

# Partition of solutes from the gas phase and from water to wet and dry di-*n*-butyl ether: a linear free energy relationship analysis†

Michael H. Abraham,\*<sup>a</sup> Andreas M. Zissimos<sup>a</sup> and William E. Acree, Jr.<sup>b</sup>

<sup>a</sup> Department of Chemistry, University College London, 20 Gordon Street, London, UK  
WC1H 0AJ

<sup>b</sup> Department of Chemistry, University of North Texas, Denton, TX 76203-0068, USA

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From literature data and from our own measurements, we have compiled a database of partition coefficients of non-electrolytes from water to wet di-*n*-butyl ether (DBE) and dry DBE, and from the gas phase to wet DBE and to dry DBE. Application of the general linear free energy relationship solvation equations shows that there are small, but significant, differences in the solvation behaviour of wet and dry DBE. In particular, the partition of acidic solutes into wet DBE is favoured over partition into dry DBE. An analysis based on the water-dragging effect of Testa *et al.* (*J. Am. Chem. Soc.*, 1993, **115**, 963) accounts quantitatively for this difference, which is shown to be due to complexation between acidic solutes and water acting as hydrogen bond base. It is suggested that even minute quantities of water may influence the solvation behaviour of non-polar solvents towards specific classes of solute.

## Introduction

The partition of solutes into wet and dry alkan-1-ols has been studied in some detail.<sup>1–4</sup> There are considerable differences in solubility properties between the wet and dry solvents for the lower alkan-1-ols, but these differences become smaller along the homologous series and are very small indeed for alkan-1-ols above decan-1-ol. No other solvent seems to have been investigated in this way in any detail, and for most solvents that dissolve only small quantities of water it is usually assumed that the dry and wet solvent can be taken as equivalent. Thus for di-*n*-butyl ether (DBE) two sets of workers<sup>5,6</sup> have analysed partition from water and have used partition into dry DBE and partition into wet DBE interchangeably. This is understandable in view of the small solubility of water in DBE, being<sup>7</sup> 0.0136 mol fraction (0.080 mol dm<sup>-3</sup>) or<sup>8</sup> 0.0108 mol fraction (0.064 mol dm<sup>-3</sup>).

However, the situation seems not to be so simple, because various workers<sup>8–10</sup> have reported on a 'water-dragging effect'. When solutes partition between water and DBE, the solubility of water in DBE is increased. Testa *et al.*<sup>8,9</sup> investigated this phenomenon in some detail and determined the increase in the quantity of water dissolved when various solutes were partitioned. From the amount of water dragged into DBE by solutes, Testa *et al.*<sup>9</sup> were able to determine 1 : 1 hydrogen bond complexation constants of water with a large number of solutes. They found that these constants were usually much larger for acidic solutes that complexed with water acting as a hydrogen bond base than for basic solutes that complexed with water acting as a hydrogen bond acid, although the reasons for this were not clear.

Since solutes are clearly capable of increasing the amount of water in DBE when partitioned between water and wet DBE, it seems possible that partition between water and wet DBE is not equivalent to partition between water and dry DBE. The purpose of the present study was to collect data on partition

between water and wet and dry DBE in an attempt to deduce the solubility properties of wet and dry DBE using linear free energy relationships (LFERs). Partitions between the gas phase and wet and dry DBE were also studied by the same method.

## Methodology

The data to be analysed are those on partition from water to wet and dry DBE, *P*, and from the gas phase to wet and dry DBE, *K*, all in the form of log *P*(*K*) values as the dependent variable, where *P* (or *K*) is the partition coefficient. It is useful to construct correlation equations in which the independent variables are similar in form to the dependent variable, that is free energy related. We have already set out<sup>11,12</sup> two such general equations; in the more recent terminology the equations are:<sup>12</sup>

$$SP = c + e.E + s.S + a.A + b.B + v.V \quad (1)$$

$$SP = c + e.E + s.S + a.A + b.B + l.L \quad (2)$$

In these equations, the dependent variable is a set of solute properties in a given system. Eqn. (1) is used for processes in condensed systems; in the present case *SP* will be log *P* for partition between water and DBE, log *P*<sup>DBE</sup>, defined through eqn. (3) where it is understood that for ionisable solutes, the concentrations refer to the unionised species

$$P = [\text{conc. of solute in DBE}]/[\text{conc. of solute in water}] \quad (3)$$

Eqn. (2) is used for gas-condensed phase processes, such as gas–water partition coefficients (equivalent to Ostwald solubility coefficients), defined through eqn. (4). If concentrations in the gas phase and solution phase are in the same units, then *K* is a dimensionless quantity; again, for ionisable solutes the concentration in water refers to that for the unionised species.

$$K = [\text{conc. of solute in DBE}]/[\text{conc. of solute in the gas phase}] \quad (4)$$

† Electronic Supplementary Information available. See <http://www.rsc.org/suppdata/cp/b1/b104682a/>

The independent variables in eqn. (1) and (2) are solute descriptors as follows.<sup>11</sup>  $E$  is the solute excess molar refractivity,  $S$  is the solute dipolarity/polarizability,  $A$  and  $B$  are the overall or summation hydrogen bond acidity and basicity,  $V$  is the McGowan characteristic volume in units of (mol dm<sup>-3</sup>)/100, and  $L$  is the logarithm of the gas-hexadecane partition coefficient. The coefficients in eqn. (1) and eqn. (2) are evaluated through multiple linear regression analysis. DBE in eqn. (3) and (4) may be either pure di-*n*-butyl ether (dry DBE) or di-*n*-butyl ether saturated with water (wet DBE). The methods used to obtain values of  $P$  and  $K$  differ markedly for partition into the dry and wet DBE. For wet DBE, the prime experimental procedure is to determine values of  $P$  through the traditional 'shake-flask' method; values of  $P^{\text{WDBE}}$ , as we shall refer to them, have been collected by Leo,<sup>13</sup> and also determined by Testa *et al.*<sup>5</sup> These  $P^{\text{WDBE}}$  values may be combined with gas-water partition coefficients,<sup>14,15</sup>  $K^{\text{W}}$ , through eqn. (5) to obtain  $K^{\text{WDBE}}$  values for partition from the gas phase to wet DBE:

$$P^{\text{WDBE}} = K^{\text{WDBE}}/K^{\text{W}} \quad (5)$$

The only values for wet DBE not obtained by this procedure were those for hydrogen, oxygen and nitrogen. In order to have more equivalent sets of data in wet and dry DBE, we estimated values of  $\log K^{\text{WDBE}}$  for these solutes from data on dry DBE, using the empirical eqn. (6), where  $X$  is the mole fraction concentration of water in the wet solvent.<sup>16</sup>

$$\log K^{\text{W, Solv}} = \log K^{\text{D, Solv}} - 0.487X \quad (6)$$

The partition data on wet DBE that we have assembled<sup>5,13</sup> are collected in Table S1†.

Partition into dry DBE is more complicated, because there is more than one prime procedure. Values of  $\log K^{\text{DDBE}}$  can be obtained by a variety of methods, including direct measurement, and calculation from infinite dilution activity coefficients,

corrected where necessary to 298 K. Once these values are known, the corresponding values of  $\log P^{\text{DDBE}}$  can be obtained through eqn. (7):

$$P^{\text{DDBE}} = K^{\text{DDBE}}/K^{\text{W}} \quad (7)$$

This procedure is restricted to solutes that are reasonably volatile; details of the calculations are in Table S2.† For less volatile solutes, it is possible to obtain values of  $P^{\text{DDBE}}$  through the ratio of solubilities in dry DBE and water,  $S_{\text{DDBE}}$  and  $S_{\text{W}}$ , provided that certain conditions are fulfilled. Once  $P^{\text{DDBE}}$  values are available in this way, the corresponding values of  $K^{\text{DDBE}}$  can be obtained through eqn. (7) or by use of the saturated vapour concentration,  $C_{\text{G}}$ . The calculation of  $P^{\text{DDBE}}$  through solubility measurements is in Table S3,† and the entire data set on dry DBE is in Table S4.†

## Results and discussion

### LFER analysis

We have assembled partition coefficients for transfer from water and the gas phase to dry DBE for 59 solutes, and for the corresponding transfers to wet DBE for 88 solutes. Application of eqn. (1) to the  $\log P$  values yields the equations summarised in Table 1 and application of eqn. (2) to the  $\log K$  values results in the equations given in Table 2. In Tables 1 and 2,  $N$  is the number of data points (*i.e.*, solutes),  $R$  is the correlation coefficient, SD is the correlation standard deviation, and  $F$  is the  $F$ -statistic; the SD values of the coefficients are given beneath the respective coefficients. The correlation statistics are reasonably good with values of  $R^2$  from 0.953 to 0.997, and SD values from 0.17 to 0.32. Note that we have fewer solutes for the equations in  $\log K$ , because we were missing a number of  $\log K^{\text{W}}$  values that were needed to calculate the  $\log K^{\text{WDBE}}$  values.

Inspection of Tables 1 and 2 shows that there are several marked differences between the equations that relate to wet

**Table 1** Equations for transfer from water to wet and dry DBE, based on eqn. (1)

DBE	$c$	$e$	$s$	$a$	$b$	$v$	$N$	$R^2$	SD	$F$
Wet	0.252	0.677	-1.506	-0.807	-5.249	4.815	87	0.953	0.31	329
	0.141	0.153	0.144	0.118	0.190	0.201				
Dry	0.203	0.369	-0.954	-1.488	-5.426	4.508	59	0.995	0.18	2150
	0.058	0.071	0.104	0.121	0.135	0.054				
Wet	0.349	0.717	-1.240	-0.964	-5.385	4.516	38	0.963	0.29	168
	0.152	0.185	0.193	0.173	0.268	0.283				
Dry	0.215	0.359	-0.886	-1.523	-5.516	4.486	38	0.990	0.19	606
	0.079	0.107	0.119	0.144	0.180	0.139				
Wet	0.389	0.600	-1.558	-0.869	-5.252	4.777	48	0.958	0.32	190
	0.197	0.194	0.193	0.161	0.270	0.255				
Dry	0.221	0.389	-0.977	-1.485	-5.373	4.483	48	0.994	0.20	1299
	0.081	0.087	0.123	0.137	0.159	0.087				

**Table 2** Equations for transfer from the gas phase to wet and dry DBE, based on eqn. (2)

System	$c$	$e$	$s$	$a$	$b$	$l$	$N$	$R^2$	SD	$F$
Gas/wet	0.369	-0.216	0.026	2.626	-0.499	1.124	83	0.983	0.294	907
	0.110	0.189	0.159	0.114	0.195	0.053				
Gas/dry	0.165	-0.421	0.760	2.102	-0.664	1.002	58	0.997	0.172	3458
	0.047	0.079	0.101	0.118	0.128	0.014				
Gas/wet	0.395	-0.061	0.127	2.565	-0.594	1.083	37	0.991	0.276	676
	0.122	0.213	0.221	0.163	0.255	0.068				
Gas/dry	0.191	-0.269	0.758	2.024	-0.732	0.985	37	0.996	0.199	1607
	0.068	0.186	0.147	0.148	0.195	0.040				
Gas/wet	0.420	-0.296	0.075	2.616	-0.632	1.127	44	0.983	0.299	439
	0.157	0.239	0.211	0.156	0.276	0.068				
Gas/dry	0.175	-0.435	0.826	2.071	-0.645	0.989	47	0.996	0.177	2234
	0.061	0.097	0.117	0.127	0.142	0.021				

and dry DBE. Thus in Table 1, the  $s$ -coefficient in eqn. (1) is markedly more negative for the wet solvent but the  $a$ - and  $v$ -coefficients are more positive. Exactly the same trend is seen for the coefficients in eqn. (2), with the  $l$ -coefficient now more positive for the wet solvent, see Table 2. However, before analysing such differences further, it is obligatory to check how representative are the two different data sets. Of course, it is not feasible to ascertain if one or another is a representative set, over all the possible compounds that might comprise a data set, but it is useful to check one set against another, and to note whether or not the descriptors in the sets cover a reasonable range. In the event, it became clear that the two data sets were not at all comparable, largely due to the different experimental methods used. As an example, we give in Fig. 1 histograms of the distribution of the  $A$ -descriptor, for both the 87 compound wet data set and the 59 compound dry data set. The wet data set contains far more compounds with large  $A$ -descriptors, and such a disparity could bias the correlations. We therefore sought to select sub-sets that had comparable distributions of all the descriptors, not just the  $A$ -descriptor, as follows. We first carried out a principal components analysis (PCA) of the descriptors in the combined two sets. The first two PCs contained about 87% of the total information, and we then plotted PC2 against PC1. On the scatter plot we identified points corresponding to the wet set and the dry set and chose pairs of points that occupied the same or nearly the same area on the plot. In this way we selected two sub-sets, each of 38 compounds, that then gave rise to more comparable histograms, as shown in Fig. 1 for the  $A$ -descriptor. We are grateful to Dr Alain Calvet who kindly used the software package DiVerse Solutions, written by Dr R. Pearlman, to select comparable sub-sets of 48 compounds;

the histogram for the  $A$ -descriptor for these sets is shown in Fig. 1.

Application of eqn. (1) and eqn. (2) to the  $\log P$  and  $\log K$  values in the 38 and 48 compound sub-sets resulted in equations summarised in Tables 1 and 2. For the 38 compound sub-sets in Table 1, the only coefficients that are now significantly different between the two sub-sets (that is, the difference is larger than the sum of the SD values of the coefficients) are the  $s$ -coefficient that is more negative for the wet solvent, and the  $a$ -coefficient that is more positive for the wet solvent. This is true also for the 48 compound sub-sets, but now the  $v$ -coefficient is more positive for the wet solvent. Very similar conclusions are reached by examination of the equations for  $\log K$  in Table 2. For our sub-sets (now for 37 compounds), the  $s$ -coefficient is more negative, the  $a$ -coefficient more positive and the  $l$ -coefficient more positive (just) for the wet solvent. Exactly the same pattern is shown by the Calvet set (now 44 or 47 solutes), but the  $l$ -coefficient is definitely more positive for transfer to the wet solvent.

Thus even when matched sub-sets are compared, the general conclusion is that there are differences between transfer into wet DBE and transfer into dry DBE. The differences are not large, and if data for wet and dry DBE were combined, it would not be very obvious that the solvation properties of the wet and dry solvent were not the same.

Even though the solvation properties of wet and dry DBE are not very different, it is not obvious why there are differences, considering the very small quantity of water required for saturating DBE.<sup>7,8</sup> Some comparisons of coefficients in eqn. (1) for alcohols that contain various quantities of water at saturation are shown in Table 3. The differences in coefficients for wet and dry alkan-1-ols become small for the higher

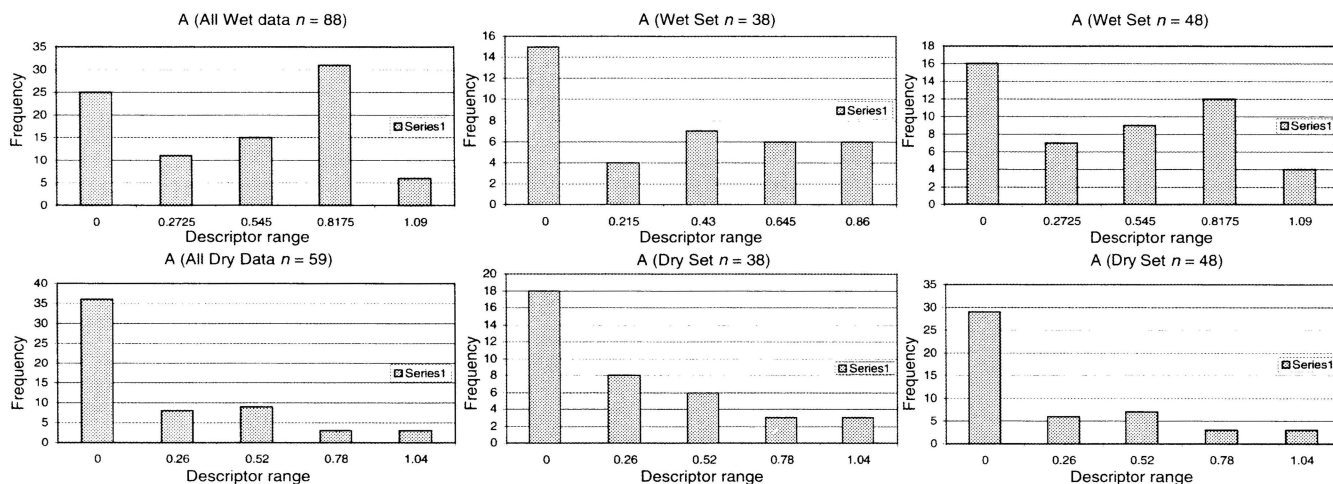


Fig. 1 Histograms showing the distribution of the  $A$ -descriptor, for all wet and dry training sets, each containing different numbers of data points (all data, 38 and 48 data points), used in this study.

Table 3 Coefficients for eqn. (1) in wet and dry alkan-1-ols

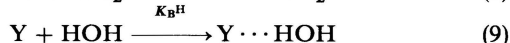
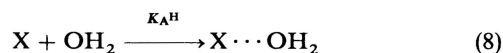
System	$c$	$e$	$s$	$a$	$b$	$v$	Water, $X^a$
Wet pentanol	0.175	0.575	-0.787	0.020	-2.837	3.249	0.326
Dry pentanol	0.080	0.521	-1.294	0.208	-3.908	4.208	
Wet hexanol	0.143	0.718	-0.980	0.145	-3.214	3.403	0.299
Dry hexanol	0.044	0.470	-1.153	0.083	-4.057	4.249	
Wet octanol	0.088	0.562	-1.054	0.034	-3.460	3.814	0.258
Dry octanol	-0.034	0.489	-1.044	-0.024	-4.235	4.218	
Wet decanol	0.008	0.485	-0.974	0.015	-3.798	3.945	0.247
Dry decanol	-0.062	0.754	-1.461	0.063	-4.053	4.293	

<sup>a</sup> Mole fraction water in the wet alkanol.

alkan-1-ols, even though the aqueous solubility is rather high. Thus the solubility of water in decan-1-ol (Table 3) is 0.247 mol fraction, or 1.29 mol dm<sup>-3</sup>, some 20 times that of the solubility of water in DBE. The different solubility properties of wet and dry DBE are therefore more likely to be due to specific effects of water, rather than to an alteration in the general properties of the solvent.

### The water dragging effect

One possible specific effect is the 'water-dragging' phenomenon, that was used by Testa *et al.*<sup>9</sup> to calculate the 1 : 1 hydrogen bond complexation constants in DBE for a solute with water, eqn. (8) where X is a solute that is a hydrogen bond acid, or eqn. (9) where Y is a solute that is a hydrogen bond base. The complexation constants are as defined before.<sup>41,42</sup>



If the solute has two functional groups, then the observed complexation constant, *K*, is the sum of the two individual constants.<sup>43,44</sup> Thus for a solute XC<sub>6</sub>H<sub>4</sub>Y,  $K = (K_A^H + K_B^H)$ . For 1 : 1 complexation in tetrachloromethane,<sup>45</sup> a very simple equation relates the complexation constant to the hydrogen bond acidity,  $\alpha_2^H$ , and hydrogen bond basicity,  $\beta_2^H$ , of the two solutes undergoing complexation:

$$\log K \text{ (in CCl}_4\text{)} = 7.354\alpha_2^H \times \beta_2^H - 1.094 \quad (10)$$

Similar equations have been constructed for complexation in other solvents,<sup>46,47</sup> and from variation of the slopes and intercepts with solvent, an estimate for those for complexation in DBE has been deduced:<sup>47</sup>

$$\log K \text{ (in DBE)} = 6.58\alpha_2^H \times \beta_2^H - 0.78 \quad (11)$$

Then taking<sup>41,42</sup>  $\alpha_2^H$  for water as 0.313 and  $\beta_2^H$  for water as 0.38, together with the values of  $\alpha_2^H$  and  $\beta_2^H$  for the various solutes,<sup>41,42</sup> we can calculate log *K* from eqn. (11); we denote these calculated values as log *K*<sub>calc</sub>. We can also estimate log *K*<sub>calc</sub> for solutes with two functional groups, as outlined above. In this way we could obtain log *K*<sub>calc</sub> values for 39 solutes out of the 56 studied. A plot of log *K* (in DBE) vs. log *K*<sub>calc</sub> (not shown) is reasonable but solutes with large  $\beta_2^H$  values are strong outliers (PhCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, PhSOMe and pyridine). These can be brought into line if  $\alpha_2^H$  for water is taken as 0.23, rather than 0.313 as before. This results in a good correlation, eqn. (12), with no outliers at all.

$$\log K \text{ (in DBE)} = 0.100 + 0.937 \log K_{\text{calc}} \quad (12)$$

$N = 39, \text{SD} = 0.17, r^2 = 0.874, F = 257$

Considering the approximations used, and the experimental error in log *K* (in DBE), 0.1 unit,<sup>9</sup> the goodness-of-fit of eqn. (12) is remarkable. That  $\alpha_2^H$  for water should be less in DBE than in solvents such as tetrachloromethane is chemically not unreasonable, because we might expect water to be itself hydrogen bonded to the very large excess of DBE molecules, as in Bu<sub>2</sub>O ··· H–O–H ··· OBu<sub>2</sub>, thus reducing the propensity of water to hydrogen bond to external bases.

Testa *et al.*<sup>8,9</sup> suggested that the water-dragging effect was dominated by the hydrogen bond acidity of solutes, although hydrogen bond basicity was also important. Our analysis through the calculation of complexation constants supports this view completely. There are two main reasons why hydrogen bond acids appear more effective. Firstly,  $\beta_2^H$  for water (0.38) is larger than  $\alpha_2^H$  for water (0.31 or 0.23) so that the factor  $6.58 \times \beta_2^H$  (2.50) is significantly larger than  $6.58 \times \alpha_2^H$  (2.04 or 1.51). Secondly, most of the functionalities studied by Testa *et al.*<sup>9</sup> have much larger hydrogen bond acidities than basicities. The result of these two effects can be seen in Table

**Table 4** Calculations of log *K* (in DBE) for 1 : 1 complexation in DBE by water acting as an acid and as a base

X	Y	$\alpha_2^H$	$\beta_2^H$	$K_A^H$	$K_B^H$	log <i>K</i> <sub>calc</sub>	log <i>K</i> <sub>obs</sub>
<i>m</i> -OH	CHO	0.720	0.415	10.47	0.70	1.05	1.0
<i>p</i> -OH	OMe	0.573	0.430	4.49	0.74	0.72	0.7
<i>p</i> -OH	CN	0.787	0.270	15.40	0.42	1.20	1.2
<i>m</i> -OH	NO <sub>2</sub>	0.785	0.210	15.22	0.34	1.19	1.4

4, where we calculate the complexation constants for compounds with two functional groups.

From our LFER analyses, there is a large effect of water on the *a*-coefficient, commensurate with the large  $K_A^H$  complexation constants and a negligible effect on the *b*-coefficient, commensurate with small  $K_B^H$  complexation constants. Thus the results of our LFER analysis agree completely with the findings of Testa *et al.*<sup>9</sup> on the water-dragging effect.

### General discussion

Both the LFER analysis and our calculation of complexation constants show that the very small amount of water in wet DBE has a considerable effect on partition of species that are hydrogen bond acids but less on the partition of hydrogen bond bases. Some calculations to illustrate this are in Table 5. Although we use equations with *N* = 38 (Table 1) for direct comparison in Table 5, we suggest that in general it is better to use the equations with the largest number of data points. That is the equations with *N* = 87 and 59 (Table 1) and equations with *N* = 83 and 58 (Table 2). The contrast between hydrogen bond acids and bases is marked; unless solutes are very strong hydrogen bond bases, there is not much difference in the two sets of partition coefficients. Since they are hydrogen bond acids, carboxylic acids are solvated differently in wet DBE. We did not include any carboxylic acids in the list of solutes for partitioning between water and dry DBE because we felt that dimerisation in the organic phase was inevitable. Indeed, for the few carboxylic acids for which we were able to obtain observed log *P*<sup>DBE</sup> values by the solubility method, the calculated values are always less than those observed, see Table 6. This is as expected if dimerisation takes place in the organic phase. Surprisingly, in view of the small solubility of water in DBE, the observed and calculated values of log *P*<sup>WDBE</sup> for partition into wet DBE of carboxylic acids are in reasonable agreement. This suggests that the carboxylic acids are not dimerised in wet DBE.

An important conclusion from our analyses is that very small amounts of water in organic solvents may have a considerable effect on the partition of polar solutes (in the case of DBE, solutes that are strong hydrogen bond acids), through formation of solute–water complexes, see for example ref. 48, especially with non-polar solvents. It is therefore unwise to assume that wet solvents have the same solubility properties

**Table 5** Comparison of calculated log *P* values for partition from water to wet and dry DBE<sup>a</sup>

Solute	Wet DBE	Dry DBE
Phenol	1.13 <sup>b</sup>	0.62
4-Nitrophenol	1.08 <sup>c</sup>	0.65 <sup>c</sup>
Hydroquinone	−0.79 <sup>d</sup>	−1.55
4-Hydroxyacetanilide	−1.25	−1.92 <sup>e</sup>
Butylamine	0.12	−0.16 <sup>f</sup>
Butanone	−0.04	−0.07 <sup>g</sup>

<sup>a</sup> Calculated using the equations with *N* = 38. <sup>b</sup> Observed value is 1.01. <sup>c</sup> Observed values are 1.19 and 0.85, respectively. <sup>d</sup> Observed value is −0.77. <sup>e</sup> Observed value is −2.11. <sup>f</sup> Observed value is −0.48. <sup>g</sup> Observed value is 0.01.

**Table 6** Calculations of log *P* values for the partition of carboxylic acids between water and wet and dry DBE

Solute	Wet DBE, calc.	Wet DBE, obs.	Dry DBE calc.	Dry DBE, obs.
Propanoic acid	-0.56	-0.43		—
Phenylacetic acid	0.65	0.76		—
4-Phenylbutanoic acid	1.85	1.79		—
3-Chlorophenylacetic acid	1.43	1.60		—
1-Naphthoic acid	2.64	2.25		—
Benzoic acid	1.24	1.86	0.75	1.35
3-Nitrobenzoic acid		—	0.55	1.17

as dry solvents, even if the quantity of water involved is very small. For example, Testa *et al.*,<sup>49</sup> studied the distribution of the zwitterionic species, cetirizine, in the water–octanol and water–dodecane systems and showed that for distribution at an aqueous pH of 7.4, the partitioning species was the zwitterion and not the neutral species, in both cases. Again, this suggests that the minute quantity of water in water-saturated dodecane ( $2.7 \times 10^{-3}$  mol dm<sup>-3</sup>) has a considerable effect on the constitution of highly polar species, and thus on their partition behaviour.

As regards the observed differences in solvation behaviour of wet and dry DBE, the larger *a*-coefficient observed in transfers to wet DBE can be explained by a specific behaviour of water in the wet solvent acting as a base and forming hydrogen bond complexes with acidic solutes. The more negative *s*-coefficient, and the more positive *v*- and *l*-coefficients for transfer to the wet solute are also likely to be due to specific effects involving solvation of the solute–water complex. Certainly, the effect of water on these coefficients for transfer to the alkan-1-ols is the reverse, see Table 3. The very large quantity of water dissolved in the wet alkan-1-ols is so large that the water simply acts as a co-solvent.

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