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 ($m_{\mathrm{Na_2SO_3}} + m_{\mathrm{Na_2SO_4}}$), and the apparent osmotic coefficient φ' calculated by means of the equation

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

It was then assumed that

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

where $\varphi_{\mathrm{Na_2SO_3}}$ and $\varphi_{\mathrm{Na_2SO_4}}$ are the osmotic coefficients of the single salt solutions at molality m. As $\varphi_{\mathrm{Na_2SO_4}}$ is known (*4*), $\varphi_{\mathrm{Na_2SO_3}}$ can be calculated. Values of $\varphi_{\mathrm{Na_2SO_3}}$ 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 $\varphi_{\mathrm{Na_2SO_3}}$ 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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Table I. Experimental Data and Osmotic Coefficients

m_{ref}	m_{acid}	φ_{acid}	m_{ref}	m_{acid}	φ_{acid}
Reference electrolyte, sodium chloride					
0.1403	0.1372	0.950	1.543	1.372	1.078
0.3438	0.3272	0.968	2.030	1.782	1.122
0.6223	0.5794	0.992	2.395	2.096	1.150
0.8917	0.8162	1.018	3.965	3.393	1.301
1.109	1.003	1.039			
Reference electrolyte, lithium bromide					
3.160	3.393	1.301	8.287	10.956	1.888
4.032	4.523	1.413	9.429	13.157	1.979
5.055	5.887	1.549	10.109	14.580	2.031
5.489	6.498	1.598	12.523	20.360	2.137
5.767	6.901	1.624	15.830	29.574	2.144
6.194	7.529	1.678	17.607	34.570	2.113
7.448	9.522	1.805	19.588	40.429	2.043

Table II. Osmotic and Activity Coefficients of Aqueous Methane Sulfonic Acid Solutions at 25°C

m/mol kg^{-1}	φ	γ	m/mol kg^{-1}	φ	γ
0.1	0.950	0.807	6.0	1.556	2.097
0.2	0.955	0.785	7.0	1.641	2.504
0.3	0.965	0.779	8.0	1.714	2.948
0.4	0.975	0.779	9.0	1.776	3.423
0.5	0.984	0.783	10.0	1.827	3.920
0.7	1.005	0.799	12.0	1.931	5.105
1.0	1.039	0.833	14.0	2.001	6.353
1.5	1.091	0.901	16.0	2.067	7.796
2.0	1.139	0.980	18.0	2.114	9.288
2.5	1.195	1.071	20.0	2.155	10.91
3.0	1.248	1.179	25.0	2.176	14.48
3.5	1.311	1.307	30.0	2.148	17.47
4.0	1.356	1.430	35.0	2.106	19.90
5.0	1.459	1.736	40.0	2.058	21.94

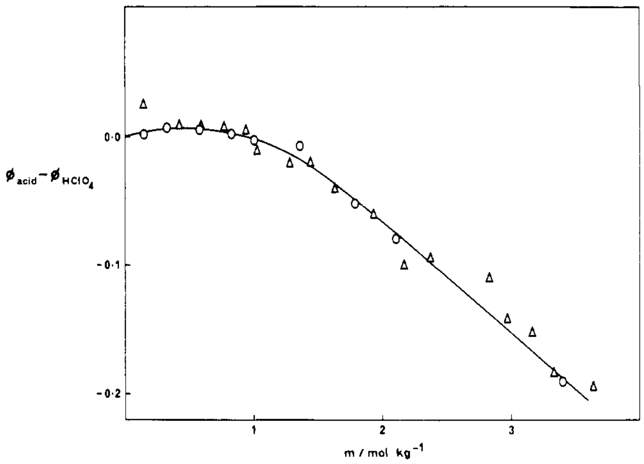

Figure 1. Osmotic coefficients of methane sulfonic acid (ϕ_{acid}) expressed as a difference with respect to those for perchloric acid in aqueous solutions at 25°C

△ Gregor et al. (*4*)
○ This work

The osmotic coefficients given in Table II can be compared with those of Gregor et al. (*4*) which extend up to 3.5*m*; the two sets of data agree with an average difference of less than 0.01 in φ (Figure 1). The corresponding activity coefficients are in agreement up to 2*m*, but the earlier values (*4*) are progressively higher at higher concentrations for reasons that have not been ascertained.

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