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*The Activity Coefficient of Sodium Sulfate in Seawater*¹

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ABSTRACT

The mean activity coefficient of sodium sulfate in artificial seawater has been measured with a sodium amalgam electrode and a lead amalgam-lead sulfate electrode. The value of 0.378 at 25°C and 35‰ salinity, and other data, suggest that a considerable fraction of the sulfate ion is tied up as a sodium sulfate complex.

Introduction. This paper, which is a continuation of activity coefficient measurements in seawater (Platford 1965), deals with the activity coefficient of sodium sulfate in seawater, measured with a sodium amalgam electrode and a lead amalgam-lead sulfate electrode. The former electrode is specific for sodium ions in seawater; the latter electrode is specific for sulfate ions, provided the carbonate concentration is small enough so that the solubility product for lead carbonate is not exceeded. The lead amalgam functions satisfactorily if the lead concentration is between 1.8% and 66% by weight (Bray 1927). Bray gives general precautions to be observed in using this electrode.

Experimental. The cell assembly is shown in Fig. 1. The general arrangement and measuring procedure were similar to those previously described (Platford 1965) except that used sodium amalgam could be drained from the cell through a stopcock fitted to the cell; this arrangement permitted several readings to be made on the same test solution. As a check, a sodium-ion glass electrode (Beckman # 39278) was substituted in some experiments for the sodium amalgam electrode.

All chemicals were "Baker Analyzed Reagent" grade. The lead amalgam, prepared electrolytically according to the method of LaMer and Parks (1931), contained about 6% lead by weight.

1. Accepted for publication and submitted to press 19 February 1965.

It was found that as much as one day was required to obtain equilibration of the lead amalgam-lead sulfate electrode at the lower temperatures.

The mean activity coefficients of solutions of pure sodium sulfate, γ_{\pm} (Harned and Hecker 1934, Robinson et al. 1941), were used to calculate the activities of the calibrating solutions, $a = 4 m^3 \gamma_{\pm}^3$, where m is the sodium

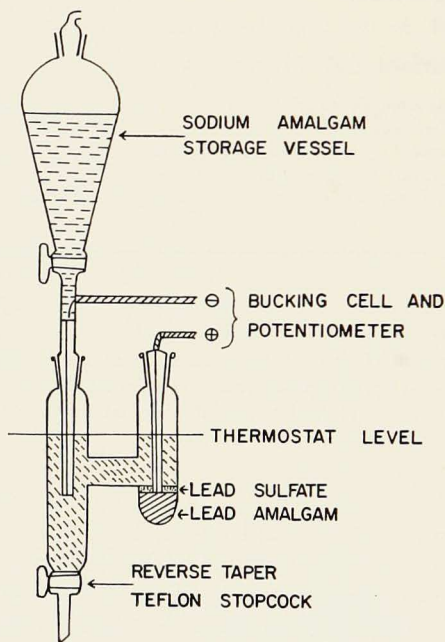


Figure 1. Cell assembly.

sulfate molality. These activities are shown in Table I. The mean activity coefficient of the sodium sulfate in seawater, $(\gamma_{\pm})_{sw}$, was then calculated from a_{sw} measured by the potential comparison method,

$$(\gamma_{\pm})_{sw} = \left[\frac{a_{sw}}{m^2_{Na^+} m_{SO_4^{2-}}} \right]^{\frac{1}{3}},$$

where m_{Na^+} and $m_{SO_4^{2-}}$ are the molalities of the sodium and sulfate ions in seawater. The slope of the line EMF versus $\log a$ varied from 23 to 28 mv/decade at 25°C, indicative of a two-electron reaction.

Results. The results with the sodium amalgam and lead amalgam-lead sulfate electrodes are given in Table II and in Figs. 2 and 3.

TABLE I. ACTIVITY COEFFICIENTS AND ACTIVITIES OF SODIUM SULFATE IN AQUEOUS SOLUTION.*

$m_{\text{Na}_2\text{SO}_4}$	15°C		25°C		35°C	
	γ_{\pm}	$4 m^3 \gamma_{\pm}^3$	γ_{\pm}	$4 m^3 \gamma_{\pm}^3$	γ_{\pm}	$4 m^3 \gamma_{\pm}^3$
0.01 ...	0.717	1.47×10^{-6}	0.715	1.46×10^{-6}	0.712	1.44×10^{-6}
0.05 ...	0.531	7.50×10^{-5}	0.529	7.40×10^{-5}	0.523	7.15×10^{-5}
0.1 ...	0.447	3.58×10^{-4}	0.445	3.52×10^{-4}	0.440	3.40×10^{-4}
0.2 ...	0.364	1.54×10^{-3}	0.365	1.56×10^{-3}	0.363	1.53×10^{-3}

* From Harned and Hecker 1934, and Robinson et al. 1941.

Activity coefficients obtained with the sodium-sensitive glass electrode were as much as 40% higher than those obtained with the sodium amalgam electrode. Because of severe drift and unexplained erratic readings with the sodium-sensitive glass electrode, the reproducibility of the activity coefficients obtained with the glass electrode coupled with the lead amalgam-lead sulfate electrode are generally not believed to be better than $\pm 20\%$. Therefore, while the glass electrode gave higher activity coefficients than the sodium amalgam electrode, it is doubtful that the differences are significant; in Table II, only the most reliable value obtained with the glass electrode is reported. Each result given for the cell $\text{Na}(\text{Hg})/\text{Na}_2\text{SO}_4/\text{PbSO}_4\text{-Pb}(\text{Hg})$ represents the mean of at least four determinations and is shown with its standard deviation.

When natural seawater was used as the test solution, the cell EMF was lower than that obtained with synthetic seawater, probably because the lead amalgam in natural seawater was acting as a lead carbonate electrode.

TABLE II. MEAN ACTIVITY COEFFICIENT OF SODIUM SULFATE IN SEAWATER.

Salinity ‰	Temperature °C	$\gamma_{\text{seawater}}^{\dagger}$		$\gamma_{\text{Na}_2\text{SO}_4}^*$	
		μ	$(\gamma_{\pm})_{sw}$	m	$(\gamma_{\pm})_{\text{Na}_2\text{SO}_4}$
34.8	25	0.72	0.378 ± 0.016	0.24	0.345
34.8**	25	0.72	0.42 ± 0.02	—	—
25	25	0.52	0.405 ± 0.016	0.17	0.385
15	25	0.31	0.435 ± 0.016	0.10	0.445
5	25	0.10	0.620 ± 0.016	0.03	0.570
34.8	35	0.72	0.408 ± 0.016	0.24	0.343
34.8	25	0.72	0.378 ± 0.016	0.24	0.345
34.8	20	0.72	0.385 ± 0.016	0.24	0.345
34.8	15	0.72	0.440 ± 0.016	0.24	0.344

† Experimental.

* After Harned and Hecker 1934, and Robinson et al. 1941.

** Glass electrode.

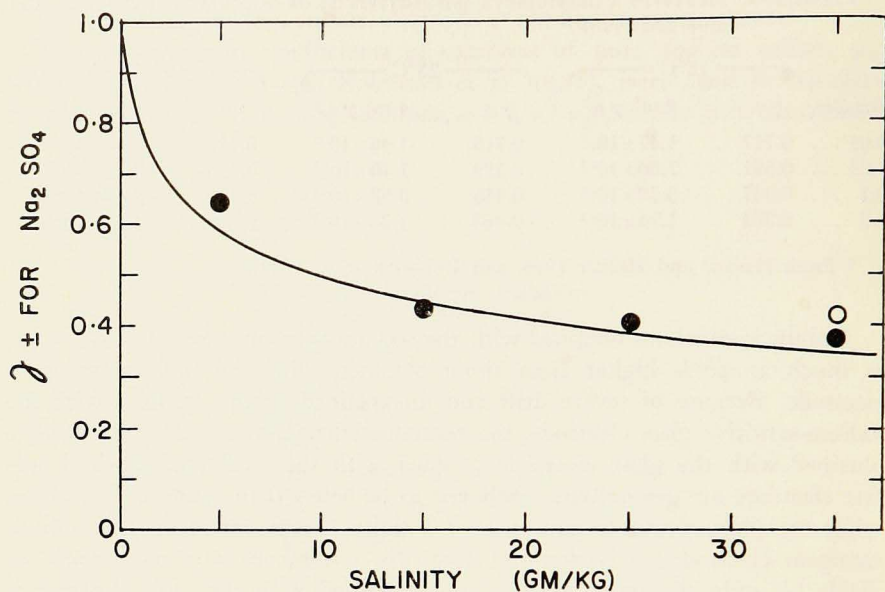


Figure 2. Mean activity coefficient of sodium sulfate in seawater as a function of salinity at 25°C. Sodium amalgam electrode (solid dots). Sodium ion glass electrode (open circle). Mean activity coefficient of pure sodium sulfate of the same ionic strength as that of seawater (solid line).

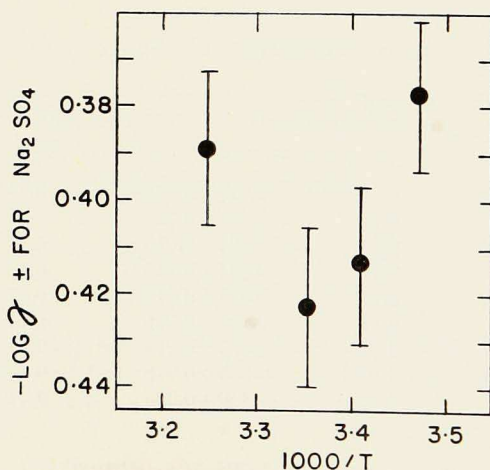


Figure 3. Mean activity coefficient of sodium sulfate in seawater as a function of temperature.

Discussion. As can be seen in Fig. 2, the mean activity coefficient of sodium sulfate in seawater is very close to that of pure sodium sulfate of the same ionic strength as the seawater. However, it should be remembered that the sulfate ion contributes only about 0.06 to the ionic strength of seawater at 35‰; therefore the above comparison is not as good as the comparison used in the study of sodium chloride. There is no way of saying what the activity coefficients in seawater "should" be in the absence of complexing, although Sillén's (1961) suggestion of 0.64 for monovalent ions and 0.16 for divalent ions is a useful guide. Unpublished work performed in this laboratory with either a sodium amalgam electrode or a glass electrode and a liquid junction indicate that the "single ion activity coefficient," γ_{Na^+} , is 0.68 ± 0.02 at 35‰ salinity and 25°C. This implies that, in seawater,

$$\gamma_{\text{SO}_4^-} = \frac{(\gamma_{\pm})_{\text{sw Na}_2\text{SO}_4}^3}{(\gamma_{\text{Na}^+})_{\text{sw}}^2} = \frac{0.378^3}{0.68^2} = 0.115.$$

The thermodynamic association constant of NaSO_4^- is reported to be 5 (Davies 1962: 169), and if we assume $\gamma_{\text{Na}^+} = \gamma_{\text{NaSO}_4^-}$, we have

$$\frac{m_{\text{NaSO}_4^-} \gamma_{\text{NaSO}_4^-}}{m_{\text{Na}^+} \gamma_{\text{Na}^+} m_{\text{SO}_4^-} \gamma_{\text{SO}_4^-}} = 5,$$

or
$$m_{\text{NaSO}_4^-} = 5 \times m_{\text{Na}^+} \times m_{\text{SO}_4^-} \times \gamma_{\text{SO}_4^-} = 8 \times 10^{-3}.$$

This calculation indicates that about 1.5% of the total sodium ion and about 27% of the sulfate ion are tied up as NaSO_4^- . Complexing of the sodium ion is too small to be detected by an anomalously low γ_{Na^+} . In view of the assumptions made in calculating these values, the values should be viewed with caution, although they provide a rough guide as to the partition of the ions involved. Agreement of these results with those calculated by Garrels and Thompson (1962) is good, but this is partly expected, since they used many of the assumptions employed here.

Although no attempt was made to estimate from Fig. 3 a partial molal heat content, it is probably safe to say that it is very small at 25°C.

Acknowledgment. The authors are grateful for technical work performed by C. C. Cunningham.

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