

Convenient Single-ion Activities

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The concept of convenient single-ion activities is described, and a basis is given for their determination. The latter involves estimations of liquid-junction potential differences. Determinations are made of such activity data for alkali-metal and ammonium chlorides in aqueous single-salt solutions of molalities 0.1–4.0 at 25 °C. The results are discussed on the basis of current theories of electrolyte solutions.

Single-ion activities are needed in evaluating ionic interactions and reactions in solutions and at interfaces. The author has repeatedly experienced such need in electrode kinetic studies. This has caused the introduction^{1,2} and subsequent use^{3–11} of a convenient scale for single-ion activities.

The present work describes the concept of convenient single-ion activities and gives a basis for their determination. It also presents and discusses such activity data for alkali-metal and ammonium chlorides in aqueous single-salt solutions of various concentrations at 25 °C.

DEFINITIONS

The convenient bare-ion activity (a'_z) of an ionic species is related to its absolute bare-ion activity (a_z) by the chosen definition:

$$a'_z = a_z r^{-z/2} \quad (1)$$

where z is the charge number (with sign) of the ion concerned, and r means a_+/a_- (or γ_+/γ_-) for potassium chloride in pure, saturated solution at the temperature concerned. Introducing $a'_z = \gamma'_z m_z/m^\circ$ and $a_z = \gamma_z m_z/m^\circ$ (where m° is 1 mol kg⁻¹), the scale definition (1) becomes:

$$\gamma'_z = \gamma_z r^{-z/2} \quad (2)$$

for convenient molal bare-ion activity coefficients (γ'_z).

From (2), the definition of mean ionic activity coefficients,¹² and the net neutrality of salts, one easily deduces:

$$\gamma'_\pm = \gamma_\pm \quad (3)$$

saying that mean-ion data are the same on the chosen convenient scale as on the absolute one. For single ions, however, there will be a difference between the two scales if r differs from unity (see below).

EQUATIONS

By the meaning of r in (1) and (2), the chosen convenient scale is particularly suited for activity determinations by potential measurements *vs.* the saturated calomel electrode (SCE). Such a determination requires a test electrode reversible to the ion whose activity is sought. The directly measured potential (E'_z) of such a test electrode *vs.* SCE should be:

$$E'_z = E_z + (\phi_l - \phi_r) - E_r \quad (4)$$

where $\phi_l - \phi_r$ is the liquid-junction potential difference between the test solution and the reference solution (saturated KCl), and E_z and E_r are the liquid-junction-free hydrogen-scale potentials of the test electrode and the reference electrode (SCE), respectively. These potentials should obey the Nernst equations:

$$E_z = E_z^\circ + (RT/zF) \ln a_z \quad (5)$$

$$E_r = E_z^\circ - (RT/F) \ln a_- \quad (6)$$

where a_z and a_- are the absolute molal activities of the test ion in the test solution and of the chloride ion in the reference solution (saturated KCl), respectively.

From $a_+ a_- = a_\pm^2$ and $a_+/a_- = r$ for the ions of the reference solution (saturated KCl), one obtains $a_- = a_\pm/r^\frac{1}{2}$ for this solution. Introducing the latter into (6), and (1) into (5), one obtains:

$$E_z = E_z^\circ + (RT/zF) \ln a'_z + (RT/2F) \ln r \quad (7)$$

$$E_r = E_r^\circ - (RT/F) \ln a_\pm + (RT/2F) \ln r \quad (8)$$

in which the E° -values and the value of a_\pm for saturated KCl generally are available from tabulated data.

At 25 °C, the recommended value for $E_r^\circ - (RT/F) \ln a_\pm$ of the saturated calomel electrode is 0.241 V.¹³ Using this value in solving (4) with (7) and (8), and remembering $a'_z = \gamma'_z m_z/m^\circ$, one obtains:

$$\gamma'_z = (m^\circ/m_z) \exp[(zF/RT) \times (E'_z - E_z^\circ - (\phi_t - \phi_r) + 0.241 \text{ V})] \quad (9)$$

as a basis for determining convenient single-ion activity data at 25 °C. Such determinations will

include estimations of the liquid-junction potential difference ($\phi_t - \phi_r$) involved.

EXPERIMENTAL

On the above basis, determinations have been made of the convenient molal chloride-ion activity coefficient (γ'_-) in aqueous solutions of x m MeCl for Me = Li, Na, K, Cs and NH_4 and $x = 0.1 - 4.0$ at 25 °C. This has been done by measuring the liquid-junction-containing potential (E'_-) of the reversible Ag/AgCl electrode ($E_-^\circ = 0.222$ V (NHE))^{12,13} in the test solutions against a saturated calomel electrode (SCE), estimating the liquid-liquid-junction potential difference ($\phi_t - \phi_r$) involved by the Henderson equation¹⁴ and mobility data,¹² and putting the outcome (Table 1) into eqn. (9). Finally, the corresponding cation activity coefficient (γ'_+) has been determined from $\gamma'_+ = \gamma_\pm^2/\gamma'_-$, using tabulated data¹² for the mean ionic activity coefficient (γ_\pm). The results are presented in Table 2.

The experiments were performed in a double-walled 100-ml Pyrex cell thermostatted at 25 °C. Ag/AgCl electrodes were made by repeated anodization of high-purity silver rods at about 1 mA/cm² in the test solutions. Commercial calomel electrodes (Metrohm) with fiber tips were used. These were also at 25 °C. Potentials were measured with a battery driven Medistor A-75A potentiometric microvoltmeter.

Table 1. Ag/AgCl reversible potentials measured vs. SCE (E'_-) and liquid-junction potentials estimated ($\Delta\phi = \phi_t - \phi_r$) for x molal aqueous solutions of alkali-metal and ammonium chlorides at 25 °C.

$x =$	0.1	0.2	0.5	1	2	3	4
LiCl							
E'_-/mV	45.2	29.9	11.0	-4.2	-19.6	-30.0	-37.2
$\Delta\phi/mV$	-1.4	-0.6	0.7	2.2	4.1	5.5	6.6
NaCl							
E'_-/mV	45.0	29.5	9.9	-5.3	-20.6	-30.7	-38.5
$\Delta\phi/mV$	-1.5	-0.9	0.1	1.1	2.5	3.5	4.2
KCl							
E'_-/mV	44.9	29.1	8.7	-7.0	-23.0	-33.1	-40.8
$\Delta\phi/mV$	-1.8	-1.5	-1.0	-0.7	-0.4	-0.2	-0.1
CsCl							
E'_-/mV	44.8	28.7	8.5	-6.5	-22.3	-31.6	-39.0
$\Delta\phi/mV$	-1.9	-1.6	-1.2	-1.0	-0.8	-0.7	-0.6
NH_4Cl							
E'_-/mV	44.9	29.2	9.0	-6.5	-22.6	-32.3	-39.6
$\Delta\phi/mV$	-1.8	-1.5	-1.0	-0.7	-0.4	-0.2	-0.1

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

$x =$	0.1	0.2	0.5	1	2	3	4
LiCl							
γ'_+	0.80	0.78 ₅	0.85	0.98	1.41	2.12	3.45
γ'_-	0.78	0.73	0.64	0.61	0.60	0.63	0.66
γ_{\pm}	0.790	0.757	0.739	0.774	0.921	1.156	1.510
NaCl							
γ'_+	0.78	0.74	0.71	0.71	0.76	0.85	0.97
γ'_-	0.78	0.73	0.65	0.61	0.59	0.60	0.63
γ_{\pm}	0.778	0.735	0.681	0.657	0.668	0.714	0.783
KCl							
γ'_+	0.77	0.72	0.65	0.60	0.57	0.57	0.57
γ'_-	0.77	0.72	0.65	0.60	0.58	0.57	0.58
γ_{\pm}	0.770	0.718	0.649	0.604	0.573	0.569	0.577
CsCl							
γ'_+	0.74	0.66	0.56 ₅	0.50	0.45	0.43	0.42
γ'_-	0.77	0.73	0.65	0.59	0.55	0.53	0.53
γ_{\pm}	0.756	0.694	0.606	0.544	0.496	0.479	0.474
NH₄Cl							
γ'_+	0.77	0.72	0.65	0.61	0.57	0.56	0.56
γ'_-	0.77	0.72	0.65	0.60	0.57	0.56	0.56
γ_{\pm}	0.770	0.718	0.649	0.603	0.570	0.561	0.560

The solutions were prepared from *p.a.* quality salts (Merck) and twice distilled water. They were deoxygenated with purified and premoistened nitrogen and kept under nitrogen atmosphere during the measurements. All glassware was cleaned with chromic acid and rinsed with twice distilled water.

RESULTS

The results of the present single-ion activity determinations are presented in Table 2 (together with previous mean-ion activity data¹² for the same conditions). These results yield the concentration dependences shown for γ'_+ , γ'_- and the ratio γ'_+/γ'_- of the various salts in Figs. 1, 2 and 3, respectively. Furthermore, to facilitate some studies of the results, a log-log plot of the ratio γ'_+/γ'_- vs. the water activity of the test solutions¹² is given in Fig. 4.

Figs. 1 and 2 show that, with increasing salt concentration, the activity sequence:

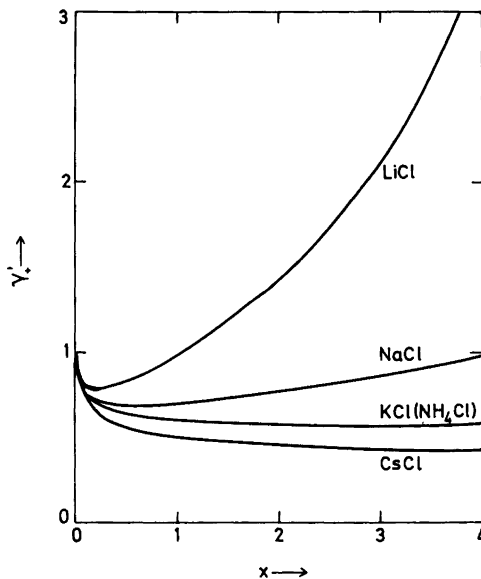


Fig. 1. Convenient molal bare-ion activity coefficient (γ'_+) for the cations of alkali-metal and ammonium chlorides in x molal aqueous single-salt solutions at 25 °C.

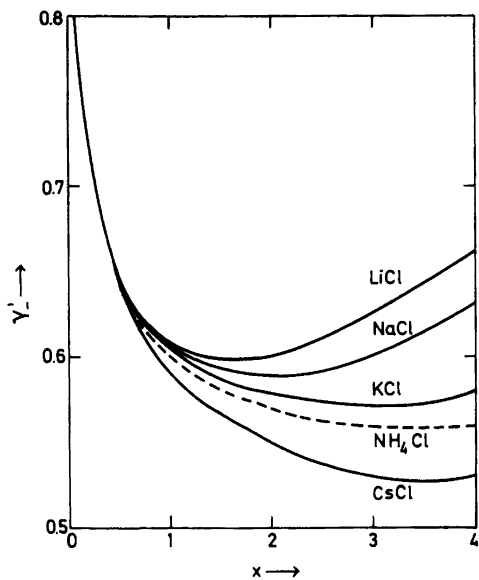


Fig. 2. Convenient molal bare-ion activity coefficient (γ'_-) for the chloride ion in x molal aqueous single-salt solutions of alkali-metal and ammonium chlorides at 25 °C.

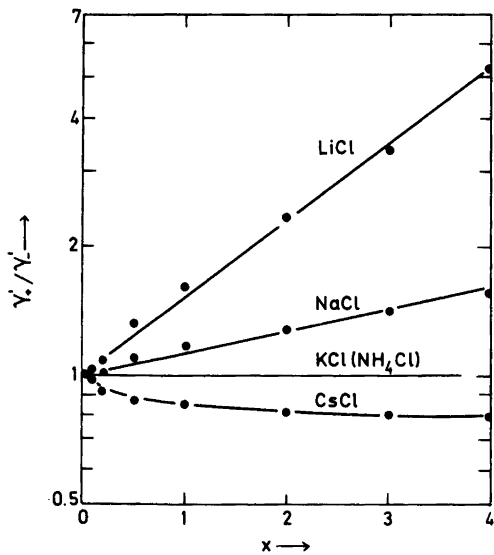


Fig. 3. Convenient molal bare-ion activity ratio (γ'_+/γ'_-) for alkali-metal and ammonium chlorides in x molal aqueous single-salt solutions at 25 °C.

is developed and strengthened both for the cations (Fig. 1) and for the common anion (Fig. 2), but most markedly so for the cations.

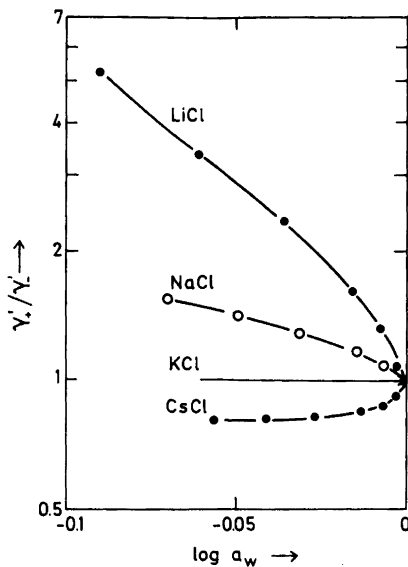


Fig. 4. Log-log plot of the convenient molal bare-ion activity ratio (γ'_+/γ'_-) vs. the water activity (a_w) of aqueous single-salt solutions of alkali-metal chlorides at 25 °C.

Fig. 3 shows that the concentration dependence of the ratio γ'_+/γ'_- (and, hence, of the ratio $\gamma_+/\gamma_- = r \gamma'_+/\gamma'_-$) steadily goes from being slightly negative for CsCl to being strongly positive for LiCl. For KCl, this dependence appears to be zero, so that $\gamma'_+/\gamma'_- = 1$ (and, hence, $\gamma_+/\gamma_- = r$) seems to apply to this salt at all concentrations. Since the Debye-Hückel value of γ_+/γ_- is unity, the observation on KCl implies that r must be unity (or nearly so). This important result is supported by γ'_+/γ'_- approaching unity (and, hence, γ_+/γ_- approaching r) at low concentration for any of the salts studied (Fig. 3).

Fig. 4 shows that a linear log-log dependence of γ'_+/γ'_- (and, hence, of $\gamma_+/\gamma_- = r \gamma'_+/\gamma'_-$) on the water activity (a_w) of the test solution, as one might anticipate from the hydrated-ion solution description by Robinson and Stokes,¹² is not obeyed (except for KCl).

DISCUSSION

The concept of convenient single-ion activities appears to be a useful one. It also seems most useful to tie the definition (1) of such activities to the ion-

activity ratio (γ_+/γ_-) of some KCl solution, since the results of the present work suggest that the convenient scale then comes close to (perhaps equal to) the absolute one. One drawback is that the determination presently proposed and applied for such single-ion activities involves estimations of liquid-junction potential differences. The reliability of the single-ion activity data then certainly depends on the validity of the estimates made in this respect. Here is room for improvement.

The determination and use of convenient single-ion activities should be of help in studies on ionic interactions and reactions in solutions and at interfaces. The author and coworkers have drawn on this in several electrode kinetic investigations.¹⁻¹¹ The present results may be useful in testing statistical theories¹⁵ for concentrated electrolyte solutions. They agree to some extent, but not completely, with recent statistical calculations¹⁶ of individual activity coefficients for the alkali-metal halides at concentrations up to 1 M.

Some further discussion of the present results is conveniently taken up in a subsequent related paper¹⁷ on ion activities of alkaline-earth chlorides in aqueous solution.

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