Nomenclature

D = molecular diffusivity, cm^2/sec
D_i° = molecular diffusivity of the limiting component in a dilute solution of solvent i, cm^2/sec
E = Taylor axial dispersion coefficient, cm^2/sec
L = length of tubing between sample injection and photometer, cm
Q = volumetric flow rate, cm^3/sec
r = radius of tubing, cm
t = time after injection, sec
$\bar{t}$ = average residence time, L/u, sec
u = average linear velocity of fluid in tube, cm/sec
x_i = mole fraction of component i

Greek Letters

σ^2 = variance of concentration vs. time curve at photometer
σ_t = standard deviation of concentration vs. time curve, sec
η = viscosity of liquid mixture, P
η_i = viscosity of solvent i, P

Subscript

i = refers to solvent i

Literature Cited

(1) Ananthakrishnan, V., Gill, W. N., Barduhn, A. J., *AIChE J.*, **11**, 1063 (1965).
(2) Barr, G., "International Critical Tables," **5**, 22 (1929).
(3) Biesenberger, A., Ouano, A. C., *J. Appl. Polym. Sci.*, **14**, 471 (1970).
(4) Bruins, H. R., "International Critical Tables," **5**, 73 (1929).
(5) Leffler, J., Cullinan, Jr., H. T., *Ind. Eng. Chem. Fundam.*, **9**, 88 (1970).
(6) Levenspiel, O., "Chemical Reaction Engineering," Wiley, New York, N.Y., 1962.
(7) Ouano, A. C., *Ind. Eng. Chem. Fundam.*, **11**, 268 (1972).
(8) Reejhsinghani, N. S., Gill, W. N., Barduhn, A. J., *AIChE J.*, **12**, 916 (1966).
(9) Reid, R. G., Sherwood, T. K., "Properties of Gases and Liquids," 2nd ed., McGraw-Hill, New York, N.Y., 1966.
(10) Tamman, G., Pillsburg, M. E., *Z. Anorg. Chem.*, **172**, 243 (1928).
(11) Taylor, G. J., *Proc. Roy. Soc.* (London), **A219**, 186 (1953).

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Enthalpy of Dilution of Aqueous Na_2SO_4 and Li_2SO_4

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The enthalpies of dilution of aqueous solutions of Na_2SO_4 and Li_2SO_4 were measured at 25°C for molalities from 3.0 to 0.09 mol/kg. Values of the excess enthalpy (H^{ex} or ϕ_L) at molalities from 0 to 3 mol/kg were derived by combining the results with the low-concentration data of Lange and Streeck and Wallace and Robinson.

Lange and Streeck (*11*) reported values for the enthalpies of dilution of aqueous solutions of Na_2SO_4 and Li_2SO_4 at 25°C at concentrations from 0.1 to 0.00016 mol/l. Wallace and Robinson (*14*) measured Na_2SO_4 enthalpies of dilution from 0.4 to 0.0006 mol/l. Results at higher concentrations are limited to two measurements by Greyson and Snell (6) (Na_2SO_4 from 1.25 to 0.0135 mol/kg) and some results of Gritsus et al. (*7*) of low accuracy. In the course of an investigation into the heats of mixing solutions of these two electrolytes, a need for excess enthalpies arose; hence, this study was undertaken.

Experimental

Preparation and analysis of solutions. The solutions were prepared from reagent-grade salts and deionized distilled water. All impurities reported by the manufacturer were less than 0.1%. The sodium sulfate was dried for 24 hr at 200°C (*2*). Solutions were prepared by weight.

The solubility of Na_2SO_4 in H_2O is reported to be 1.96 mol/kg at 25°C (*12*). Hence, a $3m$ Na_2SO_4 solution is supersaturated. It was necessary to load this solution, warmed slightly above room temperature to prevent crystallization, in the syringe and the mixing vessel.

The Li_2SO_4 was dried at 500°C in a muffle furnace for 15 hr (*1, 2, 10*). For some runs the pH was adjusted to eight or nine by the addition of a negligible amount ($<<0.1\%$) of LiOH or NaOH. No difference was detected in these runs. Both salts were prepared and measured by two different investigators (D. E. S. and P. T. T.) working independently.

The calorimeter used for these experiments, an LKB batch microcalorimeter (LKB-Produkter AB, Fack, 161 25 Bromma 1, Sweden, Model 10700-2), has been described previously (*3, 4, 13*). At the beginning of a run, the cell was rinsed with water and dried with a stream of nitrogen. One of the calorimeter compartments (compartment A) was loaded with a solution containing n_A moles of solute at a molality m_A. The other calorimeter compartment (B) was loaded with water. The two solutions were then mixed in the calorimeter, resulting in q calories of heat being released and a final molality m_F. For each of the succeeding experiments, the calorimeter was not rinsed and dried, but compartment B was emptied (by weight) with a 5-ml plastic syringe. This process left behind 10 ± 2 mg of solution if compartment B was the 2-ml side of the calorimeter and 15 ± 2 mg if compartment B was the 4-ml side of the calorimeter.

A known weight of solvent was added to compartment B, and this, when mixed with the small amount of solution left behind produced a solution containing n_B moles of solute at concentration m_B. The moles of solute (n_A)

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and concentration (m_A) retained in compartment A are calculated from the weights of solutions added and withdrawn up to this point. Mixing these solutions results in the release of q calories and a final concentration m_F. This process is continued for several cycles. The cell is not rinsed and dried after each experiment because this increases the blank heat of mixing of the calorimeter owing to heat effects associated with wetting the walls (*3, 4*).

An electrical calibration followed each experiment. In a few cases, the electrical calibration differed by more than 0.3% from the average of all calibrations. In these cases, the average of all calibrations was used which resulted in a better fit with the other data.

Treatment of data. The treatment of the data is similar to that described by Jones and Wood (*9*) and by Gibbard (*5*). If the excess enthalpy per mole of solute (H^{ex}) is represented by the equation:

$$H^{ex} = \phi_L = A_1\sqrt{m} + A_2 m + A_3 m^{3/2} + A_4 m^2 + \ldots \quad (1)$$

where A_1 is the Debye-Hückel limiting slope (A_1 = 2447.4) (*8*), then the heat associated with the mixing process in the calorimeter is calculated by the equation:

$$\Delta_m H = -q = H_F{}^{ex}(n_A + n_B) - H_A{}^{ex} n_A - H_B{}^{ex} n_B \quad (2)$$

where H^{ex} is calculated by Equation 1. Substituting Equation 1 into 2 and rearranging give:

$$\frac{q - n_A A_1\sqrt{m_A} - n_B A_1\sqrt{m_B} + n_F A_1\sqrt{m_F}}{n_A} = (A_2/n_A)(n_A m_A + n_B m_B - n_F m_F) + (A_3/n_A)(n_A m_A{}^{3/2} + n_B m_B{}^{3/2} - n_F m_F{}^{3/2}) + (A_4/n_A)(n_A m_A{}^2 + n_B m_B{}^2 - n_F m_F{}^2) + \ldots \quad (3)$$

where $n_F = (n_A + n_B)$. This equation was used in a least-squares procedure to determine the coefficients of the polynomial. The right-hand side is the heat per mole of salt in compartment A corrected for the limiting law. The fewest number of coefficients that would adequately represent the data was used; that is, if the statistical tests indicated that the last coefficient was not necessary to represent the data with 95% confidence, it was not included in the set.

For sodium sulfate the data of both Lange and Streeck (*11*) and Wallace and Robinson (*14*) were included in the least-squares fit. Thus, the results should represent the whole concentration range from 0 to 3 mol/kg. Table I lists the experimental data used for the least-squares fit. An idea of the accuracy of the results is best achieved by calculating the ΔH which would have been observed if the number of moles in compartment B had been zero.

$$\Delta H_E = \{-q + n_B[H^{ex}(m_B) - H^{ex}(m_F)]\}/n_A \quad (4)$$

This is a small correction to the experimental data (less than 0.4% for Na_2SO_4 and 2.5% for Li_2SO_4). The result (ΔH_E), together with the difference between the experimental and calculated ΔH for this process ($\Delta H_E - \Delta H_C$), is given in Table I. When all of the Na_2SO_4 data in Table I, together with the low-concentration results of Lange and Streeck (*11*) and Robinson and Wallace (*14*), were put into the least-squares program, Equation 1 with six adjustable constants represented the results with a standard deviation of 5.5 cal/mol. Individual points that differed from the calculated curve by more than two standard deviations were then removed one at a time.

Following this procedure the four experiments footnoted *e* in Table I were eliminated, and the resulting standard deviation dropped to 1.6 cal/mol. This is about the standard deviation to be expected from previous experience with this calorimeter. Although four is a rather high number of points to throw out, it is believed that this procedure gives the best estimate of the excess enthalpy of sodium sulfate. After half of the experiments were performed, the power supply for the electrical calibration of the LKB calorimeter was occasionally off by as much as 2%. Two of the points that were thrown out could have been affected in this way. Another of the points involved a 3-mol/kg sodium sulfate solution which is supersaturated. It was expected that there would be more difficulty in reproducing this point. The effect of throwing out these points is not large. It changes the final calculated excess heat contents by less than 15 cal/mol at all concentrations.

Table I. Experimental Enthalpy of Dilution of Li_2SO_4 and Na_2SO_4 at 25°C

n_A, mmol	m_A, mol kg^{-1}	n_B, μmol	m_B, mmol kg^{-1}	m_F, mol kg^{-1}	$q^{a,b}$ cal	ΔH_E,^{c} cal mol^{-1}	$\Delta H_E - \Delta H_C$,^{d} cal mol^{-1}
				Na_2SO_4			
6.055	1.578	...	...	0.9613	−2.918	481.9	−19^e
4.764	0.961	8.5	2.5	0.5726	−1.839	386.8	12^e
2.956	0.5726	5.3	2.1	0.3847	−0.650	220.0	−0.8
1.920	0.3847	3.7	1.5	0.2595	−0.285	148.6	−1.8
6.037	3.000	...	...	0.9566	−6.505	1077.6	−20^e
6.830	3.000	...	...	1.037	−6.736	986.2	0.0
5.995	3.000	...	...	1.016	−6.022	1004.5	0.1
1.845	1.016	11.0	3.2	0.3546	−1.244	675.5	28^e
9.804	2.452	...	...	1.648	−3.850	392.7	1.6
6.624	1.648	11.2	5.4	1.088	−2.603	394.6	−0.5
4.476	1.088	7.4	3.4	0.7121	−1.576	353.1	4.1
1.567	0.7121	10.9	2.7	0.2541	−0.826	527.5	−1.9
9.455	2.452	...	...	1.571	−4.176	441.7	−1.2
3.156	1.571	10.9	2.6	0.5160	−2.912	923.8	−0.7
				Li_2SO_4			
10.151	3.000	...	...	2.035	3.640	−358.6	−18^e
7.916	2.035	16.6	9.9	1.422	1.477	−188.2	0.3
5.657	1.422	12.3	7.1	0.991	0.6060	−108.6	−3.4
4.018	0.991	8.9	5.1	0.6935	0.3075	−78.0	0.2
1.172	0.6935	9.7	2.7	0.2227	0.2149	−187.5	−1.2
0.917	0.2227	2.2	1.3	0.1578	0.0469	−52.3	4.2
10.211	3.000	...	...	1.988	3.999	−391.7	0.0
7.697	1.988	16.3	9.6	1.384	1.362	−178.6	−4.8
5.707	1.401	11.8	6.7	0.982	0.5850	−104.0	−4.5
4.059	0.982	8.9	5.3	0.6987	0.2868	−72.1	−2.0
1.204	0.6987	9.7	2.4	0.2095	0.2015	−171.3	−28^e
0.875	0.2095	2.1	1.2	0.1497	0.0430	−50.2	3.4
11.698	2.998	...	...	1.909	4.876	−416.8	1.2
7.548	1.909	13.3	5.8	1.210	1.576	−210.1	6.0
4.935	1.210	9.0	3.9	0.773	0.572	−117.0	6.0
1.733	0.773	8.8	2.1	0.2687	0.3138	−183.8	0.2
0.612	0.2687	3.2	0.7	0.0914	0.1002	−166.0	15^e
11.999	2.998	...	...	1.927	4.890	−407.5	−2.2
11.764	2.998	...	...	1.914	4.883	−415.1	1.0

[a] 1 cal = 4.184 J. [b] The value of q is the negative of the enthalpy change when n_A moles (molality m_A) is mixed with n_B moles (molality m_B) to get a final solution (molality = m_F). [c] ΔH_E is the experimental change in enthalpy that would have been observed if n_A moles (molality m_A) were diluted with water to a molality m_F. [d] ΔH_C is the value calculated for the process n_A moles (molality m_A) diluted with water to a molality m_F by use of Equation 1. [e] These runs were not included in the final least-squares fit because they differed from the calculated value by much more than twice the standard deviation when included.

Table II. Excess Enthalpy of Na_2SO_4 at 25°C

	H^{ex},[a] cal/mol	
m, mol/kg	Na_2SO_4[b]	Li_2SO_4[c]
0.1	231	507
0.2	140	603
0.3	27	662
0.4	−91	708
0.5	−209	746
0.6	−323	779
0.7	−432	809
0.8	−536	837
0.9	−634	862
1.0	−726	887
1.2	−893	938
1.4	−1039	991
1.6	−1168	1049
1.8	−1283	1110
2.0	−1388	1174
2.2	−1484	1239
2.4	−1570	1305
2.6	−1645	1376
2.8	−1706	1457
3.0	−1745	1562

[a] 1 cal = 4.184 J. [b] Calculated from the results of the least-squares fit: $H^{ex}/\text{cal mol}^{-1} = 2447.4\sqrt{m} - 8237.92m + 12959.27m^{3/2} - 16570.52m^2 + 13334.22m^{5/2} - 5591.61m^3 + 933.17m^{7/2}$. [c] Calculated from the results of the least-squares fit: $H^{ex}/\text{cal mol}^{-1} = 2447.4\sqrt{m} - 1992.86m - 7808.77m^{3/2} + 27750.89m^2 - 38874.32m^{5/2} + 28295.75m^3 - 10501.18m^{7/2} + 1570.569m^4$.

The results of the least-squares fit at even concentrations are given in Table II. Greyson and Snell (*6*) made two measurements of the heat of dilution of sodium sulfate from 1.25 to 0.0135*m*. Their results differ from those calculated from the final least-squares fit by 21 and 40 cal/mol. The spread in their points is only slightly less than the difference between their points and the present results. Gritsus et al. (*7*) measured heats of dilution and heats of solution from 4.55 to 0.004*m*. The differences from the present results are as high as 500 cal/mol at 3*m*.

The reason for the discrepancy is unknown, but two things lead us to believe that the present results are correct. In the first place, the heats of solution measured by Gritsus et al. at low concentrations are not consistent with the heat of dilution data of Lange and Streeck (*11*) and Robinson and Wallace (*14*). The discrepancy is as much as 400 cal/mol. In the second place, the results of Gritsus et al. show a distinct discontinuity at the concentration at which sodium sulfate becomes supersaturated (m = 1.96 mol/kg) (*12*). This behavior is not expected if they were really measuring the properties of the supersaturated solution. We have found that the crystallization process from supersaturated solution can proceed slowly and irregularly.

When all of the Li_2SO_4 data in Table I, together with the low-concentration data of Lange and Streeck (*11*), were fit to Equation 3 by least squares, the standard deviation was 10 cal/mol for seven adjustable constants. Again, individual points that differed by more than 2 σ were discarded. When the three points (footnoted *e* in Table I) were rejected, the standard deviation dropped to 2.8 cal/mol. The results are given in Tables I and II.

The results of these experiments fit in with the normal trends. Many lithium salts of large anions have increasingly positive excess enthalpies as concentration increases, whereas the sodium salts of the same anions become negative as the concentration increases.

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Literature Cited

(1) Akerlof, G., *J. Amer. Chem. Soc.*, **48**, 1160 (1926).
(2) Duval, C., "Inorganic Thermogravimetric Analysis," pp 61, 91–92, Elsevier, New York, N.Y., 1953.
(3) Falcone, Jr., J. S., PhD dissertation, University of Delaware, Newark, Del., 1972.
(4) Falcone, Jr., J. S., Wood, R. H., *J. Solution Chem.*, **2** (1973).
(5) Gibbard, Jr., H. F., *J. Phys. Chem.*, **73**, 2382 (1969).
(6) Greyson, J., Snell, H., *J. Chem. Eng. Data*, **16**, 73 (1971).
(7) Gritsus, B. V., Akhumov, E. I., Zhilina, L. P., *Zh. Prikl. Khim.* (Leningrad), **42**, 208 (1969).
(8) Harned, H. S., Ownen, B. B., "The Physical Chemistry of Electrolyte Solutions," 3rd ed., Reinhold, New York, N.Y., 1958.
(9) Jones, F. R., Wood, R. H., *J. Phys. Chem.*, **67**, 1576 (1963).
(10) Kitajima, I., *J. Chem. Soc. Jap.*, **55**, 199 (1934).
(11) Lange, E., Streeck, H., *Z. Phys. Chem.*, **157A**, 1 (1931).
(12) Stephen, H., Stephen, J., "Solubilities of Inorganic and Organic Compounds," Vol I, Part I, p 127, Macmillan, New York, N.Y., 1963.
(13) Wädso, I., *Acta. Chem. Scand.*, **22**, 927 (1968).
(14) Wallace, W. E., Robinson, A. L., *J. Amer. Chem. Soc.*, **63**, 958 (1941).

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