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Equations for the Partition of Neutral Molecules, Ions and Ionic Species from Water to Water–Ethanol Mixtures

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Abstract Equations set up for the transfer of neutral solutes from water to water–ethanol mixtures can also be used to correlate the transfer of ions and ionic species, as $\log_{10} P$, where P is the partition coefficient. Only two additional terms are required in the equations, one for anions and one for cations. The extended equations can fit $\log_{10} P$ values for anions and cations with a standard deviation of about 0.2 to 0.3 log units for transfer of 41 anions and cations from water to various water–ethanol mixtures from 10 % ethanol to 100 % ethanol by volume. The $\log_{10} P$ values for carboxylate anions and protonated amine cations as obtained from the variation of $\mathrm{p}K_\mathrm{a}$ with solvent are quite compatible with $\log_{10} P$ values for simple anions and cations.

Keywords Water-ethanol · Partition coefficients · Ionic species · Acid dissociation constants · Ionic descriptors

1 Introduction

Properties of the water–ethanol solvent system have long been of interest. Bates [1] has reviewed acid–base properties and Hyne [2] has reviewed effects on reaction rates in this system. Effects on ionic mobilities have also been reviewed, [3] and properties of non-electrolytes [4] and electrolytes [5] in water–ethanol mixtures have been discussed. The transfer of ions from water to water–ethanol mixtures has been of particular interest and

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both Blandamer and co-workers [6] and Marcus [7] have set out lists of Gibbs energies of transfer of ions. Most of the data on transfers from water to water–ethanol mixtures have been obtained from the solubilities of electrolytes, as described by Marcus [7]. We have recently obtained descriptors for ions and ionic species, and have shown that it is possible to construct equations for the transfer of neutral molecules, ions and ionic species from water to a number of nonaqueous solvents [8–10]. We define 'ionic species' as anions derived from neutral carboxylic acids or phenols by removal of a proton, and cations derived from amines by addition of a proton. We have also set out equations for the transfer of non-electrolytes from water to water–ethanol mixtures [11], and in view of the interest in ions in water–ethanol mixtures, we wished to ascertain if it was possible to obtain equations for the transfer of non-electrolytes, ions and ionic species from water to water–ethanol mixtures. If so, then the coefficients in such equations might lead to additional insights into the nature of the water–ethanol mixtures.

2 Methodology

We start with our well-known equation for the partition of neutral molecules (non-electrolytes) from water to another solvent or solvent system,

$$\log_{10} P = c + e\mathbf{E} + s\mathbf{S} + a\mathbf{A} + b\mathbf{B} + v\mathbf{V} \tag{1}$$

In Eq. 1, the dependent variable is $\log_{10} P$, where P is the water to solvent partition coefficient for a series of non-electrolytes in a given water to solvent system. The independent variables are descriptors as follows [12, 13]. **E** is the non-electrolyte (or solute) excess molar refractivity in units of $(\text{cm}^3{\cdot}\text{mol}^{-1})/10$, **S** is the solute dipolarity/ polarizability, **A** and **B** are the overall or summation solute hydrogen bond acidity and basicity, and **V** is the solute McGowan characteristic volume in units of $(\text{cm}^3{\cdot}\text{mol}^{-1})/100$. Equation 1 has been applied to the partition coefficients of non-electrolytes between water and a very large number of organic solvents [14], and has also been used indirectly to predict the solubility of solutes in a variety of solvents, including water and ethanol [14].

For partition of non-electrolytes from water to water–ethanol mixtures, we constructed [11] Eqs. 2–11. The numbers in parenthesis in the equations refer to the volume % ethanol in the solvent and these are the compositions of the water–solvent mixtures that we shall use throughout this work.

$$\log_{10} P(100) = 0.222 + 0.471\mathbf{E} - 1.035\mathbf{S} + 0.326\mathbf{A} - 3.596\mathbf{B} + 3.857\mathbf{V} \tag{2}$$

$$\log_{10} P(90) = 0.243 + 0.213\mathbf{E} - 0.575\mathbf{S} + 0.262\mathbf{A} - 3.450\mathbf{B} + 3.545\mathbf{V} \tag{3}$$

$$\log_{10} P(80) = 0.172 + 0.175\mathbf{E} - 0.465\mathbf{S} + 0.260\mathbf{A} - 3.212\mathbf{B} + 3.323\mathbf{V} \tag{4}$$

$$\log_{10} P(70) = 0.063 + 0.085\mathbf{E} - 0.368\mathbf{S} + 0.311\mathbf{A} - 2.936\mathbf{B} + 3.102\mathbf{V} \tag{5}$$

$$\log_{10} P(60) = -0.040 + 0.138\mathbf{E} - 0.335\mathbf{S} + 0.293\mathbf{A} - 2.675\mathbf{B} + 2.812\mathbf{V} \tag{6}$$

$$\log_{10} P(50) = -0.142 + 0.124\mathbf{E} - 0.252\mathbf{S} + 0.251\mathbf{A} - 2.275\mathbf{B} + 2.415\mathbf{V} \tag{7}$$

$$\log_{10} P(40) = -0.221 + 0.131\mathbf{E} - 0.159\mathbf{S} + 0.171\mathbf{A} - 1.809\mathbf{B} + 1.918\mathbf{V} \tag{8}$$

$$\log_{10} P(30) = -0.269 + 0.107\mathbf{E} - 0.098\mathbf{S} + 0.133\mathbf{A} - 1.316\mathbf{B} + 1.414\mathbf{V} \tag{9}$$

$$\log_{10} P(20) = -0.252 + 0.042\mathbf{E} - 0.040\mathbf{S} + 0.096\mathbf{A} - 0.823\mathbf{B} + 0.916\mathbf{V} \tag{10}$$

$$\log_{10} P(10) = -0.173 - 0.023\mathbf{E} - 0.001\mathbf{S} + 0.065\mathbf{A} - 0.372\mathbf{B} + 0.454\mathbf{V} \tag{11}$$

In order to include ions and ionic species in equations of the type of Eq. 1, we devised two additional descriptors, $\mathbf{J}^+$ for anions and $\mathbf{J}^-$ for cations, leading to the general equation, Eq. 12 where j^+ and j^- are the corresponding coefficients.

$$\log_{10} P = c + e\mathbf{E} + s\mathbf{S} + a\mathbf{A} + b\mathbf{B} + v\mathbf{V} + j^+\mathbf{J}^+ + j^-\mathbf{J}^- \tag{12}$$

Thus Eq. 2 can be transformed into Eq. 12 for the transfer from water to ethanol of ions and ionic species as well as non-electrolytes. Of course, this requires knowledge of partition coefficients of ions and ionic species.

The data used to obtain partition coefficients for ions were obtained from the compilations of Gibbs energies of transfer by Blandamer et al. [6] and by Marcus [7]. For ionic species, we used the pK_a method described by us previously [8]. For anions derived from carboxylic acids, this involves use of Eq. 13 where $P(\text{A}^-)$ is the partition coefficient from water to a solvent of the carboxylate anion, $P(\text{HA})$ is the partition coefficient of the neutral carboxylic acid, $P(\text{H}^+)$ is the partition coefficient of the hydrogen ion, and pK_a(aq) and pK_a(s) are the pK_a values of the carboxylic acid in water and the given solvent.

$$\log_{10} P(\text{A}^-) = \log_{10} P(\text{HA}) - \log_{10} P(\text{H}^+) + \text{p}K_\text{a}(\text{aq}) - \text{p}K_\text{a}(\text{s}) \tag{13}$$

We devised a similar equation for the determination of partition coefficients of protonated amine cations,

$$\log_{10} P(\text{BH}^+) = \log_{10} P(\text{B}) + \log_{10} P(\text{H}^+) - \text{p}K_\text{a}(\text{aq}) + \text{p}K_\text{a}(\text{s}) \tag{14}$$

In Eq. 14, BH^+ refers to the protonated amine and B to the neutral amine. It is important to note that all values for single ions, including $\log_{10} P(\text{H}^+)$ in Eqs. 13 and 14, have to be based on some particular convention. We used the convention that $\log_{10} P$ for Ph_4As^+ or $\text{Ph}_4\text{P}^+ = \log_{10} P$ for Ph_4B^-, the so-called TATB convention employed by Blandamer et al. [6] and by Marcus [7].

3 Results and Discussion

The values of Gibbs energies of transfer of ions listed by Blandamer et al. [6] and by Marcus [7] are generally in agreement, and we used both sets of data to obtain ΔG° and then $\log_{10} P$ on the molar scale at rounded-off volume % ethanol. An exception was Pr_4N^+ where the disagreement was so large that we did not use either set of data.

In order to obtain values for ionic species from Eqs. 13 and 14, we need values of $\log_{10} P(\text{H}^+)$ and $\log_{10} P$ for the neutral species. Blandamer et al. [6] and Marcus [7] list values of the Gibbs energy of transfer of H^+ at various water–solvent compositions. The two sets of data are in good agreement, as shown in Fig. 1, where we also show our interpolated values at rounded-off water–ethanol compositions. The actual values are in Table 1. As before [8], we calculated $\log_{10} P$ for transfer from water to water–ethanol mixtures for the neutral species from known descriptors and Eqs. 2–11.

Values of pK_a for monocarboxylic acids in water–ethanol mixtures have been determined by Grunwald and Berkowitz [15], Spivey and Shedlovsky [16], Frohlinger et al. [17], Dash and Pattanaik [18], Azab et al. [19], and Thuaire [20]. For acetic acid, they are all in agreement [15–20] and we have used them to obtain values at rounded-off vol-% ethanol. There are less data for formic acid [15], propanoic acid [15, 18] and butanoic acid [15, 18]. For chloroacetic acid there are available date from Niazi [21] as well as from Grunwald and Berkowitz [15], and from Dash and Pattanaik [18].

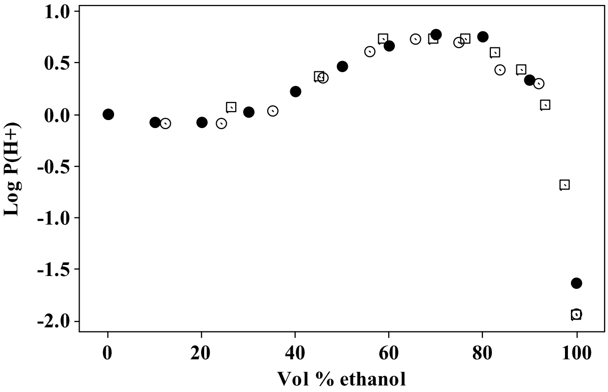

Fig. 1 A plot of $\log_{10} P(\mathrm{H}^+)$ against vol-% ethanol: ○, Ref. [6]; □, Ref. [7]; ●, values taken

Table 1 Partition coefficients, as $\log_{10} P$, for the hydrogen ion on the molar scale and the TATB assumption from water to water–ethanol mixtures, at 298 K

Vol-%	$\log_{10} P$
100	−1.60
90	0.34
80	0.64
70	0.75
60	0.67
50	0.47
40	0.22
30	0.02
20	−0.08
10	−0.08
0	0.00

Thuaire [20] has determined pK_a values for a number of substituted benzoic acids; data are available for benzoic acid [15, 20, 22, 23] and for several substituted benzoic acids as well as phenylacetic acid [18]. We only studied acids for which pK_a values could be obtained across the entire composition range, 0–100 %, and for which we had the necessary descriptors for the neutral and ionic forms. The exceptions were N-chloroacetamide and N-bromoacetamide for which Menard and Lessard [24] had measured pK_a values from 0–80 %. We included these acids in order to ascertain if the present method was general enough to include nitrogen-acids as well as the usual oxygen-acids. The $\log_{10} P$ values obtained through Eq. 13 are in Table 2; values for simple anions are also given in Table 2. Details of the pK_a values used, and the partition coefficients of the neutral species and the ionic species are given in Table S1 (see Electronic Supplementary Material).

There is much less data on pK_a values of protonated amines in the water–ethanol system. Gutbbzahl and Grunwald [25] and also Reynaud [26] have provided most of the experimental data, but comparatively few amines were studied across the whole composition region. Oszczapowicz and Czuryłowska [27] have determined pK_a values for protonated imidazole across the whole composition range, and fortunately, we have descriptors for the neutral and protonated forms [8]. Reynaud [26] measured pK_a for pyridine and *p*-bromoaniline up to 50 % ethanol, and using pK_a in ethanol of 4.00 and 4.50 respectively [28], we interpolated the intervening values. Values of $\log_{10} P$ for the protonated amines obtained through Eq. 14

Table 2 Log$_{10}$ P for partition of cations and anions from water to water–ethanol mixtures, at 298 K

	Vol-% ethanol									
	10	20	30	40	50	60	70	80	90	100
Cations										
Li$^+$	−0.336	−0.489	−0.501	−0.420	−0.306	−0.225	−0.254	−0.477	−0.989	−1.890
Na$^+$	−0.189	−0.402	−0.571	−0.667	−0.692	−0.690	−0.735	−0.941	−1.455	−2.450
K$^+$	−0.211	−0.349	−0.429	−0.477	−0.528	−0.629	−0.836	−1.217	−1.848	−2.800
Rb$^+$	−0.184	−0.319	−0.410	−0.476	−0.546	−0.661	−0.874	−1.250	−1.866	−2.800
Cs$^+$	−0.184	−0.307	−0.387	−0.446	−0.517	−0.637	−0.854	−1.221	−1.799	−2.659
Me$_4$N$^+$	−0.080	−0.017	0.092	0.168	0.149	−0.003	−0.311	−0.774	−1.377	−2.080
Et$_4$N$^+$	0.183	0.299	0.377	0.430	0.458	0.447	0.368	0.181	0.010	−1.050
Ph$_4$As$^+$	0.643	1.207	1.734	2.249	2.753	3.230	3.642	3.925	4.004	3.680
PyridineH$^+$	−0.240	−0.360	−0.380	−0.280	−0.160	−0.320	−0.520	−0.800	−1.000	−2.390
AnilineH$^+$	−0.070	−0.040	0.150	0.450	0.720	0.970	1.130	1.130	1.110	0.850
m-ToluidineH	−0.060	0.010	0.240	0.560	0.880	1.150	1.360	1.340	1.280	0.900
p-ToluidineH$^+$	0.001	0.090	0.280	0.590	0.950	1.280	1.480	1.530	1.440	0.820
4-BromoanilineH$^+$	0.001	0.140	0.440	0.800	1.190	1.540	1.760	1.920	2.050	1.440
N-MethylanilineH$^+$	−0.010	0.070	0.240	0.510	0.800	1.040	1.110	1.030	0.860	0.360
ImidazoleH$^+$	−0.330	−0.550	−0.690	−0.760	−0.820	−0.920	−1.070	−1.320	−1.560	−3.090
Anions										
F$^-$	−0.154	−0.350	−0.741	−1.224	−1.676	−2.081	−2.474	−2.934	−3.592	−4.730
Cl$^-$	−0.062	−0.149	−0.326	−0.619	−1.045	−1.381	−1.732	−2.142	−2.679	−3.510
Br$^-$	−0.040	−0.081	−0.180	−0.364	−0.639	−0.964	−1.281	−1.500	−2.060	−3.150
I$^-$	0.036	0.067	0.047	−0.080	−0.194	−0.310	−0.494	−0.829	−1.430	−2.448
BPh$_4^-$	0.643	1.207	1.734	2.249	2.753	3.230	3.642	3.925	4.004	3.680
Formate$^-$	−0.182	−0.340	−0.660	−0.974	−1.304	−1.540	−1.762	−2.217	−3.195	−3.882
Acetate$^-$	−0.117	−0.346	−0.727	−1.117	−1.432	−1.692	−1.987	−2.497	−3.422	−3.933
Chloroacetate$^-$	−0.056	−0.246	−0.492	−0.746	−0.999	−1.254	−1.544	−2.047	−2.893	−3.125
Phenylacetate$^-$	0.013	−0.001	−0.157	−0.369	−0.523	−0.772	−1.001	−1.477	−2.150	−2.540
Benzoate$^-$	0.129	0.070	−0.133	−0.365	−0.550	−0.305	−0.947	−1.350	−2.190	−2.444
3-Methylbenzoate$^-$	0.092	0.201	0.087	−0.101	−0.245	−0.545	−0.373	−0.639	−1.454	−1.941
4-Methylbenzoate$^-$	0.186	0.145	0.021	−0.133	−0.295	−0.406	−0.570	−0.986	−1.700	−1.968
3-Fluorobenzoate$^-$	0.058	0.086	−0.037	−0.318	−0.515	−0.640	−0.657	−0.749	−1.409	−1.790
4-Fluorobenzoate$^-$	0.037	0.045	−0.101	−0.122	−0.519	−0.659	−0.698	−0.835	−1.504	−1.917
4-Chlorobenzoate$^-$	0.152	0.273	0.246	0.258	0.025	−0.009	0.002	−0.106	−0.794	−1.308
3-Chlorobenzoate$^-$	0.143	0.245	0.187	0.029	−0.071	−0.070	−0.099	−0.304	−1.046	−1.395
3-Bromobenzoate$^-$	0.133	0.266	0.381	0.309	0.124	0.097	0.093	−0.018	−0.687	−1.069
4-Bromobenzoate$^-$	0.116	0.257	0.442	0.389	0.207	0.211	0.272	0.024	−0.553	−1.033
3-Methoxybenzoate$^-$	0.092	0.127	0.055	−0.215	−0.600	−0.766	−0.791	−0.938	−1.653	−2.162
4-Methoxybenzoate$^-$	0.101	0.120	0.067	−0.217	−0.602	−0.774	−0.836	−1.023	−1.816	−2.494
2-Nitrobenzoate$^-$	0.114	0.035	−0.184	−0.660	−1.014	−1.173	−1.234	−1.437	−2.261	−3.040
3-Nitrobenzoate$^-$	0.141	0.188	0.116	0.016	−0.116	−0.236	−0.447	−0.758	−1.550	−1.764
4-Nitrobenzoate$^-$	0.176	0.265	0.302	0.271	−0.021	−0.124	−0.185	−0.525	−1.332	−1.726
3-Hydroxybenzoate$^-$	−0.039	−0.140	−0.341	−0.604	−0.893	−1.204	−1.597	−2.136	−2.994	−2.946
N-Chloroacetamide$^-$	−0.132	−0.231	−0.353	−0.519	−0.768	−1.041	−1.285	−1.932	−2.670	
N-Bromoacetamide$^-$	−0.002	−0.049	−0.182	−0.398	−0.709	−1.017	−1.348	−1.790	−2.720	

are in Table 2. Details of the pK_a values and partition coefficients of the neutral bases and the protonated bases are in Table S2 (see Electronic Supplementary Material).

We decided to use exactly the same set of anions and cations for all the water–solvent compositions, except for N-chloroacetamide and N-bromoacetamide in 100 % ethanol, as mentioned above. This meant the omission of a number of ions for which we did not have data across the whole composition range or which showed marked inconsistencies at various compositions. These included the perchlorate ion and the anions derived from propanoic and butanoic acid. We were left with 26 anions and 15 cations as shown in Table 2. The coefficients c–v in Eq. 12 are exactly the same as those in Eq. 1, and so $\log_{10} P$ values for the ions must fit Eq. 12 with only one extra term for the anions and one extra term for the cations. The descriptors for the anions and cations were taken as before [8], except that those for the anions of formic acid, N-chloroacetamide and N-bromoacetamide were calculated from the equations given in Ref. [8]. The full set of descriptors for anions and cations is in Table 3.

We have 15 cations and 26 anions that have to be fitted to Eqs. 2–11. Results are in Table 4 where we give the obtained values of j^+ and j^- together with the statistics of the fit in terms of the standard deviation, SD, of the observed and fitted values. The standard deviations average around 0.2 to 0.3 log units which can be considered reasonable. For transfer from water to a number of pure solvents, similar SD values were obtained [8]. We can conclude that the general equation, Eq. 12, previously applied to transfers from water to pure solvents applies just as well to transfers from water to water–solvent mixtures. Note that the values of j^+ and j^- for ethanol itself in Table 4 obtained with a total of 39 ions or ionic species are slightly different to those we found before [8], with a total of 19 ions or ionic species ($j^+ = -3.170$ and $j^- = 3.085$).

The $\log_{10} P$ values for the ionic species, viz the carboxylate anions and the protonated amine cations, are quite compatible with $\log_{10} P$ values for the simple ions listed in Table 3. Notable exceptions are the acetate anion for which the $\log_{10} P$ values from the compilations of Blandamer et al. [6] and of Marcus [7] are completely different from those we calculate by the pK_a method. The data given by Marcus [7] are actually those of Blandamer et al. [6] and so we just compare values from the latter workers to those we obtained from the pK_a method, see Fig. 2.

There is the most remarkable disagreement between $\log_{10} P$ values from solubility measurements and those from the pK_a method—even the sign of $\log_{10} P$ differs. No anion in Table 2 has a positive $\log_{10} P$ value for transfer to 100 % ethanol (except BPh_4^-). The solubility measurements were made using potassium acetate [6]. In order to obtain $\log_{10} P$ for (K^++ acetate$^-$), it is essential that the same solid phase is in equilibrium with the saturated aqueous solution and the various saturated water–ethanol solutions. However, the solid phase in equilibrium with a saturated solution in water at 298 K is known [29] to have the composition $2CH_3CO_2K{\cdot}3H_2O$, so that it is not surprising that solubility measurements on potassium acetate yield incorrect values of $\log_{10} P(K^+$+ acetate$^-)$ and hence $\log_{10} P$ (acetate$^-$) for transfer to water–ethanol mixtures.

The specific terms associated with partition of cations and anions are $j^+\mathbf{J}^+$ and $j^-\mathbf{J}^-$. However, it must be noted that other terms make a contribution to the overall $\log_{10} P$ value. We can illustrate this by comparison of the partition of ionic species and the corresponding neutral species, term by term, giving transfers from water to ethanol as an example. In Table 5 we compare the benzoate anion with neutral benzoic acid. Although the $j^-\mathbf{J}^-$ term for the benzoate anion is very large, it is not as large numerically as the $b\mathbf{B}$ term that results from the extremely large hydrogen bond basicity ($\mathbf{B} = 2.88$) of the benzoate anion. In the case of the p-toluidine protonated cation, the $j^+\mathbf{J}^+$ term is about the same as the $s\mathbf{S}$ term.

Table 3 Descriptors for the cations and anions

	E	**S**	**A**	**B**	**V**	**J$^+$**	**J$^-$**
Cation							
Li^+	−0.020	2.11	1.30	0.00	0.0140	0.154	0.000
Na^+	−0.020	2.31	1.22	0.00	0.0330	0.316	0.000
K^+	0.000	2.57	1.21	0.00	0.0920	0.357	0.000
Rb^+	0.020	2.55	1.05	0.00	0.1300	0.477	0.000
Cs^+	0.100	2.60	1.17	0.00	0.1770	0.438	0.000
Me_4N^+	−0.100	1.31	0.68	0.00	0.7635	1.235	0.000
Et_4N^+	−0.100	1.85	0.51	0.00	1.3571	1.475	0.000
Ph_4As^+	2.220	3.20	0.07	0.91	2.8110	0.581	0.000
PyridineH$^+$	0.481	2.46	1.15	0.00	0.6968	1.050	0.000
AnilineH$^+$	0.805	1.62	1.93	0.00	0.8377	0.620	0.000
m-ToluidineH$^+$	0.796	1.92	2.05	0.00	0.9786	0.750	0.000
p-ToluidineH$^+$	0.773	1.99	1.98	0.00	0.9786	0.668	0.000
4-BromoanilineH$^+$	1.040	1.75	2.27	0.00	1.0127	0.641	0.000
N-MethylanilineH$^+$	0.798	1.87	1.53	0.00	0.9786	0.892	0.000
ImidazoleH$^+$	0.560	2.50	1.61	0.00	0.5578	1.050	0.000
Anion							
F^-	−0.050	3.76	0.00	2.42	0.1050	0.000	2.385
Cl^-	0.100	3.52	0.00	2.32	0.2280	0.000	2.363
Br^-	0.170	2.74	0.00	1.82	0.3070	0.000	1.567
I^-	0.380	3.55	0.00	1.34	0.4080	0.000	1.251
BPh_4^-	1.950	2.72	0.18	1.15	2.7000	0.000	−0.188
Formate$^-$[a]	0.493	2.30	0.00	2.50	0.3024	0.000	1.852
Acetate$^-$	0.415	2.19	0.00	2.93	0.4433	0.000	2.075
Chloroacetate$^-$	0.577	2.44	0.00	2.56	0.5657	0.000	1.860
Phenylacetate$^-$	0.880	3.05	0.00	2.97	1.0511	0.000	2.160
Benzoate$^-$	0.880	3.64	0.00	2.88	0.9102	0.000	2.395
3-Methylbenzoate$^-$	0.880	3.25	0.00	2.85	1.0511	0.000	2.228
4-Methylbenzoate$^-$	0.880	3.10	0.00	2.88	1.0511	0.000	2.167
3-Fluorobenzoate$^-$	0.952	2.96	0.00	2.73	0.9279	0.000	2.175
4-Fluorobenzoate$^-$	0.952	2.82	0.00	2.82	0.9279	0.000	2.174
4-Chlorobenzoate$^-$	0.990	3.37	0.00	2.60	1.0326	0.000	2.179
3-Chlorobenzoate$^-$	0.990	3.13	0.00	2.57	1.0326	0.000	2.034
3-Bromobenzoate$^-$	1.150	3.47	0.00	2.56	1.0852	0.000	2.197
4-Bromobenzoate$^-$	1.150	3.25	0.00	2.60	1.0852	0.000	2.148
3-Methoxybenzoate$^-$	0.980	3.32	0.00	3.00	1.1098	0.000	2.254
4-Methoxybenzoate$^-$	1.050	4.00	0.00	3.05	1.1098	0.000	2.400
2-Nitrobenzoate$^-$	1.140	3.92	0.00	2.96	1.0844	0.000	2.132
3-Nitrobenzoate$^-$	1.140	3.60	0.00	2.79	1.0844	0.000	2.217
4-Nitrobenzoate$^-$	1.140	3.50	0.00	2.79	1.0844	0.000	2.212
3-Hydroxybenzoate$^-$	1.060	3.65	0.13	3.07	0.9689	0.000	2.344
N-Chloroacetamide$^-$[a]	0.590	3.07	0.00	2.45	0.6068	0.000	1.857
N-Bromoacetamide$^-$[a]	0.770	3.33	0.00	2.45	0.6594	0.000	1.906

[a] Calculated from equations in Ref. [8]

Table 4 Statistics of the fit of $\log_{10} P$ values for ions and ionic species to Eq. 12, and the obtained values of j^+ and j^-

Vol-%	All ions				Anions		Cations	
	N	SD	j^+	j^-	N	SD	N	SD
100	39	0.144	−3.172	3.146	15	0.168	24	0.131
90	40	0.193	−2.794	2.705	15	0.164	26	0.210
80	41	0.226	−2.466	2.722	15	0.164	26	0.258
70	41	0.248	−2.203	2.550	15	0.211	26	0.274
60	41	0.284	−1.858	2.394	15	0.303	26	0.275
50	41	0.275	−1.569	2.051	15	0.317	26	0.254
40	41	0.235	−1.271	1.676	15	0.291	26	0.202
30	41	0.239	−0.941	1.290	15	0.361	26	0.136
20	41	0.148	−0.677	0.851	15	0.217	26	0.094
10	41	0.109	−0.412	0.401	15	0.163	26	0.063
0			0.000	0.000				

Table 5 A term-by-term analysis of the factors that influence partition from water to ethanol, as $\log_{10} P$

Species	Terms in Eq. 12							Total $\log_{10} P$	
	$e\mathbf{E}$	$s\mathbf{S}$	$a\mathbf{A}$	$b\mathbf{B}$	$v\mathbf{V}$	$j^+\mathbf{J}^+$	$j^-\mathbf{J}^-$	calc	obs
Benzoate	0.414	−3.767	0.000	−10.356	3.511	0.000	7.535	−2.442	−2.444
Benzoic acid	0.344	−0.932	0.192	−1.438	3.594	0.000	0.000	1.982	1.982
p-ToluidineH$^+$	0.364	−2.060	0.645	0.000	3.774	−2.119	0.000	0.827	0.820
p-Toluidine	0.435	−0.983	0.075	−1.618	3.692	0.000	0.000	1.822	1.822

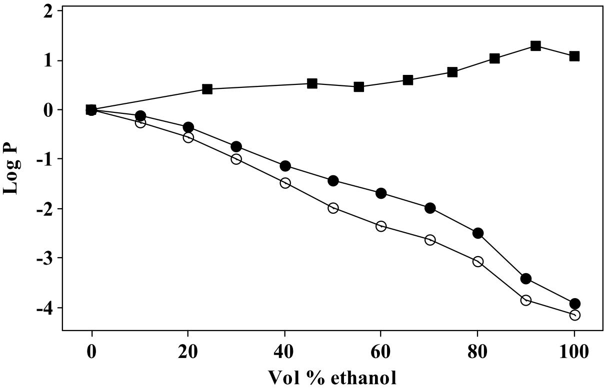

Fig. 2 Comparison of $\log_{10} P$ values for the acetate ion. ■, Experimental values from solubilities [6]; ●, experimental values by the pK_a method; ○, calculated values (this work)

The $a\mathbf{A}$ term is not so important because the *p*-toluidinium cation is not such a very strong hydrogen bond acid ($\mathbf{A} = 1.98$).

For some of the protonated amines, the $\log_{10} P$ values exhibit a maxima against the volume % ethanol around 80 or 90 %, as shown in Fig. 3 for protonated *p*-toluidine. However,

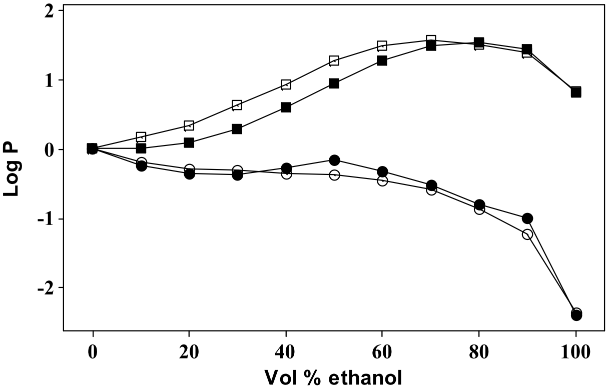

Fig. 3 Plots of $\log_{10} P$ for protonated amines against the vol-% ethanol. ■, Observed values for protonated *p*-toluidine from Table 2; □, calculated values for protonated *p*-toluidine; ●, observed values for protonated pyridine from Table 2; ○, calculated values for protonated pyridine

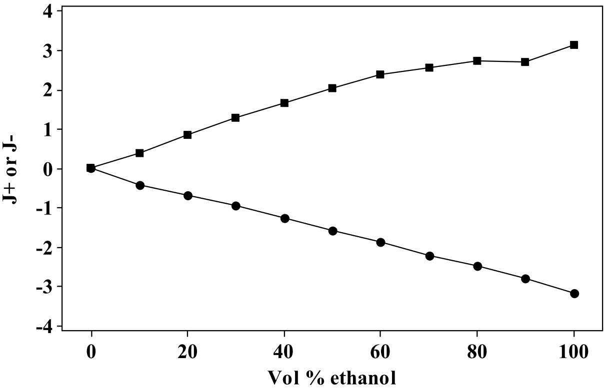

Fig. 4 Plots of the coefficients j^+ and j^- against vol-% ethanol: ●, j^+; ■, j^-

$\log_{10} P$ for protonated pyridine shows only a very small maximum at 50 % ethanol. In Fig. 3, the calculated $\log_{10} P$ values are also shown.

The two new solvent parameters are j^+ and j^-. They vary quite regularly with solvent composition as is shown in Fig. 4, with a slight decrease in j^- at 90 % ethanol. There have been numerous experimental studies of the variation of properties with solvent composition in the water–ethanol system. Excess enthalpies of mixing, velocity of sound, sound absorption coefficients, activation enthalpies for the *t*-butyl chloride solvolysis, viscosity, and the Walden product for the lithium ion show marked maxima or minima in the water-rich region, but vary smoothly with solvent composition in the ethanol-rich region [3, 4]. Indeed, the variation of $\log_{10} P$ for the hydrogen ion, Fig. 1, is the only property we have encountered with a pronounced maximum or minimum in the ethanol-rich region. Values of $\log_{10} P$ for the rather hydrophobic cations show weak maxima at various solvent compositions, for example Et_4N^+ at 50 %, anilineH$^+$ at 70–80 % and 4-bromoanilineH$^+$ at 90 %, but $\log_{10} P$ for the rather hydrophobic anions decreases regularly over the entire composition range, see Table 1. This is not reflected in the coefficients j^+ and j^-; the former plot an almost perfect straight line, and the latter shows slight deviations from linearity against vol-% ethanol. As regards the additional parameters for cations and anions, so far we have been unable to connect j^+ and j^- with other solvent properties; they remain empirical solvent parameters.

4 Conclusions

In conclusion, we have been able to show that our previous equations for the transfer of neutral molecules, ions and ionic species from water to nonaqueous solvents can be applied just as well to transfers from water to aqueous ethanol. This is the first time that a single equation has been applied for the transfer of neutral molecules and ions from water to any aqueous organic solvent. The two additional terms required for transfer of ions and ionic species vary quite regularly with solvent composition over the entire composition range. The equations that we have constructed allow for the first time predictions of $\log_{10} P$ for transfer of protonated amine cations and carboxylate anions from water to aqueous ethanol for numerous such species for which we have already determined the required solute parameters.

Electronic Supplementary Material

Tables S1 and S2 contain all the $\mathrm{p}K_\mathrm{a}$ values in the water–ethanol mixtures, partition coefficients for the neutral species and calculated partition coefficients for anionic and cationic species.

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