Short Communications

Ion Activities of Alkali — Metal Iodides in Aqueous Solution

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A convenient scale for single-ion activities has recently been described[1] and applied to alkali —metal chlorides[1] and bromides[2] and to alkaline —earth chlorides[3] in aqueous solution. Such convenient single-ion activity data contain more information than do corresponding mean-ion data, and they are closely related to true single-ion activity data. For a z-valent ion (z with sign), the relation between the convenient (γ'_z) and the true (γ_z) molal bare-ion activity coefficient is $\gamma'_z = \gamma_z r^{-z/2}$, r being the ratio γ_+/γ_- for potassium chloride in pure, saturated aqueous solution of this salt (r is not yet exactly known).

As part of a study on the energetics of alkali

—metal halide solutions,[1-4] the convenient molal bare-ion activity coefficient of the iodide ion (γ'_-) in aqueous single-salt solutions of alkali—metal iodides at 25 °C has been determined from eqn. (1)[1]

$$\gamma'_- = \frac{m^\circ}{m} \exp\left[-\frac{F}{RT}(E'_- - (\phi_t - \phi_r) - E^\circ_- + 0.241 \text{ V}) \right] \tag{1}$$

by measuring directly against a saturated calomel electrode the equilibrium potential (E'_-) of an Ag/AgI electrode (with standard hydrogen-scale potential $E^\circ_- = -0.152$ V)[5,6] in various test solutions of dimensionless molality (m/m°) 0.1 — 3.0, and estimating by means of the Henderson equation[7] and mobility data[6] the liquid-junction potential difference $(\phi_t - \phi_r)$ involved. The corresponding cation activity coefficient is subsequently obtained from $\gamma'_+ = \gamma_\pm^2/\gamma'_-$,[1] using tabulated data[6] for the mean molal bare-ion activity coefficient $(\gamma_\pm)$ of the electrolytes concerned.

Table 1. Ag/AgI potentials measured vs. SCE (E'_-) and liquid-junction potential differences estimated ($\Delta\phi = \phi_t - \phi_r$) for x molal aqueous single-salt solutions of alkali — metal iodides at 25 °C.

x =	0.1	0.2	0.5	1.0	2.0	3.0
LiI						
E'_-/mV	−327.9	−344.0	−365.1	−382.4	−400.6	(−411.6)
$\Delta\phi$/mV	−1.4	−0.7	0.6	2.0	3.9	(5.2)
NaI						
E'_-/mV	−327.6	−344.0	−364.4	−380.2	−396.9	(−408.5)
$\Delta\phi$/mV	−1.6	−1.0	−0.0	1.0	2.4	(3.3)
KI						
E'_-/mV	−327.8	−344.1	−365.2	−381.5	(−397.5)	
$\Delta\phi$/mV	−1.8	−1.5	−1.1	−0.7	(−0.4)	
CsI						
E'_-/mV	−328.0	−344.0	(−364.0)			
$\Delta\phi$/mV	−1.9	−1.6	(−1.3)			

Table 2. Molal bare-ion activity coefficients for alkali – metal iodides in x molal aqueous single-salt solutions at 25 °C.

$x =$	0.1	0.2	0.5	1.0	2.0	3.0
LiI						
γ'_+	0.89	0.89	0.98	1.16	1.84	(3.49)
γ'_-	0.75	0.72	0.69	0.71	0.78	(0.84)
$\gamma_\pm$	0.815	0.802	0.824	0.910	1.198	1.715
NaI						
γ'_+	0.84	0.79	0.79	0.86	1.05	(1.34)
γ'_-	0.74	0.71	0.66	0.63	0.64	(0.69)
$\gamma_\pm$	0.787	0.751	0.723	0.736	0.820	0.963
KI						
γ'_+	0.82	0.77	0.70	0.67	(0.69)	
γ'_-	0.74	0.70	0.65	0.62	(0.59)	
$\gamma_\pm$	0.778	0.733	0.676	0.645	0.637	
CsI						
γ'_+	0.77	0.69	(0.58)			
γ'_-	0.74	0.70	(0.62)			
$\gamma_\pm$	0.754	0.692	0.599			
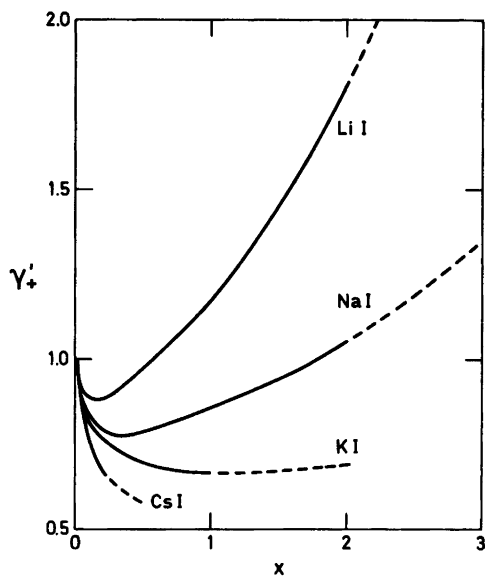
Fig. 1. Convenient molal bare-ion activity coefficient (γ'_+) for the cations in x molal aqueous single-salt solutions of alkali – metal iodides at 25 °C.
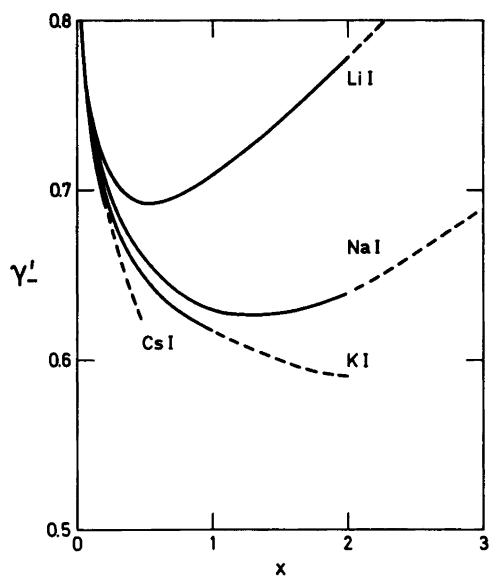
Fig. 2. Convenient molal bare-ion activity coefficient (γ'_-) for the iodide ion in x molal aqueous single-salt solutions of alkali – metal iodides at 25 °C.
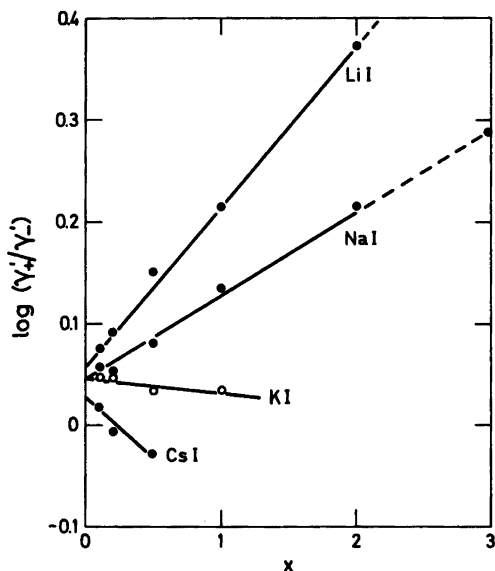
Fig. 3. Convenient molal bare-ion activity ratio (γ'_+/γ'_-) for alkali – metal iodides in x molal aqueous single-salt solutions at 25 °C.

The primary and final results of this work are presented in Tables 1 and 2, respectively. Further illustrations are given in Figs. 1 – 3. High solubility of silver iodide by complex formation[8,9] and irrelevance due to double-salt formation[9] increasingly limit, from lithium to cesium iodide, the concentration range for presently relevant measurements. Nevertheless, with increasing concentration, the activity sequence LiI > NaI > KI > CsI clearly is developed and steadily strengthened both for the cations (Fig. 1) and (to less extent) for the anion (Fig. 2). It moreover appears that all these iodides exhibit an essentially linear $\log(\gamma'_+/\gamma'_-)/m$ relationship [but not a linear $\log(\gamma'_+/\gamma'_-)/\log a_w$ relationship] with slope decreasing regularly from positive for the lithium salt to negative for the cesium salt (Fig. 3). From definitions, this slope is the same as a $\log(\gamma_+/\gamma_-)/m$ slope.

The present results for alkali – metal iodides are analogous to previous ones for alkali – metal chlorides[1] and bromides.[2] These results will be more closely compared and treated in a separate paper on excess energies and ion activities of alkali – metal halide solutions.

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