Osmotic and Activity Coefficients of Sodium Dithionate and Sodium Sulfite at 25°C

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Isopiestic vapor-pressure studies are used to obtain osmotic and activity coefficients for $Na_2S_2O_6$ and Na_2SO_3. For all practical purposes, values for the latter salt are the same as those for $Na_2S_2O_3$.

Isopiestic vapor-pressure measurements have been reported for aqueous solutions of sodium sulfate (*4*) and sodium thiosulfate (*4*) from 0.1 to 3.5 mol kg^{-1} and used to calculate osmotic coefficients. Similar data have been obtained for sodium dithionate (*1*) up to 0.05 mol kg^{-1} by means of freezing-point measurements. Isopiestic vapor-pressure measurements are now presented for sodium dithionate from 0.1 to 0.9 mol kg^{-1} and a few results for sodium sulfite.

Materials

Sodium dithionate ($Na_2S_2O_6 \cdot 2H_2O$, BDH reagent-grade material) was recrystallized once from aqueous solution and air-dried, after which it assayed 99.6%. Sodium sulfite ($Na_2SO_3 \cdot 7H_2O$, BDH reagent-grade material) was recrystallized once from aqueous solution and dried in vacuo. Precautions against oxidation of the sulfite were taken such as using nitrogen-purged water for the recrystallization and working as far as possible in an atmosphere of nitrogen. The isopiestic apparatus has been described (*2*). Sodium chloride was used as the reference electrolyte.

Results and Discussion

Table I gives the results for sodium dithionate in terms of the molalities of solutions of this salt and of solutions of sodium chloride which were in isopiestic equilibrium. Osmotic coefficients were calculated from the results of each equilibration and values interpolated at round concentrations from a large scale plot of φ vs. *m*. These osmotic coefficients are given in Table II along with corresponding values of the activity coefficient obtained by the usual procedure (*3*).

For sodium sulfite, three equilibrations were made against sodium chloride. In spite of precautions to avoid exposure to air, some oxidation of the sulfite occurred. At the end of each run, therefore, the solutions were acidified and boiled to expel sulfur dioxide, and the sulfate content was determined as barium sulfate. This, ex-

Table I. Molalities of Isopiestic Solutions

m_{NaCl}	$m_{Na_2S_2O_6}$	$\varphi_{Na_2S_2O_6}$	m_{NaCl}	$m_{Na_2S_2O_6}$	$\varphi_{Na_2S_2O_6}$
0.2071	0.1623	0.786	0.5386	0.4445	0.744
0.2558	0.2024	0.778	0.5512	0.4559	0.743
0.2992	0.2395	0.767	0.5896	0.4886	0.742
0.3293	0.2651	0.763	0.6768	0.5663	0.737
0.3669	0.2973	0.757	0.7287	0.6122	0.735
0.3738	0.3034	0.756	0.7855	0.6627	0.734
0.4012	0.3264	0.754	0.8505	0.7198	0.733
0.4613	0.3777	0.749	0.9281	0.7896	0.731
0.5106	0.4202	0.746	0.9968	0.8520	0.729

m_{NaCl}	$m_{Na_2SO_3} + m_{Na_2SO_4}$	Mol %[a] Na_2SO_4	φ'	$\varphi_{Na_2SO_3}$
0.6556	0.5564	6.1	0.726	0.729
0.7998	0.6951	4.4	0.712	0.714
1.1343	1.0130	8.5	0.701	0.706

[a] Analysis of stock solution before isopiestic run gave 1.0 mol % Na_2SO_4.

Table II. Osmotic and Activity Coefficients of Sodium Dithionate and Sodium Sulfite in Aqueous Solution at 25°C

	$Na_2S_2O_6$		Na_2SO_3 ($=Na_2S_2O_3$)	
m	φ	γ	φ	γ
0.1	0.806	0.467	0.805	0.466
0.2	0.776	0.392	0.774	0.390
0.3	0.757	0.350	0.753	0.347
0.4	0.747	0.323	0.741	0.319
0.5	0.740	0.303	0.731	0.298
0.6	0.736	0.288	0.724	0.282
0.7	0.733	0.274	0.719	0.267
0.8	0.730	0.264	0.713	0.256
0.9	0.728	0.256	0.709	0.247
1.0	...	...	0.707	0.239

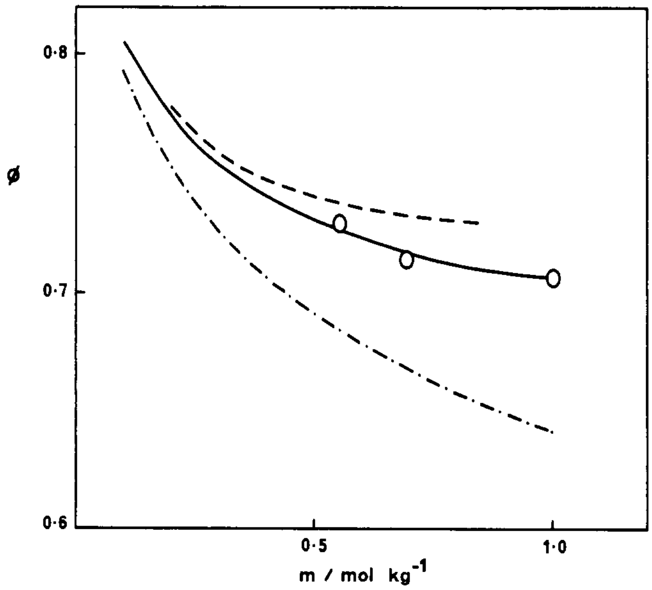

Figure 1. Osmotic coefficients in aqueous solutions of molality *m* at 25°C

--- $Na_2S_2O_6$
—— $Na_2S_2O_3$
—·—· Na_2SO_4
○ Na_2SO_3

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pressed as mol % of sodium sulfate, is given in Table I together with the molality of the reference electrolyte (NaCl), the total molality (m) of the sulfite solution ($m_{Na_2SO_3} + m_{Na_2SO_4}$), and the apparent osmotic coefficient φ' calculated by means of the equation

$$2\,\varphi_{NaCl}m_{NaCl} = 3m\varphi' \qquad (1)$$

It was then assumed that

$$m\varphi' = m_{Na_2SO_3}\varphi_{Na_2SO_3} + m_{Na_2SO_4}\varphi_{Na_2SO_4} \qquad (2)$$

where $\varphi_{Na_2SO_3}$ and $\varphi_{Na_2SO_4}$ are the osmotic coefficients of the single salt solutions at molality m. As $\varphi_{Na_2SO_4}$ is known (*4*), $\varphi_{Na_2SO_3}$ can be calculated. Values of $\varphi_{Na_2SO_3}$ are given in Table I. In spite of the correction which had to be made for the sulfate content, it is believed that these values of $\varphi_{Na_2SO_3}$ are not in error by more than 0.005. Figure 1 contains plots of the osmotic coefficients of sodium sulfate, sodium thiosulfate, and sodium dithionate, together with three points for sodium sulfite. The values for the dithionate are somewhat higher than those for the thiosulfate; moreover, they are consistent with the results of the freezing-point measurements (*1*) which gave $\varphi = 0.8288$ at the highest concentration, 0.05371 mol kg^{-1}.

The three points for sodium sulfite lie close to the plot of the thiosulfate results, and thus, for all practical purposes, the osmotic and activity coefficients of sodium thiosulfate (given in Table II) can be used for sodium sulfite.

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Osmotic and Activity Coefficients for Aqueous Methane Sulfonic Acid Solutions at 25°C

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The osmotic and activity coefficients of methane sulfonic acid in aqueous solution at 25°C are determined from 0.1 to 40 mol kg^{-1} by isopiestic vapor-pressure measurements.

Raman spectra and nmr measurements (3) indicate that methane sulfonic acid, like nitric acid, belongs to the class of electrolytes which are not as markedly weak as acetic acid but exhibit some association even in moderately concentrated solution. Thus, methane sulfonic acid is 99.7% dissociated at a concentration of 0.428 mol kg^{-1} but only 72.8% dissociated at 15.89 mol kg^{-1}. A knowledge of activity coefficient values is needed if the dissociation constant is to be calculated from the degrees of dissociation given by Raman spectra and nmr measurements. Moreover, the acid is very soluble in water, and its osmotic coefficient is of interest to the theory of concentrated solutions (*9*). Isopiestic vapor-pressure measurements have been made (*4*) up to 3.5m at 25°C, and new determinations now extend the concentration range to 40 mol kg^{-1}.

Method

An Eastman Kodak sample of methane sulfonic acid, which assayed 99.7% by titration with sodium hydroxide, was purifed by the method described by Clarke and Woodward (*1*). An aqueous solution, about 5m in concentration, was treated with an excess of activated charcoal to remove the yellow color of the original sample and then filtered through a 0.25 μm pore-size Millipore filter.

The isopiestic apparatus has been described (*2*). Sodium chloride was used as the reference electrolyte for solutions of the acid up to a concentration of 3.4 mol kg^{-1}, and lithium bromide for more concentrated solutions of the acid. Silver dishes were used to contain the reference solutions, and platinum dishes for the acid. The osmotic coefficient of lithium bromide solutions is known (*6*) up to a concentration of 20 mol kg^{-1}; at this concentration the solution was in equilibrium with the acid of concentration about 40 mol kg^{-1}.

Results and Discussion

Table I gives the concentrations of solutions in equilibrium, together with the osmotic coefficient of the solution of the acid, by use of the osmotic coefficients of sodium chloride (*8*) and lithium bromide already tabulated (*6*). Table II gives osmotic coefficients of the acid at round values of the concentrations and the activity coefficients derived therefrom, by means of the equation (*7*)

$$\ln \gamma = (\varphi - 1) + \int_0^m (\varphi - 1)\, d \ln m \qquad (1)$$

For concentrations up to 3.5m, an equation already used in the evaluation of the activity coefficient of ammonium bromide (*2*):

$$\ln \gamma/\gamma_{st} = (\varphi - \varphi_{st}) + \int_0^m [(\varphi - \varphi_{st})/m]dm \qquad (2)$$

was more convenient for calculating values of the integral. In this case, γ_{st} and φ_{st} were the activity and osmotic coefficients of perchloric acid, values of which have been tabulated (*5*).

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