PAPER www.rsc.org/njc | New Journal of Chemistry

The transfer of neutral molecules, ions and ionic species from water to ethylene glycol and to propylene carbonate; descriptors for pyridinium cations

Michael H. Abraham*[a] **and William E. Acree, Jr**[b]

Received (in Montpellier, France) 24th March 2010, Accepted 3rd June 2010
DOI: 10.1039/c0nj00222d

Equations have been constructed for the transfer of neutral solutes from water to the solvents ethylene glycol and propylene carbonate. These equations have been extended to include ions and ionic species derived from acids by loss of a proton and bases by acceptance of a proton. Only one additional term is needed for cations and one additional term for anions. The data used include literature data on the partition coefficients of simple ions, and literature data on pK_a values for carboxylic acids and amines in water, ethylene glycol and propylene carbonate from which we derive ionic partition coefficients. Descriptors have been obtained for 22 substituted pyridinium cations, and equations derived for the prediction of descriptors for further substituted pyridinium cations. Some of the pyridinium cations are the strongest hydrogen bond acids that we have encountered.

Introduction

In previous studies,[1–3] we have shown that two general equations, eqn (1) and (2), can be used for the transfer of neutral solutes from water to organic solvents and from the gas phase to organic solvents. The dependent variable in eqn (1) is log P, where P is the water to solvent partition coefficient for a series of solutes, and in eqn (2) is log K where K is the dimensionless gas phase to water partition coefficient for a series of solutes.

$$\log P_s = c + eE + sS + aA + bB + vV \qquad (1)$$

$$\log K_s = c + eE + sS + aA + bB + lL \qquad (2)$$

In eqn (1) and (2) the independent variables, or descriptors, are properties of the neutral solutes as follows:[4,5] E is the solute excess molar refraction in $cm^3\ mol^{-1}/10$, S is the solute dipolarity/polarizability, A is the overall solute hydrogen bond acidity, B is the overall solute hydrogen bond basicity, V is McGowan's characteristic molecular volume in $cm^3\ mol^{-1}/100$ and L is the logarithm of the gas to hexadecane partition coefficient at 298 K. Examples of the coefficients are shown in Table 1 for partition from water to a number of solvents.[2,3]

Recently, we have shown[6,7] that eqn (1) can be extended to include partition coefficients of ions and of ionic species; we use the latter term to describe anions derived from acids by loss of a proton, and cations derived from bases by acceptance of a proton. The descriptors for anions and cations are E, S, A, B, and V on exactly the same scales as for neutral molecules, together with an additional descriptor, J^-, for anions and an additional descriptor, J^+, for cations. The complementary solvent coefficients are j^- and j^+ so that eqn (1) is transformed into eqn (3),

$$\log P_s = c + eE + sS + aA + bB + vV + j^+J^+ + j^-J^- \qquad (3)$$

For anions $j^+ = 0$, for cations $j^- = 0$, and for neutral solutes $j^+ = j^- = 0$ so that eqn (3) then reverts to eqn (1). Values of the solvent j^+ and j^- coefficients are in Table 1,[7] and descriptors for ions and ionic species are in Table 2.

In order to set up eqn (3) for a new solvent it is necessary to obtain data on the partition of ions from water to the solvent, and also to have the corresponding equation for neutral solutes, eqn (1). Although we were able to set out the coefficients in eqn (2) for 14 solvents,[7] there were a number of important solvents for which we did not have sufficient data. These included ethylene glycol and propylene carbonate for which we had no reliable coefficients in eqn (1). Since then, Sprunger *et al.*[8] have collected data on the partition of neutral compounds from the gas phase and from water to dry ethylene glycol, and we have now collected data on partition from the gas phase and from water to dry propylene carbonate. From these data we can obtain equations corresponding to eqn (1) and (2), and it is the purpose of the present work to set out equations on the lines of eqn (3) for transfer of ions from water to ethylene glycol and to propylene carbonate. Transfers from water to dry solvents are in a sense hypothetical because they do not refer to 'practical' partitions where water and the solvent are in contact. However, partitions from water to dry solvents are of considerable utility as regards determination of the solubility of neutral solutes, and are of extreme importance in discussion of properties of ions.

---

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

Table 1 Coefficients in eqn (1) for partitions from water to solvents

Solvent	*c*	*e*	*s*	*a*	*b*	*v*	j^+	j^-
Methanol	0.276	0.334	−0.714	0.243	−3.320	3.549	−2.609	3.027
Ethanol	0.222	0.471	−1.035	0.326	−3.596	3.857	−3.170	3.085
Propan-1-ol	0.139	0.405	−1.029	0.247	−3.767	3.986	−3.077	2.834
Butan-1-ol	0.152	0.438	−1.177	0.096	−3.919	4.122	−3.605	2.685
Hexan-1-ol	0.115	0.492	−1.164	0.054	−3.971	4.131	−3.100	2.940
Propanone	0.313	0.312	−0.121	−0.608	−4.753	3.942	−2.288	0.078
Acetonitrile	0.413	0.077	0.326	−1.566	−4.391	3.364	−2.243	0.101
NMP[a]	0.147	0.532	0.275	0.840	−4.794	3.674	−1.797	0.105
DMSO[b]	−0.194	0.327	0.791	1.260	−4.540	3.361	−3.387	0.132

[a] *N*-Methylpyrrolidinone. [b] Dimethylsulfoxide.

Table 2 Descriptors for a selection of ions and ionic species[7]

Species	*E*	*S*	*A*	*B*	*V*	J^+	J^-
Li^+	−0.020	2.11	1.30	0.00	0.0140	0.154	0
Na^+	−0.020	2.31	1.22	0.00	0.0330	0.316	0
K^+	0.000	2.57	1.21	0.00	0.0920	0.357	0
Rb^+	0.020	2.55	1.05	0.00	0.1300	0.477	0
Cs^+	0.100	2.60	1.17	0.00	0.1770	0.438	0
NH_4^+	−0.011	1.77	1.80	0.00	0.2299	0.370	0
$MeNH_3^+$	0.100	2.90	1.35	0.00	0.3708	0.722	0
$EtNH_3^+$	0.086	2.84	1.30	0.00	0.5120	0.781	0
$BuNH_3^+$	0.074	1.93	1.30	0.00	0.7935	0.817	0
$Me_2NH_2^+$	0.039	2.41	1.00	0.00	0.5117	0.877	0
$Et_2NH_2^+$	0.004	2.30	0.98	0.00	0.7940	0.930	0
Me_3NH^+	−0.010	2.19	0.55	0.00	0.6526	1.064	0
Et_3NH^+	−0.049	1.93	0.60	0.00	1.0750	1.250	0
NMe_4^+	−0.100	1.31	0.68	0.00	0.7635	1.235	0
NEt_4^+	−0.100	1.85	0.51	0.00	1.3571	1.475	0
NPr_4^+	−0.100	2.02	0.42	0.00	1.9207	1.552	0
NBu_4^+	−0.100	2.82	0.61	0.00	2.4843	1.418	0
$PhNH_3^+$	0.805	1.62	1.93	0.00	0.8377	0.620	0
Ph_4P^+	2.220	3.11	0.04	0.92	2.7660	0.480	0
Ph_4As^+	2.220	3.20	0.07	0.91	2.8110	0.581	0
F^-	−0.050	3.76	0.00	2.42	0.1050	0	2.385
Cl^-	0.100	3.52	0.00	2.32	0.2280	0	2.363
Br^-	0.170	2.74	0.00	1.82	0.3070	0	1.567
I^-	0.380	3.55	0.00	1.34	0.4080	0	1.251
ClO_4^-	−0.160	5.14	0.00	0.99	0.4930	0	1.290
CN^-	0.070	1.99	0.00	1.86	0.2310	0	1.630
NO_3^-	0.170	1.98	0.00	1.97	0.3200	0	1.703
SCN^-	0.400	3.38	0.00	1.24	0.3650	0	1.242
N_3^-	0.160	3.04	0.00	1.82	0.2820	0	1.718
Ph_4B^-	1.950	2.72	0.18	1.15	2.7000	0	−0.188
Acetate	0.415	2.20	0.00	2.93	0.4433	0	2.075
Chloroacetate	0.577	2.44	0.00	2.56	0.5657	0	1.860
Phenylacetate	0.880	3.27	0.00	2.96	1.0511	0	2.153
Benzoate	0.880	3.64	0.00	2.88	0.9102	0	2.395
2-Chlorobenzoate	0.990	3.50	0.00	2.77	1.0326	0	2.160
3-Chlorobenzoate	0.990	3.13	0.00	2.57	1.0326	0	2.034
4-Chlorobenzoate	0.990	3.37	0.00	2.60	1.0326	0	2.179
4-Bromobenzoate	1.150	3.25	0.00	2.60	1.0852	0	2.148
4-Iodobenzoate	1.460	3.29	0.00	2.61	1.1684	0	2.059
3-Hydroxybenzoate	1.060	3.65	0.13	3.07	0.9689	0	2.344
4-Hydroxybenzoate	1.080	3.78	0.04	3.05	0.9689	0	2.382
2-Aminobenzoate	1.230	3.89	0.05	2.78	1.0100	0	2.146
3-Aminobenzoate	1.230	4.00	0.11	2.99	1.0100	0	2.121
4-Aminobenzoate	1.225	4.07	0.25	3.26	1.0100	0	2.357
2-Nitrobenzoate	1.140	3.92	0.00	2.96	1.0844	0	2.132
3-Nitrobenzoate	1.140	3.60	0.00	2.79	1.0844	0	2.217
4-Nitrobenzoate	1.140	3.50	0.00	2.79	1.0844	0	2.212

Methodology

There are two main methods for the determination of partition of neutral solutes from water to solvents. First, values of log K_s can be obtained from measurements of activity coefficients or Henry's law constants, or from gas–liquid chromatographic (GLC) measurements with the solvent as the stationary phase. These can be used directly in eqn (2) and can be transformed into log P_s values for use in eqn (1) through eqn (4), where log K_w is the gas to water partition coefficient. All data that we use refer to 298 K.

$$\log P_s = \log K_s - \log K_w \qquad (4)$$

The second method is through the determination of the solubility of a solute in water and the dry solvent. The ratio gives log P_s directly, with certain provisos that we have listed before.[3] Then if log K_w is known, eqn (4) can be used to obtain log K_s.

The solubility method can also be used to determine log P_s for neutral combinations of ions. The method is much more complex than for neutral solutes, and requires knowledge of the ion-pair association constant in the organic solvent as well as an estimation of the mean ionic activity coefficient of the electrolyte in the organic solvent.[6] In addition, the presence of hydrates or solvates will lead to errors in any determined log P_s value. Once log P_s for a neutral combination of ions has been obtained, it is necessary to use some particular convention to obtain values for the individual ions. We use the convention that log P_s (Ph_4P^+ or Ph_4As^+) = log P_s (Ph_4B^-), the well-known TATB assumption. In addition, we have recently developed a novel method for the determination of log P_s values of ionic species derived from acids through loss of a proton or from bases through acceptance of a proton, using eqn (5) and (6).

$$\log P_s\,(A^-) = \log P_s\,(HA) - \log P_s\,(H^+) + pK_a\,(aq) - pK_a\,(s) \qquad (5)$$

$$\log P_s\,(BH^+) = \log P_s\,(B) + \log P_s\,(H^+) - pK_a\,(aq) + pK_a\,(s) \qquad (6)$$

In eqn (5) and (6), pK_a (aq) and pK_a (s) are the pK_a values for an acid or a protonated base in water and the solvent, log P_s (HA) and log P_s (B) refer to the partition of the neutral acid or the neutral base, and log P_s (H^+) is the partition coefficient of the hydrogen ion, based on the TATB assumption. Values of pK_a (aq) and pK_a (s) are in the literature for some acids and protonated bases, and log P_s (HA) or log P_s (B) for the neutral species can be estimated from knowledge of their descriptors and the coefficients in the relevant equations, eqn (1). A main problem is the assignment of log P_s (H^+) which for many solvents has to be done by trial and error. However, there is a specific restriction on the assignment because the same value must be used in eqn (5) and (6).

Once single ion values of log P_s for permanent ions and of ionic species, log P_s (A^-) and log P_s (BH^+), have been obtained for a number of ions for which descriptors are known, Table 2, they can be fitted to the appropriate eqn (1) to give the corresponding eqn (3). Only two extra adjustable coefficients are allowed, j^+ for cations and j^- for anions.

Results

Ethylene glycol

Using data recently obtained by Sprunger *et al.*,[8] we can construct eqn (7) and (8) for 79 neutral solutes.

$$\log P_s = -0.270 + 0.578E - 0.511S + 0.715A - 2.619B + 2.729V \quad (7)$$

$$N = 79,\ R^2 = 0.978,\ SD = 0.177,\ F = 657.0$$

$$Q^2 = 0.974,\ PRESS = 2.6925,\ PSD = 0.192$$

$$\log K_s = -0.887 + 0.132E + 1.657S + 4.457A + 2.355B + 0.565L \quad (8)$$

$$N = 79,\ R^2 = 0.997,\ SD = 0.184,\ F = 4300.7$$

$$Q^2 = 0.996,\ PRESS = 3.0510,\ PSD = 0.192$$

In eqn (7) and (8), N is the number of data points (compounds), R is the correlation coefficient, SD is the regression standard deviation, and F is the F-statistic. The leave-one-out statistics are[1] Q^2, PRESS, and the predictive standard deviation, PSD.

There have been a number of reports on the partition of ions from water to ethylene glycol.[9–14] Bates[14] analysed data on the emf of cells, leading to partition coefficients for pairs of ions as follows: log P_s ($H^+ + Cl^-$) = −3.27 and log P_s ($H^+ + Br^-$) = −2.77; then using log P_s (H^+) = −1.20,[10] it follows that log P_s (Cl^-) = −2.07 and log P_s (Br^-) = −1.57, close to the values of Kundu *et al.*[13] The electrochemical data[13,14] for halide ions seem to be more reliable than data based on solubilities,[9–12] and we take the Kundu *et al.*[13] values for the halide anions as log P_s (Cl^-) = −2.07, log P_s (Br^-) = −1.62, and log P_s (I^-) = −1.10; these values of log P_s are on the molar scale at 298 K based on the TATB convention. Dash *et al.*[15] have determined pK_a values for a large number of monocarboxylic acids in ethylene glycol, and we have used eqn (5) to determine log P_s values from water to ethylene glycol for 15 carboxylate anions, exactly as before.[7] We then have 19 anions for which we have values of log P_s (A^-), Table 3, and for which we have descriptors as shown in Table 2. These anions must be fitted to eqn (7) with only one allowed extra coefficient, j^-. For the 19 anions, with j^- = 2.363, we can fit the observed log P_s (A^-) values with an absolute error AE = −0.012, an average absolute error AAE = 0.166, a root mean square error RMSE = 0.196 and a standard deviation SD = 0.201 log units. The calculated and observed values are in Table 3.

Table 3 Calculated and observed values of log P_s for transfer from water to ethylene glycol for a series of anions

	log P_s	
Anion	Calc.	Obs.
Cl^-	−1.88	−2.07
Br^-	−1.80	−1.62
I^-	−1.31	−1.10
Ph_4B^-	3.51	3.60
Acetate	−2.71	−2.42
Chloroacetate	−1.95	−1.89
Phenylacetate	−1.23	−1.31
Benzoate	−1.02	−1.23
2-Chlorobenzoate	−0.82	−0.92
3-Chlorobenzoate	−0.40	−0.37
4-Chlorobenzoate	−0.26	−0.26
3-Hydroxybenzoate	−1.29	−0.90
4-Hydroxybenzoate	−1.26	−0.97
2-Aminobenzoate	−0.96	−1.27
3-Aminobenzoate	−1.59	−1.77
4-Aminobenzoate	−1.67	−1.55
2-Nitrobenzoate	−1.37	−1.35
3-Nitrobenzoate	−0.56	−0.70
4-Nitrobenzoate	−0.52	−0.77

The situation with the alkali metal cations is more difficult. Most of the experimental data[9–12] suggest that log P_s increases in the order $Li^+ < Na^+ \approx K^+$ whereas data for transfers to all the alcohols lead to the order[7] $Li^+ > Na^+ > K^+ \approx Rb^+ < Cs^+$ and to water–alcohol mixtures the order is[10] $Li^+ > Na^+ \approx K^+ \approx Rb^+ < Cs^+$, see Table 4. Gritzner[16] has set out values for the alkali metal cations obtained by electrochemical measurements, based on the bis(biphenylchromium) convention, *viz.*: Li^+ (0.23), Na^+ (−0.25), K^+ (−0.25), and Rb^+ (−0.39). This sequence is almost the same as that found for transfers to alcohols and water–alcohol mixtures. In addition to these directly observed log P_s values, Kundu *et al.*[13] have determined pK_a values for a number of substituted ammonium ions in ethylene glycol. We can then use eqn (6) to calculate log P_s values for the protonated amines (BH^+) using the same value of −1.20 for log P_s (H^+) as before. These log P_s values are compatible with log P_s for Ph_4As^+, for which we take an average value of 3.60 log units.[9–12] For six protonated amines and Ph_4As^+ we find AE = 0.037, AAE = 0.220, RMSE = 0.258 and SD = 0.279 log units with the single adjustable constant of −1.353 for j^+. We can incorporate the values for the alkali metal cations obtained by Gritzner[16] by subtraction of 0.71 log units to convert them to the TATB convention, and to be consistent with the Kundu *et al.*[13] values for the protonated amines. For the 11 cations in Table 5, the calculated and observed values have AE = −0.010, AAE = 0.158, RMSE = 0.210 and SD = 0.220 log units using the one floating constant, j^+ = −1.352 units. However, if we take any one of the sets of data in Table 4, we obtain very poor results indeed. For example, the four cations from ref. 12 give AE = −0.212, AAE = 0.652, RMSE = 0.712 and SD = 0.822 log units with j^+ = −1.019 units. We conclude that results from the 11 cations in Table 5 are the most consistent.

Headley and Nam[17] have determined pK_a values for a series of *N*,*N*-dimethylalkyl amines relative to trimethylamine. From the observed value of log P_s for Me_3NH^+, Table 5, we can calculate that the pK_a of trimethylamine is 10.94 in ethylene

Table 4 log P_s values for transfer of cations from water to solvents and aqueous solvents[a]

	MeOH	EtOH	PrOH	EtOH $X = 0.5$	MeOH $X = 0.5$	Ethylene glycol				
Ion	7	7	7	10	10	9	10	12	13	16[b]
H^+	−1.82	−1.60	1.15			−0.88	−1.10	−1.30	−1.20	
Li^+	−0.88	−1.93	−1.98	−0.44	−0.54	0.00	−0.58	−0.39	−0.31	−0.48
Na^+	−1.40	−2.45	−2.95	−0.91	−1.07	0.35	−0.22	−0.04	0.04	−0.96
K^+	−1.75	−2.80	−3.11	−0.88	−1.10	0.35	−0.28	−0.04	0.04	−0.96
Rb^+	−1.75	−2.80	−3.39	−1.03	−1.23					−1.10
Cs^+	−1.58	−2.63	−3.06	−0.96	−1.07					
Ph_4As^+						3.68	3.73	3.30		

[a] Aqueous solvents with mol fraction water, $X = 0.5$. [b] See text.

Table 5 Calculated and observed values of log P_s for transfer from water to ethylene glycol for a series of cations

	log P_s	
Cation	Calc.	Obs.
Li^+	−0.60	−0.48[a]
Na^+	−0.93	−0.96[a]
K^+	−0.95	−0.96[a]
Rb^+	−1.10	−1.10[a]
$MeNH_3^+$	−0.69	−0.32
$EtNH_3^+$	−0.20	−0.15
$Me_2NH_2^+$	−0.55	−0.50
$Et_2NH_2^+$	0.17	−0.07
Me_3NH^+	−0.66	−0.35
Et_3NH^+	0.25	0.06
Ph_4As^+	3.97	3.60

[a] From ref. 16, see text.

glycol, and we can then obtain pK_a values for the *N*,*N*-dimethylalkylamines. We obtained the descriptors for the protonated amines from the equations we have previously set out,[7] and give them in Table 6, together with the pK_a values in ethylene glycol.

If the nine cations in Table 6 are taken with the 11 cations in Table 5, the resulting equation is eqn (9) with $j^+ = -1.300$ almost the same as that found for the 11 cations in Table 5 ($j^+ = -1.352$). For the total 20 cations, eqn (9) yields AE = 0.003, AAE = 0.141, RMSE = 0.183 and SD = 0.188 log units, and we regard this equation as the most reasonable equation for the partition of neutral compounds, anions and cations from water to ethylene glycol.

$$\log P_s = -0.270 + 0.578E - 0.511S + 0.715A - 2.619B + 2.729V - 1.300J^+ + 2.363J^- \quad (9)$$

Table 6 Descriptors and pK_a values in ethylene glycol for a series of protonated amines, Me_2NRH^+

R	*E*	*S*	*A*	*B*	*V*	J^+	pK_a
Et	−0.056	2.10	0.51	0	0.7935	1.110	11.09
Pr	−0.060	2.10	0.51	0	0.9344	1.106	11.16
iso-Pr	−0.043	2.29	0.50	0	0.9344	1.213	11.45
Bu	−0.065	2.12	0.51	0	1.0753	1.112	11.16
s-Bu	−0.120	2.27	0.53	0	1.0753	1.125	11.45
t-Bu	−0.250	2.31	0.58	0	1.0753	1.017	11.67
t-Pe	−0.250	2.31	0.58	0	1.2162	1.017	11.97
Cyclohexyl	0.220	2.44	0.59	0	1.2485	1.427	11.52
Benzyl	0.518	2.53	1.20	0	1.2604	1.277	10.50

Propylene carbonate

We had no equation available for the partition of neutral solutes from the gas phase or water to propylene carbonate, and so we collected results from the literature on data that would lead to values of log K_s. The prime set of data is that of Topphoff *et al.*[18] on activity coefficients, γ, obtained between 303 K and 333 K. We extrapolated these to 298 K through plots of log γ *vs.* $1/T$ and then calculated the corresponding values of log K_s. Activity coefficients were also obtained from Castells *et al.*,[19] Lenoir *et al.*,[20] and Vernier *et al.*,[21] supplemented by other data[22–30] on activity coefficients. The obtained values of log K_s are in Table 7. From these values log P_s values were obtained through eqn (4). We also collected solubilities of a number of solids in propylene carbonate, S_s, and determined several solubilities ourselves. Combination with corresponding solubilities in water, S_w, yields partition coefficients as shown in Table 8. The compounds in Table 8 are very important in setting out equations for log K_s and log P_s because they include strong hydrogen bond acids and strong hydrogen bond bases.

There are a total of 69 compounds in Tables 7 and 8, for which we have the necessary descriptors to obtain equations on the lines of eqn (1) and (2),

$$\log P_s = 0.004 + 0.168E + 0.504S - 1.283A - 4.407B + 3.421V \quad (10)$$

$$N = 69,\ R^2 = 0.988,\ \mathrm{SD} = 0.158,\ F = 1055.5$$

$$Q^2 = 0.984,\ \mathrm{PRESS} = 2.0826,\ \mathrm{PSD} = 0.182$$

$$\log K_s = -0.356 - 0.413E + 2.587S + 2.207A + 0.455B + 0.719L \quad (11)$$

$$N = 69,\ R^2 = 0.998,\ \mathrm{SD} = 0.143,\ F = 5052.8$$

$$Q^2 = 0.996,\ \mathrm{PRESS} = 1.9450,\ \mathrm{PSD} = 0.176$$

We can then use eqn (10) as a basis for constructing an equation for partition of ions. Compilations of Gibbs energies of transfer of ions from water to propylene glycol have been collected by Marcus[9] and by Bunakova *et al.*[35] The given values are virtually identical, although Bunakova *et al.* include a few more ions. An independent assessment[36] gives values for the halide anions as close to those of Bunakova *et al.*,[35] but

Table 7 Values of log K_s and of log P_s for volatile solutes in propylene carbonate at 298 K

Solute	log K_s	Ref.	log K_w	log P_s
Argon	−1.06	23	−1.47	0.41
Hydrogen	−1.46	22	−1.72	0.26
Nitrogen	−1.20	24	−1.80	0.60
Carbon dioxide	0.63	20	−0.08	0.71
Hydrogen sulfide	1.14	20	0.49	0.65
Sulfur dioxide	2.38	20	1.53	0.85
COS	0.84	25	−0.30	1.14
Water	3.06	26	4.69	−1.63
Methane	−0.60	20	−1.46	0.86
Ethane	0.10	20	−1.34	1.44
Propane	0.43	20	−1.44	1.87
Butane	0.88	20	−1.52	2.40
Pentane	1.22	19	−1.70	2.92
Hexane	1.53	18	−1.82	3.35
Heptane	1.88	18	−1.96	3.84
Octane	2.26	18	−2.11	4.37
Nonane	2.53	19	−2.15	4.68
Decane	2.97	18	−2.32	5.29
Isobutane	0.64	20	−1.70	2.34
2-Methylpentane	1.45	19	−1.84	3.29
2,4-Dimethylpentane	1.62	19	−2.08	3.70
2,5-Dimethylhexane	1.94	19	−2.02	3.96
2,3,4-Trimethylpentane	2.10	19	−1.88	3.98
Cyclohexane	1.95	18	−0.90	2.85
Methylcyclopentane	1.77	18	−1.17	2.94
Methylcyclohexane	2.14	18	−1.25	3.39
Ethylcyclohexane	2.50	19	−1.58	4.08
Ethene	0.18	20	−0.94	1.12
Propene	0.72	20	−0.97	1.69
Hex-1-ene	1.73	18	−1.16	2.89
Oct-1-ene	2.47	18	−1.41	3.88
2-Methylbut-2-ene	1.54	21	−0.96	2.50
1,3-Butadiene	1.44	20	−0.45	1.89
2-Methylbuta-1,3-diene	1.79	21	−0.50	2.29
Cyclohexene	2.29	18	−0.27	2.56
Benzene	2.84	18	0.63	2.21
Toluene	3.20	18	0.65	2.55
Ethylbenzene	3.53	18	0.58	2.95
o-Xylene	3.71	18	0.66	3.05
m-Xylene	3.55	18	0.61	2.94
p-Xylene	3.54	18	0.59	2.95
Diethyl ether	1.89	18	1.28	0.61
Diisopropyl ether	2.13	18	1.09	1.04
Methyl *tert*-butyl ether	2.24	18	1.45	0.79
Ethyl *tert*-butyl ether	2.24	18	1.18	1.06
Methyl *tert*-pentyl ether	2.59	18	1.31	1.28
Isopropyl *tert*-butyl ether	2.34	18	0.74	1.60
Butanone	3.18	18	2.72	0.46
Pentan-2-one	3.48	18	2.58	0.90
Dichloromethane	2.55	18	0.96	1.59
Trichloromethane	2.88	18	0.79	2.09
1,2-Dichloroethane	3.17	18	1.31	1.86
tert-Butyl chloride	2.03	27	−0.80	2.83
tert-Butyl bromide	2.43	27	−0.62	3.05
Iodoethane	2.71	28	0.54	2.17
Triethylamine	2.13	29	2.36	−0.23
Tetramethyltin	1.66	30	−1.53	3.19

Table 8 Solubilities, as log S_s, with S_s in mol dm^{-3} at 298 K for solids in propylene carbonate

Solute	log S_s	Ref.	log S_w	log P_s
Biphenyl	0.14	This work	−4.33	4.47
Anthracene	−1.61	This work	−6.43	4.82
Pyrene	−0.67	34	−6.15	5.48
Benzil	−0.01	This work	−4.02	4.03
Ferrocene	−0.82	This work	−4.47	3.65
Monouron	−0.83	This work	−2.94	2.11
Diuron	−1.00	This work	−3.74	2.74
Diphenylsulfone	−0.09	This work	−3.64	3.55
2-Methylbenzoic acid	−0.33	32	−2.06	1.73
2-Methoxybenzoic acid	0.00	31	−1.55	1.55
4-Chlorobenzoic acid	−1.42	This work	−3.56	2.14
4-Nitrobenzoic acid	−1.24	33	−2.98	1.74

log P_s values for the perchlorate anion are rather different: 0.48[35] and −0.15[36] on the TATB scale. Augustin-Nowacka *et al.*[37] have determined pK_a for a large number of substituted protonated pyridines in several solvents, including propylene carbonate. There are enough solvents to determine the descriptors for the protonated pyridinium cations, and then to use the descriptors and the pK_a values in propylene carbonate to obtain log P_s values for the pyridinium cations. Zielińska *et al.*[38] list pK_a values for protonated butylamine (16.95) and for acetic acid (18.17) in propylene carbonate. In order to make use of these pK_a values through eqn (5) and (6), a value for log P_s (H$^+$) is needed. This cannot simply be allowed to float in order to obtain agreement between observed and calculated properties, because the same value of log P_s (H$^+$) must be used in both equations. We find that log P_s (H$^+$) = −6.0 satisfies both eqn (5) and (6). With j^- = 0.341, the eight anions can be fitted with AE = −0.088, AAE = 0.248, RMSE = 0.335 and SD = 0.358 log units, as shown in Table 9. But note that the value for ClO_4^- in Table 9 is the average of 0.48[35] and −0.15.[36]

The log P_s for values for the alkali metal cations are quite scattered, see Table 10. Results based on solubilities reveal considerable differences in observed values,[36] and the set chosen[36] is markedly different to the Marcus[9] and Bunakova *et al.*[35] set. The set independently obtained by Matsuura and Umemoto[39] is not too far from Gritzner's[16] values when the latter is adjusted to the TATB convention. We decided not to use any of the quoted values except that of K$^+$. All the values for Na$^+$ are quite out of line with those we calculate, and for

Table 9 Calculated and observed values of log P_s for transfer from water to propylene carbonate for a series of anions

	log P_s	
Anion	Calc.	Obs.[a]
Cl^-	−6.85	−6.97
Br^-	−5.02	−5.25
I^-	−2.20	−2.40
ClO_4^-	0.20	0.16[b]
N_3^-	−4.91	−4.78
Ph_4B^-	5.58	6.31
Acetate	−9.51	−9.03[c]
Picrate	−1.05	−1.00

[a] Ref. 35. [b] Ref. 35 and 36. [c] Ref. 38.

Table 10 Log P_s values for transfer of cations to propylene carbonate

Ion	Ref. 35	Ref. 36	Ref. 16	Ref. 39	Calc.
Na^+	−2.56	−2.36	−2.27	−1.91	−0.92
K^+	−0.93	−0.96	−0.86	−0.24	−0.66
Rb^+	0.17	−0.30	−0.11	−0.61	−0.56
Cs^+	1.22	0.28	−0.41	−0.51	−0.44

Table 11 Calculated and observed values of log P_s for transfer of cations from water to propylene carbonate

	log P_s	
Cation	Calc.	Obs.
Na^+	−0.92	
K^+	−0.66	−0.90
Rb^+	−0.56	
Cs^+	−0.44	
$BuNH_3^+$	0.41	0.35
Et_4N^+	2.01	2.33
Pr_4N^+	3.95	3.91
2-MethylpyridineH$^+$	0.35	0.55
3-MethylpyridineH$^+$	0.48	0.40
4-MethylpyridineH$^+$	0.62	0.49
2,3-DimethylpyridineH$^+$	0.91	0.56
2,4-DimethylpyridineH$^+$	0.52	0.48
2,6-DimethylpyridineH$^+$	0.84	0.88
3,4-DimethylpyridineH$^+$	0.85	0.80
3,5-DimethylpyridineH$^+$	0.56	0.18
2-ChloropyridineH$^+$	0.51	0.76
3-ChloropyridineH$^+$	0.33	0.94
3-CyanopyridineH$^+$	0.46	0.58
4-CyanopyridineH$^+$	0.39	0.41
2-AminopyridineH$^+$	0.58	0.37
3-AminopyridineH$^+$	0.65	0.76
4-AminopyridineH$^+$	1.00	1.08
Ph_4As^+	6.36	6.31

the other cations we just took an average value of −0.90 for K^+ and did not use any other data.

Fortunately, we can use the log P_s values for pyridinium cations as shown in Table 11, and with $j^+ = -1.989$ we can fit the 20 observed values for the cations with AE = −0.006, AAE = 0.169, RMSE = 0.225 and SD = 0.231 log units. For some reason the calculated and observed values for the pyridinium cation were considerably out of line: observed value 0.91 from data in ref. 37, and calculated value −0.03 log units.

The final equation for transfer of neutral species, ions and ionic species from water to propylene carbonate is given as eqn (10),

$$\log P_s = 0.004 + 0.168E + 0.504S - 1.283A - 4.407B + 3.421V - 1.989J^+ + 0.341J^- \qquad (12)$$

Discussion

The statistics for the equations for partition of neutral species from the gas phase to the two solvents and from water to the two solvents are good, and these equations can be used to predict further values of log K_s and log P_s with an estimated error given by the various predicted standard deviations, PSD. The equations for transfer to ethylene glycol show that this solvent acts as a somewhat stronger hydrogen bond base than methanol and an appreciably stronger hydrogen bond acid; compare the coefficients in eqn (7) with those in Table 1. Propylene carbonate as a solvent is a surprisingly weak hydrogen bond base, somewhere between propanone and acetonitrile, but seems to have a small, although statistically significant, hydrogen bond acidity.

Although data on the transfer of anions from water to ethylene glycol are reasonably self-consistent, there is considerable scatter in values of log P_s for cations, see Table 4. Much of the data on the alkali metal cations have been derived from the solubility of electrolytes in water and ethylene glycol, but there has been little regard to the possibility of solvate formation in the organic solvent. Interestingly, the electrochemical results for anions, in which solvate formation is irrelevant, seem to be more self-consistent than data derived from solubilities. In the event, the two additional descriptors needed to convert eqn (7) into eqn (9) are compatible with those for transfers into alcohols. For ethylene glycol, $j^+ = -1.300$ and $j^- = 2.363$, as compared to values for the alcohols from −2.609 to −3.605 and from 2.940 to 3.085, see Table 1.

The same problem over the alkali metal cations occurs in transfers to propylene carbonate, but for this solvent, the large amount of electrochemical data on protonated amines and pyridines enable j^+ to be evaluated without any great reliance on the data for alkali metal cations. The final equation for partition of neutral molecules, ions and ionic species, eqn (12), contains $j^+ = -1.989$ and $j^- = 0.341$; compare values for other aprotic solvents in Table 1 as −3.387 to −1.797 and 0.078 to 0.132 respectively. Thus propylene carbonate and ethylene glycol follow the trend that j^- is large and positive for hydroxylic solvents but very small for aprotic solvents.

This has the effect that log P_s for a given anion will be much more negative in an aprotic solvent than in a hydroxylic solvent. However, this is not the only large effect, and a breakdown for the transfers of the chloride ion and the acetate ion are given in Table 12. The bB term is very important for both transfer of the chloride and the acetate anion. This arises because water is a stronger hydrogen bond acid than ethylene glycol but is a very much stronger hydrogen bond acid than propylene carbonate. Hence hydrogen bond bases prefer ethylene glycol (EG) to propylene carbonate (PC) to the extent of 4.15 log units for the chloride anion and 5.24 log units for the acetate anion.

Table 12 A breakdown of the factors that influence partition of the chloride and acetate anions

System	Ion	eE	sS	bB	vV	j^-J^-	Calc.[a]	Obs
Water → EG	Chloride	0.06	−1.80	−6.07	0.62	5.58	−1.88	−2.07
Water → PC	Chloride	0.02	1.77	−10.22	0.78	0.80	−6.85	−6.97
EG → PC	Chloride	−0.04	3.57	−4.15	0.16	−4.78	−4.97	−4.90
Water → EG	Acetate	0.24	−1.12	−7.67	1.21	4.90	−2.71	−2.42
Water → PC	Acetate	0.07	1.11	−12.91	1.51	0.71	−9.51	−9.03
EG → PC	Acetate	−0.17	2.23	−5.24	0.30	−4.19	−6.80	−6.61

[a] Including the constant −0.27 in eqn (9) and 0.00 in eqn (12).

Table 13 Descriptors for substituted pyridinium cations

Substituent	E	S	A	B	V	J^+
Pyridine	0.481	2.250	1.210	0.000	0.6968	1.045
2-Methyl	0.448	2.000	1.090	0.000	0.8377	1.110
3-Methyl	0.481	2.290	1.290	0.000	0.8377	0.988
4-Methyl	0.480	2.280	1.150	0.000	0.8377	1.008
2,3-Dimethyl	0.507	2.290	1.160	0.000	0.9786	1.100
2,4-Dimethyl	0.484	2.050	1.200	0.000	0.9786	1.210
2,6-Dimethyl	0.457	1.900	1.040	0.000	0.9786	1.110
3,4-Dimethyl	0.526	3.050	1.700	0.000	0.9786	0.930
3,5-Dimethyl	0.509	2.250	1.420	0.000	0.9786	1.100
2-Chloro	0.588	4.100	2.700	0.000	0.8192	0.500
3-Chloro	0.582	1.870	1.250	0.000	0.8192	0.960
4-Chloro	0.590	1.950	1.260	0.000	0.8192	0.950
2-Bromo	0.771	5.330	3.500	0.000	0.8718	0.300
3-Bromo	0.755	3.200	2.080	0.000	0.8718	0.670
4-Bromo	0.750	2.650	1.620	0.000	0.8718	0.780
3-Cyano	0.600	7.160	4.650	0.000	0.8515	0.101
4-Cyano	0.600	6.470	4.200	0.000	0.8515	0.250
2-Acetyl	0.580	5.780	3.890	0.000	0.9943	0.350
4-Dimethylamino	0.830	6.710	3.750	0.000	1.0784	0.191
2-Amino	0.830	4.100	2.600	0.000	0.7966	0.512
3-Amino	0.830	4.500	2.970	0.000	0.7966	0.340
4-Amino	0.830	2.800	1.440	0.000	0.7966	0.720

Previously, we have set out descriptors for a number of permanent ions, carboxylate anions, protonated amine cations[7] and phenoxide anions.[40] In our list of protonated amines,[7] we included pyridine and a few substituted pyridines. However, descriptors for the substituted pyridinium cations were based on very few data, and so we used the pK_a values of Augustin-Nowacka *et al.*[37] to determine log P_s for the cations through eqn (6), and then used the log P_s values to obtain the descriptors given in Table 13. As before,[7] for protonated bases we took E as 0.15 units less than that for the neutral pyridine, and V as 0.0125 units more than that for the neutral pyridine. This leaves three descriptors, S, A and J^+ to be obtained, since B is zero in all cases. The obtained descriptors, Table 13, for the 2-halopyridinium cations are substantially different to those for the 3- and 4-halopyridinium cations, but this is reflected in the quoted[37] pK_a values. For example, in acetonitrile pK_a values are 6.80 (2-chloropyridine) and 10.01 (3-chloropyridine), and in propylene carbonate they are 5.51 (2-chloropyridine) and 8.28 (3-chloropyridine). Some of the functionally substituted pyridinium cations are extraordinarily strong hydrogen bond acids. Many of the cations have A-values larger than 3.5, which makes them even stronger hydrogen bond acids than 3-nitroaniline (A = 3.06)[7] and the strongest hydrogen bond acids that we have encountered. The dipolarity/polarizability descriptor, S, is also very large indeed for many of the pyridinium cations.

Since we had descriptors for 22 pyridinium cations, we thought it useful to set out equations that could be used to predict values of these descriptors for other substituted pyridinium cations. As independent variables, we used descriptors for the neutral compounds, together with the pK_a values of the neutral compounds in water. In order to avoid confusion between the two sets of descriptors, we refer to those for the pyridinium cations with the subscript 'i'; the descriptors E, S, B and V that are independent variables in eqn (14)–(16) refer to the neutral pyridines. The predictive standard deviations, PSD, are reasonably small and suggest that eqn (14)–(16) can be used to predict values of the ionic descriptors for other substituted pyridinium cations.

$$E_i = -0.15 + 1.00E \tag{13}$$

$$S_i = -7.783 - 3.120E + 10.978S + 2.398B + 2.277V \tag{14}$$

$$N = 22,\ R^2 = 0.995,\ \mathrm{SD} = 0.138,\ F = 835.8$$

$$Q^2 = 0.991,\ \mathrm{PRESS} = 0.5438,\ \mathrm{PSD} = 0.179$$

$$A_i = -4.844 - 0.463E + 5.447S + 3.405B + 1.356V - 0.175\mathrm{p}K_a\ (\text{in water}) \tag{15}$$

$$N = 22,\ R^2 = 0.997,\ \mathrm{SD} = 0.069,\ F = 1230.0$$

$$Q^2 = 0.995,\ \mathrm{PRESS} = 0.13649,\ \mathrm{PSD} = 0.093$$

$$J^+ = 2.745 - 0.498E - 1.473S - 0.774B + 0.0396\mathrm{p}K_a\ (\text{in water}) \tag{16}$$

$$N = 22,\ R^2 = 0.982,\ \mathrm{SD} = 0.053,\ F = 230.5$$

$$Q^2 = 0.968,\ \mathrm{PRESS} = 0.08525,\ \mathrm{PSD} = 0.071$$

$$V_i = 0.0215 + 1.00V \tag{17}$$

Experimental

As part of the study, we measured the solubility of biphenyl, anthracene, benzil, ferrocene, monuron, diuron, diphenyl sulfone and 4-chlorobenzoic acid in propylene carbonate at 298 K. Excess solute and solvent were placed in amber glass bottles and allowed to equilibrate in a constant temperature water bath at 298.15(± 0.05) K for at least three days (often longer) with periodic shaking in order to facilitate dissolution of the solid. Attainment of equilibrium was verified by repetitive measurements after a minimum of three additional days and by approaching equilibrium from supersaturation by pre-equilibrating the solutions at a slightly higher temperature. Aliquots of saturated solutions were transferred through a coarse filter into a tared volumetric flask to determine the amount of sample and then diluted quantitatively with methanol for spectrophotometric analysis on a Bausch and Lomb Spectronic 2000. Concentrations of the dilute solutions were determined from a Beer–Lambert law absorbance *versus* concentration working curve. The analysis wavelengths and concentration ranges used for each solute were reported earlier.[41–47] Results are in Table 8.

Conclusion

Equations for the partition of neutral compounds from the gas phase and from water to ethylene glycol and propylene carbonate have been constructed. The statistics indicate that these equations can usefully be used to predict further values of partition coefficients for neutral species. Examination of data in the literature has enabled us to extend the equations to the partition of ions and ionic species from water. However, the literature data on ionic transfers, especially for simple cations, are quite scattered, and only by incorporation of partition coefficients derived from the variation of pK_a with solvent can any reliable equations be developed. Descriptors for substituted pyridinium cations have been obtained, and a set of equations derived that can be used to predict further values. This considerably extends our data base of descriptors for ionic species derived from the protonation of amines.

References

1 M. H. Abraham, W. E. Acree, Jr. and J. E. Cometto-Muñiz, *New J. Chem.*, 2009, **33**, 2034–2043.
2 L. M. Sprunger, S. S. Achi, R. Pointer, B. H. Blake-Taylor, W. E. Acree, Jr. and M. H. Abraham, *Fluid Phase Equilib.*, 2009, **286**, 170–174.
3 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.
4 M. H. Abraham, *Chem. Soc. Rev.*, 1993, **22**, 73–83.
5 M. H. Abraham, A. Ibrahim and A. M. Zissimos, *J. Chromatogr., A*, 2004, **1037**, 29–47.
6 M. H. Abraham and Y. H. Zhao, *J. Org. Chem.*, 2004, **69**, 4677–4685.
7 M. H. Abraham and W. E. Acree, Jr., *J. Org. Chem.*, 2010, **75**, 1006–1015.
8 L. M. Sprunger, S. S. Achi, W. E. Acree, Jr. and M. H. Abraham, *Fluid Phase Equilib.*, 2010, **288**, 139–144 (Supporting information).
9 Y. Marcus, *Pure Appl. Chem.*, 1983, **55**, 977–1021.
10 C. Kalidas, G. Hefter and Y. Marcus, *Chem. Rev.*, 2000, **100**, 819–852.
11 Y. Marcus, *Chem. Rev.*, 2007, **107**, 3880–3897.
12 A. K. Das and K. K. Kundu, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, 1978, **16**, 467–470.
13 K. K. Kundu, A. K. Rakshit and M. N. Das, *Electrochim. Acta*, 1972, **17**, 1921–1937.
14 R. G. Bates, in *Hydrogen-bonded solvent systems*, ed. A. K. Covington and P. Jones, Taylor and Francis, London, 1968.
15 U. N. Dash, S. P. Kalia and M. K. Mishra, *J. Electrochem. Soc. India*, 1988, **37**, 323–331.
16 G. Gritzner, *J. Chem. Eng. Data*, 2010, **55**, 1914–1920.
17 A. D. Headley and J. Nam, *J. Phys. Org. Chem.*, 2002, **15**, 62–68.
18 M. Topphoff, D. Gruber and J. Gmehling, *J. Chem. Eng. Data*, 1999, **44**, 1355–1359.
19 C. B. Castells, D. I. Eikens and P. W. Carr, *J. Chem. Eng. Data*, 2000, **45**, 369–375.
20 J.-Y. Lenoir, P. Renault and H. Renon, *J. Chem. Eng. Data*, 1971, **16**, 340–342.
21 P. Vernier, C. Raimbault and H. Renon, *J. Chim. Phys. Phys.-Chim. Biol.*, 1969, **66**, 429–436.
22 Solubility Data Project, *Hydrogen and Deuterium*, ed. C. L. Young, Pergamon, Oxford, 1981, vol. 5/6.
23 Solubility Data Project, *Argon*, ed. H. L. Clever, Pergamon, Oxford, 1980, vol. 4.
24 R. Battino, T. R. Rettich and T. Tominaga, *J. Phys. Chem. Ref. Data*, 1984, **13**, 563–600.
25 C. W. Sweeney, *Chromatographia*, 1984, **18**, 663–667.
26 B. G. Cox, A. J. Parker and W. E. Waghorne, *J. Am. Chem. Soc.*, 1973, **95**, 1010–1014.
27 M. H. Abraham, P. L. Grellier, A. Nasehzahdeh and R. A. C. Walker, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1717–1724.
28 M. H. Abraham and P. L. Grellier, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1735–1741.
29 M. H. Abraham and A. Nasehzadeh, *J. Chem. Thermodyn.*, 1981, **13**, 549–556.
30 M. H. Abraham and A. Nasehzadeh, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 321–340.
31 K. R. Hoover, D. W. Stovall, E. Pustejovsky, R. Coaxum, K. Pop, W. E. Acree, Jr. and M. H. Abraham, *Can. J. Chem.*, 2004, **82**, 1353–1360.
32 R. Coaxum, K. R. Hoover, E. Pustejovsky, D. W. Stovall, W. E. Acree, Jr. and M. H. Abraham, *Phys. Chem. Liq.*, 2004, **42**, 313–322.
33 K. R. Hoover, R. Coaxum, E. Pustejovsky, D. W. Stovall, W. E. Acree, Jr. and M. H. Abraham, *Phys. Chem. Liq.*, 2004, **42**, 339–347.
34 W. E. Acree, Jr. and M. H. Abraham, *Fluid Phase Equilib.*, 2002, **201**, 245–258.
35 L. V. Bunakova, L. A. Kova and L. I. Krishtalik, *Russ. J. Electrochem.*, 2005, **41**, 287–293.
36 M. H. Abraham, *Monatsh. Chem.*, 1979, **110**, 517–524.
37 D. Augustin-Nowacka, M. Makowski and L. Chmurzyński, *Anal. Chim. Acta*, 2000, **418**, 233–240.
38 J. Zielińska, M. Makowski, K. Maj, A. Liwo and L. Chmurzyński, *Anal. Chim. Acta*, 1999, **401**, 317–321.
39 N. Matsuura and K. Umemoto, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 1334–1337.
40 M. H. Abraham and W. E. Acree, Jr., *J. Org. Chem.*, 2010, **75**, 3021–3026.
41 C. E. Green, M. H. Abraham, W. E. Acree, Jr., K. M. De Fina and T. L. Sharp, *Pest Manage. Sci.*, 2000, **56**, 1043–1053.
42 K. M. De Fina, C. Ezell and W. E. Acree, Jr., *Phys. Chem. Liq.*, 2001, **39**, 699–710.
43 W. E. Acree, Jr. and M. H. Abraham, *J. Solution Chem.*, 2002, **31**, 293–303.
44 K. M. De Fina, T. L. Sharp and W. E. Acree, Jr., *Can. J. Chem.*, 1999, **77**, 1589–1593.
45 M. V. Marthandan and W. E. Acree, Jr., *J. Chem. Eng. Data*, 1987, **32**, 301–303.
46 K. M. De Fina, T. T. Van, K. A. Fletcher and W. E. Acree, Jr., *Can. J. Chem.*, 2000, **78**, 449–453.
47 C. R. Daniels, A. K. Charlton, R. M. Wold, W. E. Acree, Jr. and M. H. Abraham, *Can. J. Chem.*, 2003, **81**, 1492–1501.