Gibbs Transfer Energies of Some Uni-Univalent Salts in Water – N-Methyl-2-Pyrrolidinone Solvent Mixtures at 30 °C

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The standard Gibbs transfer energies of some uni-univalent electrolytes like potassium picrate, tetraphenylarsonium picrate, potassium and silver tetraphenyl borate were determined in water + N-Methyl-2-Pyrrolidinone mixtures from solubility measurements at 30 °C. They were split into respective ionic values on the basis of the reference electrolyte method using tetraphenylarsonium tetraphenylborate. The variation of transfer energies of the ions with composition of solvent are examined and discussed in terms of the possible ion – solvent interactions.

Introduction

The elucidation of ion-solvent interactions in pure and mixed solvents is important from a fundamental and technological view point and has wide ranging applications from biology to electrochemical power sources [1–4]. The Gibbs transfer energy of a given species from a reference solvent to the solvent in question is the most relevant parameter for the understanding of such interactions. In the present work, the Gibbs transfer energies of a number of ions have been determined in water – N-Methyl-2-Pyrrolidinone mixtures on the basis of the reference electrolyte method [5–7] using tetraphenylarsonium tetraphenylborate. The results are discussed and compared with those based on the nLJP method employed earlier on these solvent mixtures [8].

Experimental

(I) Materials

N-Methyl-2-Pyrrolidinone (NMP) (SISCO Research Laboratories, extra pure > 99.5%) was purified following the procedure described in [9]. The purified sample had a boiling point of 76 °C at a pressure of 5 mm of Hg a density of $d^{30} = 1.0330\ \mathrm{gcm}^{-3}$ (as reported), and a refractive index $_{\mathrm{D}}\eta^{30} = 1.4705$, (reported $_{\mathrm{D}}\eta^{30} = 1.471$ [9]. It had a water content of 84.5 ppm from analysis by the Karl Fischer method. Sodium tetraphenyl borate (AR, Merck) was dried before use. Potassium picrate (KPic), tetraphenylarsonium picrate (Ph_4AsPic) and potassium tetraphenyl borate ($KBPh_4$) were prepared and purified as described in [10]. Silver tetraphenyl borate was prepared according to [11].

Methods Employed

1. Solubility Measurements

The saturation solubilities of KPic, Ph_4AsPic and $KBPh_4$ in different solvent mixtures were determined spectrophotometrically using a PMQ II Carl-Zeiss spectrophotometer. The solubility measurements of the tetraphenylborate salts were carried out in thoroughly deaerated solutions by flushing them with nitrogen at every stage of the experiment.

The solubility of silver tetraphenylborate at various solvent compositions was determined by an Inductively Coupled plasma atomic spectrometry (Argon flame, wavelength 328.06 nm for silver) (ICP-AES, ARL-3410 with mini torch) [12]. The method of preparation of saturated solutions has been described in [13]. An appropriate volume of the clear saturated solution was taken and diluted suitably in all measurements. The solutions were then analysed. The concentration of silver was obtained from a calibration curve prepared earlier with various standard solutions of silver (I) nitrate in a suitable range of compositions. In all cases, the solubility measurements were repeated at least twice independently for each solvent composition. The agreement between the duplicates was better than ±0.1%. All measurements were carried out at 30 ± 0.1 °C.

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Table 1. Solubilities (S) and solubility products ($pKsp$) of various electrolytes in water–NMP mixtures at 30 °C

X_{NMP}	D[a]	KPic		Ph_4AsPic		$KBPh_4$		$AgBPh_4$	
		$S \times 10^2$/ mol kg^{-1}	$pKsp$	$S \times 10^4$/ mol kg^{-1}	$pKsp$	$S \times 10^4$/ mol kg^{-1}	$pKsp$	$S \times 10^8$/ mol kg^{-1}	$pKsp$
0.0	76.3	0.22	5.36	0.29	9.07	0.23	9.28	0.12	17.8
0.1	69.2	0.67	4.43	0.69	8.34	0.70	8.32	0.39	16.8
0.3	56.4	0.89	4.21	1.57	7.63	3.87	6.85	1.46	15.7
0.5	46.1	1.12	4.04	2.39	7.27	7.84	6.25	4.56	14.7
0.7	38.5	1.32	3.93	4.16	6.80	34.50	5.02	46.10	12.1
0.9	33.2	1.47	3.87	7.97	6.25	45.80	4.80	98.40	12.0
1.0	31.5	1.68	3.79	8.79	6.18	76.50	4.40	932.00	10.1

[a] Dielectric constant.

Table 2. Gibbs transfer energies of various electrolytes from water to water+NMP mixtures at 30 °C (Molal scale).

X_{NMP}	$\Delta_t G^{\circ a}$/kJ mol^{-1}				
	KPic	Ph_4AsPic	$KBPh_4$	$AgBPh_4$	Ph_4AsBPh_4
0.0	0.0	0.0	0.0	0.0	0.0
0.1	−5.4	−4.3	−5.6	−5.7	−4.5
0.3	−6.7	−8.4	−14.1	−12.4	−15.8
0.5	−7.6	−10.5	−17.6	−18.2	−20.4
0.7	−8.3	−13.2	−24.8	−29.8	−29.7
0.9	−8.6	−16.4	−26.0	−33.6	−33.8
1.0	−9.1	−16.8	−28.3	−44.9	−36.0

[a] Accurate upto ±0.2 kJ mol^{-1}.

Results and Discussion

The solubilities obtained as above were used for calculating the solubility products, Ksp, employing the relation

$$Ksp = S^2 \gamma \pm^2, \tag{1}$$

where S is the solubility in mol kg^{-1} and $\gamma\pm$ the mean molal activity coefficient of the salt, calculated using the modified Debye-Hückel equation

$$-\log \gamma_{\pm} = \frac{A Z_+ Z_- \mu^{1/2}}{1 + a B \mu^{1/2}}, \tag{2}$$

where A and B are the Debye-Hückel constants, μ is the ionic strength of the solution and a is the ion size parameter with $a = 6$ Å for KPic, $a = 8$ Å for Ph_4AsPic, $KBPh_4$ and $a = 7.5$ Å for $AgBPh_4$ [14].

The solubility (S) and solubility product ($pKsp$) for all the salts are given in Table 1.

The Gibbs transfer energy of the salts $\Delta_t G^\circ$ from water to water–NMP mixtures was calculated from

$$\Delta_t G^\circ(\text{salt}) = -2.303\, RT \log \left[\frac{Ksp(\text{water}+\text{NMP})}{Ksp(\text{water})}\right]. \tag{3}$$

$\Delta_t G^\circ$ of Ph_4AsBPh_4 in the various solvent mixtures was obtained from the equation

$$\begin{aligned} \Delta_t G^\circ(Ph_4AsBPh_4) &= \Delta_t G^\circ(Ph_4AsPic) \\ &\quad + \Delta_t G^\circ(KBPh_4) - \Delta_t G^\circ(KPic). \end{aligned} \tag{4}$$

The transfer energies of tetraphenyl arsonium [$\Delta_t G^\circ(Ph_4As^+)$ and tetraphenyl borate [$\Delta_t G^\circ(BPh_4^-)$ ions were obtained from the equations

$$\begin{aligned} \Delta_t G^\circ(Ph_4As^+) &= \Delta_t G^\circ(BPh_4^-) \\ &= 1/2\, \Delta_t G^\circ(Ph_4AsBPh_4), \\ \Delta_t G^\circ(K^+) &= \Delta_t G^\circ(KBPh_4) - \Delta_t G^\circ(BPh_4^-), \\ \Delta_t G^\circ(Pic^-) &= \Delta_t G^\circ(KPic) - \Delta_t G^\circ(K^+), \\ \Delta_t G^\circ(Ag^+) &= \Delta_t G^\circ(AgBPh_4) - \Delta_t G^\circ(BPh_4^-), \end{aligned} \tag{5}$$

Variation of Transfer Energies of the Salts

The transfer energies of all the salts are negative and decrease continuously with the addition of NMP (Table 2) indicating that their transfer from water to water+NMP mixtures and pure NMP is a thermodynamically favoured process. The stabilisation arises mainly due to the increased dispersive interactions of the salts in the mixed solvents compared to that in water.

Table 3. Gibbs transfer energies of various ions from water to water + NMP mixtures at 30 °C (molal scale).

X_{NMP}	$\Delta_t G^{\circ a}$/kJ mol^{-1}				
	K^+	Ph_4As^+	Ag^+	Pic^-	BPh_4^-
0.0	0.0	0.0	0.0	0.0	0.0
0.1	−3.3 (−2.3)*	2.3 (−1.2)	−3.5 (−2.4)	−2.1 (−3.1)	−2.3 (−3.3)
0.3	−6.2 (−8.1)	−7.9 (−9.8)	−4.5 (−6.4)	−0.5 (1.4)	−7.9 (−6.0)
0.5	−7.4 (−10.6)	−10.2 (−13.4)	−8.0 (−11.2)	−0.3 (3.0)	−10.2 (−7.0)
0.7	−9.9 (−10.9)	−14.9 (−15.8)	−15.0 (−15.9)	1.6 (2.6)	−14.9 (−13.9)
0.9	−9.2 (−10.3)	−16.8 (−18.1)	−16.8 (−17.9)	0.5 (1.7)	−16.8 (−15.7)
1.0	−5.8 (−1.8)	−22.5 (−10.3)	−26.9 (−18.4)	3.3 (−7.3)	−22.5 (−26.5)

* Values in parentheses refer to $\Delta_t G^\circ$ from nLJP method.

[a] Accurate to ± 0.2 kJ mol^{-1}.

Variation of Transfer Energies of Ions Based on the TATB Method

The transfer energies of all the ions calculated according to (5) are given in Table 3. The $\Delta_t G^\circ$ values of these ions, calculated on the basis of the nLJP method using the $\Delta_t G^\circ$ (Ag^+) reported in [8] are included in the table in parentheses. It is seen that there is very good agreement between the data on the two assumptions except in pure NMP. It is observed that (Table 3) the transfer energies of Ph_4As^+, BPh_4^- ions are negative and decrease with the addition of NMP. The solvation of these large ions, where the central charge remains "buried" deep inside the ion, seems to be governed mainly by the dispersion interactions with the organic co-solvent molecules [15]. The transfer energy values are also affected to a considerable extent by the cavity formation effect associated with the large sized ions [16] apart from the water structure disruption around these large ions caused by the addition of NMP [17].

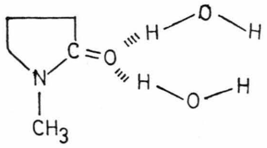
The transfer energy of the picrate anion is initially negative and increases (becomes less negative) with the addition of NMP. The initial negative values of $\Delta_t G^\circ$ of this ion, which become positive subsequently may be attributed to the weakening of the H-bonded interactions between the picrate ion and water as the composition of NMP is increased. This is further aided by the electron withdrawing nitro groups in the picrate ion as well as the increased solvent-solvent interactions on addition of NMP, which results in the disruption of the water structure around this large ion [17].

A comparison of $\Delta_t G^\circ$ values of picrate and tetraphenyl borate ions shows that they are less negative (more positive) in the case of picrate ion as compared to the latter in these mixtures. The smaller extent of solvation of the picrate ion in the mixed solvents (relative to the tetraphenylarsonium or borate ions) may be attributed to the opposing effects of increasing dispersive interactions of the phenyl group, water structure disruption around the large ions by the addition of NMP [17] and decreased hydrogen bonding strength.

The $\Delta_t G^\circ$ of K^+ is negative and decreases continuously with the addition of NMP upto $X_{\mathrm{NMP}} = 0.7$ and then increases (becomes less negative), These results indicate that K^+ is better stabilised in water + NMP mixtures than in water. The strong electrostatic interactions of ion-dipole type between K^+ and NMP and the disruption of the structure of water molecules packed around this ion by the added NMP [17] due to solvent–solvent interactions contribute to the stability. The negative $\Delta_t G^\circ$ of K^+ is further aided by the fact that the enthalpy of transfer of this ion from water to these mixtures and to NMP is exothermic and outweighs any unfavourable effects due to entropy changes in the transfer process [18].

The transfer energies of Ag^+ are negative and decrease continuously with the addition of NMP, which suggests that the transfer of this ion from water to water-NMP mixtures and to pure NMP is thermodynamically favoured. It may therefore be inferred that the silver ion is selectively solvated by NMP in these mixtures, which can be explained in terms of the HSAB principle. The softer nature of NMP compared to water facilitates its interactions with Ag^+ [19]. Ag^+ has d^{10} configuration and is thus capable of experiencing a variety of covalent interactions, including backbonding with suitable ligands [18]. In addition, its small size ($r_{Ag^+} = 1.26$ Å) enables strong electrostatic interactions with NMP through the negative end of carbonyl oxygen of the molecule.

Though Ph_4As^+, K^+, Ag^+, and Pic^- are initially solvated by water, on addition of NMP formation of the 2:1 complex between water and NMP [20]



favours the disruption of water structuring around these ions.

Table 4. Comparison of $\Delta_t G^\circ$ for some selected ions in various solvent mixtures

Solvent	Donor number	$\Delta_t G^\circ$/kJ mol^{-1}			
		Ph_4As^+	K^+	Ag^+	Pic^-
NMP	27.3[a]	−22.8[c]	−5.8[c]	−26.9[c]	3.3[c]
DMSO	29.8[b]	−37.4[d]	−13.0[d]	−44.3[e]	–
Pyridine	33.1[b]	−38.0[a]	6.0[d]	−52.9[f]	−5[d]

[a] [22], [b] [23], [c] Present study, [d] [24], [e] [25], [f] [26].

A comparison of $\Delta_t G^\circ$ data of the cations (water → pure organic solvent) in the three solvents NMP, DMSO and Pyridine along with their donor numbers is given in Table 4. As the donor number of a solvent increases, the transfer energies of soft cations like Ag^+ and Ph_4As^+ generally become more negative, which reflects the behaviour of these solvents towards such ions. In the case of K^+, both DMSO and NMP interact with it through the oxygen of the solvents, while pyridine interacts through the nitrogen atom. The interaction of K^+ with DMSO and NMP may be expected to be stronger compared to pyridine because these solvents contain an oxygen atom which carries excess negative charge, and further they are relatively free of groups which might interfere with their structuring about K^+. However, as mentioned earlier, disruption of the structure of the smaller water molecules which are packed around small ions like K^+ or Ag^+ in large numbers and their replacement by NMP molecules in the transfer process is also an important factor which affects $\Delta_t G^\circ$ between the two solvents [17, 21]. A comparison of $\Delta_t G^\circ$ of K^+ in DMSO and NMP shows that it is more negative in DMSO than in NMP, which can be explained on the basis of the HSAB principle. K^+ interacts with DMSO more strongly than with NMP because of the hard–hard interactions, whereas NMP is comparatively softer in nature [19].

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