Transfer Gibbs energies for ClO_3^- , BrO_3^- , IO_3^- , ClO_4^- and $IO_4^$ anions for water-methanol and water-propan-2-ol mixtures: Some quantum-chemical aspects of ionic solvation

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The transfer Gibbs energies, $\Delta_{trs} G^{\circ}$, of KClO₃, KBrO₃, KIO₃, KClO₄, KIO₄ and the corresponding caesium salts have been obtained through gravimetric measurements of the solubility in aqueous mixtures with methanol (MeOH) and propan-2-ol (PrⁱOH) at 298.2 K. In addition, the solubility of Ph₄P(pic) (pic = picrate anion) as well as K(pic) and KBPh₄ and the corresponding caesium salts are reported in these mixtures at 298.2 K. Single-ion values of $\Delta_{trs} G^{\circ}$ have been calculated using the tetraphenylphosphonium tetraphenylborate (TPTB) assumption. The semiempirical quantum-chemical AM1 method was used for calculations of interaction energy of BPh₄⁻ and Ph₄P⁺ with a series of five solvent molecules and energy demands associated with a deformation of these ions. Trends observed for $\Delta_{trs} G^{\circ}$ are discussed in terms of specific ion-solvent interactions and the structural effect of solvent mixtures.

Transfer properties of a single ion such as Gibbs energies, enthalpies and entropies of the transfer reflect the specific interactions of solvent molecules with cations and anions in solution. The examination of transfer parameters of ions provides a basis for analysis of the kinetic data for reactions involving ions in such solvents. All single-ion transfer properties are extrathermodynamic quantities and their values depend on a suitable reference electrolyte.

The aim in the present study is twofold. First, to investigate the behaviour of oxoanions of halogens in H_2O -MeOH and H_2O -PrⁱOH mixtures and to compare the transfer Gibbs energies of the investigated ions with recently reported results in H_2O -acetonitrile (AN) and H_2O -Bu⁴OH mixtures.¹ Second, to provide an analysis of the extrathermodynamic TPTB assumption used in calculation of single-ion thermodynamic properties comparing the $\Delta_{trs} G^o$ data for the selected K^+ and Cs^+ salts and evaluating the interaction energy of Ph_4P^+/BPh_4^- with a series of solvent molecules. In these semiempirical quantum-chemical calculations we were inspired by the recent critical study of thermodynamic splitting based on the TPTB assumption which was published for water and $Pr^iOH.^2$

Experimental

Materials

The compounds NaBrO₃, (>99.8%), CsNO₃ (>99.0%), PrⁱOH (>99.7%), MeOH (>99%) Lachema Brno, H₅IO₆ (>99.5%), HClO₄, HIO₃ (>97%), KClO₄ (>99.5%), KIO₄ (>99.8%), KBrO₃ (99.8%), KIO₃ (>99.5%), NaBPh₄ (>99.5%) Merck and Ph₄PCl (>98%) Fluka (% purity in parentheses) were of analytical grade. Caesium salts (CsIO₃, CsIO₄ and CsClO₄) were prepared from CsNO₃ and the appropriate acid. Addition of CsNO₃ to saturated solutions of NaClO₃ and NaBrO₃ resulted in precipitation of CsClO₃ and $CsBrO_3$, respectively. $KBPh_4$ was prepared by treating $NaBPh_4$ with an excess of KCl in water. It was recrystallized three times from acetone-water (3:1) and dried in vacuo at 80 °C. CsBPh₄ was prepared in a similar way. K(pic) and Cs(pic) were prepared by treating a stoichiometric amount of the purified picric acid (purification was made according the literature³) with the corresponding standard aqueous hydroxide. CsOH was prepared on Dowex 2×800 (200-400 mesh)

in OH⁻ form using CsCl. $Ph_4P(pic)$ was prepared by treating an equimolar amount of the purified picric acid with Ph_4PCl and purified by recrystallisation from methanol-water mixtures. All salts were recrystallized from water prior to use and their purity was checked by elemental analysis (halogens titrimetrically and alkali metals using flame photometry). All solvents were redistilled before use.

Solubilities

The concentrations of potassium and caesium oxohalogenide salts were determined gravimetrically. Evaporation of the solvent was performed carefully and slowly under an IR lamp to prevent any loss in the salt weight. Solubility values were averages of three independent measurements. The solubilities of K(pic), Cs(pic), KBPh₄, CsBPh₄ as well as Ph₄P(pic) in water and in aqueous-organic mixtures were determined spectrophotometrically at 360 nm ($\varepsilon = 1396 \text{ m}^2 \text{ mol}^{-1}$) for the picrate salt and at 266 and 274 nm ($\varepsilon = 325$, 206 m² mol⁻¹) for tetraphenylborate salts at 298.2 K.⁴ For the rapid attainment of the equilibrium between the solid phase of KBPh₄, $CsBPh_4$ and $Ph_4P(pic)$ and their solutions, an ultrasonic generator Tesla UC 005 AJ1 with an output of 30 W of 50 kHz frequency was used. The duration of the ultrasonic agitation did not exceed 30 min. The standard errors in solubility determinations using gravimetry and spectrophotometry were 1 and 3%, respectively. According to these standard errors of solubility determinations, the errors in $\Delta_{trs} G^{\circ}(salt)$ were ± 0.07 and ± 0.21 kJ mol⁻¹. The error in $\Delta_{trs} G^{o}(salt)$ was calculated by the total differential method.5

Semiempirical quantum-chemical calculations

Intermolecular interactions between BPh_4^{-}/Ph_4P^+ and solvent/cosolvent can play an important role in the applicability of the TPTB assumption. They determine the build-up of the solvation sphere around the reference ion and its modification upon an addition of the cosolvent. Recently, Taniewska-Osińska has raised arguments against the applicability of the TPTB assumption based on an interpretation of the enthalpies of the transfer of ions from water to water-PrⁱOH mixtures and on the MNDO calculations of charge distribution in BPh_4^- and $Ph_4P^{+,2}$ Her main theoretical objections were based purely on electrostatics arising from the Published on 01 January 1996. Downloaded by State University of New York at Stony Brook on 31/10/2014 14:22:12.

							S/10 ⁻² mo	l dm ⁻³						
x(MeOH)	KCI04	KI04	KClO ₃	KBrO ₃	KIO ₃ "	K(pic)	Ph4P(pic)	CsCI04	CsIO4	CsCIO3	CsBrO ₃	CsIO ₃	Cs(pic)	CsBPh4
0	15.1	2.26	68.5	47.9	42.6 (41.8)	2.47	0.00447	8.89	5.67	35.5	14.1	8.25	1.13	0.00447
0.047	12.7	1.83	52.6	34.5	25.9 (23.9)	1.90	0.00738	7.16	4.72	28.5	10.4	5.81	0.89	0.00626
0.100	10.1	1.56	39.4	23.3	15.7 (15.1)	1.61	0.0108	6.17	4.01	21.6	7.54	3.84	0.86	0.00650
0.160	7.91	1.14	29.6	14.4	8.02 (7.24)	1.55	0.0204	4.90	3.06	15.5	4.79	2.32	0.80	06600.0
0.229	6.76	1.00	20.9	9.98	4.84 (3.78)	1.48	0.0370	4.30	2.71	12.2	3.42	1.65	0.77	0.0139
0.309	5.09	0.82	12.9	5.3	2.13 (2.14)	1.42	0.100	3.38	2.22	7.86	1.96	0.68	0.79	0.0246
^a Data in par	rentheses from	ı ref. 14.												
				Table 2	Solubilities of the	salts investic	oated in water a	nd H .O–PriO	H mixtures :	at 298.2 K				

		CsBPh ₄	0.00405	0.00415	0.00431	0.00461	0.0177	0.0342
		Cs(pic)	1.01	0.88	0.85	0.85	1.08	1.40
		CsIO ₃	6.23	4.82	3.52	2.60	1.62	0.975
		CsBrO ₃	12.2	9.82	7.73	6.30	4.48	3.21
98.2 K	$S/10^{-2}$ mol dm ⁻³	CsClO3	30.6	26.3	22.4	19.1	16.0	12.0
mixtures at 2		CsIO ₄	4.95	4.44	3.90	3.62	3.43	3.35
ed in water and H ₂ O-Pr ⁱ OH		CsClO ₄	7.56	6.79	5.94	4.90	4.73	4.34
		Ph ₄ P(pic)	0.0064	0.0072	0.0108	0.0154	0.0421	0.115
s investigate		$KBPh_4$	0.0206	0.0206	0.0218	0.0240	0.0591	0.151
es of the salt		K(pic)	2.11	1.90	1.87	1.83	2.15	2.70
Solubiliti		LIO ₃	31.2	23.5	16.0	11.5	6.93	3.88
Table 2		KBrO ₃	40.9	32.0	24.9	19.9	13.8	9.66
		KCIO ₃	59.3	49.0	39.9	34.5	25.9	20.6
		KIO4	1.99	1.75	1.56	1.42	1.37	1.25
		KClO4	13.1	11.5	10.0	9.02	7.90	6.78
		x(Pr ⁱ OH)	0.012	0.025	0.040	0.056	0.092	0.136

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		IO ₃ - b (K ⁺)	1.31 (1.7) 2.79 (2.8) 5.02 (5.4) 6.18 (7.4) 9.18 (9.4)
		$\operatorname{BrO}_{3^{-b}}^{\mathbf{b}}$	(0.8) (1.8) (3.4) (4.3)
		$\operatorname{BrO}_{3}^{-}$ (Cs ⁺)	0.76 1.45 2.85 3.70 5.40
	-	BrO ₃ ⁻ (K ⁺)	0.54 1.66 2.91 3.52 5.44
		CIO ₃ ⁻ (Cs ⁺)	0.43 1.01 2.38 3.41
		CIO ₃ - (K ⁺)	0.40 1.01 2.06 3.33
		IO ₄ ⁻ (Cs ⁺)	0.20 0.14 0.71 0.56 0.65
	01-1	IO_4^{-} (K ⁺)	0.07 0.26 0.15 0.38 0.37
	G°/kJ mo	CIO4 ⁻ (Cs ⁺)	0.27 0.18 0.15 0.58 0.66
nu potassium au	Δ	CIO4 ^{- a} (K ⁺)	-0.21 (-0.04) 0.05 (0.06) -0.08 (0.02) -0.29 (-0.10) -0.13 (-0.07)
OIDS CVALUATION		Cs ⁺ a	0.74 (0.95) 1.61 (1.30) 2.37 (2.75) 3.15 (3.80) 4.08 (4.60)
sugarca i		K + a	$\begin{array}{c}(1.10)\\(2.10)\\(3.20)\\(4.40)\\(4.40)\end{array}$
		pic ⁻ (Cs ⁺)	0.43 -0.44 -0.62 -2.06 -2.14
		pic ^{- a} (K ⁺)	$\begin{array}{c} 0.17 \ (0.20) \\ 0.00 \ (0.02) \\ -0.86 \ (-0.94) \\ -1.76 \ (-1.91) \\ -2.60 \ (-2.66) \end{array}$
		BPh ₄ ⁻ (Cs ⁺)	-2.94 -4.01 -6.86 -9.31 -13.19
-		$_{(\mathbf{K}^{+})}^{\mathbf{BPh}_{4}}$	-2.20 ^a -4.10 ^a -6.30 ^a -9.35 ^a -12.50 ^a
		x(MeOH)	0.047 0.100 0.160 0.229 0.309

0.95 2.06 3.68 8.12 8.12

 O_3^{-1}

ereise for investigated ions evaluated from notassium and caesium safts in H-O-MeOH mixtures corrected to infinite dilution at 298.2 K Table 3 Transfer Gibbs

^a Data interpolated from ref. 13 in parentheses. ^b Data from ref. 14 in parentheses.

Table 4 Transfer Gibbs energies for investigated ions evaluated from potassium and caesium salts in H₂O-PrⁱOH mixtures corrected to infinite dilution at 298.2 K

	$\begin{array}{ccc} 0_{3}^{-} & IO_{3}^{-} \\ K^{+}) & (Cs^{+}) \end{array}$	0.75 0.21 1.67 0.88 2.62 1.35 3.49 2.07 5.03 3.71 7.86
	BrO ₃ ⁻ I((Cs ⁺) []	-0.04 0.10 0.25 0.52 0.52 3.98 3.98 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9
	$\operatorname{BrO_3^-}(\mathrm{K^+})$	0.01 0.68 1.14 1.62 3.46 5.71
$\Delta_{\rm trs} G^{\circ}/{\rm kJ} {\rm mol}^{-1}$	CIO ₃ - (Cs ⁺)	-0.33 -0.07 -0.34 -0.13 1.29 3.60
	CIO ₃ ⁻ (K ⁺)	0.01 0.54 0.75 0.85 2.57 4.24
	IO_4^- (Cs ⁺)	-0.46 -0.47 -0.96 -1.16 -0.39 0.60
	${{ m IO}_4}^-$ (K ⁺)	-0.24 -0.10 -0.49 -0.73 -0.40 0.52
	CIO_4^- (Cs ⁺)	- 0.39 - 0.38 - 0.35 - 0.53 - 0.40 1.47
	CIO4 ⁻ (K ⁺)	-0.14 0.10 -0.21 -0.43 0.49 1.70
	Cs^+	1.14 1.70 3.46 4.12 2.44
	K +	0.87 1.40 2.33 3.06 3.01
	pic ⁻ (Cs ⁺)	- 0.58 - 0.46 - 1.29 - 2.67 3.02
	pic ⁻ (K ⁺)	- 0.09 - 1.0 - 1.46 - 2.04 2.63
	BPh ₄ ⁻ (Cs ⁺)	-1.20 -1.88 -3.10 -8.44 -13.08
	$BPh_4^{-}(K^+)$	-1.70 -2.23 -3.45 -4.65 -9.07
	x(Pr ⁱ OH)	0.012 0.025 0.040 0.056 0.092 0.136

Table 5 Selected smallest atom-atom distances r(Å) and averages R(Å) over six directions for ion-solvent interaction

		BP	h ₄ ⁻	Ph	$_{4}\mathbf{P}^{+}$
solvent	3	$r(\mathbf{B}, \mathbf{X})^a$	<i>R</i> (B, X)	$r(\mathbf{P}, \mathbf{Y})^b$	<i>R</i> (P, Y)
water	(78.5)	4.08	5.45	4.36	5.64
AN	(36.2)	4.70	6.18	5.08	5.99
MeOH	(32.6)	5.22	6.42	5.20	6.45
Pr ⁱ OH	(18.3)	7.07	7.77	6.70	6.76
Bu ^t OH	(10.9)	6.22	7.15	6.58	6.97

^a X for water and alcohols is oxygen, for acetonitrile is methyl group carbon, ^b Y for water and alcohols is oxygen, for acetonitrile is nitrogen.

Mulliken population analysis (changes in net charge distributions) for isolated benzene, BPh_4^- and Ph_4P^+ . Strictly speaking, Taniewska-Osińska claims that interaction of solvent molecules with both reference ions (binding energy, penetration into the sphere of the ion, deformation of BPh_4^{-}/Ph_4P^+ geometry) may considerably differ, however, this statement is supported only by coulombic and spatial considerations of isolated subsystems and ignores the other components of the interaction energy (e.g., delocalization, exchange repulsion and charge transfer). The different properties of these ions are attributed also to presumed more hindered rotation of phenyl groups in the BPh₄⁻ anion compared with the Ph_4P^+ cation.⁶ There is no doubt that subtle details of the BPh_4^{-}/Ph_4P^+ solvation must differ. In our opinion, one has to investigate also the pair interactions connected with the solvation since they can lead to a plausible estimate of the most important structures and energetics. According to the literature, $^{1,7-9}$ there is a lot of experimental evidence that the TPTB assumption works well for a large variety of mixtures up to ca. 40 vol.% of the cosolvent. In order to contribute with some molecular based arguments we decided to: (i) tackle the problem more systematically and calculate interaction energies of BPh_4^- and Ph_4P^+ with a series of five solvent molecules and (ii) investigate the energy demands associated with the deformation of these ions.

In this context, the orientation of the solvent molecule, its penetration on docking at the ion and the deformation extent of the ion are of importance. Our primary intention is to compare the trends in binding energies for both reference ions with the molecule of the cosolvent. We are aware that this type of the calculation cannot answer all questions related to the TPTB assumption (solvent-solvent, cosolvent-cosolvent and solvent-cosolvent interactions), nevertheless, we believe that they can assist in conclusions based on our experimental findings.

We have selected the following solvent molecules: water, MeOH, Pr^iOH , Bu'OH, AN. Geometries of subsystems, optimized separately, have been used in the construction of the starting structures in the ion-solvent complex. In order to get at least a coarse sampling of the configuration space around BPh_4^- and Ph_4P^+ we have optimized the ion-solvent pair for six different approaches of the solvent molecule to the ion. They approximately coincide with six directions associated with the axes of the cartesian coordinate system. For each direction we have completely optimized all internal coordinates of the ion-solvent complex allowing BPh_4^- (Ph_4P^+) to relax its geometry in the presence of the solvent and vice versa. Altogether we obtained 60 structures. The geometry convergence criterion (largest component of the energy gradient) was required to lie below $2.5 \times 10^{-4} E_{\rm h}/a_0$. We have investigated also two aspects of the deformation of BPh₄⁻ and Ph₄P⁺, namely, the bending of the angle C-B-C or C-P-C and the rotation of one phenyl along the B-C-C or P-C-C axis while keeping the other phenyls fixed. The former calculations include the variations of the total energy with respect to the 'tetrahedral' angle in the range $\pm 20^{\circ}$, the latter cover the rotation barrier in the range 0–180°. All quantum-chemical calculations were performed using the semiempirical AM1 method¹⁰ as implemented in the GAMESS program system¹¹ on Convex 3410 at the Computing Centre of the Faculty of Science, Comenius University.

Results

Measured solubilities of potassium and caesium salts in H_2O and in aqueous-organic mixtures containing MeOH and Pr^iOH are given in Tables 1 and 2. The solubilities of the salts in water S_w and in solvent mixtures S_x are related to the transfer Gibbs energy of the salt by

$$\Delta_{\rm trs} G^{\rm o} = 2RT \, \ln(S_{\rm W} \gamma_{\rm W}^{\pm} / S_{\rm X} \gamma_{\rm X}^{\pm}) \tag{1}$$

The solubilities were corrected to infinite dilution using the activity coefficients, γ^{\pm} , calculated from the Davies equation:

$$\log \gamma^{\pm} = -A[I^{1/2}/(1+I^{1/2})+0.3I]$$
(2)

where A is the Debye-Hückel parameter and I is the ionic strength. A was calculated from the known relative permittivities of H_2O -MeOH and H_2O -PrⁱOH mixtures.¹²

Transfer Gibbs energies of the investigated anions can be calculated using eqn. (3)-(5)

$$\{\Delta_{\rm trs} G^{\circ}[\rm Ph_4P(pic)] + \Delta_{\rm trs} G^{\circ}(\rm KBPh_4) - \Delta_{\rm trs} G^{\circ}[\rm K(pic)]\}/2$$

$$= \Delta_{\rm trs} G^{\rm o}({\rm Ph}_4 {\rm P}^+) = \Delta_{\rm trs} G^{\rm o}({\rm BPh}_4^-) \quad (3)$$

$$\Delta_{\rm trs} \, G^{\rm o}({\rm K}^+) = \Delta_{\rm trs} \, G^{\rm o}({\rm KBPh}_4) - \Delta_{\rm trs} \, G^{\rm o}({\rm BPh}_4^-) \tag{4}$$

$$\Delta_{\rm trs} G^{\rm o}({\rm XO}_3^{-}) = \Delta_{\rm trs} G^{\rm o}({\rm KXO}_3) - \Delta_{\rm trs} G^{\rm o}({\rm K}^+)$$
(5)

where X is a halogen. We have determined the transfer Gibbs energies of $Ph_4P(pic)$ as well as K(pic) and $KBPh_4$ and corresponding caesium salts from water to aqueous methanol and propan-2-ol so that it was possible to calculate independently two sets of single ion $\Delta_{trs} G^o$ values (Tables 3 and 4).

Table 6 AM1 binding energies (kJ mol⁻¹) for ion-solvent interaction

		BPh ₄ ⁻		Ph ₄ P ⁺			
solvent	$\Delta E_{\rm max}$	ΔE_{\min}	ΔE_{av}	$\Delta E_{\rm max}$	ΔE_{\min}	ΔE_{av}	$ \delta\Delta E_{av} $
H ₂ O AN MeOH Pr ⁱ OH Bu'OH	-16.4 -9.1 -9.6 -14.9 -6.1	-22.9 -18.1 -15.9 -19.9 -14.7	- 19.7 - 12.8 - 12.0 - 17.5 - 10.0	-7.9 -14.4 -9.7 -20.5 -7.8	18.6 15.2 14.4 28.4 16.4	-12.5 -14.8 -12.7 -22.9 -11.0	7.2 2.0 0.7 5.4 1.0

Discussion

The results in Tables 1 and 2 show that all electrolytes investigated are more soluble in water than in the H₂O-MeOH and H₂O-PrⁱOH mixtures. The salting out effect observed is higher for halate salts than for perhalate ones and this effect increases in the order $S(ClO_3^-) > S(BrO_3^-) > S(IO_3^-)$. The solubility decrease with increasing cosolvent concentration shows the significant participation of the solvent effect in the dissolution of the investigated salts. Information about a change of the solvent effect on going from water to watercosolvent mixtures was gained from Gibbs transfer functions (Tables 3 and 4). Table 3 indicates that our $\Delta_{trs} G^{\circ}$ data for pic⁻, Cs⁺, BrO₃⁻ and ClO₄⁻ ions appear to be in good agreement with the available literature data.^{13,14} In H₂O-PrⁱOH mixtures there are only limited data available in the literature^{15,16} which span the required concentration range.

The transfer of halate anions from H₂O to H₂O-PrⁱOH as well as to H₂O-MeOH mixtures is non-spontaneous as indicated by the positive $\Delta_{trs} G^{\circ}$ values. Values of $\Delta_{trs} G^{\circ}$ becomes increasingly positive in the order $\Delta_{trs} G^{\circ}(ClO_3^{-}) < \Delta_{trs} G^{\circ}(BrO_3^{-}) < \Delta_{trs} G^{\circ}(IO_3^{-})$ but the reverse order $\Delta_{trs} G^{\circ}(I^{-}) < \Delta_{trs} G^{\circ}(Br^{-}) < \Delta_{trs} G^{\circ}(Cl^{-})^{13,15,16}$ is observed (Fig. 1 and 2). The ion size, the distribution of charge on the surface of the



Fig. 1 Gibbs energies of transfer to water–MeOH mixtures at 298.2 K. Data for Cl⁻ (1), Br⁻ (2) and I⁻ (3) ions are from the literature.¹³ $IO_3^{-}(\bigcirc)$, BrO₃⁻ (\bigtriangleup), ClO₃⁻ (\square), ClO₄⁻ (\blacksquare), IO₄⁻ (\blacklozenge).



Fig. 2 Gibbs energies of transfer to water– $Pr^{i}H$ mixtures at 298.2 K. Data for Cl⁻ (1) and Br⁻ (2) ions were recalculated from the literature.^{15,16} IO₃⁻ (\bigcirc), BrO₃⁻ (\triangle), ClO₃⁻ (\square), ClO₄⁻ (\blacksquare), IO₄⁻ (\bullet).

ion and the geometry are important factors in $\Delta_{trs} G^{\circ}$ values. For monatomic halide ions with a spherical shape, the $\Delta_{trs}G^{\circ}$ values decrease with an increasing anion radius. From this point of view the $\Delta_{trs} G^{\circ}$ order for polyatomic XO_3^{-} anions is unexpected. However, the literature data¹⁷ estimate the IO₃⁻ radius to be smaller by about 10 pm than BrO_3^- and 19 pm than ClO₃⁻. Similar order of the halate ion radii is given in ref. 18. The calculation of the XO_3^- radii on a basis of the behaviour of their electrostatic potential¹⁹ shows the reverse order, $r(ClO_3^-) < r(BrO_3^-)$, but the values do not incorporate the relativistic effect. However, it is supposed that the relativistic effect may not shrink BrO3⁻ so much as to make it smaller than ClO_3^{-} . From available literature data, it is rather difficult to rationalize why IO₃⁻ could be smaller than BrO_3^{-} and ClO_3^{-} . But if the order of the halate ion radii¹⁷ is an approximation of the true dimension of ions in an aqueous environment, the order of their transfer functions $\Delta_{trs} G^{\circ}$ is not surprising. The convenient partial volume in water at 25 °C has the same order as the halate ion radii, $\overline{V}^{\circ}(\text{ClO}_{3}^{-}) = 36.6$, $\overline{V}^{\circ}(\text{BrO}_{3}^{-}) = 35.3$ and $\overline{V}^{\circ}(\text{IO}_{3}^{-}) = 25.3$ cm³ mol⁻¹.²⁰

The XO_3^- ions should be more influenced by their surroundings than XO_4^{-} . Halate ions with an electron lone pair on halogen suitable for charge transfer to the solvent can be better stabilised by water. The stabilisation in water is reduced on going from XO^- to XO_4^- and this might be due to the reduction in electron density on halogen.²¹ Addition of an organic cosolvent into the solvent influences the H₂O-H₂O interactions. At low alcohol concentrations, alcohol molecules are monomeric and enhance H₂O-H₂O interactions near the non-polar alkyl group – hydrophobic interaction.²² IR measurements²³ indicate a structural integrity of water in this alcohol concentration region. The destabilisation of XO_3^- is probably connected with particular difficulties in the formation of solvation shells in the region of the hydrophobically ordered structure of the solvent. These conclusions correspond with trends for these anions being transferred to other binary aqueous media. Fig. 3 shows that $\Delta_{trs} G^{\circ}$ of ClO₃⁻ and ClO₄⁻ becomes more positive with increasing hydrophobicity of cosolvent in the order $\Delta_{trs} G^{\circ}(Bu^{t}OH) > \Delta_{trs} G^{\circ}(Pr^{i}OH) >$ $\Delta_{trs} G^{\circ}(MeOH)$. The ordering of plots for other investigated anions is very similar but in general, anions are more destabilised on adding Bu'OH than on adding a comparable amount of MeOH.

The $\Delta_{trs} G^{\circ}$ variations in mixed solvents are commonly simpler than those of $\Delta_{trs} H^{\circ}$ and $T\Delta_{trs} S^{\circ}$. Unfortunately, only limited enthalpy and entropy data for oxoanions of halogens



Fig. 3 Transfer Gibbs energies for (a) ClO_3^- and (b) ClO_4^- to water-rich binary solvent mixtures at 298.2 K. Bu'OH (\bigcirc), Pr'OH (\triangle), MeOH (\blacktriangle) and AN ($\textcircled{\bullet}$). $\Delta_{\text{trs}} G^\circ$ Data in H₂O-Bu'OH and H₂O-AN are published values.¹

in mixed solvents are available. The values of $T\Delta_{trs}S^{\circ}$ for ClO_3^- , BrO_3^- , ClO_4^- and IO_4^- in H_2O -MeOH were evaluated from published $\Delta_{trs} H^{\circ}$ data⁷ and from $\Delta_{trs} G^{\circ}$ data in this work. Fig. 4 shows that the transfer process for the investigated ions is endothermic, $\Delta_{trs} H^{\circ} > 0$, therefore the solutesolvent interactions are probably weaker than the solvent-solvent ones. The main contribution to $\Delta_{trs} H^o$ is probably the cavity formation in the solvent to accommodate the solute. However, at concentration $x_2(MeOH) > 0.16$ the transfer process for halate ions is exothermic, $\Delta_{trs} H^o < 0$. Within this methanol concentration range the transfer process is accompanied by a decrease in the disorder on going from water to an H₂O-MeOH mixture and the entropy deficiency effect dominates in the transfer Gibbs energy. The presence of $\Delta_{trs} H^{\circ}$ maxima in a water-rich region has been attributed to the hydrophobic effect of the organic component.⁶ The differences of positions of $\Delta_{trs} H^o$ maxima for XO_3^- and XO_4^- are probably connected with different perturbation effects of these anions on the structure of the mixed solvent. $\Delta_{trs} H^o$ and $T\Delta_{trs} S^{\circ}$ of perhalate ions are largely compensated in their contributions to $\Delta_{trs} G^{\circ}$ values in the whole investigated range of the cosolvent concentration. The changes of $\Delta_{trs} H^o$, $T\Delta_{trs} S^o$ have probably a common origin in the change of the solvent structure caused by adding cosolvent. The difference in behaviour of XO₃⁻ and XO₄⁻ probably results from stronger relative affinity to water in the case of XO_3^- due to the existence of a lone pair on the halogen atom.

In the case of BPh₄⁻ all solvent molecules act as proton donors with some tiny conformational differences. The AM1 calculations indicate that water prefers bifurcated orientation over the bent hydrogen bond; MeOH and Bu'OH utilize both methyl and hydroxy hydrogens to attach to the ion's surface, PrⁱOH and AN prefer exclusively CH₃ connection to BPh₄⁻. One can notice a gradual increase of an average contact distance with the size of the solvent molecule (Table 5), or more precisely, with the size of its accessible part. There is one apparent exception, Bu'OH vs. Pr'OH, caused probably by steric factors since Bu^tOH docks at BPh_4^- also by hydroxy, while $Pr^{i}OH$ only by methyls. In the solvation of $Ph_{4}P^{+}$, water and alcohols offer oxygen lone pairs to attach to the ion's surface and acetonitrile offers nitrogen as a proton acceptor. In a few cases, PrⁱOH and BuⁱOH use one CH₃ group to stabilize additionally their position at the π system of phenyl. Generally, deformations of ions and solvent molecules are very small. For example, the energy change associated with the bending of near-tetrahedral CBC/CPC angles in ions (for deformations not exceeding $\pm 5-10^{\circ}$) is comparable with binding energies but dramatically rises for larger angle



Fig. 4 Transfer enthalpies, $\Delta_{trs} H^{\circ}$, (open symbols) and entropies, $-T\Delta_{trs} S^{\circ}$, (filled symbols) for $ClO_{3}^{-}(\Delta, \blacktriangle)$, $ClO_{4}^{-}(\bigcirc, \bigoplus)$, $BrO_{3}^{-}(\diamondsuit, \bigstar)$ and $IO_{4}^{-}(\Box, \blacksquare)$ to water-MeOH mixtures. All transfer enthalpy data are published values.⁷

changes. This is in accord with relatively large contact distances that indicate a very shallow penetration. Even water, the smallest solvent molecule, cannot penetrate deeper between the phenyl groups. According to our results, it approaches the shell delimited by hydrogen-carbon bonds of C₆H₅ groups, but not so much as anticipated by Marcus.²⁴ The minimal values r(B/P, O) differ by 0.32 Å, the averages R(B/P, O) by 0.21 Å (Table 5). Evidently, more compact hydrogen atoms can approach the reference ion closer than diffuse lone-pair side of oxygen. Concerning other solvent molecules, they attach to the outer shell of the ion and practically do not penetrate. As can be seen in Fig. 5, intramolecular rotation of one phenyl group (that could perhaps assist in deeper penetration of the solvent) is strongly hindered. The barrier for Ph_4P^+ is predicted to be 100 kJ mol⁻¹ higher than for BPh_4^- , *i.e.* opposite as considered by Taniewska-Osinska.⁶

Let us briefly judge the TPTB assumption with respect to binding energies (Table 6). First, it should be noted that absolute ΔE values are relatively small, lying in the range 10–20 kJ mol⁻¹. The values $|\delta\Delta E_{av}|$ indicating differences between cation and anion are significant only for water and PrⁱOH and reflect subtle differences in solvation sites around both ions for these two solvent molecules. Both exhibit a completely different orientation in binding to Ph₄P⁺/BPh₄⁻ and in addition, water can penetrate deeper than PrⁱOH.

The behaviour of Ph_4P^+/BPh_4^- on going from water to water-organic mixtures is illustrated in Fig. 6. The transfer enthalpies for aqueous mixtures with MeOH,¹³ PrⁱOH,²



Fig. 5 Barrier of rotation of one C_6H_5 group in BPh₄⁻ and Ph₄P⁺



Fig. 6 Transfer enthalpies, $\Delta_{trs} H^{\circ}$, (open symbols) and entropies, $-T\Delta_{trs} S^{\circ}$, (filled symbols) for BPh₄⁻/Ph₄P⁺ in water-MeOH (\triangle , \blacktriangle), water-Bu'OH (\bigcirc , $\textcircled{\bullet}$), water-AN (\diamondsuit , \blacklozenge) and water-Pr'OH (\square , \blacksquare) mixtures.

AN²⁵ and Bu^tOH²⁶ were taken from literature. The $T\Delta_{trs}S^{\circ}$ values were calculated using published estimates of $\Delta_{trs} G^{\circ}$ (aqueous MeOH and PriOH from Tables 3 and 4, aqueous AN^{27} and aqueous Bu^tOH²⁸) and $\Delta_{trs}H^{\circ}$ for corresponding ions. Fig. 6 shows that the overcompensating contribution from $T\Delta_{trs} S^{\circ}$ leads to $\Delta_{trs} G^{\circ} < 0$. Similar behaviour was found in water-urea mixtures.²⁹ $\Delta_{trs} H^{\circ}$ and $T\Delta_{trs} S^{\circ}$ values exhibit extremes whose position can be treated as measures of the hydrophobic effect. The high enthalpy extrema for electrolytes with organic ions such as Ph_4P^+/BPh_4^- (in contrast to the enthalpy extrema for XO_3^- and XO_4^- , Fig. 4) can probably be attributed to a competition between organic cosolvent and organic ions for those water molecules needed to form hydration shells or quasi-clathrates. The transfer enthalpy, Fig. 6, reflects the sum of all interactions occurring between dissolved ions and solvent. According to the semiempirical AM1 calculation method (Table 5) the difference between interaction energies of Ph_4P^+/BPh_4^- -water and of Ph_4P^+/BPh_4^- -alcohol or acetonitrile is small. From the comparison of $\Delta_{trs} H^{\circ}$ and difference of interaction energies mentioned above it follows that the latter does not play a decisive role. Although the ion-solvent interaction energy is not the main part of interaction in solution, the results in Table 5 do not exclude validity of the extrathermodynamic splitting criteria.

The results obtained for $\Delta_{trs}\,G^o$ of the investigated anions calculated from solubilities of K^+ and Cs^+ salts (Tables 3 and 4) suggest that the TPTB method in both investigated mixtures is, in this case, suitable for evaluation of properties of individual ions in solution at a low cosolvent concentration. It should be noted that $\Delta_{trs} G^{o}$ values for the reference electrolyte Ph₄P⁺BPh₄⁻ were obtained directly from solubilities of potassium and corresponding caesium salts. A similar observation was made for halate and perhalate ions with common cations (K⁺ or Cs⁺) in water-AN and water-Bu'OH mixtures.¹ In addition, the additivity of ionic contribution in the transfer enthalpy of different sodium and potassium salts from water to water-MeOH⁷ and to water-Bu^tOH⁸ was verified. A good agreement was found for $\Delta_{trs} H^o$ of acetate and propionate ions estimated from the dissociation enthalpy of acid and from solution heats of sodium salts in water-Bu'OH mixtures.³⁰ The transfer enthalpy values of hydrohalogenic acids (determined from dilution heat) and their potassium salts (determined from solution heat) support an applicability of the extrathermodynamic assumption up to 40% Bu^tOH.³¹ The additivity test of ionic contribution in the transfer Gibbs energies from water to water-MeOH was done in the literature.¹⁴

Our pilot AM1 calculations have shown that interactions with both reference ions exhibit similar trends, with relatively small binding energies. We consider these calculations as the first step in developing suitable effective pair potentials which can be used in molecular based studies of mixtures including these ions. Computer simulations utilizing such potentials would enable us to investigate a larger variety of systems at more realistic conditions and bring theoretical data closer to experimental ones.

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