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IONIC SOLVATION IN WATER + CO-SOLVENT MIXTURES. PART 16. FREE ENERGIES OF TRANSFER OF LARGE SINGLE IONS WITH THE "NEUTRAL" COMPONENT REMOVED FROM WATER INTO WATER + ETHANOL MIXTURES

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ABSTRACT

The method developed previously for deriving free energies of transfer of the charge only on large single ions from water into water-rich water + co-solvent mixtures $\Delta G_t^\ominus(i)_e$ has now been applied to water + ethanol mixtures. This derivation depends only on the experimental pK values of a large acidic positive ion producing a neutral base or of a large neutral acid producing a negative ion and on the total free energy of transfer of the proton, $\Delta G_t^\ominus(H^+)$. Water + ethanol has been chosen for this investigation as $\Delta G_t^\ominus(H^+)$ for mole fractions of ethanol ~ 0.28–0.40 is largely independent of the assumptions used in either the spectrophotometric solvent sorting method or in the reference ion method using $\Delta G_t^\ominus(Ph_4As^+) = \Delta G_t^\ominus(BPh_4^-)$ for calculating $\Delta G_t^\ominus(H^+)$. The significance of the variation of $\Delta G_t^\ominus(i)_e$ with ionic size, the sign of the charge and the extent of the distribution of the charge over the bulk of the ion in this composition range x_2 ~ 0.28–0.40 is discussed.

INTRODUCTION

In calculating and interpreting the free energy of transfer of single ions from water into either another pure solvent or into a mixture of water with a co-solvent, the extent to which the charge and the ionic bulk contribute to the final result has been the subject of considerable discussion. One method which has been used extensively to calculate free energies of transfer of single ions $\Delta G_t^\ominus(i)$ from water into pure liquids and aqueous mixtures assumes for a salt such as Ph_4AsBPh_4 consisting solely of large ions that the free energy of transfer can be divided equally (or nearly equally) [1–3]

$$\Delta G_t^\ominus(Ph_4As^+) = \Delta G_t^\ominus(BPh_4^-) = \tfrac{1}{2}\,\Delta G_t^\ominus(Ph_4AsBPh_4) \tag{1}$$

It is assumed by comparison with the free energies of transfer of similarly sized and structured neutral species, Ph_4Ge for Ph_4As^+ and Ph_4C for BPh_4^-, that $\Delta G_t^\ominus(\text{salt})_e$ arising from the transfer of the charges on the ions alone is about 15–25% of the total $\Delta G_t^\ominus(\text{salt})$ for transfers from water into

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water + acetonitrile, into water + N,N-dimethylformamide or into pure methanol, with the remaining larger portion attributable to the transfer of the neutral bulk $\Delta G_t^\ominus(\text{salt})_n$ [2,3]. Moreover, it is concluded [2,3] that the small $\Delta G_t^\ominus(\text{salt})_e$ can be divided equally (or nearly equally) in magnitude and sign between the large positive and negative ions in the salt. The weakness of this approach is that it does not investigate the free energy of transfer of the charge on the ion, $\Delta G_t^\ominus(i)_e$, in the presence of the actual neutral bulk on which it resides.

An alternative approach to the separation of $\Delta G_t^\ominus(\text{salt})$ into $\Delta G_t^\ominus(i)$ for the individual ions involves the determination of the free energy of transfer of the hydrated proton [4–7]. In this method [4], the small contribution deriving from the transfer of the spherical $H^+(H_2O)_5$ from water into the mixture is calculated using the Born Charging relationship and the free energy change arising from the subsequent re-arrangement of solvent molecules via

$$\{H^+(H_2O)_x\}_{\text{solv}} + S_{\text{solv}} \rightleftharpoons \{(H_2O)_{x-1}S\}H^+_{\text{solv}} + H_2O_{\text{solv}}$$

for the co-solvent molecule S is determined experimentally from the competitive equilibria of $\{H^+(H_2O)_x\}_{\text{solv}}$ and $\{(H_2O)_{x-1}S)H^+\}_{\text{solv}}$ for a trace concentration of a base, 4-nitroaniline. The total $\Delta G_t^\ominus(H^+)$ is then the sum of both components. This method is unfortunately restricted to water-rich mixtures of water with S and has been applied to a wide range of co-solvents [4–7]. In all cases where values are available, $\Delta G_t^\ominus(\text{PhAs}^+)$ has larger negative values than $\Delta G_t^\ominus(\text{BPh}_4^-)$, but frequently $\Delta G_t^\ominus(\text{Ph}_4\text{As}^+) = \Delta G_t^\ominus(\text{Ph}_4\text{P}^+)$ [4–7]. However, this method has been used to determine $\Delta G_t^\ominus(i)_e$ for the charge on the ion on the neutral bulk on which it resides without reference to $\Delta G_t^\ominus(i)_n$ for the transfer of neutral molecules other than the molecule under consideration.

For a large organic cationic acid A^+, the conjugate base B involved in the acid-base equilibrium

$$A^+_{\text{solv}} \overset{K}{\rightleftharpoons} B_{\text{solv}} + H^+_{\text{solv}} \tag{2}$$

resembles A^+ very closely in size and structure, and indeed as close as is possible without being identical, so that

$$\Delta G_t^\ominus(A^+)_e = \Delta G_t^\ominus(A^+) - \Delta G_t^\ominus(A^+)_n = \Delta G_t^\ominus(A^+) - \Delta G_t^\ominus(B) \tag{3}$$

will apply with $\Delta G_t^\ominus(A^+)_n = \Delta G_t^\ominus(B)$. The free energy of transfer of the whole equilibrium (2) from water into a water + co-solvent mixture = $RT\ \ln(K_w/K_s)$, where subscript w and s indicate water and the mixture, respectively, and is given by

$$RT\ \ln(K_w/K_s) = \Delta G_t^\ominus(B) + \Delta G_t^\ominus(H^+) - \Delta G_t^\ominus(A^+) \tag{4}$$

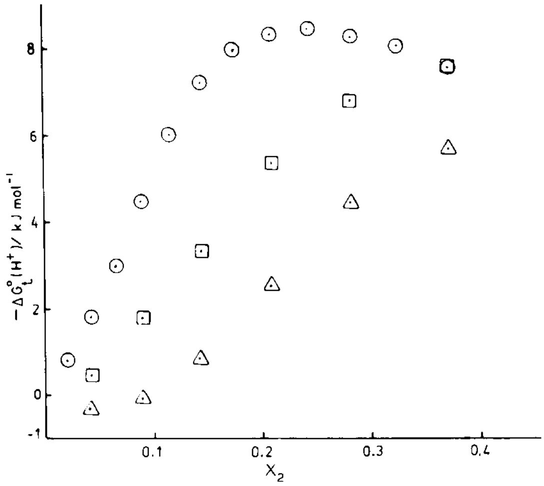


Fig. 1. The variation of $\Delta G_t^\ominus(H^+)$ for water + ethanol mixtures with the mole fraction of ethanol in water-rich conditions derived using the spectrophotometric solvent sorting method (⊙) and the reference ion methods, $\Delta G_t^\ominus(Ph_4As^+) = \Delta G_t^\ominus(BPh_4^-)$ (△) and $\Delta G_t^\ominus$(triisoamyl-(n-Bu)N^+) = $\Delta G_t^\ominus(BPh_4^-)$ (⊡).

Substituting from eqn. (3) and re-arranging gives

$$\Delta G_t^\ominus(A^+)_e = RT\ \ln(K_s/K_w) + \Delta G_t^\ominus(H^+) \qquad (5)$$

Similarly, for an equilibrium

$$A \overset{K}{\rightleftharpoons} B^- + H^+ \qquad (6)$$

involving a large neutral organic acid A, eqn. (7) can be derived,

$$\Delta G_t^\ominus(B^-)_e = RT\ \ln(K_w/K_s) - \Delta G_t^\ominus(H^+) \qquad (7)$$

with $\Delta G_t^\ominus(B^-)_n = \Delta G_t^\ominus(A)$. Equations (5) and (7) have been applied extensively to such acids A^+ and A in water + methanol [8], water + acetone [9] and water + dioxane [6], and to a few acids in water + dimethyl sulphoxide and in mixtures of water with other alcohols [10] and in mixtures of water with tetrahydrofuran and with dimethylformamide [5]. We now apply this procedure to the extensive literature of pK values for acids in water + ethanol, for, as Fig. 1 shows, $\Delta G_t^\ominus(H^+)$ derived by this method for individual ions in water + ethanol converge in the region mole fraction of ethanol x_2 ~ 0.28–0.40 with $\Delta G_t^\ominus(H^+)$ derived using either the assumption $\Delta G_t^\ominus(Ph_4As^+) = \Delta G_t^\ominus(BPh_4^-)$ or $\Delta G_t^\ominus$(triisoamyl(n-Bu)N^+) = $\Delta G_t^\ominus(BPh_4^-)$ [1]. Therefore, conclusions drawn for the variations of $\Delta G_t^\ominus(A^+)_e$ and $\Delta G_t^\ominus(B^-)_e$ with the structure and size of A and B in the range x_2 ~ 0.28–0.40 will be largely independent of the assumptions on which the derivations of $\Delta G_t^\ominus(H^+)$ are based.

TABLE 1

Variation of $\Delta G_t^{\ominus}(B^-)_e$ in water + ethanol mixtures at 25 °C (kJ mol^{-1})

Ion B^-	Ref for p*K*	Mole fraction of ethanol																						
		0.028	0.032	0.042	0.068	0.072	0.091	0.109	0.116	0.144	0.149	0.157	0.163	0.172	0.182	0.207	0.214	0.233	0.242	0.281	0.299	0.316	0.370	0.390
$HCOO^-$	12	–	–	–	–	–	–	–	–	8.9	–	–	–	–	–	–	–	–	–	11.6	–	–	–	–
$HCOO^-$	13	–	–	–	–	–	–	–	–	5.6	–	–	–	10.0	–	–	–	–	–	12.2	–	–	–	–
CH_3COO^-	14	–	–	2.57	–	–	6.5	–	–	–	–	–	–	–	–	12.1	–	–	–	–	–	–	13.8	–
CH_3COO^-	12	–	–	–	–	–	–	–	–	9.8	–	–	–	–	–	–	–	–	–	13.0	–	–	–	–
CH_3COO^-	15	–	–	–	–	4.65	–	–	–	–	–	–	–	11.0	–	–	–	12.8	–	–	13.8	–	–	14.9
CH_3COO^-	13	–	–	–	–	–	6.2	–	–	–	–	–	–	11.0	–	–	–	–	–	13.5	–	–	–	–
CH_3COO^-	16	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	12.4	–	–	–	–	–
CH_3COO^-	17	–	–	–	–	–	–	–	–	–	–	–	10.4	–	–	–	–	–	–	–	13.2	–	–	–
$CH_3CH_2COO^-$	12	–	–	–	–	–	–	–	–	10.6	–	–	–	–	–	–	–	–	–	14.0	–	–	–	–
$CH_3CH_2COO^-$	13	–	–	–	–	–	6.7	–	–	–	–	–	–	11.8	–	–	–	–	–	14.6	–	–	–	–
$CH_3CH_2CH_2COO^-$	13	–	–	–	–	–	6.8	–	–	–	–	–	–	12.2	–	–	–	–	–	14.9	–	–	–	–
$(CH_3)_2CHCH_2COO^-$	13	–	–	–	–	–	6.9	–	–	–	–	–	–	12.7	–	–	–	–	–	15.6	–	–	–	–
$PhCH_2COO^-$	18	–	–	–	–	–	–	–	–	11.2	–	–	–	–	–	–	–	–	–	14.7	–	–	–	–
Ph_2CHCOO^-	18	–	–	–	–	–	–	–	–	13.2	–	–	–	–	–	–	–	–	–	17.0	–	–	–	–
$PhCOO^-$	18	–	–	–	–	–	–	–	–	11.7	–	–	–	–	–	–	–	–	–	15.7	–	–	–	–
$PhCOO^-$	13	–	–	–	–	–	7.3	–	–	–	–	–	–	13.1	–	–	–	–	–	16.3	–	–	–	
$PhCOO^-$	17	–	–	–	–	–	–	–	–	–	–	–	12.5	–	–	–	–	–	–	–	15.9	–	–	–
$ClCH_2COO^-$	13	–	–	–	–	–	6.3	–	–	–	–	–	–	11.2	–	–	–	–	–	13.6	–	–	–	–
$CNCH_2COO^-$	13	–	–	–	–	–	5.8	–	–	–	–	–	–	10.6	–	–	–	–	–	12.6	–	–	–	–
CH_2OHCOO^-	13	–	–	–	–	–	6.2	–	–	–	–	–	–	11.1	–	–	–	–	–	13.2	–	–	–	–
$CH_3CH_2OHCOO^-$	13	–	–	–	–	–	5.6	–	–	–	–	–	–	10.5	–	–	–	–	–	12.7	–	–	–	–
$2\text{-}NO_2PhCOO^-$	17	–	–	–	–	–	–	–	–	–	–	–	14.4	–	–	–	–	–	–	–	17.1	–	–	–
$3\text{-}NO_2PhCOO^-$	17	–	–	–	–	–	–	–	–	–	–	–	10.7	–	–	–	–	–	–	–	13.7	–	–	–
$4\text{-}NO_2PhCOO^-$	17	–	–	–	–	–	–	–	–	–	–	–	10.7	–	–	–	–	–	–	–	13.6	–	–	–
$2\text{-}BrPhCOO^-$	17	–	–	–	–	–	–	–	–	–	–	–	14.0	–	–	–	–	–	–	–	17.6	–	–	–
$3\text{-}BrPhCOO^-$	17	–	–	–	–	–	–	–	–	–	–	–	12.1	–	–	–	–	–	–	–	15.3	–	–	–
$4\text{-}BrPhCOO^-$	17	–	–	–	–	–	–	–	–	–	–	–	11.9	–	–	–	–	–	–	–	14.8	–	–	–
$2\text{-}CH_3PhCOO^-$	17	–	–	–	–	–	–	–	–	–	–	–	14.1	–	–	–	–	–	–	–	17.9	–	–	–
$3\text{-}CH_3PhCOO^-$	17	–	–	–	–	–	–	–	–	–	–	–	12.8	–	–	–	–	–	–	–	16.4	–	–	–
$4\text{-}CH_3PhCOO^-$	17	–	–	–	–	–	–	–	–	–	–	–	12.7	–	–	–	–	–	–	–	16.3	–	–	–

2-ClPhCOO$^-$	17	–	–	–	–	–	–	–	–	–	–	–	14.0	–	–	–	–	–	–	–	17.6	–	–	–
3-ClPhCOO$^-$	17	–	–	–	–	–	–	–	–	–	–	–	12.4	–	–	–	–	–	–	–	15.7	–	–	–
4-ClPhCOO$^-$	17	–	–	–	–	–	–	–	–	–	–	–	11.9	–	–	–	–	–	–	–	15.0	–	–	–
2-CH$_3$OPhCOO$^-$	17	–	–	–	–	–	–	–	–	–	–	–	13.3	–	–	–	–	–	–	–	16.9	–	–	–
3-CH$_3$OPhCOO$^-$	17	–	–	–	–	–	–	–	–	–	–	–	12.5	–	–	–	–	–	–	–	16.3	–	–	–
4-CH$_3$OPhCOO$^-$	17	–	–	–	–	–	–	–	–	–	–	–	12.6	–	–	–	–	–	–	–	16.2	–	–	–
2-FPhCOO$^-$	17	–	–	–	–	–	–	–	–	–	–	–	14.3	–	–	–	–	–	–	–	18.3	–	–	–
3-FPhCOO$^-$	17	–	–	–	–	–	–	–	–	–	–	–	12.0	–	–	–	–	–	–	–	15.5	–	–	–
4-FPhCOO$^-$	17	–	–	–	–	–	–	–	–	–	–	–	11.6	–	–	–	–	–	–	–	15.0	–	–	–
2-HOPhCOO$^-$	17	–	–	–	–	–	–	–	–	–	–	–	11.2	–	–	–	–	–	–	–	13.4	–	–	–
2-HOPhCOO$^-$	19		2.39	–	–	–	–	8.5	–	–	–	–	–	–	–	–	–	–	13.1	–	–	–	–	–
2-HOPhCOO$^-$	13	–	–	–	–	–	5.3	–	–	–	–	–	–	10.7	–	–	–	–	–	13.0	–	–	–	–
2-HSPhCOO$^-$	19	–	–	2.78	–	–	–	8.5	10.4	–	–	–	–	–	–	–	–	–	14.7	–	–	–	–	–
CH$_2$(COOH)COO$^-$	13	–	–	–	–	–	6.3	–	–	–	–	–	–	10.8	–	–	–	–	–	13.5	–	–	–	–
(CH$_2$)$_2$(COOH)COO$^-$	13	–	–	–	–	–	6.4	–	–	–	–	–	–	11.4	–	–	–	–	–	13.5	–	–	–	–
(CH$_2$)$_3$(COOH)COO$^-$	13	–	–	–	–	–	5.7	–	–	–	–	–	–	11.0	–	–	–	–	–	13.5	–	–	–	–
(CH$_2$)$_3$(COOH)COO$^-$	20	–	–	–	–	–	7.9	–	–	–	–	–	–	–	–	12.6	–	–	–	–	–	–	15.1	–
(CH$_2$)$_4$(COOH)COO$^-$	20	–	–	–	–	–	8.2	–	–	–	–	–	–	–	–	12.9	–	–	–	–	–	–	15.1	–
(CH$_2$)$_5$(COOH)COO$^-$	20	–	–	–	–	–	8.3	–	–	–	–	–	–	–	–	13.3	–	–	–	–	–	–	15.8	–
(CH$_2$)$_6$(COOH)COO$^-$	20	–	–	–	–	–	8.5	–	–	–	–	–	–	–	–	13.6	–	–	–	–	–	–	15.7	–
(CH$_2$)$_7$(COOH)COO$^-$	20	–	–	–	–	–	8.5	–	–	–	–	–	–	–	–	13.7	–	–	–	–	–	–	16.0	–
(CH$_2$)$_8$(COOH)COO$^-$	20	–	–	–	–	–	8.7	–	–	–	–	–	–	–	–	14.6	–	–	–	–	–	–	15.9	–
PhO$^-$	12	–	–	–	–	–	–	–	–	11.4	–	–	–	–	–	–	–	–	–	14.9	–	–	–	–
2-CH$_3$PhO$^-$	12	–	–	–	–	–	–	–	–	12.4	–	–	–	–	–	–	–	–	–	15.6	–	–	–	–
3-CH$_3$PhO$^-$	12	–	–	–	–	–	–	–	–	11.8	–	–	–	–	–	–	–	–	–	15.3	–	–	–	–
4-CH$_3$PhO$^-$	12	–	–	–	–	–	–	–	–	11.7	–	–	–	–	–	–	–	–	–	15.3	–	–	–	–
2,3-(CH$_3$)$_2$PhO$^-$	12	–	–	–	–	–	–	–	–	12.5	–	–	–	–	–	–	–	–	–	16.2	–	–	–	–
2,4-(CH$_3$)$_2$PhO$^-$	12	–	–	–	–	–	–	–	–	12.4	–	–	–	–	–	–	–	–	–	16.0	–	–	–	–
2,5-(CH$_3$)$_2$PhO$^-$	12	–	–	–	–	–	–	–	–	12.4	–	–	–	–	–	–	–	–	–	16.2	–	–	–	–
2,6-(CH$_3$)$_2$PhO$^-$	12	–	–	–	–	–	–	–	–	12.6	–	–	–	–	–	–	–	–	–	16.2	–	–	–	–
3,4-(CH$_3$)$_2$PhO$^-$	12	–	–	–	–	–	–	–	–	12.2	–	–	–	–	–	–	–	–	–	15.7	–	–	–	–
3,5-(CH$_3$)$_2$PhO$^-$	12	–	–	–	–	–	–	–	–	12.3	–	–	–	–	–	–	–	–	–	15.9	–	–	–	–
4-NO$_2$PhO$^-$	21	–	–	–	3.64	–	–	6.4	–	–	–	8.9	–	–	–	–	10.4	–	–	–	–	–	–	–
2,6-(NO$_2$)$_2$PhO$^-$	22	1.29	–	2.11	–	–	4.92	–	–	–	–	–	–	–	8.4	–	–	–	–	–	–	–	–	10.7
2,4,6-(NO$_2$)$_3$PhO$^-$	23	–	–	–	–	–	–	–	–	7.1	–	–	–	–	–	–	–	–	–	8.2	–	–	–	–

TABLE 2

Variation of $-\Delta G_t^{\ominus}(A^+)_e$ in water + ethanol mixtures at 25 °C (kJ mol^{-1})

Ion A^+	Ref. for pK	Mole fraction of ethanol																					
		0.032	0.042	0.070	0.091	0.109	0.116	0.144	0.149	0.157	0.163	0.172	0.182	0.207	0.214	0.233	0.242	0.281	0.299	0.316	0.370	0.390	0.400
NH_4^+	24	–	–	–	2.60	–	–	–	3.95	–	–	–	–	–	–	–	–	–	3.88	–	–	–	1.58
NH_4^+	25	–	–	–	3.77	–	–	–	–	–	–	3.59	–	–	–	–	–	1.57	–	–	–	–	–
NH_4^+	12	–	–	–	–	–	–	4.82	–	–	–	–	–	–	–	–	–	3.80	–	–	–	–	–
$CH_3NH_3^+$	25	–	–	–	3.94	–	–	–	–	–	–	3.82	–	–	–	–	–	1.97	–	–	–	–	–
$CH_3NH_3^+$	12	–	–	–	–	–	–	4.14	–	–	–	–	–	–	–	–	–	2.60	–	–	–	–	–
$CH_3CH_2NH_3^+$	25	–	–	–	4.22	–	–	–	–	–	–	4.27	–	–	–	–	–	2.31	–	–	–	–	–
$CH_3CH_2NH_3^+$	12	–	–	–	–	–	–	4.48	–	–	–	–	–	–	–	–	–	2.60	–	–	–	–	–
$CH_3CH_2CH_2NH_3^+$	12	–	–	–	–	–	–	3.63	–	–	–	–	–	–	–	–	–	2.08	–	–	–	–	–
$CH_3(CH_2)_3NH_3^+$	12	–	–	–	–	–	–	3.85	–	–	–	–	–	–	–	–	–	1.63	–	–	–	–	–
$CH_3(CH_2)_4NH_3^+$	12	–	–	–	–	–	–	3.46	–	–	–	–	–	–	–	–	–	1.28	–	–	–	–	–
$CH_3(CH_2)_5NH_3^+$	12	–	–	–	–	–	–	3.34	–	–	–	–	–	–	–	–	–	0.89	–	–	–	–	–
$(CH_3)_2NH_2^+$	25	–	–	–	3.77	–	–	–	–	–	–	3.59	–	–	–	–	–	1.57	–	–	–	–	–
$(CH_3)_2NH_2^+$	12	–	–	–	–	–	–	4.20	–	–	–	–	–	–	–	–	–	1.97	–	–	–	–	–
$(CH_3)_3NH^+$	25	–	–	–	3.65	–	–	–	–	–	–	3.44	–	–	–	–	–	0.83	–	–	–	–	–
$(CH_3)_3NH^+$	12	–	–	–	–	–	–	3.91	–	–	–	–	–	–	–	–	–	1.17	–	–	–	–	–
$PhNH_3^+$	25	–	–	–	2.85	–	–	–	–	–	–	4.77	–	–	–	–	–	3.03	–	–	–	–	–
$PhNH_3^+$	12	–	–	–	–	–	–	4.48	–	–	–	–	–	–	–	–	–	3.17	–	–	–	–	–
$PhNH_3^+$	21	0.73	–	1.98	–	3.64	–	–	–	4.24	–	–	–	–	4.26	–	–	–	–	–	–	–	–
$PhNH_3^+$	15	–	–	2.26	–	–	–	–	–	–	–	5.1	–	–	–	4.75	–	–	3.63	–	–	2.37	–
$Ph\overset{+}{N}H_2CH_3$	12	–	–	–	–	–	–	4.03	–	–	–	–	–	–	–	–	–	1.68	–	–	–	–	–
$Ph\overset{+}{N}H_2CH_3$	21	0.67	–	1.75	–	3.24	–	–	–	3.74	–	–	–	–	3.12	–	–	–	–	–	–	–	–
$Ph\overset{+}{N}H_2CH_2CH_3$	12	–	–	–	–	–	–	4.25	–	–	–	–	–	–	–	–	–	1.80	–	–	–	–	–
$Ph\overset{+}{N}H_2CH_2CH_3$	21	–	–	2.49	–	4.15	–	–	–	4.77	–	–	–	–	4.03	–	–	–	–	–	–	–	–
$Ph\overset{+}{N}H_2CH_2CH_3$	15	–	–	2.14	–	–	–	–	–	–	–	4.75	–	–	–	4.23	–	–	2.71	–	–	1.34	–
$Ph\overset{+}{N}H_2CH_2CH_2CH_3$	12	–	–	–	–	–	–	7.2	–	–	–	–	–	–	–	–	–	8.2	–	–	–	–	–
$Ph\overset{+}{N}H_2CH_2CH_2CH_3$	15	–	–	2.03	–	–	–	–	–	–	–	4.52	–	–	–	3.26	–	–	1.97	–	–	0.43	–
$Ph\overset{+}{N}H_2CH_2CH_2CH_2CH_3$	15	–	–	1.86	–	–	–	–	–	–	–	3.89	–	–	–	3.26	–	–	1.80	–	–	0.31	–
$Ph\overset{+}{N}H_2CH(CH_3)_2$	21	–	–	1.52	–	2.95	–	–	–	3.57	–	–	–	–	2.83	–	–	–	–	–	–	–	–
$Ph\overset{+}{N}H_2CH(CH_3)_2$	15	–	–	2.09	–	–	–	–	–	–	–	4.86	–	–	–	4.29	–	–	2.66	–	–	0.94	–
$Ph\overset{+}{N}H_2C(CH_3)_3$	21	–	–	1.92	–	–	3.52	–	–	4.14	–	–	–	–	3.46	–	–	–	–	–	–	–	–
$Ph\overset{+}{N}H(CH_3)_2$	25	–	–	–	4.11	–	–	–	–	–	–	3.13	–	–	–	–	–	0.26	–	–	–	–	–
$Ph\overset{+}{N}H(CH_2CH_3)_2$	21	–	–	1.70	–	3.07	–	–	–	3.51	–	–	–	–	2.43	–	–	–	–	–	–	–	–
$Ph\overset{+}{N}H(CH(CH_3)_2)_2$	21	–	–	1.58	–	2.67	–	–	–	2.94	–	–	–	–	1.75	–	–	–	–	–	–	–	–
$2\text{-}CH_3Ph\overset{+}{N}H_3$	25	–	–	–	4.39	–	–	–	–	–	–	4.33	–	–	–	–	–	2.66	–	–	–	–	–

$2\text{-}CH_3Ph\overset{+}{N}H_3$	12	–	–	–	–	–	–	4.82	–	–	–	–	–	–	–	–	–	3.22	–	–	–	–	–
$3\text{-}CH_3Ph\overset{+}{N}H_3$	25	–	–	–	4.28	–	–	–	–	–	–	4.39	–	–	–	–	–	2.66	–	–	–	–	–
$3\text{-}CH_3Ph\overset{+}{N}H_3$	12	–	–	–	–	–	–	4.82	–	–	–	–	–	–	–	–	–	3.34	–	–	–	–	–
$4\text{-}CH_3Ph\overset{+}{N}H_3$	12	–	–	–	–	–	–	4.71	–	–	–	–	–	–	–	–	–	3.40	–	–	–	–	–
$2,3\text{-}(CH_3)_2Ph\overset{+}{N}H_3$	12	–	–	–	–	–	–	4.91	–	–	–	–	–	–	–	–	–	3.57	–	–	–	–	–
$2,4\text{-}(CH_3)_2Ph\overset{+}{N}H_3$	12	–	–	–	–	–	–	4.88	–	–	–	–	–	–	–	–	–	3.28	–	–	–	–	–
$2,5\text{-}(CH_3)_2Ph\overset{+}{N}H_3$	12	–	–	–	–	–	–	4.88	–	–	–	–	–	–	–	–	–	3.51	–	–	–	–	–
$2,6\text{-}(CH_3)_2Ph\overset{+}{N}H_3$	12	–	–	–	–	–	–	4.60	–	–	–	–	–	–	–	–	–	2.77	–	–	–	–	–
$3,4\text{-}(CH_3)_2Ph\overset{+}{N}H_3$	12	–	–	–	–	–	–	5.05	–	–	–	–	–	–	–	–	–	3.68	–	–	–	–	–
$4\text{-}BrPh\overset{+}{N}H_3$	21	0.73	–	1.64	–	3.07	–	–	–	3.57	–	–	–	–	3.00	–	–	–	–	–	–	–	–
$4\text{-}BrPh\overset{+}{N}H(CH_3)_2$	21	0.56	–	1.35	–	2.15	–	–	–	1.63	–	–	–	–	0.38	–	–	–	–	–	–	–	–
$4\text{-}BrPh\overset{+}{N}H(CH_2CH_3)_2$	21	–	–	1.30	–	1.98	–	–	–	1.12	–	–	–	–	−0.65	–	–	–	–	–	–	–	–
$4\text{-}BrPh\overset{+}{N}H(CH(CH_3)_2)_2$	21	–	–	3.21	–	5.7	–	–	–	7.5	–	–	–	–	8.3	–	–	–	–	–	–	–	–
$4\text{-}NO_2Ph\overset{+}{N}H_3$	31	–	0.41	–	1.37	–	–	–	–	–	–	–	–	1.05	–	–	–	–	–	–	–	–	–
phenanthrolinium	26	0.39	–	1.34	–	–	2.42	–	–	–	–	3.07	–	–	–	1.78	–	–	–	–	–	–	–
pyridinium	21	–	–	1.41	–	2.55	–	–	–	7.6	–	–	–	–	8.3	–	–	–	–	−0.25	–	–	–
quinolinium	21	–	–	0.95	–	1.81	–	–	–	1.69	–	–	–	–	0.61	–	–	–	–	–	–	–	–
isoquinolinium	21	–	–	1.13	–	1.98	–	–	–	1.86	–	–	–	–	0.81	–	–	–	–	–	–	–	–
acridinium	21	–	–	0.10	–	0.55	–	–	–	0.32	–	–	–	–	−0.76	–	–	–	–	–	–	–	–
imidazolinium	27	–	0.93	–	3.53	–	–	4.93	–	–	–		–	3.23	–	–	−0.26	–	–	–	−0.50	–	–
$HOCH_2CH_2\overset{+}{N}H_3$	28	–	–	–	2.75	–	–	–	–	–	–	–	–	4.82	–	–	–	–	–	–	2.30	–	–
$HOCH_2CH_2\overset{+}{N}H_3$	29	–	–	–	2.96	–	–	–	–	–	–	–	–	–	–	–	–	3.85	–	–	–	–	–
$HOCH_2CH_2\overset{+}{N}H_2CH_3$	29	–	–	–	3.42	–	–	–	–	–	–	–	–	–	–	–	–	3.65	–	–	–	–	–
$HOCH_2CH_2\overset{+}{N}H_2CH_2CH_3$	29	–	–	–	3.42	–	–	–	–	–	–	–	–	–	–	–	–	3.23	–	–	–	–	–
$HOCH_2CH_2\overset{+}{N}H(CH_3)_2$	29	–	–	–	3.25	–	–	–	–	–	–	–	–	–	–	–	–	2.31	–	–	–	–	–
$HOCH_2CH_2\overset{+}{N}H(CH_2CH_3)_2$	29	–	–	–	3.36	–	–	–	–	–	–	–	–	–	–	–	–	1.91	–	–	–	–	–
$HOCH_2CH_2\overset{+}{N}H_2CH_2CH_2OH$	29	–	–	–	3.13	–	–	–	–	–	–	–	–	–	–	–	–	3.74	–	–	–	–	–
$HOCH_2CH_2\overset{+}{N}H(CH_2CH_2OH)_2$	29	–	–	–	3.47	–	–	–	–	–	–	–	–	–	–	–	–	3.63	–	–	–	–	–
$HOCH_2CH_2\overset{+}{N}H(CH_3)(CH_2CH_2OH)$	29	–	–	–	3.25	–	–	–	–	–	–	–	–	–	–	–	–	3.45	–	–	–	–	–
$HOCH_2CH_2\overset{+}{N}H_2Ph$	29	–	–	–	3.45	–	–	–	–	–	–	–	–	–	–	–	–	3.05	–	–	–	–	–
$HOCH_2CH_2\overset{+}{N}H(Ph)(CH_2CH_3)$	29	–	–	–	2.50	–	–	–	–	–	–	–	–	–	–	–	–	−0.89	–	–	–	–	–
$HOCH_2CH_2\overset{+}{N}H(Ph)(CH_2CH_2OH)$	29	–	–	–	3.25	–	–	–	–	–	–	–	–	–	–	–	–	2.26	–	–	–	–	–
$(4\text{-}(CH_3CH_2)_2\overset{+}{N}HPh)(Ph)_2COH$	18	0.39	–	0.96	–	1.52	–	–	–	1.17	–	–	–	–	0.04	–	–	–	–	–	–	–	–
$(4\text{-}\overset{+}{N}H_3Ph)(Ph_2COH$	18	0.61	–	1.58	–	3.24	–	–	–	4.03	–	–	–	–	3.75	–	–	–	–	–	–	–	–
$(4\text{-}((CH_3)_2CH)_2\overset{+}{N}HPh)(Ph)_2COH$	18	–	–	0.50	–	1.24	–	–	–	1.00	–	–	–	–	−0.19	–	–	–	–	–	–	–	–

(continued)

TABLE 2 (continued)

Ion A^+	Ref. for p*K*	Mole fraction of ethanol																					
		0.032	0.042	0.070	0.091	0.109	0.116	0.144	0.149	0.157	0.163	0.172	0.182	0.207	0.214	0.233	0.242	0.281	0.299	0.316	0.370	0.390	0.400
$CH_3CO\overset{+}{N}H_2Cl$	30	–	–	–	–	–	8.3	–	–	–	–	–	–	–	–	–	–	12.2	–	–	–	–	–
$ICH_2CO\overset{+}{N}H_2Cl$	30	–	–	–	–	–	8.4	–	–	–	–	–	–	–	–	–	–	12.8	–	–	–	–	–
$BrCH_2CO\overset{+}{N}H_2Cl$	30	–	–	–	–	–	7.9	–	–	–	–	–	–	–	–	–	–	12.1	–	–	–	–	–
$ClCH_2CO\overset{+}{N}H_2Cl$	30	–	–	–	–	–	7.7	–	–	–	–	–	–	–	–	–	–	11.6	–	–	–	–	–
$FCH_2CO\overset{+}{N}H_2Cl$	30	–	–	–	–	–	7.7	–	–	–	–	–	–	–	–	–	–	11.2	–	–	–	–	–
$Cl_2CHCO\overset{+}{N}H_2Cl$	30	–	–	–	–	–	8.1	–	–	–	–	–	–	–	–	–	–	12.1	–	–	–	–	–
$Cl_3CCO\overset{+}{N}H_2Cl$	30	–	–	–	–	–	8.1	–	–	–	–	–	–	–	–	–	–	13.9	–	–	–	–	–
$F_3CCO\overset{+}{N}H_2Cl$	30	–	–	–	–	–	7.4	–	–	–	–	–	–	–	–	–	–	10.2	–	–	–	–	–
$CH_3CO\overset{+}{N}H_2Br$	30	–	–	–	–	–	7.8	–	–	–	–	–	–	–	–	–	–	12.8	–	–	–	–	–
$CH_3CH_2OCO\overset{+}{N}H_2Br$	30	–	–	–	–	–	8.5	–	–	–	–	–	–	–	–	–	–	13.7	–	–	–	–	–
$CH_3CH_2OCO\overset{+}{N}H_2Cl$	30	–	–	–	–	–	9.1	–	–	–	–	–	–	–	–	–	–	14.9	–	–	–	–	–

EVALUATION OF $\Delta G_t^{\ominus}(i)_e$

If values for the acid dissociation constants for acids A^+ and A are available for a range of water + ethanol compositions, eqns. (5) and (7) can be used to produce values for $\Delta G_t^{\ominus}(A^+)_e$ or $\Delta G_t^{\ominus}(B^-)_e$ respectively using $\Delta G_t^{\ominus}(H^+)$. If the p*K* data are on the molality scale (superscript m), values for $\Delta G_t^{\ominus}(A^+)_e$ and $\Delta G_t^{\ominus}(B^-)_e$ on the mole fractions scale at 25 °C are given by

$$\Delta G_t^{\ominus}(A^+)_e = 5.71(pK_w^m - pK_s^m) + \Delta G_t^{\ominus}(H^+) - 5.71\log\left(\frac{18.015}{M_s}\right) \tag{8}$$

$$\Delta G_t^{\ominus}(B^-)_e = 5.71(pK_s^m - pK_w^m) - \Delta G_t^{\ominus}(H^+) + 5.71\log\left(\frac{18.015}{M_s}\right) \tag{9}$$

where $M_s = 100/\{(W/46.07) + ((100 - W)/18.015)\}$ and W is the weight % of ethanol in the mixture. If, however, the p*K* data are on the molar scale (superscript c), $\Delta G_t^{\ominus}(H^+)_e$ and $\Delta G_t^{\ominus}(B^-)_e$ on the mole fraction scale at 25 °C are given by

$$\Delta G_t^{\ominus}(A^+)_e = 5.71(pK_w^c - pK_s^c) + \Delta G_t^{\ominus}(H^+) - 5.71\log\left(\frac{18.015d_s}{M_s d_w}\right) \tag{10}$$

$$\Delta G_t^{\ominus}(B^-)_e = 5.71(pK_s^c - pK_w^c) - \Delta G_t^{\ominus}(H^+) + 5.71\log\left(\frac{18.015d_s}{M_s d_w}\right) \tag{11}$$

where d_w and d_s are the densities of pure water and the mixture at 25 °C. Values for d_s were interpolated from the data given by Bates [11]. The values for $\Delta G_t^{\ominus}(A^+)_e$ and $\Delta G_t^{\ominus}(B^-)_e$ calculated in this way using $\Delta G_t^{\ominus}(H^+)$ determined previously [7] from the spectrophotometric solvent sorting method are assembled in Tables 1 and 2. The references from which the p*K* data are taken are also given in Tables 1 and 2. These tables show a similar distribution of values for $\Delta G_t^{\ominus}(i)_e$ to that found previously for water + methanol [8] water + acetone [9] and water + dioxane [6], with, broadly, $\Delta G_t^{\ominus}(B^-)_e$ being positive and $\Delta G_t^{\ominus}(A^+)_e$ negative in water-rich conditions.

COMPARISON OF VALUES FOR $\Delta G_t^{\ominus}(A^+)_e$ and $\Delta G_t^{\ominus}(B^-)_e$

The charges on some negative ions lead to positive values for $\Delta G_t^{\ominus}(B^-)_e$ which are high, notably for phenate and substituted phenates, the monocaboxylate anions and the carboxylate anions containing another –COOH group; high negative values for $\Delta G_t^{\ominus}(A^+)$ are found with the amide cations. In the composition region $x_2 \sim 0.28$–0.40, where $\Delta G_t^{\ominus}(H^+)$ is reasonably independent of the sets of assumptions used in its evaluation, for the phenates $\Delta G_t^{\ominus}(B^-)_e \sim 15$ kJ mol^{-1} at $x_2 \sim 0.28$, for the monocarboxylates

$\Delta G_t^{\ominus}(\mathrm{B^-})_e \sim$ 10–15 kJ mol^{-1} at $x_2 \sim 0.28$ and for the carboxylates which also contain an additional –COOH group $\Delta G_t^{\ominus}(\mathrm{B^-})_e \sim 15$ kJ mol^{-1} at $x_2 \sim 0.37$; for $\Delta G_t^{\ominus}(\mathrm{A^+})$ at $x_2 \sim 0.28$, the cations $\mathrm{XCH_2CO\overset{+}{N}H_2Cl}$ (where X = H, I, Br, Cl or F) give -11 to -13 kJ mol^{-1}, $\mathrm{BrOCO\overset{+}{N}H_2Cl}$ gives -12 kJ mol^{-1}, $\mathrm{X_3CCO\overset{+}{N}H_2Cl}$ (for X = Cl, H or F) give -10 to -14 kJ mol^{-1} and $\mathrm{EtOCO\overset{+}{N}H_2X}$ (for X = Cl or F) give -14 to -15 kJ mol^{-1}. Therefore, many of the charges, even on quite large molecules, have substantial effects on the free energy of transfer.

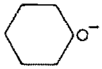
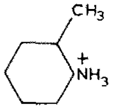
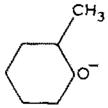
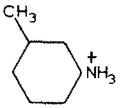
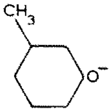
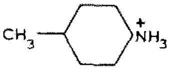
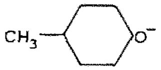
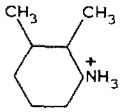
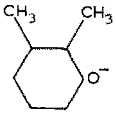
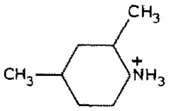
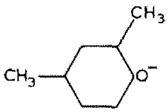
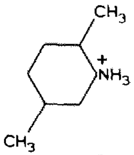
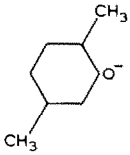
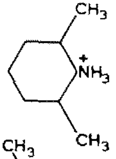
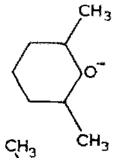
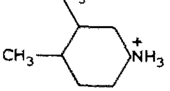
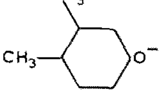
Two effects may independently influence this contribution of the charge to $\Delta G_t^{\ominus}(i)$; the size of the molecule on which the charge resides and the extent of the distribution of the charge over this bulk. A change in the size of the ion at the same time as a change in the extent of the distribution of the charge appears to have little effect on $\Delta G_t^{\ominus}(i)_e$ (kJ mol^{-1}), with all comparisons at $x_2 \sim 0.28$ except the last one at $x_2 \sim 0.20$: $\mathrm{HCOO^-}$ (11.5), $\mathrm{CH_3COO^-}$ (13), $\mathrm{PhCOO^-}$ (15.7); phenate (14.7), 4-nitrophenate (12.5), 2,4-dinitrophenate (12.5) and 2,4, 6-trinitrophenate (8.0); $\mathrm{Me\overset{+}{N}H_3}$ (-2.6), $\mathrm{Ph\overset{+}{N}H_3}$ (-3); $\mathrm{CH_2OHCH_2\overset{+}{N}H_2Me}$ (-3.6), $\mathrm{CH_2OHCH_2\overset{+}{N}H_2Ph}$ (-3.0), $\mathrm{CH_2OHCH_2\overset{+}{N}H(Ph)}$ (Et) (-1); pyridine (-2), quinoline (-0.7) and acridine ($+0.7$).

Likewise, a change in the size of the ion with little change in the extent of the distribution of the charge has little effect: for $x_2 \sim 0.22$, 4-bromoanilinium (-3.0), *N*,*N*-dimethyl-4-bromoanilinium (-0.4), *N*,*N*-diethyl-4-bromoanilinium ($+0.65$); for $x_2 \sim 0.28$, phenate (14.0), cresate (15.5), xylenate (16.2); for $x_2 \sim 0.28$, $\mathrm{HCOO^-}$ (11.5), $\mathrm{CH_3COO^-}$ (13.0), $\mathrm{PhCH_2COO^-}$ (14.7), $\mathrm{Ph_2CHCOO^-}$ (17.0); for $x_2 \sim 0.28$, $\mathrm{CH_2OHCH_2\overset{+}{N}H_3}$ (-3.8), $\mathrm{CH_2OHCH_2\overset{+}{N}H_2Me}$ (-3.6), $\mathrm{CH_2OHCH_2\overset{+}{N}H_2Et}$ (-3.2); for $x_2 \sim 0.28$, $\mathrm{CH_2OHCH_2\overset{+}{N}H_3}$ (-3.8), $\mathrm{CH_2OHCH_2\overset{+}{N}H_2Me}$ (-3.6), $\mathrm{CH_2OHCH_2\overset{+}{N}HMe_2}$ (-2.3); for $x_2 \sim 0.28$, $\mathrm{CH_2OHCH_2\overset{+}{N}H_3}$ (-3.8), $\mathrm{CH_2OHCH_2\overset{+}{N}H_2Et}$ (-3.2), $\mathrm{CH_2OHCH_2\overset{+}{N}HEt_2}$ (-1.9); for $x_2 \sim 0.22$, $\mathrm{(4\text{-}\overset{+}{N}H_3Ph)Ph_2COH}$ (-3.8), $\mathrm{(4\text{-}Et_2\overset{+}{N}HPh)Ph_2COH}$ ($\sim$ zero), $\mathrm{(4\text{-}isoPr_2\overset{+}{N}HPh)Ph_2COH}$ ($+0.2$); for $x_2 \sim 0.39$, $\mathrm{Ph\overset{+}{N}H_3}$ (-2.4), $\mathrm{Ph\overset{+}{N}H_2Et}$ (-1.3), $\mathrm{Ph\overset{+}{N}H_2Pr}$ (-0.4), $\mathrm{Ph\overset{+}{N}H_2isoPr}$ (-1.0), $\mathrm{Ph\overset{+}{N}H_2n\text{-}Bu}$ (-0.3); for $x_2 \sim 0.28$, $\mathrm{Ph\overset{+}{N}H_3}$ (-3.2), $\mathrm{Ph\overset{+}{N}H_2Me}$ (-1.7), $\mathrm{Ph\overset{+}{N}H_2Et}$ (-1.8), $\mathrm{Ph\overset{+}{N}HMe_2}$ (-0.31); for $x_2 \sim 0.37$, $\mathrm{HOOC(CH_2)_{\mathit{n}}COO^-}$, for $n = 1$–8, (15–16); for $x_2 \sim 0.28$, $\mathrm{\overset{+}{N}H_4}$ (-3.8), $\mathrm{Me\overset{+}{N}H_3}$ (-2.6), $\mathrm{Pr\overset{+}{N}H_3}$ (-2.1), $\mathrm{Bu\overset{+}{N}H_3}$ (-1.6), $\mathrm{pentyl\overset{+}{N}H_3}$ (-1.3), $\mathrm{hexyl\overset{+}{N}H_3}$ (-0.9); for $x_2 \sim 0.28$, $\mathrm{Ph\overset{+}{N}H_3}$ (-3.2), $\mathrm{4\text{-}MePh\overset{+}{N}H_3}$ (-3.4), xylidinium ions (-3.7).

Moreover, a change in the extent of the distribution of the charge over the ion accompanying little change in size, illustrated for $x_2 \sim 0.28$ by

TABLE 3

Values for $\Delta G_t^{\ominus}(\mathrm{B}^-)_e - \Delta G_t^{\ominus}(\mathrm{A}^+)_e$ and $\Delta G_t^{\ominus}(\mathrm{B}^-)_e + \Delta G_t^{\ominus}(\mathrm{A}^+)_e$ (kJ mol^{-1}) at 25 °C for pairs of ions having the same size and extent of distribution of the charge

A^+	B^-	$\Delta G_t^{\ominus}(\mathrm{B}^-)_e - \Delta G_t^{\ominus}(\mathrm{A}^+)_e$ for mole fractions of EtOH		$\Delta G_t^{\ominus}(\mathrm{B}^-)_e + \Delta G_t^{\ominus}(\mathrm{A}^+)_e$ for mole fractions of EtOH	
		$x_2 = 0.144$	$x_2 = 0.281$	$x_2 = 0.144$	$x_2 = 0.281$
		15.9	18.0	6.5	12.0
		17.2	18.8	7.6	12.6
		16.6	18.6	7.0	12.3
		16.4	18.7	7.0	11.9
		17.4	19.8	7.6	12.6
		17.3	19.3	7.5	12.7
		17.3	19.7	7.5	12.7
		17.2	19.0	8.0	13.4
		17.3	19.4	7.2	12.0

$PhCH_2COO^-$ (14.7) and $PhCOO^-$ (15.7), appears to produce little variation in $\Delta G_t^\ominus(i)_e$.

However, despite the relative insensitivity of $\Delta G_t^\ominus(i)_e$ to the changes along the above series, we have the initial observation of high positive values for $i = B^-$ and negative values, sometimes high, for $i = A^+$. This has particular significance for the reference ion or TATB method of assigning values of $\Delta G_t^\ominus(i)$ for individual ions by assuming an equal, or nearly equal, split $\Delta G_t^\ominus(Ph_4As^+) = \Delta G_t^\ominus(BPh_4^-)$, with only a small contribution of $\Delta G_t^\ominus(Ph_4As^+)_e$ to $\Delta G_t^\ominus(Ph_4As^+)$ and of $\Delta G_t^\ominus(BPh_4^-)_e$ to $\Delta G_t^\ominus(BPh_4^-)$. In Table 3, values for $(\Delta G_t^\ominus(B^-)_e - \Delta G_t^\ominus(A^+)_e)$ for large similarly sized, but not completely identical A and B, with a similar spread of charge over A or B from a charged atom, are presented, with only the identity of the charged group varying within each pair. This difference shows very significant values for each pair, again illustrating that $\Delta G_t^\ominus(i)_e$ is not a small contribution to $\Delta G_t^\ominus(i)$ for these large ions. Particularly interesting is $(\Delta G_t^\ominus(B^-)_e - \Delta G_t^\ominus(A^+)_e) \sim 18$–$20$ kJ mol^{-1} for $x_2 \sim 0.28$, where the derivation of $\Delta G_t^\ominus(i)_e$ is independent of the particular source of the values for $\Delta G_t^\ominus(H^+)$. This explains, perhaps, the difference $\Delta G_t^\ominus(BPh_4^-) - \Delta G_t^\ominus(Ph_4As^+) \sim 7$ kJ mol^{-1} found [7] for this solvent composition, $x_2 \sim 0.28$. Clearly, the contribution of $\Delta G_t^\ominus(i)_e$ to $\Delta G_t^\ominus(i)$ is not small and is markedly dependent on the sign of the charge, so that $\Delta G_t^\ominus(A^+)_e \not\approx \Delta G_t^\ominus(B^-)_e$. Of interest too are the values of $\Delta G_t^\ominus(B^-)_e + \Delta G_t^\ominus(A^+)_e$ for large ions of similar size and with a similar distribution of charge over the bulk of A^+ and B^- in each pair, since this sum is independent of $\Delta G_t^\ominus(H^+)$ and therefore of the method used in deriving it. These are also contained in Table 3: for $x_2 \sim 0.28$, $\Delta G_t^\ominus(B^-)_e + \Delta G_t^\ominus(A^+)_e \sim 12$–$13$ kJ mol^{-1}, determined without reference to data for any other molecules but B and A themselves. This can be contrasted with the sum of the total free energies of transfer [7] for pairs of large oppositely charged ions, with $\Delta G_t^\ominus(Ph_4As^+) + \Delta G_t^\ominus(BPh_4^-) \sim -33$ kJ mol^{-1} and $\Delta G_t^\ominus(Ph_4As^+) + \Delta G_t^\ominus(\text{picrate}) \sim -21$ kJ mol^{-1} for the same composition.

REFERENCES

1 O. Popovych, Crit. Rev. Analyt. Chem., 1 (1970) 73; O. Popovych, A. Gibofsky and D.H. Berne, Analyt. Chem., 44 (1972) 811.

2 J.I. Kim, J. Phys. Chem., 82 (1978) 191; Z. Phys. Chem. N. F., 113 (1978) 129.

3 J.I. Kim, A. Cecal, H.-J. Born and E. A. Gomaa, Z. Phys. Chem. N. F., 110 (1978) 209.

4 C.F. Wells, Australian J. Chem., 36 (1983) 1739; I.M. Sidahmed and C.F. Wells, J. Chem. Soc. Faraday Trans. 1 , 82 (1986) 2577.

5 C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 69 (1973) 984; 70 (1974) 694; 71 (1975) 1868; 72 (1976) 601; 77 (1981) 1515; G.S. Groves and C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 81 (1985) 1985, 3091; G.S. Groves, K.H. Halawani and C.F. Wells, 83 (1987) 1281; I.M. Sidahmed and C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 83 (1987) 439; 84 (1988) in press.

6 C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 74 (1978) 1569.

7 C.F. Wells, J. Chem. Soc. Faraday Trans. 1, 80 (1984) 2445.
8 C.F. Wells, J. Chem. Soc. Faraday Trans, 1, 74 (1978) 636.
9 C.F. Wells, Thermochim. Acta, 53 (1982) 67.
10 C.F. Wells, Adv. Chem. Ser., 177 (1979) 53.
11 R.G. Bates, in A.K. Covington and P. Jones (Eds.), Hydrogen-Bonded Solvent Systems, Taylor and Francis, London, 1968, p. 49.
12 W.J. Gelsema, C.L. de Ligny and G.F. Visserman, Rec. Trav. Chim., 84 (1965) 1129.
13 E. Grunwald and B.J. Berkowitz, J. Am. Chem. Soc., 73 (1951) 4939.
14 H.O. Spivey and T. Shedlovsky, J. Phys. Chem., 71 (1967) 2171.
15 G. Douhéret, Bull. Soc. Chim. Fr., (1967) 1412.
16 J.O. Frohliger, R.A. Gartska, H.W. Irwin and O.W. Steward, Anal. Chem., 40 (1968) 1408.
17 R. Thuaire, J. Chim. Phys., 67 (1970) 1076.
18 R. Reynaud, Bull. Soc. Chim. Fr., (1967) 2686.
19 S. Aditya, A.K. Roy and S.C. Lahiri, Z. Phys. Chem., 258 (1977) 1033.
20 G. Bonhomme, Bull. Soc. Chim. Fr., (1968) 60.
21 R. Reynaud, Bull. Soc. Chim. Fr., (1967) 4597.
22 G. Kortum and M. Buck, Z. Elektrochem., 62 (1958) 1083.
23 A.L. De and A.K. Atta, Can. J. Chem., 63 (1985) 3129.
24 A.V. Nevskii, V.A. Shormanov and G.A. Krestov, Russ. J. Phys. Chem., 58 (1984) 97.
25 B. Gutbezahl and E. Grunwald, J. Am. Chem. Soc., 75 (1953) 559.
26 S.C. Lahiri, G. Biswas and S. Aditya, Thermochim. Acta, 9 (1974) 365.
27 J. Oszczapowicz and M. Czurylowska, Talanta, 31 (1984) 559.
28 G. Douhéret, Bull. Soc. Chim. Fr., (1967) 2969.
29 G. Douhéret and J.-C. Pariaud, J. Chim. Phys., 59 (1962) 1013.
30 H. Menard and J. Lessard, J. Chem. Eng. Data, 23 (1978) 64.
31 H. Sadek, M.S.A. Elamayem and I.M. Sidahmed, Suomen Kemistilehti, B39 (1966) 225.