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Enthalpies of Transfer of Monovalent Ions from Water to Water-Acetonitrile Mixtures

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Synopsis. Ionic enthalpies of transfer from water to water–acetonitrile mixtures were estimated for Na^+, K^+, Rb^+, Cs^+, Ag^+, Tl^+, Me_4N^+, Et_4N^+, n-Pr_4N^+, n-Bu_4N^+, Ph_4As^+, Ph_4B^-, Cl^-, Br^-, I^-, NCS^-, NO_3^-, ClO_4^-, and picrate ion on the basis of the assumption $\Delta H^\circ_t(Ph_4As^+)=\Delta H^\circ_t(Ph_4B^-)$.

Several papers are concerned with enthalpies of solution in water-aprotic solvent mixtures.[1] In connection with the conductivity measurement,[2] we measured enthalpies of solution for twenty-three electrolytes in water–acetonitrile (W–AN) mixtures.

Experimental

Tetraphenylarsonium salts were recrystallyzed from acetone.[3] Tetraalkylammonium salts were purified according to the literature.[4] The other salts were of reagent grade and purified by the standard methods. The method for purification of solvents were reported elsewhere.[2] Enthalpies of solution were measured at 25.00±0.02 °C by using a heat-exchange type calorimeter.[5] They were independent of electrolyte concentration (10^{-2}—10^{-3} mol dm^{-3}) within experimental error. Usually three to five measurements were made and the average of values agreeing within ±0.4 kJ mol^{-1} was taken to be the standard enthalpies of solution (ΔH°_s).

Results and Discussion

The ΔH°_s values in Table 1 agree with those in the literature[6] within ±0.7 kJ mol^{-1} in aqueous solutions except for CsI and Et_4NPi (Pi=picrate) and within ±1.1 kJ mol^{-1} in acetonitrile solutions except for Me_4NBr, respectively. The ΔH°_t values for ions estimated on the basis of the assumption $\Delta H^\circ_t(Ph_4As^+)=\Delta H^\circ_t(Ph_4B^-)$ are given in Table 2. The differences between the $\Delta H^\circ_t(W\rightarrow AN)$ values and those in the literature[3,6] are less than ±1.0 kJ mol^{-1} for Na^+, K^+, Me_4N^+, Et_4N^+, n-Pr_4N^+, n-Bu_4N^+, Ph_4As^+, Ph_4B^-, Br^-, and I^- ions, and $-2._7$, $+1._5$, and $+2._0$ kJ mol^{-1} for Rb^+, Cl^-, and ClO_4^- ions, respectively.

Table 1. Enthalpies of solution for electrolytes in water–acetonitrile mixtures. ΔH°_s/kJ mol^{-1}

Electrolyte	x_{AN}							
	0	0.1	0.2	0.4	0.6	0.8	0.9	1.0
NaCl	$+3.8_9$	$+1.0_9$	-1.0_9	-7.1_1	$-11._7$			
NaBr	-0.6_3	-4.7_3	-7.7_9	$-12._6$	$-17._7$	$-21._3$	$-20._0$	
NaI	-7.4_9	$-12._9$	$-17._8$	$-23._4$	$-28._9$	$-34._6$	$-36._1$	$-28._1$
NaSCN	$+6.7_4$	0	-5.3_2	$-11._8$	$-17._5$	$-22._4$	$-24._2$	$-11._2$
$NaPh_4B$	$-19._8$	$-14._6$	$-43._6$	$-51._8$	$-50._1$	$-51._5$	$-53._4$	$-43._5$[a]
KI	$+20._2$	$+12._1$	$+6.7_4$	$+0.8_0$	-5.4_0	$-11._3$	$-14._2$	$-10._7$
KNO_3	$+34._7$		$+26._0$	$+21._5$	$+15._9$	$+11.0$		
RbI	$+25._6$	$+16._9$	$+11._4$	$+5.1_1$	-0.4_6	-6.9_5	-9.7_1	-7.9_1
CsI	$+32._3$	$+23._4$	$+18._0$	$+11._3$	$+5.9_4$	$+0.8_8$	-1.7	
$AgNO_3$	$+22._7$	$-14._3$	$-18._8$	$-22._4$	$-25._4$	$-28._7$	$-28._5$	$-22._7$
$TlNO_3$	$+40._7$	$+36._0$	$+31._5$	$+26._8$				
Me_4NBr	$+24._5$		$+20._6$	$+17._5$	$+14._1$	$+11._9$	$+12._8$	$+20._3$
Me_4NI	$+43._1$		$+35._8$	$+30._8$	$+28._0$	$+25._3$	$+21._3$	
Et_4NCl	$-12._9$			-8.1_2	$-10._7$	$-11._2$	-8.7_5	$+5.8_6$
Et_4NBr	$+5.6_5$		$+9.2_1$	$+8.5_4$	$+5.9_9$	$+3.4_3$	$+3.6_8$	$+11._5$
Et_4NI	$+27._3$		$+27._6$	$+26._2$	$+23._0$	$+18._7$	$+16._8$	$+18._8$
Et_4NClO_4	$+31._9$	$+33._2$	$+27._0$	$+24._0$	$+20._8$	$+15._9$	$+14._4$	$+12._8$
Et_4NPi	$+33._5$	$+40._6$	$+34._8$	$+30._7$	$+30._2$	$+29._7$	$+29._9$	$+30._8$
n-Pr_4NI	$+11._0$	$+24._4$	$+24._2$	$+22._4$	$+19._5$	$+14._4$	$+12._6$	$+14._0$
n-Bu_4NBr	-9.2_9	$+17._1$	$+16._4$	$+13._5$	$+11._4$	$+9.4_6$	$+8.8_7$	$+16._0$
n-Bu_4NI	$+16._7$[b]	$+41._9$	$+39._7$	$+35._1$	$+32._9$	$+28._9$	$+25._9$	$+27._1$
Ph_4AsBr	$+7.7_0$	$+19._8$	$+11._4$	$+6.2_4$	$+2.6_4$	0	-0.8_4	$+6.2_8$
Ph_4AsI	$+34._7$[c]	$+44._9$	$+33._3$	$+27._8$	$+24._2$	$+18._4$	$+15._1$	$+16._3$

a) Ref. 6. b) Ref. 1a. c) Ref. 7.

Table 2. Ionic enthalpies of transfer from water to water–acetonitrile mixtures. ΔH°_t/kJ mol^{-1}

Ion	x_{AN}						
	0.1	0.2	0.4	0.6	0.8	0.9	1.0
Li^+[a]	$-6._2$	$-15._8$	$-22._0$	$-26._2$	$-28._9$		$-14._4$
Na^+	$-5._3$	$-16._8$	$-20._8$	$-20._9$	$-21._8$	$-22._3$	$-13._0$
K^+	$-7._9$	$-19._4$	$-23._9$	$-25._1$	$-25._6$	$-26._9$	$-23._3$
Rb^+	$-8._4$	$-20._1$	$-25._0$	$-25._5$	$-26._6$	$-27._8$	$-25._9$
Cs^+	$-8._6$	$-20._3$	$-25._5$	$-25._9$	$-25._5$	$-26._4$	
Ag^+	$-39._5$	$-52._1$	$-55._5$	$-54._4$	$-55._3$	-54	$-55._3$[b]
Tl^+	$-7._2$	$-19._9$	$-24._5$				
Me_4N^+		$-13._6$	$-16._5$	$-14._5$	$-14._3$	$-14._3$	$-13._6$
Et_4N^+		$-6._1$	$-6._0$	$-3._8$	$-3._3$	$-3._8$	$-2._2$
n-Pr_4N^+	$+13._7$	$+7._2$	$+7._0$	$+9._1$	$+9._4$	$+9._2$	$+10._6$
n-Bu_4N^+	$+25._2$	$+16._2$	$+13._7$	$+16._8$	$+17._6$	$+16._1$	$+16._9$
Ph_4As^+,Ph_4B^-	$+10._6$	$-6._9$	$-11._1$	$-9._4$	$-9._9$	$-11._9$	$-10._8$
Cl^-	$+2._5$	$+11._8$	$+10._3$	$+5._7$	$+5._0$	$+8._0$	$+21._6$
Br^-	$+1._3$	$+10._1$	$+9._3$	$+4._1$	$+1._7$	$+3._3$	$+9._4$
I^-	$-0._3$	$+6._0$	$+4._5$	$-0._6$	$-5._9$	$-7._6$	$-7._6$
NCS^-	$-1._4$	$+4._7$	$+2._2$	$-3._3$	$-7._5$	$-8._6$	$-4._9$
NO_3^-	$+2._5$	$+10._7$	$+10._7$	$+6._3$	$+1._9$	$+3$	$+9._9$
ClO_4^-	$+1._2$	$+2._1$	$-1._0$	$-6._5$	$-11._7$	$-12._7$	$-16._0$
Pi^-	$+6._1$	$+7._4$	$+3._2$	$+0._4$	$-0._5$	$+0._2$	$-0._5$

a) The ionic values for Li^+ ion were calculated from ΔH°_s for $LiClO_4$[1b]. b) Ref. 6.

As Cox *et al.* have suggested,[1e] there is no doubt that a rapid decrease in ΔH°_t for Ag^+ ion in W-rich region is due to the selective solvation by acetonitrile and an increase in ΔH°_t for Na^+ and Cl^- ions in AN-rich region is due to the selective hydration. Since the specific interaction of Ag^+ ion with acetonitrile at x_{AN} (mole fraction of acetonitrile) =0—1.0 has been established,[8] a slight increase in ΔH°_t at x_{AN}=0.3—0.8 and a decrease at x_{AN}=0.8—1.0 can be concluded to be characteristic of the type of ion, the cosphere of which is enriched with more acetonitrile than water relative to the bulk composition of solvent mixtures. The ΔH°_t values for alkali metal ions at x_{AN}=0.2 follow the order: $Li^+>Na^+>K^+>Rb^+\approx Cs^+$. This is consistent with that of decreasing ΔH°_t-increase in AN-rich region. A marked decrease in ΔH°_t at x_{AN}=0.2—0.8 for Li^+ ion can be concluded to be characteristic of a selectively hydrated ion. An endothermic maximum for n-Bu_4N^+, Ph_4As^+, and Ph_4B^- ions at x_{AN}=0.05—0.1 is common to a hydrophobic structure-making ion in W-aprotic solvent mixtures.[1a,1g] In contrast to the positive values for n-Bu_4N^+ ion at x_{AN}=0—1.0, those for Ph_4As^+ ion are negative at x_{AN}= 0.15—1.0. The extent of endothermicity for tetraalkylammonium ions decreases with decreasing size, and Me_4N^+ ion behaves like alkali metal ions.[9]

Anions show a variety of ΔH°_t dependences: The ΔH°_t values for all the anions reach a maximum at x_{AN}=0.15—0.3, decrease in an intermediate region, and, except for ClO_4^- and Pi^- ions, reach a minimum at x_{AN}=0.7—0.95. From the ΔH°_t-increase in AN-rich region the order in decreasing hydration can be concluded: $\mathrm{Cl^-} > \mathrm{NO_3^-} > \mathrm{Br^-} > \mathrm{NCS^-} > \mathrm{I^-} > \mathrm{Pi^-} > \mathrm{ClO_4^-}$. The x_{AN} value corresponding to $\Delta H^\circ_{\mathrm{t}}$ minimum shifts to a higher value from $\mathrm{Cl^-}$ through $\mathrm{Br^-}$ to $\mathrm{I^-}$. However, the $\Delta H^\circ_{\mathrm{t}}$ maximum appears at nearly equal x_{AN}. The extent of endothermicity follows the order: $\mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{I^-}$. As compared with aqueous solution, the solvent structure at $x_{\mathrm{AN}} = ca.\ 0.3$ may be the least favorable for the hydration of halide ions owing to the destruction of water lattice caused by the addition of acetonitrile.[10] In contrast to the positive $\Delta H^\circ_{\mathrm{t}}$ values for $\mathrm{Cl^-}$ and $\mathrm{Br^-}$ ions at $x_{\mathrm{AN}} = 0$—1.0, those for $\mathrm{I^-}$ ion are negative at $x_{\mathrm{AN}} = 0$—0.1 and 0.6—1.0. The behavior of $\mathrm{NCS^-}$ ion as a softer ion than $\mathrm{I^-}$ ion at $x_{\mathrm{AN}} = 0$—0.95 and as a harder ion at $x_{\mathrm{AN}} = 0.95$—1.0 may be related to the fact that linear $\mathrm{NCS^-}$ ion has two kinds of terminal atoms. The behavior of $\mathrm{NO_3^-}$ ion resembles that of $\mathrm{Br^-}$ ion. The $\Delta H^\circ_{\mathrm{t}}$ values for $\mathrm{Pi^-}$ ion suggest that it interacts weakly with either water or acetonitrile.

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