Subscripts

av = average
e = experimental
r = reference
s = smooth

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Isopiestic Measurements on the System H_2O–NaCl–Na_2SO_4 at 25° C.

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The mean activity coefficients and the Harned coefficients for the system H_2O–NaCl–Na_2SO_4 have been calculated from isopiestic vapor pressure measurements for ionic strengths up to 6*m*. The results for NaCl in the system agree with those reported using e.m.f. measurements. Values for α_c in Harned's equation were −0.008, −0.010, −0.032, and −0.040 at I = 0.7, 1, 3, and 6, respectively.

TERNARY systems consisting of aqueous NaCl and another salt are important sea water analogs; this paper presents activity coefficients for the system H_2O-NaCl-Na_2SO_4 for comparison with results from the systems H_2O-NaCl-$MgSO_4$ *(5)* and H_2O-NaCl-$MgCl_2$ *(6)*.

Activity and osmotic coefficients of pure Na_2SO_4 solutions at 25° C. have been reported for concentrations up to 4*m* *(7)* although the solubility of this salt is reported *(10)* to be only 1.96*m* at 25° C. Anhydrous Na_2SO_4 liberates enough heat on solution in water so that the warm solution is unsaturated, and on cooling to room temperature the solution becomes supersaturated with respect to $Na_2SO_4 \cdot 10H_2O$, which is the stable solid phase at 25° C. The system H_2O-NaCl—Na_2SO_4 is the first ternary system supersaturated with one of its components that has been studied by the isopiestic method.

EXPERIMENTAL

Reagents. Sodium chloride was precipitated with HCl and fused in a platinum dish. Sodium sulfate was recrystallized twice from distilled water and dried at 100° C. to give the anhydrous salt. The solubility of $Na_2SO_4 \cdot 10H_2O$ was determined by evaporating to dryness solutions saturated at 25° C. The mean of seven runs was 1.9503 ± 0.0020*m*.

Method. Solutions were equilibrated in seven silver cups resting in depressions in a gold plated copper block *(5)*. The block fitted snugly in a 10-cm. Dry Seal desiccator sealed with a rubber O-ring. The desiccator was evacuated with a water aspirator and rotated for from 4 to 7 days at an angle in a water bath kept at 25° ± 0.005° C.

Solution concentrations were determined by weighing dry pure salts into the cups, adding water, and reweighing at the end of each run. One cup usually contained pure NaCl solution, another contained pure Na_2SO_4 solution, the rest were aqueous mixtures of the two salts.

Solutions were easily supersaturated with Na_2SO_4 by adding an appropriate amount of water to the anhydrous

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salt contained in one of the isopiestic dishes. During solution the temperature increased enough to dissolve all the salt, and when the solution was cooled to 25° C., it became supersaturated and remained so for the duration of the run. Each of these solutions was tested for supersaturation by seeding with a crystal of $Na_2SO_4 \cdot 10H_2O$.

Treatment of Data. The isopiestic ratio was computed as a power series in x_C (*4*) using a polynomial curve fitting program.

Robinson (*8*) has shown that if

$$R_B = 1 - ax_C - bx_C^2 \tag{1}$$

then

$$\log \gamma_B = \log \Gamma_B + \log R_B + \frac{x_C^2}{2.303} \int_0^{M_B\phi_B} \frac{b}{M_B}\, d(M_B\phi_B) \tag{2}$$

and

$$\log \gamma_C = \log \Gamma_C + \log R_C + \frac{(1-x_C)^2}{2.303} \int_0^{M_B\phi_B} \frac{b}{M_B}\, d(M_B\phi_B) \tag{3}$$

The integral was evaluated numerically and log γ_B and γ_C were evaluated at several values of I_B/I, where I is the ionic strength of the mixture.

RESULTS AND DISCUSSION

Typical plots of R_B *vs.* x_C are shown in Figure 1. The values of R_B at $x_C = 1$ and for $M_B > 2m$ are slightly higher (by less than 0.5%) than those calculated from literature (*9*) values. Using literature values would have changed the log γ by less than 0.002. The coefficients for Equation 1 are shown in Table I and the integral in Equations 2 and 3 is shown in Figure 2.

In Table I, set 13 is a combination of four runs with saturated Na_2SO_4 as the reference solution. The scatter (Table I and Figure 1) is quite large partly because two of the runs were done with dried A.R. grade chemicals instead of the purified reagents. More important was that temperature changes of 0.005° C. combined with the large temperature coefficient of solubility of sodium sulfate could have caused concentration changes of 0.002*m* in the reference solution from run to run. Even so, set 13 is not out of line with the other sets. A solid phase was found in the Na_2SO_4 reference solution after two of the runs (set 21, Table I). Although enough of this solution was not available for analysis, the concentration of NaCl (about 3.62*m*) in isopiestic equilibrium with the Na_2SO_4 solution indicated that it was about 3.64*m* Na_2SO_4. The solid phase was probably the metastable hydrate $Na_2SO_4 \cdot 7H_2O$, which has a reported (*10*) solubility of 3.73*m*. Set 21 is included for interest's sake; it is not as reliable as the other sets as its solution compositions were probably continuously changing.

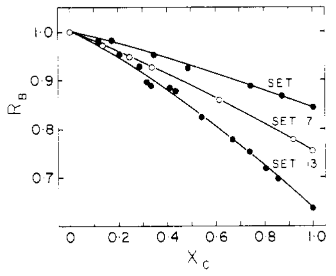

Figure 1. Isopiestic ratio vs. ionic fraction for the system H_2O–NaCl–Na_2SO_4

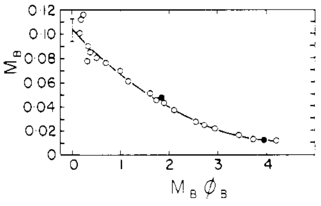

Figure 2. The integral in Equations 2 and 3

● Solutions in contact with solid phase

The uncertainty in the integral in Equations 2 and 3 was estimated from Figure 2 to be 0.005 or less, depending on the values of M_B and x_C; the uncertainty in each of the log Γ and log R terms was about 0.001, so that the uncertainty in log γ was usually about 0.005.

A cubic equation gave a slightly better fit to the data in Table I than a binomial equation, but this would have

Table I. Coefficients of Equation 1 and Integral Arguments of Equations 2 and 3

Set	M_B	M_C	a	b	$\overline{\Delta}$[c]	$M_B\phi_B$	b/M_B
1	0.1466	0.1156	0.1429	0.0148	0.20	0.136	0.101
2	0.2012	0.1626	0.1500	0.0225	0.09	0.186	0.112
3	0.2552	0.2102	0.1580	0.0296	0.12	0.235	0.116
4	0.3288	0.2753	0.1782	0.0257	0.02	0.302	0.078
5	0.3378	0.2826	0.1740	0.0303	0.05	0.311	0.090
6	0.4035	0.3446	0.1844	0.0343	0.04	0.371	0.085
7	0.5399	0.4770	0.2017	0.0430	0.03	0.498	0.080
8	0.7669	0.7100	0.2201	0.0590	0.05	0.711	0.077
9	1.0625	1.0356	0.2403	0.0743	0.05	0.995	0.070
10	1.2286	1.2210	0.2539	0.0753	0.08	1.059	0.061
11	1.6562	1.7105	0.2697	0.0837	0.04	1.598	0.0505
12	1.7858	1.8536	0.2752	0.0813	0.04	1.736	0.0455
13	1.8704	1.9503[a]	0.2770	0.0885	0.47	1.826	0.0475
14	1.9066	1.9905	0.2775	0.0828	0.04	1.865	0.0435
15	2.1096	2.2075	0.2844	0.0778	0.05	2.088	0.037
16	2.5080	2.6256	0.2938	0.0690	0.03	2.543	0.0275
17	2.6451	2.7588	0.2949	0.0655	0.03	2.703	0.025
18	2.8402	2.9472	0.2971	0.0606	0.04	2.940	0.0215
19	3.2348	3.3163	0.2962	0.0535	0.04	3.429	0.0165
20	3.4534	3.5109	0.3015	0.0425	0.02	3.712	0.0123
21	3.62	3.64[b]	0.2986	0.0405	0.60	3.910	0.0112
22	3.8147	3.8140	0.2926	0.0413	0.06	4.200	0.0108

[a] $Na_2SO_4 \cdot 10H_2O$. [b] $Na_2SO_4 \cdot 7H_2O$. [c] $\overline{\Delta}$ = Average of $|R_B\ (\text{calcd.}) - R_B\ (\text{obsd.})| \times 100$.

Table II. Mean Activity Coefficients in the System H_2O–NaCl(*B*)–Na_2SO_4(C) at 25° C.

$m_B + m_C$	$-\log \gamma_B$ E.m.f.	$-\log \gamma_B$ Isopiestic	$-\log \gamma_C$, Isopiestic
0.70	0.176	0.176	0.447
0.49 + 0.07		0.186	0.447
0.28 + 0.14		0.201	0.444
0.175 + 0.175		0.209	0.446
0.07 + 0.21		0.220	0.447
0.233	0.215[a]	0.233	0.452
1.0	0.182	0.182	0.491
0.7 + 0.1		0.196	0.496
0.4 + 0.2		0.214	0.495
0.25 + 0.25		0.227	0.495
0.1 + 0.3		0.240	0.497
0.33	0.243[b]	0.250	0.500
3.0	0.146	0.146	0.594
2.1 + 0.3		0.189	0.628
1.2 + 0.6		0.232	0.655
0.75 + 0.75		0.257	0.669
0.3 + 0.9		0.287	0.682
1.0	0.307[b]	0.308	0.692
6.0	0.006	0.006	. . .
4.2 + 0.6		0.082	. . .
2.4 + 1.2		0.172	0.720
1.5 + 1.5		0.217	0.752
0.6 + 1.8		0.270	0.789
2.0	0.306[b]	0.314	0.811

[a] From Gieskes (*2*). [b] From Lanier (*3*).

Table III. Coefficients in Harned's Equation

	$I = 0.7$	$I = 1$	$I = 3$	$I = 6$	Ref.
α_B	Not constant but agrees with (*1–3*)				This work
		0.0605	0.0537	0.0500	(*3*)
	0.0557				(*2*)
		0.0453	0.0490		(*1*)
α_C	−0.008	−0.010	−0.032	−0.040	This work
		−0.0141	−0.0205	−0.0333	(*3*)
		−0.0431	−0.0319		(*1*)

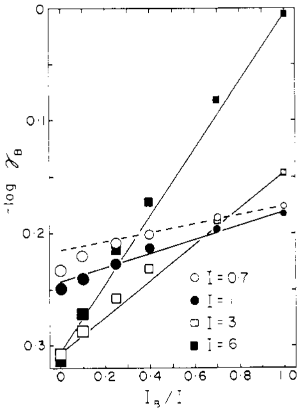

Figure 3. Mean activity coefficients of sodium chloride in the system H_2O-NaCl-Na_2SO_4
———— e.m.f. Lanier (3)
— — — — e.m.f. Gieskes (2)

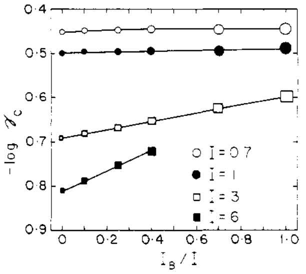

Figure 4. Mean activity coefficients of sodium sulfate in the system H_2O-NaCl-Na_2SO_4

complicated the treatment of the data and would probably have not increased the reliability of the results.

The calculated activity coefficients are shown in Table II and are plotted in Figures 3 and 4. The values for γ_B as derived from e.m.f. measurements (*1–3*) are shown in Figure 3 and Table III for comparison. The isopiestic results agree with the e.m.f. results within 0.01 in $\log \gamma_B$, although curvature in the plots of isopiestic $\log \gamma_B$ *vs.* I_B/I at low I_B lead to slightly different values of $\log \gamma_B$ at $I_B = 0$ between the two methods.

Values for α_B and α_C in Harned's equation ($\log \gamma_C = \log \gamma_C^0 - \alpha_C I_B$) are compared with literature values in Table III. There are large differences between these α_C values and those reported by Lanier (*3*) and Butler *et al.* (*1*) all of whom calculated their values by assuming Harned's rule applied to both salts in the system. Part of this difference is due to the rather large uncertainities in α_C and also to the present author's observation that Harned's rule is not exactly obeyed for NaCl at the higher ionic strengths.

At $I = 0.7$ (the ionic strength of normal sea water) both salts in the system follow Harned's rule, while in the system (*5*) H_2O-NaCl-$MgSO_4$, neither salt does. The ion pair $MgSO_4^0$ in the later system must account for part of this difference.

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NOMENCLATURE

γ_B = activity coefficient of NaCl in a mixed solution of m_B molal NaCl and m_C molal Na_2SO_4
γ_C = activity coefficient of Na_2SO_4 in the same mixed solution
Γ_B = activity coefficient of NaCl in M_B molal NaCl solution which is in isopiestic equilibrium with the mixed solution
Γ_C = activity coefficient of Na_2SO_4 in M_C molal Na_2SO_4 solution which is in isopiestic equilibrium with the mixed solution (and also with the M_B molal NaCl solution)
R_B = isopiestic ratio $M_B/(m_B + 1.5m_C)$
R_C = $1.5\ M_C/(m_B + 1.5m_C)$
x_C = $1.5\ m_C/(m_B + 1.5m_C)$
ϕ_B = osmotic coefficient of M_B molal NaCl solution.

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