Single-Ion Activities of Sodium Sulfate in Aqueous Solution

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The single-ion activity coefficients of sodium and sulfate ions in aqueous 0.1–2.0 molal solutions of sodium sulfate at 25 °C have been determined by a liquid-junction approach. The results are compared to previous ones from a double-layer approach. The two approaches mutually agree at low sodium sulfate concentration ($<0.2\ m$). The liquid-junction approach gives the most likely results at higher concentration. It gives a linear log (f_+^4/f_-) vs. m dependence with positive slope. This is interpreted by a hydration-energy involving treatment of ionic activities.

It has long been known that single-ion activities are indeterminable,[1-3] unless extra thermodynamic means be introduced.[4-9] An interesting approach to such determinations uses double-layer data as extra means.[7,10,11] It directly yields single-ion activity coefficients (γ_i).[10] Another approach draws on estimations of liquid-junction potential differences.[8,12] It primarily yields convenient single-ion activity coefficients (γ_i') defined by eqn. (1)

$$\gamma_i' = \gamma_i\, r^{-z_i/2} \tag{1}$$

where z_i is the charge number (with sign) of the ion concerned, and r means γ_+/γ_- for potassium chloride in pure, saturated solution of this salt at the temperature concerned.[12] At 25 °C, the value of r appears to be[12,13] close to unity or[14] slightly lower.

The present work aims at testing the above two approaches against each other for sodium sulfate in aqueous solution. Such solutions have already been studied by the double-layer approach.[11] Corresponding studies by the liquid-junction approach are presented below. The present studies especially add to previous ones on aqueous solutions of magnesium and zinc sulfates.[15]

EXPERIMENTAL

The experimental work comprises measurements of the liquid-junction containing equilibrium potential (E') of the Hg/Hg_2SO_4 electrode in aqueous 0.1–2.0 molal Na_2SO_4 solutions against the saturated calomel electrode (sce) under isothermal conditions at 25 °C. The solutions were made from p.a. quality salt (Merck) and twice distilled water, and the measurements were performed with equipment and procedures essentially as previously described.[12,15]

TREATMENT

From potential data at 25 °C, the convenient molal activity coefficient (γ_-') of the sulfate ion is obtained by eqn. (2)

$$\gamma_-' = (m^\circ/m)\ \exp[-(2F/RT)$$
$$(E'-\Delta\phi-E^\circ+0.241\ \text{V})] \tag{2}$$

where m/m° is the dimensionless sulfate-ion molality concerned, E° is the molal standard hydrogen-scale potential of the Hg/Hg_2SO_4 electrode, and $\Delta\phi=\phi_t-\phi_r$ is the liquid-junction potential difference between the test solution concerned (ϕ_t) and the saturated KCl solution of the calomel reference electrode (ϕ_r).[12-15] In the present work, 0.612 V is used for E°[15,16] and $\Delta\phi$ is estimated[8] from the Henderson equation[17] with limiting mobility data[18] for the ions.

The convenient molal activity coefficient (γ_+') of the sodium ion is subsequently obtained from γ_-' by eqn. (3)

Table 1. Potential and activity data for aqueous x m Na_2SO_4 solutions at 25 °C (see text).

Measured		Liquid-junction based			Ref. 18	Double-layer based[11]		
x	E'/mV	$\Delta\phi/mV$	γ'_-	γ'_+	$\gamma_\pm$	γ_+	γ_-	$\Delta\phi/mV$
0.1	419.7	−1.9	0.19	0.67	0.445	0.665	0.199	−1.6
0.2	415.9	−1.8	0.13	0.61	0.365	0.599	0.136	−1.3
0.5	413.3	−1.8	0.065	0.53	0.266	0.500	0.075	0.1
0.7	412.5	−1.9	0.049	0.50	0.233	0.458	0.060	0.8
1.0	412.1	−2.0	0.035	0.48	0.201	0.410	0.048	2.1
1.5	411.8	−2.1	0.024	0.45	0.170			
2.0	411.5	−2.3	0.018	0.44	0.152			

$$\gamma'_+=(\gamma_\pm^3/\gamma'_-)^{1/2} \tag{3}$$

using accepted data [18] for the mean molal ionic activity coefficient ($\gamma_\pm$) of sodium sulfate in aqueous solution.[12,13] These activity coefficients are all bare-ion ones.[19]

RESULTS

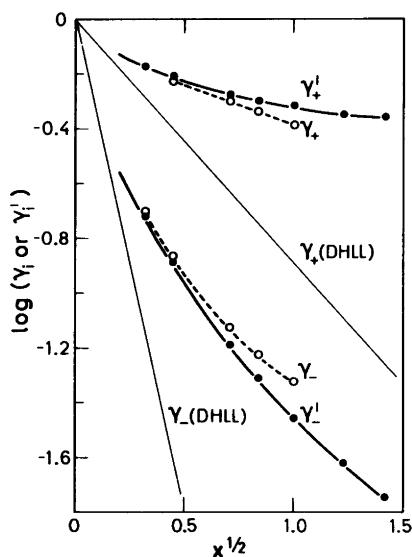The results of the present work are summarized in Table 1. This table also compares

Fig. 1. Log γ_i (double-layer based) [11] and log γ'_i (liquid-junction based) vs. $x^{1/2}$ for aqueous x m Na_2SO_4 solutions at 25 °C. Comparison to the Debye-Hückel limiting law (DHLL) for sodium and sulfate ions.

the present liquid-junction based data with previous [11] double-layer based ones. The last column of Table 1 gives the values resulting for $\Delta\phi$ from eqn. (2) on accepting the latter activity data, the present potential data (E', $E°$) and $r=1$ [eqn. (1)].

The results of the liquid-junction approach and of the double-layer approach to single-ion activities mutually agree well at the lowest concentrations covered. With increasing salt concentration, however, the two approaches give increasingly differing results. This is illustrated in Figs. 1 and 2.

In Fig. 1, the results of the two approaches are compared both mutually and to the Debye-Hückel limiting law [19] for the ions involved. The logarithm of the activity coefficients is there plotted against the square root of the dimensionless salt molality ($x=m/m°$). This reveals that the liquid-junction approach shows somewhat larger deviation from the Debye-Hückel limiting law for the sodium ion (and somewhat smaller for the sulfate ion) than does the double-layer approach (assuming $r=1$).

In Fig. 2, use is made of rational (mol fraction) activity coefficients obtained by eqn. (4)

$$f_i(\text{resp. } f'_i)=[1+(3x/55.51)]\gamma_i (\text{resp. } \gamma'_i) \tag{4}$$

where $x/55.51$ is the mol ratio of Na_2SO_4 to H_2O in solution.[19] The functions $\log(f_+^4/f_-)$ and $\log((f'_+)^4/f'_-)$ from the double-layer and the liquid-junction approach, respectively, are there plotted vs. the dimensionless salt molality (x). The former function follows a curve with varying negative slope, whereas the latter function essentially follows a line with positive slope. These
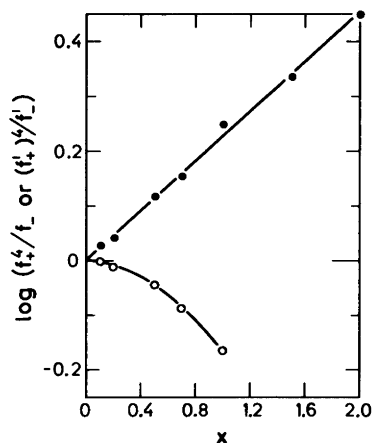
Fig. 2. (○) log (f_+^4/f_-), double-layer based,[11] and (●) log $((f_+')^4/f_-')$, liquid-junction based, vs. x for aqueous x m Na_2SO_4 solutions at 25 °C.

results are mutually incompatible. With decreasing salt concentration (x→0), both functions approach zero. This agrees with Debye-Hückel values being $f_+^4/f_-=1$ and $(f_+')^4/f_-'=r^{-3}$, and it supports previous findings[12,13] that r be close to unity.

DISCUSSION

At low salt concentration (x<0.2), the present liquid-junction approach and the previous[11] double-layer approach to single-ion activities for sodium sulfate in aqueous solution give essentially coinciding results. This matching is good enough to strongly support[12,13] that r of eqn. (1) be close to unity. With increasing salt concentration, however, the two approaches give increasingly diverging results. It then is a question which one of the two sets of data (Table 1) comes nearest to the truth.

Basically, the double-layer approach[10,11] appears to the author as the better one of the two. However, the data obtained with this approach for sodium sulfate solutions of higher concentration[11] are hard to swallow. This especially applies to the values emerging from these data for $\Delta\phi$ (last column of Table 1) and for f_+^4/f_- (Fig. 2). It seems unreasonable that $\Delta\phi$ should become more and more positive and d log $(f_+^4/f_-)/dx$ more and more negative with increasing sodium sulfate concentration. The results

from the liquid-junction approach are in these respects more likely. For $\Delta\phi$, this goes to the heart of the latter approach itself (to the estimate of the sign for $d(\Delta\phi)/dx$). For f_+^4/f_-, some elaboration is needed.

The treatment of ionic activities is often based on an extended Debye-Hückel equation like eqn. (5)

$$\log f_i = -z_i^2 A\sqrt{I}/(1+aB\sqrt{I})+b_i m \qquad (5)$$

where I is the ionic strength of the solution, A and B are temperature dependent universal constants, a is a salt dependent constant and b_i is a salt and ion dependent constant.[19] For single-salt solutions of sodium sulfate, this yields eqn. (6)

$$\log(f_+^4/f_-)=(4b_+-b_-)m \qquad (6)$$

for the function considered. This prescribes the function to be linear in m (or in $x=m/m°$) as presently obtained with the liquid-junction based data, but not with the double-layer based data (Fig. 2).

From a hydration-energy involving treatment of ionic activities,[20] one easily deduces that eqn. (7)

$$b_i = bz_i^2/r_i \qquad (7)$$

where b is a positive constant and r_i the effective radius of the dissolved i-ion, should apply to the ions of a single-salt solution. For sodium sulfate, this prescribes the sign of d $\log(f_+^4/f_-)/dx$ to be that of $r_+^{-1}-r_-^{-1}$, which most likely is positive. Also this favours the present results from the liquid-junction approach over those from the double-layer approach (see Fig. 2).

A weakness in the present liquid-junction approach is the simplification of directly using concentrations and limiting mobilities in estimating $\Delta\phi$ from the Henderson equation. Even though this practice has been given some justification by considerations of diffusion contra conduction in liquid junctions,[8] it still carries uncertainty with it. The double-layer approach avoids this uncertainty, but involves other ones. Here is room for improvement and a need for additional testing methods.

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