Thermodynamics of bromate and iodate of potassium in dioxane-water mixtures from conductance measurements

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Summary. The free energy of transfer (ΔG_t^0) of $KBrO_3$ and KIO_3 from water to 10, 20 and 30% dioxane-water mixtures have been studied from conductometric measurements. The ΔG_t^0 values are in the order of $BrO_3^- > IO_3^-$.

Studies of electrolytic conductance in dioxane-water media of varying dioxane content were initiated by us[2] at 30, 35, 40 and 45 °C 0.01. In the present communication, attempts have been made to evaluate the thermodynamic function ΔG_t for the transfer of $KBrO_3$ and KIO_3 from water to the respective dioxane + water media, which would give some information regarding ionic solvation.

Materials and methods. The salts and dioxane used were of E. Merck, 'extra-pure' varieties. Purification of dioxane, preparation of solvents, solutions and measurements of the conductance have been reported earlier[2]. The conductance measurement was of an accuracy of ±2 in 1000. The concentration range was from 0.01 to 0.001 moles · l^{-1}.

The plot of ΔG_t^0 vs. r^{-1} for KCl, KBr and KNO_3 in dioxane + water mixtures[6] are found to be linear. Knowing the ΔG_t^0 values of $KBrO_3$ and KIO_3, the ionic radii of BrO_3^- and IO_3^- could be estimated from the above plot. They are 2.5 Å and 3.2 Å respectively. Utilising these values, the ΔG_t^0 has been split up into 2 parts according to Roy et al.[7]. It consists of an electrostatic part $\Delta G_{t(el)}^0$ corresponding to a charge in the dielectric constant of the medium, and another nonelectrostatic part or chemical contribution, $\Delta G_{t(Ch)}^0$ arising from the specific chemical interactions between the ions and the solvent, and is, therefore, solvent dependent. The $\Delta G_{t(el)}^0$ has been calculated from the Born's[8] equation utilizing the values of ionic radii obtained. The $\Delta G_{t(Ch)}^0$ was then evaluated. These values are presented in table 2. It is evident that the $\Delta G_{t(Ch)}^0$ values are mostly negative in case of KIO_3, which indicates that the transfer of KIO_3 from water to dioxane + water is favoured as far as the chemical interactions are concerned. In case of $KBrO_3$ it is positive, suggesting the transfer as unfavourable as far as chemical interactions are concerned. $\Delta G_{t(el)}^0$ is positive in both cases and is of the order $BrO_3^- > IO_3^-$ and hence the ionic solvation is of the reverse order.

Table 1. Free energy of transfer of $KBrO_3$ and KIO_3 from water to dioxane + water mixtures at different temperatures

Mass fraction of dioxane	ΔG_t^0/J · mole^{-1}					
	$KBrO_3$			KIO_3		
	10%	20%	30%	10%	20%	30%
30	1012	2012	3043	612	1152	1853
35	1113	2313	3443	714	1215	1954
40	1265	2756	3354	1080	1356	2134
45	1313	2754	3603	1016	1646	2754

Table 2. Electrical and chemical part of the thermodynamic quantities accompanying the transfer of $KBrO_3$ and KIO_3 from water to dioxane + water mixtures at different temperatures

	$\Delta G_{t(el)}^0$/J · mole^{-1}			$\Delta G_{t(Ch)}^0$/J · mole^{-1}		
	$KBrO_3$					
30	904	1560	2578	108	452	465
35	696	1452	2484	417	961	959
40	830	1597	2656	435	1159	1688
45	577	1428	2504	736	1296	1099
	KIO_3					
30	836	1442	2384	− 224	− 290	− 531
35	643	1343	2297	71	− 127	− 342
40	768	1476	2455	312	− 120	− 321
45	541	1321	2315	575	322	439

Results and discussion. The plot of λ vs $C^{1/2}$ was found to be linear and $\lambda°$ has been obtained from the extrapolated values[2]. Since dielectric constant of the medium is low, the dissociation constant K has been calculated by Fuous and Krauss[3] and Shedlovsky's[4] method. The values obtained by both the methods are in good agreement. The standard thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ have been calculated. The plots of $\Delta G°$, $\Delta H°$ and $\Delta S°$ vs. solvent compositions were found to be linear. The extrapolated values gave the thermodynamic parameters for water. The standard thermodynamic quantities (ΔG_t^0) from water to dioxane + water mixtures could be calculated from the values of water and dioxane + water mixtures by Feakins method[5]. These are tabulated in table 1. The probable uncertainties in ΔG_t^0 are ± 15 J · mole^{-1}.

The ΔG_t^0 values are observed to be positive at all solvent compositions and at all temperatures. The positive value indicates that the salts are in a higher free energy state in dioxane + water mixtures than in water, suggesting that water has more affinity for the salts for dioxane + water mixtures.

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