The hydrogen bond properties of water from 273 K to 573 K; equations for the prediction of gas-water partition coefficients

Michael H. Abraham^{*a} and William E. Acree Jr.^b

Received 21st February 2012, Accepted 28th March 2012

DOI: 10.1039/c2cp40542c

An equation due to Plyasunov and Shock for the calculation of gas to water partition coefficients, as $\log K_w$, at high temperature requires knowledge of experimental values of $\log K_w^{298}$, ΔH_w^{298} the standard enthalpy of hydration at 298 K, $\Delta C_{p_w}^{298}$ the heat capacity of hydration at 298 K and b' that is a constant that refers to the variation of ΔC_{p_w} with temperature. Linear free energy relationships based on Abraham descriptors for solutes have been constructed for all of these four input quantities, so that $\log K_w$, ΔH_w^{298} , $\Delta C_{p_w}^{298}$ and b' can be estimated. Known values of the four input quantities, where available, together with estimated values enabled values of $\log K_w$ from 273 to 573 K to be calculated for 555 solutes. At various fixed temperatures LFERs again based on Abraham descriptors were constructed from the obtained $\log K_w$ values for the 555 solutes. These LFERs can then be used to estimate further values of $\log K_w$ between 273 and 573 K for any solute with already determined descriptors, so that knowledge of experimental values of $\log K_w^{298}$, ΔH_w^{298} , $\Delta C_{p_w}^{298}$ and b' is no longer necessary. The obtained LFERs show how the solvation properties of water vary with temperature. Both water hydrogen bond acidity and hydrogen bond basicity towards solutes decrease substantially with increase of temperature until at 573 K the hydrogen bond properties of water resemble those for solvents such as nitrobenzene and acetonitrile at 298 K. A characteristic property of water at ambient temperatures is that water will not solvate non-polar solutes, thus leading to large Henry's law constants and small values of K_w . Although this property also decreases with increase of temperature, our results indicate that it still remains to some extent even at 573 K, so that the general solvation properties of water at 573 K do not resemble the solvation properties of organic solvents at 298 K.

Introduction

Following the recent work of Nilsson *et al.*,^{1–4} there has been renewed interest in the structure of water.⁵ Models such as the two-state model of Nilsson *et al.*^{1–4} lead to explanations for remarkable properties of water, including anomalous heat capacity, compressibility and variation in density. The two-state model consists of patches of water structures with strong near-tetrahedral hydrogen bonds surrounded by more distorted water molecules with non-directional hydrogen bonds. Although the proportion of the two species alters with temperature, Nilsson *et al.*⁴ make the remarkable suggestion that the extreme differences in hydrogen bonding of the two species remain in bulk water almost up to the boiling point.

Hydrogen bond properties of water and liquid solvents in general can be manifested in a number of ways. Not only do

they relate to structural properties of liquids, but they result in particular chemical properties of solvents. Thus if the hydrogen bond differences suggested by Nilsson *et al.*⁴ still remain at high temperatures, then the chemical properties of water that depend on hydrogen bonding should also remain at high temperatures. These chemical properties will include how well do acidic and basic compounds dissolve in water at high temperatures, as compared to their solubility in water (and in other solvents) at ambient temperatures. In order to address this problem, some methodology that relates solubility of solutes to properties of solvents, including hydrogen bond properties, is required. There are only two methods that have been applied quite generally: those of Kamlet and Taft^{6–8} and of Abraham.^{9–12} In the former method, hydrogen bond properties of solvents are obtained through uv/visible measurements of indicators in solvents, thus enabling scales of solvent hydrogen bond acidity and hydrogen bond basicity to be developed. In principle, the Kamlet–Taft method could be extended to high temperatures, but this has never been pursued and we now consider the alternative method.

^a Department of Chemistry, University College London, 20 Gordon St, London WC1H 0AJ, UK. E-mail: m.h.abraham@ucl.ac.uk

^b Department of Chemistry, 1155 Union Circle Drive #305070, University of North Texas, Denton, TX 76203-5017, USA. E-mail: bill.acree@unt.edu

Methods

In the method developed by Abraham *et al.*,^{9–12} it is solutes that are assigned a number of properties including hydrogen bond acidity and hydrogen bond basicity. These are used as descriptors in two linear free energy relationships, LFERs, eqn (1) and (2).

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

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

The independent variables, or descriptors, in eqn (1) and (2) are properties of solutes as follows:^{9–12} E is an excess molar refraction in $\text{cm}^3 \text{mol}^{-1}/10$, S is a combined dipolarity/polarizability descriptor, A is the overall solute hydrogen bond acidity, B is the overall solute hydrogen bond basicity, V is McGowan's¹³ characteristic molecular volume in $\text{cm}^3 \text{mol}^{-1}/100$ and L is the gas to hexadecane partition coefficient at 298 K, as log L . The dependent variable, SP , is a set of solute properties in a given system. Thus SP could be K , the gas to solvent partition coefficient for a series of solutes in a given solvent. The set of coefficients, c , e , s , a , b , v and l characterise the system and are determined by multiple linear regression analysis. These coefficients are not just fitting coefficients, but represent the complimentary properties of the solvent: e gives the contribution in eqn (1) and (2) of the solute–solvent phase general dispersion interaction, s is the solvent dipolarity (plus some polarizability), a is the solvent hydrogen bond basicity (the complimentary property to solute hydrogen bond acidity) and b is the solvent hydrogen bond acidity (the complimentary property to solute hydrogen bond basicity). The coefficients v and l reflect general dispersion interactions that aid solubility of a solute and the solvent–solvent interactions that oppose solubility.

The gas to solvent partition coefficient, K , is defined through eqn (3) and is dimensionless. It is the inverse of the solute Henry's Law coefficient, with due regard to the units of the latter.

$$K = \frac{\text{concentration of solute (mol dm}^{-3}\text{) in solvent}}{\text{concentration of solute (mol dm}^{-3}\text{) in the gas phase}} \quad (3)$$

For solution of gases in organic solvents, eqn (2) is invariably statistically better than eqn (1), but for solution of gases in water there is little difference. We give in Table 1 the coefficients in eqn (2) with $SP = K$ for solution of gases in solvents at 298 K, and for solution of gases in water at 298 K and at 310 K. In the present context, the coefficients a and b are of most interest. From Table 1 it can be seen that the hydrogen bond basicity of water (the a -coefficient) at 298 K is no larger than that for many alcohols and polar solvents. On the other hand, the hydrogen bond acidity (the b -coefficient) of water is larger than any other solvent we have studied—even larger than that of ethylene glycol or 2,2,2-trifluoroethanol. The equation coefficients for solution of gases into water-ethanol solvents are very informative. As the proportion of ethanol in the solvent gets smaller, so the coefficients approach those of pure water, showing that there is a gradation in the hydrogen bond properties of the water-ethanol solvents.

Table 1 Coefficients in eqn (2), $SP = K$, for the solubility of gases in solvents at 298 K

	c	e	s	a	b	l
Gas–water	−1.271	0.822	2.743	3.904	4.814	−0.213
Gas–water, 310	−1.347	0.928	2.795	3.717	4.297	−0.254
10% Ethanol	−1.497	0.422	2.452	4.050	4.500	−0.016
20% Ethanol	−1.426	0.407	2.274	4.047	4.124	0.092
30% Ethanol	−1.292	0.36	2.061	4.045	3.687	0.218
40% Ethanol	−1.089	0.238	1.873	4.021	3.210	0.351
50% Ethanol	−0.861	0.103	1.640	4.045	2.733	0.481
60% Ethanol	−0.640	0.002	1.459	4.037	2.386	0.587
70% Ethanol	−0.448	−0.155	1.356	4.015	2.103	0.669
80% Ethanol	−0.272	−0.118	1.200	3.946	1.851	0.724
90% Ethanol	−0.119	−0.161	1.056	3.900	1.601	0.782
Methanol	−0.039	−0.338	1.317	3.826	1.396	0.773
Ethanol	0.017	−0.232	0.867	3.894	1.192	0.846
Propan-1-ol	−0.042	−0.246	0.749	3.888	1.076	0.874
Butan-1-ol	−0.004	−0.285	0.768	3.705	0.879	0.890
Pentan-1-ol	−0.002	−0.161	0.535	3.778	0.960	0.900
Hexan-1-ol	−0.014	−0.205	0.583	3.621	0.891	0.913
Heptan-1-ol	−0.056	−0.216	0.554	3.596	0.803	0.933
Octan-1-ol	−0.147	−0.214	0.561	3.507	0.749	0.943
Nonan-1-ol	−0.100	−0.150	0.491	3.532	0.734	0.952
Decan-1-ol	−0.139	−0.090	0.356	3.547	0.727	0.958
Hexadecan-1-ol ^a	−0.152	−0.185	0.742	2.436	0.339	0.980
Hexadecan-1-ol,373 ^a	0.134	0.131	0.233	1.537	0.363	0.578
Formamide	−0.800	0.310	2.292	4.130	1.933	0.442
<i>N</i> -Methylformamide	−0.249	−0.142	1.661	4.147	0.817	0.739
Ethylene glycol	−0.887	0.132	1.657	4.457	2.355	0.565
Trifluoroethanol	−0.092	−0.547	1.339	2.213	3.807	0.645
Dimethylformamide	−0.391	−0.869	2.107	3.774	0.000	1.011
DMSO	−0.556	−0.223	2.903	5.037	0.000	0.719
Acetonitrile	−0.007	−0.595	2.461	2.085	0.418	0.738
Nitromethane	−0.340	−0.297	2.689	2.193	0.514	0.728
Nitrobenzene	−0.296	0.092	1.707	1.147	0.443	0.912
Propanone	0.127	−0.387	1.733	3.060	0.000	0.866
Ethyl acetate	0.182	−0.352	1.316	2.891	0.000	0.916
Diethylether	0.288	−0.347	0.775	2.985	0.000	0.973
THF	0.189	−0.347	1.238	3.289	0.000	0.982
Benzene	0.107	−0.313	1.053	0.457	0.169	1.020
Toluene	0.085	−0.400	1.063	0.501	0.154	1.011
Tetrachloromethane	0.217	−0.435	0.554	0.000	0.000	1.069
Octane	0.215	−0.049	0.000	0.000	0.000	0.967
Hexadecane	0.000	0.000	0.000	0.000	0.000	1.000

^a This work, see text.

In order to construct equations for the solubility of solute gases and vapours into water, K_w , at elevated temperature, it is necessary to know log K_w for a wide range of solutes as a function of temperature. Previously¹⁴ we used an equation due to Plyasunov and Shock¹⁷ for the Gibbs energy of hydration in J mol^{-1} , eqn (4); ΔH_w^{298} is the standard enthalpy of hydration at 298 K in J mol^{-1} , $\Delta C_p_w^{298}$ is the heat capacity of hydration at 298 K in $\text{J K}^{-1} \text{mol}^{-1}$ and b' refers to the variation of ΔC_p_w with temperature.

$$\begin{aligned} \Delta G_w^{\circ T} = & (T/298.15) * \Delta G_w^{\circ 298} - ((T-298.15)/298.15) * \Delta H_w^{\circ 298} \\ & + (\Delta C_p_w^{298} - b' * 298.15) * (T-298.15 - T * \ln(T/298.15)) \\ & - b' * (T-298.15)^2 / 2 \end{aligned} \quad (4)$$

Eqn (4) refers specifically to a total pressure of 0.1 MPa and to solute standard states of 0.1 MPa in the gas phase and unit molal concentration in solution. To be compatible with our previous work on the solubility of gases¹⁴ we converted eqn (4) into an equation for log K_w , the gas to water partition coefficient with standard states of unit concentration in

the gas phase and unit concentration in water, so that K_w is dimensionless.

In order to use eqn (4) for the prediction of $\log K_w$ at temperatures other than 298 K, we used equations for the prediction of ΔH_w^{298} by Mintz *et al.*¹⁸ and equations for the prediction of ΔCp_w^{298} by Abraham and Acree,¹⁴ all based on eqn (1) and eqn (2).

$$\Delta H_w^{298} = -6.952 + 1.412 E - 2.859 S - 34.086 A - 42.686 B - 22.720 V \quad (5)$$

$$\Delta H_w^{298} = -13.310 + 9.910 E + 2.836 S - 32.010 A - 41.816 B - 6.354 L \quad (6)$$

$$\Delta Cp_w^{298} = 103.6 - 65.3 E - 91.6 S - 3.1 A - 119.3 B + 404.0 V \quad (7)$$

$$\Delta Cp_w^{298} = 222.3 - 197.6 E - 183.4 S - 46.4 A - 119.1 B + 105.4 L \quad (8)$$

We already had to hand a large number of values of $\log K_w^{298}$ and where they were not available we could use equations that we had already derived¹⁹ for prediction of $\log K_w^{298}$, eqn (9) and (10).

$$\text{Log } K_w^{298} = -0.994 + 0.577 E + 2.549 S + 3.813 A + 4.841 B - 0.869 V \quad (9)$$

$$\text{Log } K_w^{298} = -1.271 + 0.822 E + 2.743 S + 3.904 A + 4.814 B - 0.213 L \quad (10)$$

Then through eqn (4) together with eqn (5), (7) and (9) or eqn (6), (8) and (10) we could calculate $\log K_w^T$ for a wide range of solutes between 273 K and 373 K.¹⁴ However, for temperatures much above 373 K it is necessary^{15–17} to take into account any possible temperature variation of ΔCp_w itself. Plyasunov and Shock¹⁷ suggested eqn (11) where the coefficients a' and b' depend on the solute.

$$\Delta Cp_w^T = a' + b' * T \quad (11)$$

$$a' = \Delta Cp_w^{298} - b' * 298.15 \quad (12)$$

Thus in order to incorporate the temperature variation of ΔCp_w for solutes in general it seems necessary to have to predict a' and b' . However, we can recast eqn (11) as eqn (12) and since we have reasonable equations, eqn (7) and (8), for the prediction of ΔCp_w^{298} , there is no need to invoke a' at all and we need only to predict b' in eqn (4). Unfortunately, only few values of b' are known, but we were able to correlate the b' values of Plyasunov and Shock¹⁷ through eqn (13)

$$b' = -0.220 + 0.851 E - 0.031 S + 0.319 A + 0.751 B - 1.210 V \quad (13)$$

$$N = 34, \text{SD} = 0.207, R^2 = 0.848, F = 31.4$$

Here and elsewhere, N is the number of data points, that is the number of solutes, SD is the regression standard deviation, R is the correlation coefficient and F is the Fischer F-statistic.

Results and discussion

We now have to hand eqn (4) for the calculation of $\Delta G_w^{\circ T}$, and hence of $\log K_w^T$, for any solute for which we have the descriptors in eqn (1) and eqn (2). Values of ΔH_w^{298} and ΔCp_w^{298} values were taken from a number of compilations,^{20–35} and $\log K_w^{298}$ from our previous work. If experimental values of $\log K_w^{298}$, ΔH_w^{298} and ΔCp_w^{298} were not available, they were calculated through eqn (5), (7) and (9) or through eqn (6), (8) and (10). In all cases b' was calculated through eqn (13). As a test we used data from Čenský *et al.*²⁰ who determined $\log K_w^T$ for a number of phenols and anilines from 298 to 573 K. Results for two typical solutes, phenol and m-toluidine, are shown in Fig. 1. There is good agreement between our calculated values and experimental values up to 573 K.

We then applied our method to 555 solutes covering a very wide range of compound, from simple aliphatic compounds as alkanes and alkenes to more complicated compounds such as ethylene glycol dibutanoate, hexafluoropropan-2-ol, and diethyl disulfide as well as heterocyclic compounds such as pyridine, pyrrole and pyrazine. The resulting values of $\log K_w^T$ at a number of specific temperatures from 272 K to 573 K were correlated against our descriptors through the LFER eqn (1) and (2). Although results in terms of eqn (2) are the more useful in terms of comparison with other solvents, eqn (1) has an advantage that the L -descriptor need not be determined. We therefore list in Table 2 the coefficients in the LFER equations for both eqn (1) and (2) using values for all 555 solutes from 273 K to 573 K. The input parameters refer to a pressure of 0.1 MPa and hence the LFER equations will do the same.

The statistics of the LFERs summarized in Table 2 are remarkably good, even up to 573 K. As expected, the regression standard deviation is at a minimum near to 298 K and gradually increases up to 573 K. Even at the latter temperature, the two LFERs can correlate the calculated values of $\log K_w^T$ to about 0.30 log units. Kühne *et al.*³⁶ used an LFER method to calculate $\log K_w^T$ values between 273 K and 293 K, starting from known values of $\log K_w^{298}$. They obtained a standard error of 0.21 log units for 462 compounds as compared to our SD of 0.13–0.15 and 0.11–0.13 log units for 555 compounds at 273 K and 298 K. Furthermore, we do not need a known

Fig. 1 $\log K_w^T$ for phenol: ● experimental values;²² ○ calculated values. $\log K_w^T$ for m-toluidine: ■ experimental values;²² □ calculated values.

Table 2 Coefficients in eqn (1) and (2) applied to $\log K_w^T$ for 555 solutes at temperatures from 273 to 573 K

T	<i>c</i>	<i>e</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>l</i>	SD	R ²	F
573.15	−0.872	0.650	1.368	1.385	0.722	0.026	0.297	0.953	2223
523.15	−1.068	0.675	1.682	1.588	1.163	−0.067	0.253	0.973	3965
473.15	−1.255	0.748	1.996	1.875	1.716	−0.163	0.213	0.986	7679
423.15	−1.407	0.850	2.294	2.265	2.400	−0.249	0.180	0.993	15568
373.15	−1.482	0.937	2.545	2.784	3.236	−0.303	0.152	0.997	31945
323.15	−1.383	0.925	2.693	3.471	4.252	−0.280	0.134	0.998	63208
310.15	−1.314	0.887	2.703	3.683	4.549	−0.252	0.132	0.998	71345
298.15	−1.227	0.832	2.697	3.894	4.836	−0.216	0.133	0.998	78151
273.15	−0.958	0.636	2.626	4.383	5.477	−0.095	0.146	0.999	80294
573.15 ^a	−0.964	0.752	1.434	1.423	0.731	−0.033	0.300	0.952	2166

T	<i>c</i>	<i>e</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>v</i>	SD	R ²	F
573.15	−0.919	0.645	1.392	1.400	0.662	0.186	0.294	0.953	2243
523.15	−1.013	0.555	1.625	1.571	1.113	−0.180	0.250	0.973	3982
473.15	−1.096	0.512	1.856	1.825	1.676	−0.558	0.209	0.986	7886
423.15	−1.153	0.511	2.080	2.185	2.372	−0.901	0.170	0.994	17198
373.15	−1.162	0.541	2.284	2.686	3.223	−1.123	0.134	0.997	40965
323.15	−1.080	0.573	2.450	3.380	4.258	−1.067	0.109	0.999	93759
310.15	−1.035	0.575	2.482	3.601	4.561	−0.973	0.109	0.999	106654
298.15	−0.982	0.572	2.507	3.824	4.854	−0.846	0.111	0.999	111743
273.15	−0.825	0.543	2.538	4.354	5.509	−0.418	0.134	0.999	95552
573.15 ^a	−0.956	0.672	1.406	1.417	0.669	−0.029	0.293	0.953	2205

^a At 20 MPa.

value at 298 K at all, since this can be calculated through eqn (9) or eqn (10). Goss³⁷ again started with known values of $\log K_w^{298}$ and used the same descriptors that we use to obtain LFERs for 217 compounds between 298 K and 318 K with SDs of less than 0.15 log unit. By comparison, our LFERs for 555 compounds lead to SDs of 0.13 or 0.11 log unit over the same temperature range.

The LFERs at 298 K for 555 solutes, Table 2, are essentially the same as the LFER equations we developed before¹⁹ using 408 solutes, eqn (1), and 392 solutes, eqn (2). Similarly, the LFERs at 310 K for 555 solutes are essentially the same as those we previously obtained³⁸ using 350 solutes.

We use data from Dohnal and Fenclová³³ to assess how well the LFERs in Table 2 can estimate $\log K_w^T$. We use no experimental input data at all and calculate input data through eqn (5), (7) and (9) or through eqn (6), (8) and (10) using descriptors for the phenols. Results are compared in Table 4 to those calculated from equations given by Dohnal and Fenclová³³ (see their Table 7). AE is the average error, AAE is the average absolute error and RMSE is the root mean square deviation of our calculated values and the experimental values. The LFERs yield reasonable estimates of $\log K_w^T$ at 373 K, with SD values of 0.12 and 0.14 log units. Of course, the SD values in Table 3 include the errors in the correlation equations of Dohnal and Fenclová,²² which amount to 0.02 to 0.06 log units on average, and probably more at the highest temperature studied.

We therefore have a method using our LFERs for the estimation of $\log K_w^T$ at high temperatures that can be applied quite generally to inorganic and organic compounds. The estimation using calculated thermodynamic quantities through our descriptors is especially useful because we have published descriptors for a very large number of compounds. These descriptors, together with the LFERs in Table 2 are all that are needed to estimate $\log K_w^T$ values. We omit from our

Table 3 Comparison of calculated values of $\log K_w^T$ at 373 K with experimental values for 10 phenols

Solute	Ref. 33 Exp.	Calc. this work ^a	
		LFER, eqn (1)	LFER, eqn (2)
Phenol	2.93	3.02	3.04
2-Methylphenol	2.52	2.59	2.63
3-Methylphenol	2.79	2.88	2.90
4-Methylphenol	2.78	2.76	2.78
2,3-Dimethylphenol	2.49	2.55	2.58
2,4-Dimethylphenol	2.39	2.57	2.60
2,5-Dimethylphenol	2.37	2.55	2.58
2,6-Dimethylphenol	2.02	2.17	2.20
3,4-Dimethylphenol	2.78	2.84	2.83
3,5-Dimethylphenol	2.66	2.71	2.73
AE		−0.09	−0.11
AAE		0.10	0.11
RMSE		0.11	0.13
SD		0.12	0.14

^a All input values of $\log K_w^{298}$, ΔH_w^{298} and $\Delta C_{p_w}^{298}$ were calculated.

LFERs a number of small hydrophobic solutes that are known¹⁹ to be outliers. These are the rare gases, hydrogen, nitrogen, oxygen, nitrous oxide and carbon monoxide. We include other inorganic compounds such as carbon dioxide, nitric oxide, chlorine, arsine and phosphine. We had to exclude ethyne that was an outlier in all our LFERs; we have no explanation for this at all. We did not include the polychlorobiphenyls, but we did include polyaromatic hydrocarbons, PAHs. Some of the PAHs were outliers and so results of calculations for PAHs should be regarded as only provisional. Otherwise, $\log K_w^T$ can be estimated for any compound for which there are reliable descriptors. Our list of 555 solutes includes examples of organic compounds that contain most of the common functional groups in monofunctional and polyfunctional compounds, as well as representatives of many of the common heterocyclic compounds. A full list of the 555 compounds

together with their descriptors and the thermodynamic quantities that we used is given in the supplementary material.

All the results so far refer to a pressure of 0.1 MPa, but experimental measurements on the solubility of compounds are mostly carried out at pressures corresponding to the water vapor pressure on the vapor-liquid phase boundary. At 573 K this is 8.57 MPa, and so at temperatures above 373 K a correction is necessary to convert $\log K_w^T$ at 0.1 MPa to $\log K_w^T$ at a higher pressure. The correction is quite small, but we thought it useful to check if the coefficients in our LFER equations did vary with pressure. The correction follows the identity $(dGdP)_T = V$ which leads to eqn (14).

$$\Delta \log K_w^T = -\Delta P V_w^T / 2.303RT \quad (14)$$

For argon in water at 298 K, an increase in pressure of 7.9 MPa leads to a decrease in $\log K_w$ of 0.067 log units,³⁹ so the correction along the water vapor-liquid boundary will be quite small. Since eqn (14) includes a term in V_w^T , the correction is not constant but alters with solute volume; V_w^T is the partial molal volume of a solute in water at the particular temperature. It seems almost impossible to devise an equation for the estimation of V_w^T that would cover our 555 solutes, and so we resorted to the use of V_w^{298} as an approximation. It turns out that V_w^{298} is very close to V_w^{298} , the liquid molar volume at 298 K, and so we estimated both V_w^{298} and V_w^{298} through eqn (15) and (16); the units of the volumes are $\text{cm}^3 \text{mol}^{-1}$. We found it useful to incorporate an indicator variable, NF , that takes a value of the number of fluorine atoms in the molecule.

$$V_w^{298}(\text{cm}^3 \text{mol}^{-1}) = 8.52 - 7.06 E - 1.071 S - 6.81 A \\ - 3.72 B + 112.30 V + 2.13 NF \quad (15)$$

$$N = 319, \text{SD} = 2.34, R^2 = 0.995, F = 11061$$

$$V_w^{298}(\text{cm}^3 \text{mol}^{-1}) = 19.40 - 14.09 E - 7.78 S - 9.95 A \\ - 3.13 B + 116.78 V + 1.32 NF \quad (16)$$

$$N = 476, \text{SD} = 1.90, R^2 = 0.999, F = 56824$$

It makes little difference if we use eqn (15) or eqn (16). We used eqn (16) to calculate V_w^{298} as an approximation to V_w^T in eqn (14). We can test this approximation by calculating $\log K_w^T$ at 573 K and at various pressures and comparing the results to the experimental values obtained by Čenský *et al.*²⁰ at 20 MPa and 40 MPa. Results are in Table 4. Two sets of calculations are given, one using equations in V and the other using equations in L . Use of V_w^{298} from eqn (16) instead of V_w^T in eqn (14) leads to reasonable estimations of the pressure dependence of $\log K_w^T$ at 573 K.

We can now use eqn (14) and (16) to calculate the correction from 0.1 MPa to 20 MPa at 573 K for all 555 solutes and can then obtain two LFERs for $\log K_w^T$ at 573 K and 20 MPa. The coefficients and statistics are in Table 2. There are only minor changes to the coefficients from 0.1 MPa to 20 MPa (well beyond the water vapor pressure on the vapor-liquid phase boundary, 8.57 MPa at 573 K) and so the variation of pressure hardly alters the hydrogen bond coefficients. We can then take the coefficients in our LFER equations at 0.1 MPa as defining

Table 4 Calculation of $\log K_w^T$ at 298 K and at 573 K and various pressures; comparison with experimental values from Čenský *et al.*²⁰

Solute	298 0.1 MPa	573 0.1 MPa	573 8.6 MPa	573 20 MPa	573 40 MPa
Phenol, exp	4.94		2.10	1.96	1.72
Phenol, calc ^a	4.85	1.97	1.93	1.82	1.66
Phenol, calc ^b	4.85	1.97	1.92	1.82	1.66
o-Cresol, exp	4.54		1.90	1.73	1.45
o-Cresol, calc	4.31	1.66	1.58	1.47	1.28
o-Cresol, calc	4.31	1.74	1.66	1.56	1.37
m-Cresol, exp	4.86		2.03	1.85	1.57
m-Cresol, calc	4.60	1.98	1.90	1.79	1.60
m-Cresol, calc	4.76	1.98	1.90	1.79	1.60
Aniline, exp	4.39		1.88	1.73	1.48
Aniline, calc	4.30	1.54	1.46	1.37	1.21
Aniline, calc	4.30	1.54	1.46	1.37	1.21
m-Toluidine, exp	4.31		1.81	1.62	1.33
m-Toluidine, calc	4.23	2.05	1.97	1.86	1.66
m-Toluidine, calc	4.23	1.93	1.85	1.74	1.54

^a Equations in V . ^b Equations in L .

Fig. 2 The variation of coefficients in eqn (2) for $\log K_w^T$ as a function of temperature: ○ e-coefficient; □ s-coefficient; ● b-coefficient; ● a-coefficient; ■ l-coefficient.

the solvation properties of water up to 573 K. The coefficients in eqn (2) specifically relate to solvent (water)–solute interactions that lead to the solvation (hydration) of gaseous solutes. Plots of the coefficients against temperature are shown in Fig. 2. Of especial interest are the a -coefficient that refers to the hydrogen bond basicity of the solvent, and the b -coefficient that refers to the hydrogen bond acidity of the solvent with regard to solvent–solute interactions. Both coefficients decrease regularly with increase in temperature, with the b -coefficient decreasing from 5.48 at 273 K down to 0.72 at 573 K. At 573 K water has a quite small hydrogen bond acidity with respect to interaction with external hydrogen bond bases and yet at ambient temperature water is an extraordinarily strong hydrogen bond acid, see Table 1. The l -coefficient for water at ambient temperatures is negative, but for all organic solvents the l -coefficient is markedly positive. This size of the l -coefficient is determined by general solvent–solute dispersion interactions that aid solvation of gaseous species, and the energy required to break solvent–solvent interactions and form a cavity in the solvent; this energy requirement opposes solution. For water at ambient temperature, it is the cavity effect that dominates, and this sets water apart from organic solvents. But the l -coefficient for water is still negative at 523 K and is only

Table 5 The gas-solvent systems used in comparison of coefficients^a

System	No	System	No
Water, 573	1	Ethanol	20
Water, 523	2	Decan-1-ol	21
Water, 473	3	Hexadecan-1-ol	22
Water, 423	4	Hexadecan-1-ol, 373	23
Water, 373	5	Formamide	24
Water, 323	6	<i>N</i> -Methylformamide	25
Water, 310	7	Ethylene glycol	26
Water, 298	8	Trifluoroethanol	27
Water, 273	9	Dimethylformamide	28
10% Ethanol	10	DMSO	29
20% Ethanol	11	Acetonitrile	30
30% Ethanol	12	Nitrobenzene	31
40% Ethanol	13	Benzonitrile	32
50% Ethanol	14	Chlorobenzene	33
60% Ethanol	15	Propanone	34
70% Ethanol	16	Diethylether	35
80% Ethanol	17	THF	36
90% Ethanol	18	Tetrachloromethane	37
Methanol	19	Hexadecane	38

^a Systems studied at 298 K except where indicated otherwise.

slightly positive at 573 K. The present results indicate that the unusual combination of large cavity effects and small dispersion effects persists in water even at high temperature.

A general comparison of LFERs for $\log K_w^T$ with gas-solvent LFERs for $\log K_s$ values can be carried out using the standard eqn (2). In preliminary work we found that the coefficients in LFERs for long chain alkan-1-ols at 298 K tended to approach those for water at 573 K, and so we collected data on $\log K_w^T$ for hexadecan-1-ol at 298 K and 373 K.^{40–43} Data at 298 K were extrapolated from higher temperatures and so the LFER equation is not particularly good, but sufficiently so to use for comparison. The obtained LFERs for hexadecan-1-ol are in Table 1. Coefficients for the various gas-solvent systems are in Table 1 and those for the gas-water systems are in Table 2. The systems we shall consider are listed and numbered in Table 5. There are two well-known methods for a quantitative comparison of coefficients in LFER equations.^{44,45} In both of these methods a ‘standard’ system is defined and coefficients in the other systems studied are compared to those in the ‘standard’ system. In the present work we do not wish to relate coefficients to any particular standard system but to compare coefficients between several systems. It is then more practical to use principal components analysis, PCA. Five columns of coefficients, *e*, *s*, *a*, *b* and *l*, for the 37 systems in Table 5 are converted into five PCs. The first two PCs contain 84% of the total information (in the present case) and so a plot of PC2 against PC1 will provide an estimate of how close the coefficients are for the various systems, and hence how close are the systems as regards chemical effects on solvation of gaseous species; the plot is shown in Fig. 3. The points for water at various temperatures and the points for alcohols and aqueous alcohols at 298 K, together with the point for hexadecan-1-ol at 373 K form a rather well defined ‘ring’. Judging from hexadecan-1-ol at 298 K and at 373 K, it seems quite likely that hexadecan-1-ol at even higher temperatures will approach water at 573 K in general solvation characteristics. As things stand, none of the solvents listed in Table 1 and Table 5 can be considered to be near to water at 573 as regards solvation

Fig. 3 Plot of the scores of PC2 against the scores of PC1 for the systems in Table 5: ● solvent water systems No 1–No 9; ■ solvent water-ethanol systems No 10–No 18, and alcohol systems No 19–No 23; □ protic organic solvents No 24–No 27; ○ aprotic organic solvents No 28–No 38.

Fig. 4 Plot of the *a*-coefficient against the *b*-coefficient for the systems in Table 5: ● solvent water systems No 1–No 9; ■ solvent water-ethanol systems No 10–No 18, and alcohol systems No 19–No 23; □ protic organic solvents No 24–No 27; ○ aprotic organic solvents No 28–No 38.

of gaseous species. Even hexadecan-1-ol at 3573 K and nitrobenzene at 298 K are quite far away.

In terms just of hydrogen bond properties, it can be seen from Fig. 4 that hexadecan-1-ol at 373 K and nitrobenzene at 298 K are quite close to water at 573 K. Both organic solvents are mediocre hydrogen bond acids (with *b*-coefficients 1.54 and 1.15) and poor hydrogen bond bases (with *a*-coefficients 0.36 and 0.44). However, the substantial positive *l*-coefficient (0.578) of hexadecan-1-ol at 373 K indicates that in terms of cavity effects and general dispersion interactions at this temperature hexadecan-1-ol solvent behaves as a typical organic solvent; for example, ethylene glycol has an *l*-coefficient of 0.565. The unusual behavior of water solvent in this respect can be seen by a term-by-term analysis of solvation of three solutes: pentane a non-polar solute, pentylamine a strong hydrogen bond base and butanoic acid a strong hydrogen bond acid. Details are in Table 6. Pentane is solvated far more strongly by hexadecan-1-ol at 373 K and by nitrobenzene at 298 K than it is by water at any temperature. This unusual feature of water that is exhibited at ambient temperature is thus retained up to 573 K, albeit to a less extent. It is manifested in

Table 6 A term-by-term comparison of solvation of pentane, pentylamine and butanoic acid

Term in LFERs:	<i>c</i>	<i>e.E</i>	<i>s.S</i>	<i>a.A</i>	<i>b.B</i>	<i>l.L</i>	Total
Pentane							
Water, 298	-1.27	0.00	0.00	0.00	0.00	-0.46	-1.73
Water, 573	-0.87	0.00	0.00	0.00	0.00	0.06	-0.81
Hexadecan-1-ol, 373	0.13	0.00	0.00	0.00	0.00	1.25	1.38
Nitrobenzene, 298	-0.30	0.00	0.00	0.00	0.00	1.97	1.68
Pentylamine							
Water, 298	-1.27	0.17	0.96	0.62	2.94	-0.67	2.76
Water, 573	-0.87	0.14	0.48	0.22	0.44	0.08	0.49
Hexadecan-1-ol, 373	0.13	0.03	0.08	0.25	0.22	1.81	2.52
Nitrobenzene, 298	-0.30	0.02	0.60	0.18	0.27	2.86	3.64
Butanoic acid							
Water, 298	-1.27	0.17	1.76	2.38	2.17	-0.59	4.62
Water, 573	-0.87	0.14	0.88	0.84	0.32	0.07	1.38
Hexadecan-1-ol, 373	0.13	0.03	0.15	0.94	0.16	1.59	3.00
Nitrobenzene, 298	-0.30	0.02	1.09	0.70	0.20	2.51	4.22

the *l.L* term which is less positive for all solutes in water than it is for the solutes in organic solvents. Other effects are more straightforward. The most positive term for pentylamine is the *b.B* term that occurs for solvation in water at 298 K, because at this temperature water is a very strong hydrogen bond acid. For butanoic acid the *a.A* term is very large for water at 298 K because water at ambient temperature is a strong hydrogen bond base. Butanoic acid is also a hydrogen bond base and so the *a.A* term is large at 298 K. As the temperature increases, these hydrogen bond terms for solvation in water become smaller, and at 573 K are of the same importance as the corresponding terms for solvation in nitrobenzene at 298 K.

The *l*-coefficient, and also the *v*-coefficient, reaches a minimum value at around 373 K, consistent with the observation that Henry's law constants for non-polar compounds exhibit a maximum^{46,47} and hence that values of $\log K_w^T$ for non-polar compounds exhibit a minimum. This is shown in Fig. 5 where $\log K_w^T$ for pentane calculated through eqn (6), (8), (10) and (13) goes through a minimum near 373 K. For the polar solutes pentylamine and butanoic acid the effect of the *l.L* term is over ridden by the *a.A* and *b.B* terms that both lead to a large reduction in $\log K_w^T$ with increase in temperature, see Fig. 5. For a solute that is only a poor hydrogen bond acid or poor hydrogen bond base, we would expect that the effect of the *l.L* term might still lead to a minimum in the value of $\log K_w^T$. Fig. 5 shows exactly this effect for methyl

Fig. 5 Plots of calculated values of $\log K_w$ against temperature for: ● pentane; ○ methyl propyl ether; ■ pentylamine; □ butanoic acid.

propyl ether ($A = 0$ and $B = 0.43$); there is a slight minimum in our calculated values of $\log K_w^T$ around 425 K. This indicates again that the unusual solvation effects of water at ambient temperature towards non-polar compounds still persist at much higher temperatures.

We conclude that as the temperature increases, the hydrogen bond acidity and the hydrogen bond basicity of water greatly decrease. At 573 K, the hydrogen bond properties of water as regards solvation of solutes are about the same as organic solvents such as nitrobenzene, nitromethane or acetonitrile at 298 K, see Table 1. Amongst solvents in general, water is distinguished at ambient temperatures by its extremely poor solvation of non-polar solutes. Gaseous solutes such as the alkanes, alkenes, alkylbenzenes, and the PAHs have very small gas-water partition coefficients, and conversely have large Henry's law constants. This unusual behavior of water does not disappear as the temperature increases but can still be seen at 573 K, although to a less extent than at ambient temperature.

References

- 1 Ph. Wernet, D. Nordlund, U. Bergmann, M. Cavalleri, M. Odelius, H. Ogasawara, L. A. Näslund, T. K. Hirsh, L. Ojamäe, P. Glatzel, L. G. M. Pettersson and A. Nilsson, *Science*, 2004, **304**, 995–999.
- 2 T. Tokushima, Y. Harada, O. Takahashi, Y. Senba, H. Ohashi, L. G. M. Pettersson, A. Nilsson and S. Shin, *Chem. Phys. Lett.*, 2008, **460**, 387–400.
- 3 M. Leetmaa, T. K. Wikfeldt, M. P. Ljungberg, M. Odelius, J. Swenson, A. Nilsson, L. G. M. Pettersson and G. M. Lars, *J. Chem. Phys.*, 2008, **129**, 084502.
- 4 C. Huang, K. T. Wikfeldt, T. Tokushima, D. Nordlund, Y. Harada, U. Bergmann, M. Niebuhr, T. M. Weiss, Y. Horikawa, M. Leetmaa, M. P. Ljungberg, O. Takahashi, A. Lenz, L. Ojamäe, A. P. Lyubartsev, S. Shin, L. G. M. Pettersson and A. Nilsson, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 15214–15218.
- 5 E. Cartledge, *New Sci.*, 2010, **205**, 32–35.
- 6 M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877–2887.
- 7 M. J. Kamlet, R. M. Doherty, J.-L. M. Abboud, M. H. Abraham and R. W. Taft, *ChemTech*, 1986, **16**, 566–576.
- 8 M. J. Kamlet, *Prog. Phys. Org. Chem.*, 1993, **19**, 295–317.
- 9 M. H. Abraham, *Chem. Soc. Rev.*, 1993, **22**, 73–83.
- 10 M. H. Abraham, A. Ibrahim and A. M. Zissimos, *J. Chromatogr., A*, 2004, **1037**, 29–47.
- 11 M. H. Abraham, R. E. Smith, R. Luchtefeld, A. J. Boorem, R. Luo and W. E. Acree, Jr., *J. Pharm. Sci.*, 2010, **99**, 1500–1515.
- 12 T. W. Stephens, A. N. Quay, V. Chou, M. Loera, C. Shen, A. Wilson, W. E. Acree, Jr. and M. H. Abraham, *Global J. Phys. Chem.*, 2012, **3**, 1–42.
- 13 M. H. Abraham and J. C. McGowan, *Chromatographia*, 1987, **23**, 243–246.
- 14 M. H. Abraham and W. E. Acree, Jr., *Fluid Phase Equilib.*, 2007, **262**, 97–110.
- 15 A. V. Plyasunov, J. P. O'Connell and R. H. Wood, *Geochim. Cosmochim. Acta*, 2000, **64**, 495–512.
- 16 A. V. Plyasunov and E. L. Shock, *Geochim. Cosmochim. Acta*, 2000, **64**, 2811–2833.
- 17 A. V. Plyasunov and E. L. Shock, *Geochim. Cosmochim. Acta*, 2003, **67**, 4981–5009.
- 18 C. Mintz, M. Clark, W. E. Acree, Jr. and M. H. Abraham, *J. Chem. Inf. Model.*, 2007, **47**, 115–121.
- 19 M. H. Abraham, J. Andonian-Haftvan, G. S. Whiting, A. Leo and R. W. Taft, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1777–1791.
- 20 M. Čenský, J. Šedlbauer, V. Majer and V. Růžicka, *Geochim. Cosmochim. Acta*, 2007, **71**, 580–603.
- 21 S.-O. Nilsson and I. Wadsö, *J. Chem. Thermodyn.*, 1986, **18**, 673–681.
- 22 D. Hallén, *J. Chem. Thermodyn.*, 1993, **25**, 519–524.

-
- 23 C. H. Rochester and J. R. Symonds, *J. Chem. Soc., Faraday Trans. 1*, 1973, **69**, 1577–1585.
- 24 S. Cabani, P. Gianni, V. Mollica and L. Lepori, *J. Solution Chem.*, 1981, **10**, 563–595.
- 25 A. V. Plyasunov and E. L. Shock, *J. Chem. Eng. Data*, 2001, **46**, 1016–1019.
- 26 A. V. Plyasunov, J. P. O'Connell, R. H. Wood and E. L. Shock, *Fluid Phase Equilib.*, 2001, **183–184**, 133–142.
- 27 A. V. Plyasunov, N. V. Plyasunova and E. L. Shock, *J. Chem. Eng. Data*, 2004, **49**, 1152–1167.
- 28 N. V. Plyasunova, A. V. Plyasunov and E. L. Shock, *J. Chem. Eng. Data*, 2005, **50**, 246–253.
- 29 A. V. Plyasunov, N. V. Plyasunova and E. L. Shock, *J. Chem. Eng. Data*, 2006, **51**, 276–290.
- 30 A. V. Plyasunov, N. V. Plyasunova and E. L. Shock, *J. Chem. Eng. Data*, 2006, **51**, 1481–1490.
- 31 D. Fenclová, V. Dohnal, P. Vrbka and V. Laštovka, *J. Chem. Eng. Data*, 2007, **52**, 989–1002.
- 32 M. Fujisawa, T. Matsushita, Y. Matsui, K. Akasaka and T. Kimura, *J. Therm. Anal. Calorim.*, 2004, **77**, 225–231.
- 33 V. Dohnal and D. Fenclová, *J. Chem. Eng. Data*, 1995, **40**, 478–483.
- 34 V. Dohnal, P. Vrbka, K. Řehák, A. Böhme and A. Paschke, *Fluid Phase Equilib.*, 2010, **295**, 194–200.
- 35 E. Badea and G. D. Gatta, *J. Chem. Eng. Data*, 2011, **56**, 4778–4785.
- 36 R. Kühne, R.-U. Ebert and G. Schüürmann, *Environ. Sci. Technol.*, 2005, **39**, 6705–6711.
- 37 K.-U. Goss, *Chemosphere*, 2006, **64**, 1369–1374.
- 38 M. H. Abraham, A. Ibrahim and W. E. Acree, Jr., *Fluid Phase Equilib.*, 2007, **251**, 93–109.
- 39 R. P. Kennan and G. L. Pollack, *J. Chem. Phys.*, 1990, **93**, 2724–2735.
- 40 G. L. Pollack, J. F. Himm and J. J. Enyeart, *J. Chem. Phys.*, 1984, **81**, 3239–3246.
- 41 D. Colson and D. Vanhove, *J. Chem. Thermodyn.*, 1990, **22**, 1217–1222.
- 42 K. Fukuchi, K. Miyoshi, T. Watanabe, S. Yonezawa and Y. Arai, *Fluid Phase Equilib.*, 1999, **156**, 197–206.
- 43 H. Xian, Y. D. Lei and F. Wania, *J. Chem. Eng. Data*, 2006, **51**, 338–346.
- 44 Y. Ishihama and N. Asakawa, *J. Pharm. Sci.*, 1999, **88**, 1305–1312.
- 45 M. H. Abraham and F. Martins, *J. Pharm. Sci.*, 2004, **93**, 1508–1523.
- 46 J. L. Heidman, C. Tsionopoulos, C. J. Brady and G. M. Wilson, *AIChE J.*, 1985, **31**, 376–384.
- 47 C. Tsionopoulos and G. M. Wilson, *AIChE J.*, 1983, **29**, 990–999.