3) nor R_2 in equation (4) were significant, and so both equations reduce to a three-parameter equation in π^{*}_{2}, α^{H}_{2}, and log L^{16}. The 45 solutes studied are listed in Table 1, and a summary of the regressions is in Table 2. Gmehling and co-workers[6] repeated some of their measurements of V°_{G} but since there is excellent agreement between the old[4] and the new[6] sets, we took V°_{G} all from the earlier set, for convenience. We also investigated use of equation (5), and details are collected in Table 3.

Equations (3) and (4), with δ_2, R_2, and β^{H}_{2} non-significant, reproduce the log V°_{G}-values with an overall standard deviation of 0.1 log units, at the various temperatures given. Considering that this represents 'all solute' correlations, with no outliers at all, agreement between observed and calculated log V°_{G} is quite satisfactory. These equations could therefore be used to predict further log V°_{G}-values for a large number of solutes for which the necessary parameters are available.

Gmehling and co-workers also reported V°_{G}-values in NMP for 31 solutes at 323.4, 333.2, and 343.4 K. We have similarly analysed these data, as log V°_{G}, and have also extrapolated the V°_{G}-values down to 298.2 K to obtain another regression equation. As with NFM, the parameters δ_2, R_2, and β^{H}_{2} in equations (3) and (4) were not significant, and the latter parameter was not significant in equation (5). Details are in Tables 4 and 5. Once again equations (3) and (4) reproduce the log V°_{G}-values to *ca.* 0.1 log unit, with again no solutes being excluded. Thus equations (3) and (4) with the constants in Table 4 can be used to predict log V°_{G} for further solutes.

In the case of NMP, there is a very considerable quantity of literature data available, mostly on vapour–liquid equilibria,[14–24] and we have recast these data in terms of log L_{NMP} at 298 K. Here, L_{NMP} refers to the Ostwald solubility coefficient of a solute in NMP solvent, see equation (1). Some of these data overlap with those of Gmehling and co-workers,[4,6] but in order to have as independent a set of results as possible,

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[†] Neither NFM nor NMP can act as hydrogen-bond acids, and hence solute hydrogen-bond basicity plays no part in any solute–solvent interactions.

[‡] Calculated from high pressure data given in ref. 14.

[§] Taking $\gamma^{\infty} = 1$, by definition.

Table 7. Correlations of log L for 60 solutes[a] in NMP at 298 K.

	c	d	r	s	q	a	l	SD	R
Equation (3)	−0.276	−0.170		2.157		5.134	0.870	0.148	0.995
	0.043	0.089		0.072		0.229	0.017		
Equation (4)	−0.283		0.454	1.998		5.085	0.851	0.137	0.996
	0.040		0.121	0.072		0.212	0.016		
Equation (5)	−0.195		1.458		0.126	5.676	0.839	0.247	0.985
	0.071		0.198		0.009	0.377	0.029		

[a] These are the 60 data entries in Table 6.

Table 8. Correlations of log L for 53 solutes[a] in DMF at 298 K.

	c	d	r	s	q	a	l	SD	R
Equation (3)	−0.231	−0.366		2.561		4.612	0.839	0.149	0.994
	0.047	0.109		0.090		0.165	0.021		
Equation (4)	−0.207			2.482		4.585	0.829	0.164	0.993
	0.051			0.096		0.182	0.023		
Equation (5)	−0.145		1.387		0.119	5.830	0.823	0.233	0.986
	0.072		0.193		0.008	0.244	0.034		

[a] These are the 53 data entries in Table 6.

Table 9. Correlations of log L for 27 solutes[a] in DMA at 298 K.

	c	d	r	s	q	a	l	SD	R
Equation (3)	−0.045	−0.346		2.229		4.984	0.802	0.169	0.992
	0.114	0.168		0.128		0.261	0.052		
Equation (4)	−0.001			2.196		4.864	0.782	0.181	0.991
	0.120			0.136		0.271	0.054		
Equation (5)	−0.003		1.158		0.115	6.222	0.796	0.145	0.994
	0.096		0.153		0.006	0.201	0.044		

[a] These are the 27 data entries in Table 6.

Table 10. Comparison of characteristic constants for solvents and GLC stationary phases, equation (4).

Solvent	T/K	$r \cdot R_2$	$s \cdot \pi_2^*$	$a \cdot \alpha_2^H$	$l \cdot \log L^{16}$
NFM[a]	298		2.31	4.33	0.708
NMP[b]	298	0.45	2.00	5.09	0.851
DMF[c]	298		2.48	4.58	0.829
DMA[d]	298		2.20	4.86	0.782
NFM[e]	393		1.52	2.24	0.442
NMP[e]	393		1.42	2.70	0.472
Carbowax[f]	393	0.26	1.37	2.11	0.442
DEGS[f]	393	0.35	1.70	1.92	0.396
PPE[f]	393	0.19	0.98	0.59	0.552
TCEP[f]	393	0.23	2.12	1.94	0.379
ZE7[f]	393	−0.38	1.61	0.70	0.442

[a] Table 2. [b] Table 7. [c] Table 8. [d] Table 9. [e] Extrapolated data from results in Tables 2 and 4. [f] From ref. 10.

we have used Gmehling's data as an additional source only.* Details of the log L_{NMP}-values are in Table 6, and a summary of our obtained regression equations is in Table 7. Bearing in mind the different set of solutes studied, there is quite good agreement between the various equations in Table 7 and those given before in Tables 4 and 5 (the 31 solutes of Tables 4 and 5 are a subset of the 60 solutes in Table 7).

We shall consider in more detail the actual constants listed in Table 7, but now set out values of log L for a range of solutes in *N*,*N*-dimethylformamide (DMF) and in *N*,*N*-dimethylacetamide (DMA). These are two additional *N*-substituted amides for which there are a large number of log L-values at 298 K that can be obtained from a variety of additional literature sources.[25–34] Values of log L_{DMF} and log L_{DMA} are collected in Table 6. Although there are a reasonable number of hydrogen-bond bases in these two sets, there are but few hydrogen-bond acids. Since these are very important in characterising phases or solvents that are themselves hydrogen-bond bases, we determined a few values of log L_{DMF} and log L_{DMA} for alcohols by the method of headspace analysis, exactly as we have detailed before.[11]

We have to hand log L-values for 53 assorted solutes in DMF and for 27 solutes in DMA (Table 6), and give summaries of the obtained regression equations in Tables 8 and 9. Bearing in mind the diverse sources of the data used, the correlation equations (3) and (4) lead to quite satisfactory results. These equations could be used as 'all solute' correlations to predict further log L-values for a variety of solutes. For both DMF and DMA the $r \cdot R_2$ term in equation (4) is not significant, but this

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* We calculated log L_{NMP} at 298 K by using the equation log L_{NMP} = log V_G° + 0.0499.

Table 11. Solute parameters used in the regressions.

No.	Compound	δ_2	R_2	μ_2^2	π_2^*	α_2^H	log L^{16}
3	Argon	0.00	0.000	0.000	0.00	0.00	−0.688
11	Hydrogen	0.00	0.000	0.000	0.00	0.00	−1.200
15	Nitrogen	0.00	0.000	0.000	0.00	0.00	−0.978
18	Ammonia	0.00	0.139	2.074	0.34	0.10	0.680
21	Carbon monoxide	0.00	0.000	0.010	0.02	0.00	−0.812
50	Methane	0.00	0.000	0.000	0.00	0.00	−0.323
51	Ethane	0.00	0.000	0.000	0.00	0.00	0.492
52	Propane	0.00	0.000	0.000	0.00	0.00	1.050
53	n-Butane	0.00	0.000	0.000	0.00	0.00	1.615
54	Isobutane	0.00	0.000	0.000	0.00	0.00	1.409
55	n-Pentane	0.00	0.000	0.000	0.00	0.00	2.162
56	2-Methylbutane	0.00	0.000	0.000	0.00	0.00	2.013
58	n-Hexane	0.00	0.000	0.000	0.00	0.00	2.668
63	n-Heptane	0.00	0.000	0.000	0.00	0.00	3.173
72	n-Octane	0.00	0.000	0.000	0.00	0.00	3.677
86	2,2,4-Trimethylpentane	0.00	0.000	0.000	0.00	0.00	3.120
91	n-Nonane	0.00	0.000	0.000	0.00	0.00	4.182
126	n-Decane	0.00	0.000	0.000	0.00	0.00	4.686
284	Cyclopentane	0.00	0.263	0.000	0.00	0.00	2.447
288	Methylcyclopentane	0.00	0.225	0.000	0.00	0.00	2.771
287	Cyclohexane	0.00	0.305	0.000	0.00	0.00	2.913
293	Methylcyclohexane	0.00	0.244	0.000	0.00	0.00	3.252
308	1,2-*trans*-Dimethylcyclohexane	0.00	0.227	0.000	0.00	0.00	3.550
307	1,2-*cis*-Dimethylcyclohexane	0.00	0.281	0.000	0.00	0.00	3.760
312	1,4-*trans*-Dimethylcyclohexane	0.00	0.191	0.000	0.00	0.00	3.550
311	1,4-*cis*-Dimethylcyclohexane	0.00	0.204	0.000	0.00	0.00	3.700
313	Ethylcyclohexane	0.00	0.263	0.000	0.00	0.00	3.590
314	n-Propylcyclohexane	0.00	0.257	0.000	0.00	0.00	3.930
315	n-Butylcyclohexane	0.00	0.255	0.000	0.00	0.00	4.270
370	Ethene	0.00	0.107	0.000	0.08	0.00	0.289
371	Propene	0.00	0.103	0.134	0.08	0.00	0.946
373	But-1-ene	0.00	0.100	0.116	0.08	0.00	1.491
380	Pent-1-ene	0.00	0.093	0.116	0.08	0.00	2.013
383	3-Methylbut-1-ene	0.00	0.063	0.250	0.08	0.00	1.910
379	2-Methylbut-2-ene	0.00	0.159	0.116	0.08	0.00	2.190
392	Hex-1-ene	0.00	0.078	0.116	0.08	0.00	2.547
409	Oct-1-ene	0.00	0.094	0.116	0.08	0.00	3.591
387	Buta-1,3-diene	0.00	0.320	0.068	0.20	0.00	1.543
389	2-Methylbuta-1,3-diene	0.00	0.313	0.144	0.20	0.00	2.130
390	2,3-Dimethylbuta-1,3-diene	0.00	0.352	0.270	0.20	0.00	2.690
385	(*E*)-Penta-1,3-diene	0.00	0.385	0.342	0.20	0.00	2.250
384	(*Z*)-Penta-1,3-diene	0.00	0.345	0.250	0.20	0.00	2.280
427	Cyclopentadiene	0.00	0.417	0.281	0.35	0.00	2.222
454	Pent-1-yne	0.00	0.172	0.740	0.20	0.13	2.010
751	Benzene	1.00	0.610	0.000	0.59	0.00	2.803
752	Toluene	1.00	0.601	0.130	0.55	0.00	3.344
753	2-Xylene	1.00	0.663	0.384	0.51	0.00	3.937
754	3-Xylene	1.00	0.623	0.160	0.51	0.00	3.864
755	4-Xylene	1.00	0.613	0.000	0.51	0.00	3.858
766	Ethylbenzene	1.00	0.613	0.348	0.53	0.00	3.765
768	Isopropylbenzene	1.00	0.602	0.152	0.53	0.00	4.105
551	Chloromethane	0.00	0.249	3.764	0.40	0.00	1.163
552	Dichloromethane	0.50	0.387	2.624	0.82	0.13	2.019
553	Trichloromethane	0.50	0.425	1.020	0.58	0.20	2.480
605	Bromoethane	0.00	0.366	4.121	0.48	0.00	2.120
651	Iodomethane	0.00	0.676	2.624	0.40	0.00	2.106
655	Iodoethane	0.00	0.640	2.924	0.50	0.00	2.573
1351	Dimethyl ether	0.00	0.000	1.664	0.27	0.00	1.090
1421	1,4-Dioxane	0.00	0.329	8.500	0.67	0.00	2.797
1553	Butanal	0.00	0.187	7.398	0.65	0.00	2.270
1554	2-Methylpropanal	0.00	0.144	7.290	0.65	0.00	2.060
1555	Pentanal	0.00	0.163	6.760	0.65	0.00	2.770
1570	(*E*)-But-2-enal	0.00	0.387	12.530	0.75	0.00	2.570
1651	Acetone	0.00	0.179	8.294	0.71	0.04	1.760
1653	Pentan-2-one	0.00	0.143	7.290	0.65	0.00	2.755
1654	Pentan-3-one	0.00	0.154	7.398	0.65	0.00	2.811
1662	4-Methylpentan-2-one	0.00	0.111	7.290	0.65	0.00	3.050
1860	Methyl acetate	0.00	0.142	2.958	0.60	0.00	1.960
1861	Ethyl acetate	0.00	0.106	3.168	0.55	0.00	2.376
1862	n-Propyl acetate	0.00	0.092	3.420	0.55	0.00	2.878
1882	Ethyl propanoate	0.00	0.087	3.240	0.55	0.00	2.881

Table 11 (*continued*).

No.	Compound	δ_2	R_2	μ_2^2	π_2^*	α_2^H	$\log L^{16}$
1888	Ethyl butanoate	0.00	0.106	3.240	0.55	0.00	3.379
1880	Vinyl acetate	0.00	0.223	2.890	0.55	0.00	2.600
2201	Acetonitrile	0.00	0.237	15.366	0.75	0.09	1.560
2202	Propanonitrile	0.00	0.162	16.000	0.70	0.00	2.050
2101	Nitromethane	0.00	0.313	11.972	0.85	0.12	1.892
2301	Methylamine	0.00	0.250	1.664	0.32	0.00	1.300
2321	Dimethylamine	0.00	0.189	0.941	0.25	0.00	1.600
2340	Trimethylamine	0.00	0.140	0.375	0.15	0.00	1.620
2346	Triethylamine	0.00	0.101	0.490	0.15	0.00	3.077
3601	Thiophene	1.00	0.687	0.325	0.60	0.00	2.943
4561	Tetramethyltin	0.00	0.000	0.000	0.00	0.00	2.920
3351	Water	0.00	0.000	3.497	0.43	0.65	0.260
3352	Methanol	0.00	0.278	2.890	0.40	0.37	0.922
3353	Ethanol	0.00	0.246	2.856	0.40	0.33	1.485
3354	Propan-1-ol	0.00	0.236	2.822	0.40	0.33	2.097
3355	Propan-2-ol	0.00	0.212	2.756	0.40	0.32	1.821
3356	Butan-1-ol	0.00	0.224	2.756	0.40	0.33	2.601
3357	Butan-2-ol	0.00	0.217	2.723	0.40	0.32	2.338
3359	t-Butyl alcohol	0.00	0.180	2.657	0.40	0.32	2.018
3497	2,2,2-Trifluoroethanol	0.50	0.015	4.121	0.73	0.57	1.224
2854	*N*-methylpyrrolidin-2-one	0.00	0.481	16.728	0.92	0.00	4.320
2503	*N*,*N*-dimethylformamide	0.00	0.367	14.900	0.88	0.00	3.173
2509	*N*,*N*-dimethylacetamide	0.00	0.363	13.838	0.88	0.00	3.717

may be due to lack of solutes with high R_2-values in the correlations. In general, however, the correlation equations for DMF and DMA follow closely those for NMP (*cf.* Tables 8 and 9 with Table 7). This is exactly as expected, because all three of these amides are quite dipolar and all three are quite strong hydrogen-bond bases. From the results shown in Tables 7–9, the amides NMP, DMF, and DMA are of quite similar dipolarity with *s*-constants 2.00, 2.48, and 2.20, respectively, in equation (4), and *q*-constants 0.126, 0.119, and 0.115, respectively, in equation (5). The hydrogen-bond basicities of these amides are also very similar, being for NMP, DMF, and DMA in the sequence of *a*-values 5.09, 4.58, and 4.86 (compare the solvent hydrogen-bond β_1 basicity values of 0.77, 0.69, and 0.76, respectively).[35] The other amide studied, NFM, is of about the same dipolarity but of somewhat lower basicity than NMP, DMF, and DMA; see the collected results in Table 10.

We have previously[10] characterised a number of stationary phases used in gas–liquid chromatography (GLC), and it would be of considerable interest to compare such phases with common solvents. The GLC phases were studied at 393 K, but we have found that the constants in equation (4) obtained for NFM and NMP at lower temperatures can be extrapolated to 393 K through excellent plots against $1/T$(K); see Table 10.

It is quite clear from results in Table 10, and from results in Tables 2–5, that characteristic constants in equations such as (4) alter markedly with temperature. In general, it is to be expected that solute–solvent interactions would decrease with a rise in temperature, simply as a result of increased thermal motion. Indeed, hydrogen-bond complexation constants between a given acid and a given base do invariably decrease with increase in temperature. In the present case, any decrease in solute–solvent interactions could be due both to effects on the solute and on the solvent. We have no means of separating these, and hence adopt the convention that any change in a characteristic constant with temperature is due to a change in solvent property only. This does not matter as regards inter-solvent comparisons, which is what we are concerned with, but it would be important if absolute values of solvent properties were required.

In Table 10 we report constants in equation (4) at 393 K for NFM and NMP, together with those for five GLC phases.[10] Our above-stated comments on temperature effects are very relevant: at 298 K both NFM and NMP appear to be more dipolar and very much more basic than any of the GLC phases. However, at a common temperature of 393 K, NFM and NMP are somewhat less dipolar than tricyano(ethoxy)propane (TCEP), diethyleneglycol succinate (DEGS), and Zonyl E-7® (ZE7), although more dipolar than poly(phenyl ether) (PPE). At 393 K, the hydrogen-bond basicity of NFM and NMP is not a great deal larger than that of the more basic GLC phases: Carbowax®, TCEP, and DEGS. The *l*-constant represents a combination of cavity effects and general dispersion interactions,[10] but as regards GLC separations its importance lies in the separation of members of homologous series. The larger the *l*-constant, the greater will be the separation. There are no very remarkable values of the *l*-constant in Table 10: as might be expected, PPE has a reasonably high value of 0.55, DEGS and TCEP the lowest values, with the amides and the other GLC phases in between.

We can conclude that equations (3)–(5) yield useful information on solute–solvent interactions and that the constants in equation (4), especially, can be used to characterise solvents in terms of such interactions. Together with previous results,[10] we can demonstrate that the constants in equation (4) are useful in a general method for characterising condensed phases, and lead, for the first time, to a comparison of GLC stationary phases with common solvents.

Table 12. Calculation of the solute–solvent interactions that influence log *L*-values in DMF at 298 K, *via* equation (4).

Solute	$s \cdot \pi_2^*$	$a \cdot \alpha_2^H$	$l \cdot \log L^{16}$	Dispersion[a]	Cavity[a]
Butane	0	0	1.35	3.38	−1.47
Octane	0	0	3.05	6.42	−2.69
Benzene	1.46	0	2.32	4.29	−1.56
Propanone	1.76	0	1.46	2.65	−1.19
Propan-1-ol	0.99	1.51	1.74	2.86	−1.29

[a] Obtained by analysis of the $l \cdot \log L^{16}$ term according to Abraham and Fuchs.[36] The two effects do not exactly add up to $l \cdot \log L^{16}$ because of omission of a constant term, and a small dipole-induced dipole term.

Finally, we collect in Table 11 all the solute parameters used in the regression analysis. Note that, for 1,4-dioxane, an 'effective' value of 8.5 is used for μ_2^2 and one of 0.67 for π_2^*.

Solute–Solvent Interactions.—Our preferred equation (4) can be used to separate out the various contributions to the observed log *L*-values for any particular solute. Details for solutes in DMF at 298 K are in Table 12, with a number of compounds taken as examples. The $l \cdot \log L^{16}$ term is always very large, and only if the solute π_2^*-value or α_2^H-value is substantial do the $s \cdot \pi_2^*$ and $a \cdot \alpha_2^H$ terms make comparable contributions. Abraham and Fuchs[36] separated out various contributions to the $\log L^{16}$ term itself, the two main ones being an exoergic dispersion interaction that leads to an increase in $\log L^{16}$, and an endoergic cavity term that leads to a decrease in $\log L^{16}$. If we assume that, as a first approximation, the relative sizes of these effects is the same in DMF, we can further subdivide the $l \cdot \log L^{16}$ term into dispersion and cavity effects; see Table 12. The results show very clearly that, of the exoergic solute–solvent effects we have considered, the general dispersion interaction is always the most important.

In terms of GLC analyses, separations of adjacent members of an homologous series will be governed by differences in dispersion interactions and cavity effects. These two influences are together contained in the $l \cdot \log L^{16}$ term—the larger the value of *l*, the greater will be the separation between members of a homologous series. Interactions of the dipole–dipole and hydrogen-bonding types will obviously influence separations of solutes of different functionalities, even though in general they are not so large as general dispersion effects.

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