

Ion Activities of Alkali–Metal Bromides in Aqueous Solution

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Convenient single-ion activity coefficients have been determined for alkali–metal bromides in 0.1–4.0 molal aqueous single-salt solutions at 25 °C. The results are discussed through comparisons both among themselves and to corresponding chloride data. Support is found for the convenient activity scale used being close to a true one, and for the excess hydration energy of an ion being a most important term in governing the individuality of its activity behaviour.

A convenient scale for single-ion activities has recently been described¹ and applied to alkali–metal¹ and alkaline–earth² chlorides in aqueous solution. The results obtained, and also a subsequent excess-energy study³ of concentrated aqueous solutions of alkali–metal halides, call for more such single-ion data, which contain more information than do corresponding mean-ion data. As part of a study on the energetics of alkali–metal halide solutions, the present work pursues this to aqueous single-salt solutions of alkali–metal bromides at 25 °C. The molality range covered is 0.1–4.0.

EQUATIONS

A determining equation for the convenient molal bare-ion activity coefficient ($\gamma'_z = r^{-z/2}\gamma_z$) of a z -valent ion at 25 °C is given by eqn. (1),¹ where m° is

$$\gamma'_z = \frac{m^\circ}{m_z} \exp \left[\frac{zF}{RT} (E'_z - (\Phi_i - \Phi_r) - E_z^\circ + 0.241 \text{ V}) \right] \quad (1)$$

the standard molality (1 mol kg⁻¹), m_z is the actual ion molality, E'_z is the directly measured potential *vs.* SCE (saturated calomel electrode) of an electrode reversible to the ion concerned and placed in the test solution, E_z° is the conventional

standard hydrogen-scale potential of the latter electrode, and $(\Phi_i - \Phi_r)$ is the liquid-junction potential difference between the test solution and the saturated KCl solution of the calomel reference electrode (*i.e.* the liquid-junction potential difference included in E'_z), all at 25 °C.

Eqn. (1) is presently used to the bromide ion ($z = -1$) after measuring the potential (E'_-) of an Ag/AgBr electrode ($E_-^\circ = 0.071 \text{ V (NHE)}$)^{4–6} in various test solutions against a saturated calomel electrode, and estimating by means of the Hender-son equation⁷ and mobility data⁶ the liquid-junc-tion potential difference $(\Phi_i - \Phi_r)$ involved. This yields values for γ'_- of the bromide ion in the alkali–metal bromide solutions tested. The corre-sponding cation activity coefficient (γ'_+) is then obtained from eqn. (2),¹ using tabulated data⁶ for

$$\gamma'_+ = \gamma_{\pm}^2 / \gamma'_- \quad (2)$$

the mean molal bare-ion activity coefficient (γ_{\pm}) of the alkali–metal bromides in single-salt solu-tions.

EXPERIMENTAL

Solutions were made from *p.a.* quality salts and twice distilled water. They were deoxygenated with purified and premoistened nitrogen and kept under nitrogen atmosphere during measurements. The measurements were performed with procedures and equipment recently described¹ for analogous studies on alkali–metal chlorides. All measurements apply to solutions and electrodes at 25 °C.

RESULTS

The intermediate and final results of the present activity determinations are given in Tables 1 and 2,

Table 1. Ag/AgBr potentials measured vs. SCE (E'_-) and liquid-junction potential differences estimated ($\Delta\phi = \phi_1 - \phi_r$) for x molal aqueous single-salt solutions of alkali-metal bromide at 25 °C.

| $x =$ | 0.1 | 0.2 | 0.5 | 1 | 2 | 3 | 4 |
|-----------------|--------|--------|--------|--------|--------|--------|--------|
| LiBr | | | | | | | |
| E'_-/mV | -104.4 | -120.1 | -140.1 | -156.4 | -173.9 | -185.8 | -195.7 |
| $\Delta\phi/mV$ | -1.4 | -0.7 | 0.6 | 2.1 | 4.0 | 5.3 | 6.4 |
| NaBr | | | | | | | |
| E'_-/mV | -105.2 | -120.6 | -140.8 | -156.8 | -173.5 | -184.0 | -192.8 |
| $\Delta\phi/mV$ | -1.6 | -1.0 | 0.1 | 1.1 | 2.5 | 3.4 | 4.2 |
| KBr | | | | | | | |
| E'_-/mV | -105.4 | -120.5 | -141.4 | -157.5 | -174.4 | -185.1 | -192.8 |
| $\Delta\phi/mV$ | -1.8 | -1.5 | -1.0 | -0.6 | -0.2 | 0 | 0.2 |
| CsBr | | | | | | | |
| E'_-/mV | -104.4 | -120.1 | -140.3 | -155.5 | -172.6 | -183.3 | -190.1 |
| $\Delta\phi/mV$ | -1.9 | -1.6 | -1.3 | -1.0 | -0.8 | -0.7 | -0.7 |

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

| $x =$ | 0.1 | 0.2 | 0.5 | 1 | 2 | 3 | 4 |
|---------------|-------|-------|-------|-------|-------|-------|-------|
| LiBr | | | | | | | |
| γ'_+ | 0.86 | 0.84 | 0.89 | 1.01 | 1.52 | 2.37 | 4.14 |
| γ'_- | 0.74 | 0.70 | 0.64 | 0.64 | 0.68 | 0.76 | 0.87 |
| γ'_\pm | 0.796 | 0.766 | 0.753 | 0.803 | 1.015 | 1.341 | 1.897 |
| NaBr | | | | | | | |
| γ'_+ | 0.82 | 0.78 | 0.76 | 0.76 | 0.85 | 1.00 | 1.20 |
| γ'_- | 0.75 | 0.70 | 0.64 | 0.62 | 0.63 | 0.66 | 0.72 |
| γ'_\pm | 0.782 | 0.741 | 0.697 | 0.687 | 0.731 | 0.812 | 0.929 |
| KBr | | | | | | | |
| γ'_+ | 0.79 | 0.76 | 0.69 | 0.63 | 0.60 | 0.59 | 0.61 |
| γ'_- | 0.75 | 0.69 | 0.63 | 0.60 | 0.59 | 0.60 | 0.61 |
| γ'_\pm | 0.772 | 0.722 | 0.657 | 0.617 | 0.593 | 0.595 | 0.608 |
| CsBr | | | | | | | |
| γ'_+ | 0.79 | 0.72 | 0.61 | 0.53 | 0.44 | 0.40 | 0.39 |
| γ'_- | 0.72 | 0.67 | 0.60 | 0.55 | 0.54 | 0.54 | 0.53 |
| γ'_\pm | 0.754 | 0.694 | 0.603 | 0.538 | 0.486 | 0.465 | 0.457 |

respectively. These results yield the specificities and concentration dependences shown for γ'_+ in Fig. 1 and for γ'_- in Fig. 2. Clearly, with increasing concentration, the activity sequence (3) is developed



and steadily strengthened both for the cations (Fig. 1) and for the common anion (Fig. 2) of the single-

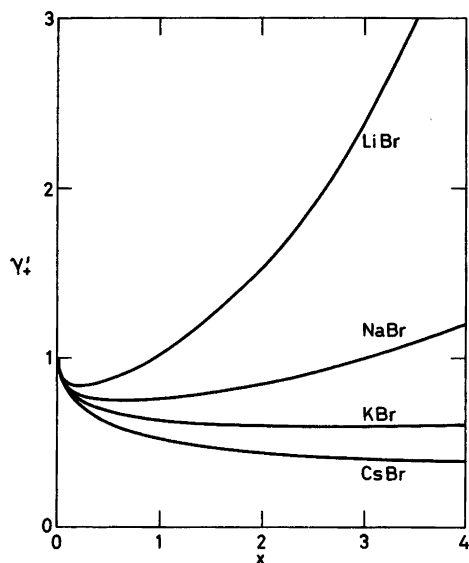


Fig. 1. Convenient molal bare-ion activity coefficient (γ'_+) for the cations in x molal aqueous single-salt solutions of alkali-metal bromides at 25 °C.

salt solutions studied. This occurs much more strongly for the cations than for the anion, however.

According to definitions,¹ $\gamma'_+/\gamma'_- = r^{-1} \gamma_+/\gamma_-$ where γ_+ and γ_- are the corresponding true

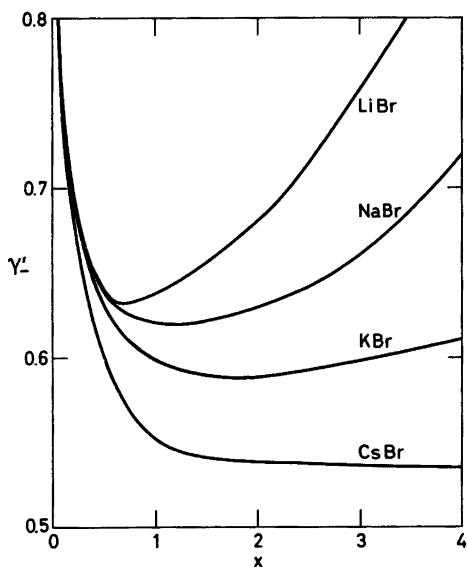


Fig. 2. Convenient molal bare-ion activity coefficient (γ'_-) for the bromide ion in x molal aqueous single-salt solutions of alkali-metal bromides at 25 °C.

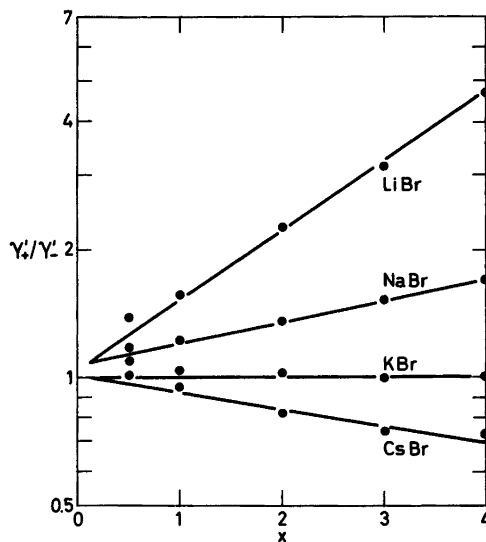


Fig. 3. Convenient molal bare-ion activity ratio (γ'_+/γ'_-) for alkali-metal bromides in x molal aqueous single-salt solutions at 25 °C.

activity coefficients and r is the ratio γ_+/γ_- for KCl in pure saturated aqueous solution. Since the Debye-Hückel value of γ_+/γ_- for a 1:1 salt is unity,⁶ γ'_+/γ'_- should approach r^{-1} at low concentration. In Fig. 3, a semilogarithmic plot is given of values presently obtained for γ'_+/γ'_- vs. molality of the various alkali-metal bromides. These results support previous findings^{1,2} of r being close to unity, but do not allow a more precise determination of this important parameter.

DISCUSSION

The present observations on alkali-metal bromides add to previous results on alkali-metal¹ and alkaline-earth² chlorides in elucidating the convenient scale used for single-ion activities and in building up a bank of such data for ions in single-salt aqueous solutions. Important is that these results all agree that the chosen convenient scale be close to a true one (by r being close to unity). The single-ion data obtained, however, to some extent depend on estimations of liquid-junction potential differences involved in their determination. Here is room for improvement.

All through the molality range covered, the mean-ion activity coefficient for the alkali-metal bro-

mides decreases with increasing bare-cation size (*i.e.* from Li to Cs), and more markedly so the higher is the concentration.⁶ The present results show that these changes are carried mostly by the cations themselves (Fig. 1) and much less by the anion (Fig. 2). The same applies to alkali-metal¹ and alkaline-earth² chlorides. These observations match expectations from differences in excess hydration energy³ of equally (or oppositely) charged ions determining the activity-coefficient relations between them.

All the alkali-metal bromides exhibit an essentially linear $\log(\gamma'_+/\gamma'_-)/m$ relationship with slope decreasing from highly positive for lithium bromide to negative for cesium bromide (Fig. 3). Correspondingly the same largely applies to alkali-metal chlorides.¹ Also these observations match expectations from the hydration-energy treatment³ mentioned above. A linear $\log(\gamma'_+/\gamma'_-)/\log a_w$ relationship of the type expected from the hydrated-ion description of electrolyte solutions,⁶ is not obeyed by the alkali-metal bromides (nor by the corresponding chlorides¹). Here, a_w means the water activity of the solutions.

A more thorough discussion will be postponed until convenient single-ion data have been produced also for alkali-metal iodides.

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