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**THE SOLVATION PROPERTIES OF THE ALIPHATIC ALCOHOLS**Michael H. ABRAHAM<sup>a1,\*</sup>, Joelle LE<sup>a</sup> and William E. ACREE, Jr.<sup>b</sup><sup>a</sup> *Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.; e-mail: <sup>1</sup> m.h.abraham@ucl.ac.uk*<sup>b</sup> *Department of Chemistry, University of North Texas, Denton, TX 76203-0068, U.S.A.; e-mail: acree@unt.edu*Received July 1, 1999  
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Solubilities of solute gases and vapours, as  $\log L$ , where  $L$  is the Ostwald solubility coefficient, in the alkan-1-ols from methanol to decan-1-ol have been correlated through the solvation equation of Abraham. It is shown that there is a regular progression of solvent properties from methanol to decan-1-ol, except for the solvent hydrogen-bond basicity that remains the same along the series, and, indeed, is the same as that of water. A slightly different solvation equation is used to correlate the partition of solutes from water to the dry alkanols. For the longer chain alkanols, the coefficients in the solvation equations approach those in equations for partition from water to the wet (water-saturated) alkanols, showing that the solvation properties of the wet and dry alkanols are quite close for the higher alkanol homologues.

**Key words:** Hydrogen bonding; Solvation equations; Gas-water partition; Water-alkanol partition.

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The alcohols occupy a somewhat peculiar position in the rank of solvents. They resemble water in being highly associated liquids with a three-dimensional network of hydrogen bonds, but in terms of properties such as polarisability, molar refraction, surface tension, and the Hildebrand cohesive energy density, the higher alcohols in particular are akin to aprotic solvents. It is therefore of theoretical interest, as well as practically useful, to investigate the solubility properties of the alcohols. One possible method is to correlate the solubility of a given solute in a range of alcohols with properties of the alcohols. However, almost any given property in a series of alcohols is usually well correlated with any other property. Hence very little can be deduced from such an approach. A much better method is to correlate the solubility of a series of solutes in a given alcohol with properties (or

descriptors) of the solutes. Solute properties are not constrained to be co-linear, and therefore correlations through multiple linear regression analysis (MLRA) can be set up. These have an advantage over methods such as principle components, partial least squares or neural networks in that correlation equations obtained by MLRA are easier to interpret.

Our procedure is therefore to collect solubilities of a series of solutes in a given solvent and to regress these data against solute descriptors. As a measure of solubility, we use the Ostwald solubility coefficient,  $L$ , defined through Eq. (1). If concentrations in the solvent and the gas phase are in the same units, for example  $\text{mol dm}^{-3}$ , then  $L$  is a dimensionless quantity;  $L$  is also referred to as the gas-liquid partition coefficient,  $K$ :

$$L = [\text{concentration in solvent}]/[\text{concentration in the gas phase}]. \quad (1)$$

Experimental values of  $L$  can be obtained as follows. (i)  $L$  can be obtained by a direct determination of the concentration of the solute in the headspace above a dilute solution of the solute in a given alcohol. (ii) From vapour-liquid equilibria it is possible to obtain the activity coefficient of a solute in an alcohol, and extrapolation to zero solute concentration will yield the infinite dilution activity coefficient,  $\gamma^\infty$ . Then the Henry's Law constant is given by  $K^H = \gamma^\infty P^0$ , where  $P^0$  is the solute saturated vapour pressure (taken as equivalent to fugacity), and  $K^H$  is the inverse of  $L$ , with due regard to units. (iii) For sparingly soluble compounds,  $L$  can be obtained as the ratio of the concentration of solute in the saturated solution to the vapour concentration of the gaseous solute. We have previously studied methanol<sup>1</sup>, ethanol<sup>2</sup>, propan-1-ol<sup>3</sup>, and octan-1-ol<sup>4</sup>, as well as water<sup>5</sup>, and in the present work we complete our analysis of solubility in the alkan-1-ols through a study of butan-1-ol, pentan-1-ol, hexan-1-ol, heptan-1-ol, and decan-1-ol. There was not enough data available to study nonan-1-ol.

## METHODOLOGY

The  $L$  values, as  $\log L$ , for a series of solutes in a given alcohol at 298 K are used as the dependent variable in Eq. (2), the solvation equation of Abraham<sup>6</sup>:

$$\log L = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^H + l \log L^{16}. \quad (2)$$

The independent variables are solute descriptors as follows<sup>6</sup>.  $R_2$  is an excess molar refraction,  $\pi_2^H$  is the dipolarity/polarisability,  $\Sigma\alpha_2^H$  is the overall or summation hydrogen-bond acidity and  $\Sigma\beta_2^H$  is the overall or summation hydrogen-bond basicity;  $L^{16}$  is the Ostwald solubility coefficient on hexadecane at 298 K (ref.<sup>7</sup>), defined as in Eq. (1). Because the descriptors used in Eq. (2) are chemically based, the coefficients in the equation encode specific chemical information. The  $r$  coefficient indicates the propensity of solutes to interact with solvent molecules *via*  $\sigma$  and  $\pi$  electron pairs (with hexadecane as a standard solvent). The  $s$  coefficient is a measure of the solvent dipolarity/polarisability, the  $a$  coefficient is a measure of the solvent hydrogen-bond basicity, and the  $b$  coefficient is a measure of the solvent hydrogen-bond acidity. The important  $l$  coefficient is a measure of the solvent lipophilicity, that is how near the solvent lipophilicity is to that of hexadecane for which  $l = 1$  by definition.

Values of  $\log L$  on the alcohols were obtained using all three methods above. Inorganic gas data were mostly from Battino *et al.*<sup>8</sup>, activity coefficients were from a variety of sources<sup>9</sup> and were combined with vapour pressure data given by Stephenson and Malinowski<sup>10</sup>, and solubilities used in method (iii) were from Acree *et al.*<sup>11</sup> and other sources<sup>12</sup>. Even with these various methods, we were restricted to 38 solutes in the case of heptan-1-ol.

Once values of  $L$  for gases and vapours have been obtained for a particular alcohol, they may be combined with the corresponding  $L^W$  values in water<sup>5,13</sup> at 298 K to give values for the partition between water and the (dry) alcohol, through Eq. (3):

$$L/L^W = P \quad \text{or} \quad \log L - \log L^W = \log P. \quad (3)$$

As we have shown before<sup>1-6</sup>, water-solvent  $\log P$  values are better correlated through the alternative solvation equation, Eq. (4):

$$\log P = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^H + vV_x, \quad (4)$$

where the final descriptor is the McGowan characteristic volume<sup>14</sup>,  $V_x$ .

Our aim is therefore to assemble enough values of  $\log L$  for gas-alcohol partitions and enough values of  $\log P$  for water-alcohol partitions to be able to apply Eqs (2) and (4) and hence to characterise the solubility behav-

four of aliphatic alcohols. We shall then be in a position to compare such behaviour with those of water and other solvents.

## RESULTS AND DISCUSSION

### *Gas-Alcohol Partitions*

For butan-1-ol we were able to assemble 92 values of  $\log L$ , covering a wide range of solutes. Application of Eq. (2) to the 92  $\log L$  values, denoted as  $\log L^{\text{BuOH}}$ , leads to the correlation equation:

$$\log L^{\text{BuOH}} = -0.039 - 0.276 R_2 + 0.539 \pi_2^{\text{H}} + 3.781 \Sigma\alpha_2^{\text{H}} + 0.995 \Sigma\beta_2^{\text{H}} + 0.934 \log L^{16}, \quad (5)$$

$n = 92$ ,  $r^2 = 0.9966$ , s.d. = 0.158,  $F = 5\,099$ .

Here,  $n$  is the number of data points (solutes),  $r$  is the correlation coefficient, s.d. is the standard deviation, and  $F$  is the  $F$ -statistic. The statistical fit of Eq. (5) is good, and suggests that the equation could be used to predict further values of  $\log L^{\text{BuOH}}$ . We shall discuss the coefficients in the regression equations for all the alcohols together.

In the case of pentan-1-ol, we still had a reasonable number of  $\log L^{\text{PeOH}}$  values, some 61 in all, leading to the equation:

$$\log L^{\text{PeOH}} = -0.042 - 0.277 R_2 + 0.526 \pi_2^{\text{H}} + 3.779 \Sigma\alpha_2^{\text{H}} + 0.983 \Sigma\beta_2^{\text{H}} + 0.932 \log L^{16}, \quad (6)$$

$n = 61$ ,  $r^2 = 0.9994$ , s.d. = 0.076,  $F = 19\,143$ .

However, for hexan-1-ol, heptan-1-ol, and decan-1-ol, we could obtain values for only 38–46 solutes:

$$\log L^{\text{HexOH}} = -0.035 - 0.298 R_2 + 0.626 \pi_2^{\text{H}} + 3.726 \Sigma\alpha_2^{\text{H}} + 0.729 \Sigma\beta_2^{\text{H}} + 0.936 \log L^{16}, \quad (7)$$

$n = 46$ ,  $r^2 = 0.9996$ , s.d. = 0.089,  $F = 18\,181$ .

$$\log L^{\text{HeptOH}} = -0.062 - 0.168 R_2 + 0.429 \pi_2^{\text{H}} + 3.541 \Sigma\alpha_2^{\text{H}} + 1.181 \Sigma\beta_2^{\text{H}} + 0.927 \log L^{16}, \quad (8)$$

$n = 38$ ,  $r^2 = 0.9998$ , s.d. = 0.067,  $F = 23\ 045$ .

$$\log L^{\text{DecOH}} = -0.136 - 0.068 R_2 + 0.325 \pi_2^{\text{H}} + 3.674 \Sigma\alpha_2^{\text{H}} + 0.767 \Sigma\beta_2^{\text{H}} + 0.947 \log L^{16}, \quad (9)$$

$n = 45$ ,  $r^2 = 0.9996$ , s.d. = 0.090,  $F = 15\ 984$ .

The statistics of Eqs (6)–(9) are all good, and these equations could be used to predict further  $\log L$  values to rather less than 0.1 log unit for solutes within the descriptor space used in setting up the correlation equations.

We can compare the coefficients in Eqs (6)–(9) with those we have obtained previously for the solution of gases and vapours in other alcohols<sup>1-4</sup>,

TABLE I  
Coefficients in the  $\log L$  equation for gas-solvent partitions at 298 K

| Solvent     | $c$    | $r$    | $s$   | $a$   | $b$   | $l$    | $n^a$ |
|-------------|--------|--------|-------|-------|-------|--------|-------|
| Water       | -1.271 | 0.822  | 2.743 | 3.904 | 4.814 | -0.213 | 392   |
| Methanol    | -0.004 | -0.215 | 1.173 | 3.701 | 1.432 | 0.769  | 93    |
| Ethanol     | 0.012  | -0.206 | 0.789 | 3.635 | 1.311 | 0.853  | 68    |
| Propan-1-ol | -0.028 | -0.185 | 0.648 | 4.022 | 1.043 | 0.869  | 77    |
| Butan-1-ol  | -0.039 | -0.276 | 0.539 | 3.781 | 0.995 | 0.934  | 92    |
| Pentan-1-ol | -0.042 | -0.277 | 0.526 | 3.779 | 0.983 | 0.932  | 61    |
| Hexan-1-ol  | -0.035 | -0.298 | 0.626 | 3.726 | 0.729 | 0.936  | 46    |
| Heptan-1-ol | -0.062 | -0.168 | 0.429 | 3.541 | 1.181 | 0.927  | 38    |
| Octan-1-ol  | -0.120 | -0.204 | 0.564 | 3.582 | 0.694 | 0.939  | 156   |
| Decan-1-ol  | -0.136 | -0.068 | 0.325 | 3.674 | 0.767 | 0.947  | 45    |
| Chloroform  | 0.116  | -0.467 | 1.203 | 0.138 | 1.432 | 0.994  | 134   |
| DMF         | -0.161 | -0.189 | 2.327 | 4.756 | 0.000 | 0.808  | 72    |

<sup>a</sup> Number of compounds in the correlation equation.

and also in water<sup>5</sup>, see Table I. From methanol to decan-1-ol, there is little change in either the constant term or the  $r$  coefficient. The  $s$  coefficient gets slightly smaller as the carbon number increases, with the value for octan-1-ol rather out-of-line. The  $a$  coefficient, a measure of the solvent hydrogen-bond basicity, is almost constant amongst all the alcohols, at  $3.715 \pm 0.142$ ; including water, the average value is  $3.734 \pm 0.146$ . This is quite remarkable, considering that the fraction of OH groups decreases very considerably from methanol to decan-1-ol, and decreases even more from water to decan-1-ol. There is a gradual decline in the  $b$  coefficient from methanol to decan-1-ol, but the value for heptan-1-ol is out-of-line. The  $l$  coefficients increase with increase in the alkyl chain, and there is a reasonable plot (not given) of the  $l$  coefficient vs the Hildebrand cohesive energy density, CED, again as expected. Thus the coefficients in Eq. (2) for solubility of gases and vapours in the alkan-1-ols fall into a reasonably coherent pattern. One or two coefficients are out-of-line, but this is probably due to different sets of solutes being used in the various equations.

All the alkan-1-ols are characterised as having moderate-to-weak dipolarity/polarisability, very considerable hydrogen-bond basicity and moderate hydrogen-bond acidity. The  $l$  coefficients indicate that the behaviour of the alcohols towards nonpolar solutes is no different to the behaviour of standard aprotic organic solvents. Coefficients in Eq. (2) for the common organic solvents chloroform<sup>15</sup> and *N,N*-dimethylformamide<sup>16</sup>, DMF, are in Table I for comparison.

We can show how the various solute-solvent interactions contribute towards the overall solubility of a gaseous solute through a term-by-term analysis of the various solvation equations. Details are in Table II for solution in water, ethanol, decan-1-ol, and DMF. There are two peculiarities of water as a solvent that should be noted: the  $c$  constant is very much more negative than for any nonaqueous solvent, and the  $l$  coefficient is negative. These are probably a consequence of the cavity effects in water, and result in very low solubilities for any hydrophobic solute.

Thus the hydrophobic solutes, ethane and octane, are poorly soluble in water, but much more soluble in the three nonaqueous solvents. The alcohols behave quite similarly to aprotic nonaqueous solvents as regards solvation of hydrophobic solutes. For acetic acid, which is polar, and is both a hydrogen-bond acid and a hydrogen-bond base, the three polar terms ( $s\pi_2^H$ ,  $a\Sigma\alpha_2^H$ , and  $b\Sigma\beta_2^H$ ) are all very positive and considerably aid solution in water. However the  $l \log L^{16}$  term and the constant term are both negative, with the result that the total  $\log L$  value in water is hardly greater than that in ethanol, and only 0.56 log units greater than in decan-1-ol. In the basic

solvent, DMF, the  $a\Sigma\alpha_2^H$  term is very large and so is the  $\pi\pi_2^H$  term, leading to a very large calculated  $\log L$  value indeed. The  $l \log L^{16}$  term and the constant term again play a part in the solution of trimethylamine in water: the  $b\Sigma\beta_2^H$  term is due to interaction between the solute strong hydrogen-bond base and the solvent strong hydrogen-bond acid, and so is very large. But

TABLE II  
A term-by-term analysis of solvation of gaseous solutes at 298 K

|                                   | $rR_2$ | $\pi\pi_2^H$ | $a\Sigma\alpha_2^H$ | $b\Sigma\beta_2^H$ | $l \log L^{16}$ | Total             |       |
|-----------------------------------|--------|--------------|---------------------|--------------------|-----------------|-------------------|-------|
|                                   |        |              |                     |                    |                 | calc <sup>a</sup> | obs   |
| Solvent water                     |        |              |                     |                    |                 |                   |       |
| Ethane                            | 0.00   | 0.00         | 0.00                | 0.00               | -0.10           | -1.37             | -1.34 |
| Octane                            | 0.00   | 0.00         | 0.00                | 0.00               | -0.78           | -2.05             | -2.11 |
| CH <sub>3</sub> CO <sub>2</sub> H | 0.22   | 1.78         | 2.38                | 2.11               | -0.37           | 4.85              | 4.91  |
| Me <sub>3</sub> N                 | 0.11   | 0.55         | 0.00                | 3.22               | -0.35           | 2.26              | 2.35  |
| Solvent ethanol                   |        |              |                     |                    |                 |                   |       |
| Ethane                            | 0.00   | 0.00         | 0.00                | 0.00               | 0.42            | 0.43              | 0.44  |
| Octane                            | 0.00   | 0.00         | 0.00                | 0.00               | 3.14            | 3.15              | 3.17  |
| CH <sub>3</sub> CO <sub>2</sub> H | -0.06  | 0.52         | 2.22                | 0.55               | 1.49            | 4.74              | -     |
| Me <sub>3</sub> N                 | -0.03  | 0.16         | 0.00                | 0.87               | 1.38            | 2.37              | 2.67  |
| Solvent decanol                   |        |              |                     |                    |                 |                   |       |
| Ethane                            | 0.00   | 0.00         | 0.00                | 0.00               | 0.47            | 0.33              | -     |
| Octane                            | 0.00   | 0.00         | 0.00                | 0.00               | 3.48            | 3.35              | 3.30  |
| CH <sub>3</sub> CO <sub>2</sub> H | -0.02  | 0.21         | 2.24                | 0.34               | 1.66            | 4.29              | -     |
| Me <sub>3</sub> N                 | -0.01  | 0.07         | 0.00                | 0.51               | 1.53            | 1.96              | -     |
| Solvent DMF                       |        |              |                     |                    |                 |                   |       |
| Ethane                            | 0.00   | 0.00         | 0.00                | 0.00               | 0.40            | 0.24              | 0.22  |
| Octane                            | 0.00   | 0.00         | 0.00                | 0.00               | 2.97            | 2.81              | 2.81  |
| CH <sub>3</sub> CO <sub>2</sub> H | -0.05  | 1.51         | 2.90                | 0.00               | 1.41            | 5.61              | -     |
| Me <sub>3</sub> N                 | -0.03  | 0.46         | 0.00                | 0.00               | 1.31            | 1.58              | 1.77  |

<sup>a</sup> Includes the intercept term of -1.27 (water), 0.01 (ethanol), -0.14 (decan-1-ol), and -0.16 (DMF). The total refers to the sum of all the terms, including the intercept.

because of the unfavourable  $l \log L^{16}$  and constant term, the total  $\log L$  value is smaller than that in ethanol, where the  $b\Sigma\beta_2^H$  term is much less. All-in-all, the solvation of solutes in the alcohols more resembles solvation in nonaqueous polar solvents than solvation in water.

The one great oddity in the results shown in Table I, is the almost identical hydrogen-bond basicity of the alcohols and water (as shown by the  $a$  coefficient). We have commented on the similar hydrogen-bond basicity of the lower alkan-1-ols and water, before<sup>1-4</sup>, and have shown that this similarity is quite contrary to other measures of solvent hydrogen-bond basicity such as the Kamlet-Taft solvatochromic parameter<sup>17</sup>,  $\beta$ . We have little to add to our previous discussion except to point out that the present method does yield very consistent results for all the alkan-1-ols from methanol to decan-1-ol.

### *Water-Alcohol Partitions*

Having assembled the  $\log L$  values for solutes in the alkanol solvents, we can use Eq. (3) to calculate the corresponding partition coefficients from water to the dry alkanols, and then apply our alternative solvation equation, Eq. (4) to the  $\log P$  values. Although these  $\log P$  values are for the hypothetical partition from pure water to the pure alkanol, they are useful in a number of ways, (i) they provide another measure of the solubility properties of the alkanols, this time with reference to water, (ii) they can be compared to practical partitions from water to water-saturated alkanols, and (iii) they are very useful in the correlation and prediction of solubilities of solids<sup>18</sup>.

A summary of the correlation equations with  $\log P$  as the dependent variable is given in Table III. The statistical fits of the  $\log P$  equations are always worse than those of the corresponding  $\log L$  equations. This is as expected, because most of the  $\log P$  values have been obtained through Eq. (3) which introduces an additional experimental error in the  $\log L^W$  values. However, the correlation equations are reasonably self-consistent. In particular, they all confirm our conclusion, above, as to the hydrogen-bond basicity of the alkanols: the  $a$  coefficient, which is a measure of the difference in hydrogen-bond basicity of the alkanol and water, is very close to zero. Thus, again, the hydrogen-bond basicity of the alkan-1-ols is shown to be essentially constant from methanol to decan-1-ol, and to be very nearly the same as that of solvent water. The other coefficients shown in Table III can be interpreted on exactly the same lines as the coefficients in the  $\log L$  equations.



It is of some consequence to ascertain the effect of water on the solubility properties of the alkan-1-ols. We have previously obtained correlation equations for  $\log P$  values in the practical partitions between water and a number of the higher alkan-1-ols<sup>19</sup>. These practical partitions refer to partition between water saturated with the alkanol and the alkanol saturated with water. The solubility of the higher alkanols in water is comparatively small, and so differences in partition between water and dry alkanols, and practical partition will very largely be due to the water in the water-saturated alkanol. In Fig. 1 we plot coefficients for the water-dry alkanol partitions shown in Table III, and for the practical partitions we have previously studied, against the carbon number,  $N$ , of the alkan-1-ols. For convenience we take water as having  $N = 0$ , but this does not affect the general conclusions as regards wet and dry alkanols. It is very clear that as the carbon number increases, the coefficients for the water-dry alkanol partitions approach those for the water-wet alkanol partitions. Indeed for partitions into decan-1-ol, the two sets of coefficients are statistically indistinguishable. Thus for the various solutes used to construct the solvation equations, the solvation properties of dry decan-1-ol and wet decan-1-ol are practically the same.

Most of the previous studies on the solvation properties of wet and dry alkan-1-ols refer to octan-1-ol, which has been extensively investigated by Cabani *et al.*<sup>20</sup> and by Dallas and Carr<sup>21</sup>. The former workers found differ-

TABLE III  
Coefficients in the  $\log P$  equation for water-(dry) solvent partitions

| Solvent     | $c$    | $r$   | $s$    | $a$    | $b$    | $v$   | $n$ | $r^2$  | s.d.  | $F$   |
|-------------|--------|-------|--------|--------|--------|-------|-----|--------|-------|-------|
| Methanol    | 0.329  | 0.299 | -0.671 | 0.080  | -3.389 | 3.512 | 93  | 0.9880 | 0.160 | 1 440 |
| Ethanol     | 0.208  | 0.409 | -0.959 | 0.186  | -3.645 | 3.928 | 64  | 0.9809 | 0.170 | 1 205 |
| Propan-1-ol | 0.149  | 0.436 | -1.098 | 0.389  | -3.893 | 4.036 | 76  | 0.9952 | 0.130 | 2 892 |
| Butan-1-ol  | 0.153  | 0.438 | -1.177 | 0.096  | -3.919 | 4.122 | 88  | 0.9940 | 0.125 | 2 719 |
| Pentan-1-ol | 0.080  | 0.521 | -1.294 | 0.208  | -3.908 | 4.208 | 59  | 0.9960 | 0.112 | 2 597 |
| Hexan-1-ol  | 0.044  | 0.470 | -1.153 | 0.083  | -4.057 | 4.249 | 46  | 0.9978 | 0.114 | 3 775 |
| Heptan-1-ol | -0.026 | 0.491 | -1.258 | 0.035  | -4.155 | 4.415 | 38  | 0.9972 | 0.081 | 2 333 |
| Octan-1-ol  | -0.034 | 0.489 | -1.044 | -0.024 | -4.235 | 4.218 | 153 | 0.9933 | 0.144 | 4 362 |
| Decan-1-ol  | -0.062 | 0.754 | -1.461 | 0.063  | -4.053 | 4.293 | 45  | 0.9980 | 0.123 | 3 843 |

ences up to 0.79 log units for partition into wet and dry octan-1-ol, but in the work of Dallas and Carr the maximum difference was only 0.13 log units. More recently, Kristl and Vesnaver<sup>22</sup> have shown that the solubility ratio of a number of drug molecules between water and dry octan-1-ol and between octanol-saturated water and water-saturated octanol could be as large as 0.99 log units. However, the solubility ratio method will yield consistent results only if the same solid phase is in equilibrium with the various solvents under study. The conclusion seems to be that solvation in wet and dry octan-1-ol is generally quite similar, but that there may be specific instances where this is not so. Indeed, it might be expected that solutes with very hydrophilic functional groups might complex with the water in water-saturated octan-1-ol and bring about a decrease in the standard Gibbs energy. From our studies, we suggest that water and octan-1-ol have similar hydrogen-bond basicities, so it is unlikely that a solute with an acidic functional group will preferentially complex with the water in water-saturated octan-1-ol. But the hydrogen-bond acidity of water is very much greater than that of octan-1-ol (see the  $b$  coefficients in Table I), so that functional groups that are strong hydrogen-bond bases might complex preferentially with water in the water-saturated octan-1-ol.

Kristl<sup>23</sup> also found very different solubility ratios for drug molecules in the other dry and wet alkanols, heptan-1-ol and nonan-1-ol. Whether these ratios are due to complexation with the water in the water-saturated

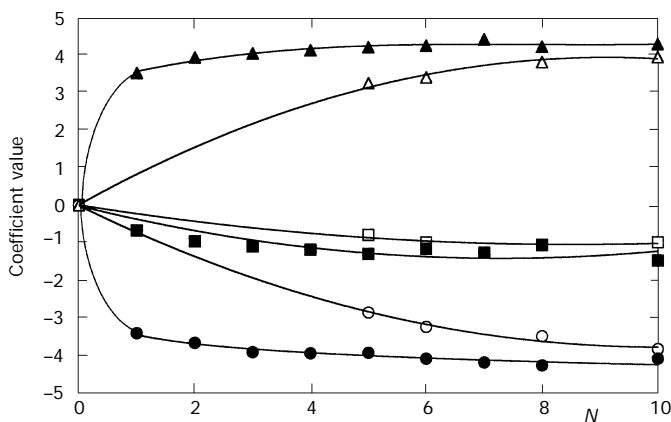


FIG. 1

Plot of the coefficients in Eq. (4) for partitions between water and dry alkanols,  $N = 1-10$ , and for partitions between water and wet alkanols,  $N = 5-10$ , against the carbon number of the alcohol: ■  $s$  coefficient, ●  $b$  coefficient, ▲  $v$  coefficient. Closed symbols are for the dry alkanols, open symbols are for the wet alkanols

alkan-1-ols, or to solvate (or hydrate) formation, or to both, is not really known. If they are due to complexation, then this work of Kristl will illustrate again that there is always a possibility that certain compounds will be solvated differently in wet alkan-1-ols than in dry alkan-1-ols.

The two solvation equations, Eqs (2) and (4) both contain descriptors that refer to solute size. The  $\log L^{16}$  descriptor is related to solute size, and the  $V_x$  descriptor is obviously a measure of solute size. However, neither of the equations contains any descriptor that refers to the solute shape. The set of solutes we have considered includes molecules of quite different shape, for example spherical molecules such as helium and sulfur hexafluoride, long chain alkanes and alkan-1-ols, and a variety of other shaped compounds including diisopropyl ether, benzene, pyrene, diuron, and diphenyl sulfone. Thus, effects due to solute shape in the simple transport processes we have considered seem to be relatively small. This has also been found for the solvation of conformational isomers by organic solvents<sup>24</sup>, and for the solvation of structural isomers by hexadecane and olive oil<sup>7</sup>. In the latter work, the solvation of the three dimethoxybenzenes or the three dimethylbenzenes or the *cis/trans* isomers of 1,2-dichloroethene are essentially the same. We suggest, therefore, that predictions of gas-solvent and water-solvent partitions through Eqs (2) and (4) should be valid for any compound that is within the descriptor space used to set up the correlations provided, possibly, that the compound is not of a very unusual shape.

## CONCLUSIONS

The two general solvation equations we have used, through Eqs (2) and (4) can be applied very successfully to the correlation of gas-alkanol and water-alkanol partition coefficients. The correlation equations are useful as regards prediction of further  $\log L$  and  $\log P$  values, but are also of value in the understanding of the solvation properties of the alkan-1-ols, and how these properties compare to other solvent systems. Our general conclusions are that solvation in the alkan-1-ols is not different in principle to solvation in polar aprotic solvents, bearing in mind that the alkan-1-ol solvents are quite strong hydrogen-bond bases but are not very strong hydrogen-bond acids.

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