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THERMODYNAMICS OF AQUEOUS SODIUM DODECYL SULFATE

By

Robert L. Berg

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Energy Research and Development Administration
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ABSTRACT

A flow microcalorimeter system has been assembled and is being used in a thermodynamic study of surfactant systems as part of the Energy Research and Development Administration's enhanced oil recovery program. Enthalpies of dilution and demicellization of sodium dodecyl sulfate have been measured over a temperature range of 20° to 35° C. This surfactant has also been studied with cosurfactant and salt backgrounds. The critical micelle concentrations (cmc) have been determined and are in excellent agreement with those in the literature. Studies below the cmc suggest the possible formation of a dimer. Work on alkyl sulfonates and alkylbenzene sulfonates is planned.

INTRODUCTION

The development of a successful micellar-polymer oil recovery program is dependent on supporting research which will allow oilfield flooding to be carried out with an optimal utilization of chemicals to produce significant quantities of residual oil. The process of micellar flooding has been described in the literature (6,14).² At present, still unanswered are numerous fundamental questions concerning the stability of micellar systems with temperature

¹ Research chemist.

² Underlined numbers in parentheses refer to items in the list of references at the end of this report.

and pressure, with brine background, cosurfactant, and hydrocarbons. The purpose of this continuing study of the thermodynamics of oil recovery surfactant systems is to answer the questions: What is the structure of a micelle? What is the mechanism of micelle formation? and What causes the special properties of micellar systems?

Thermodynamics is a valuable tool for the understanding of the reactions occurring between micellar systems and oil-reservoir fluids in oilfield flooding. By the use of calorimetry, it is possible to determine the strength of the interactions between micelles and brine systems and to give additional information to the petroleum engineer about the stability of micellar solutions. The effect of a cosurfactant on micellar structure is still largely conjecture; yet the blending of surfactant and cosurfactant is one of the few parameters which can be controlled in micellar flooding. Knowledge of the thermodynamic interactions of surfactant and cosurfactant would be of great value in the planning of oil recovery processes. Earlier thermodynamic studies of surfactants show wide discrepancies both in terms of experimental results and of theoretical interpretation.

The intent of this thermodynamic research is to obtain an understanding of micellar interactions to allow more knowledgeable planning of oilfield recovery processes.

This report describes the strategy and apparatus being used in the experimental thermodynamic study of micellar systems and presents the results of measurements on a simple well-defined surfactant system. This initial study of a simple surfactant system does not answer the questions mentioned above; however, considerable information about micelle behavior already has been obtained in the course of this investigation. The work has also raised additional questions concerning micelle structure such as the extent of premicellar association and the nature of solubilization effects.

The surfactant chosen for this initial study was sodium dodecyl sulfate, $\text{NaC}_{12}\text{H}_{25}\text{SO}_4$. Although sodium dodecyl sulfate shows little promise as an oilfield chemical, its physical and chemical properties have been extensively studied. Mukerjee and Mysels (16), in their 1966 tabulation of critical micelle concentrations (cmc), list more than 600 measurements of the cmc by more than 50 methods. Since 1966, additional work has appeared including thermodynamic measurements and calculations. Because of this extensive study, sodium dodecyl sulfate served as a test surfactant for this initial calorimetric study.

Various background conditions were used which demonstrate the ability of thermodynamic measurements to provide information concerning the effect of salt and cosurfactant backgrounds on micellar behavior. Calorimetric measurements of enthalpies of dilution and demicellization are reported for sodium dodecyl sulfate in:

water at 20°, 25°, 30°, and 35° C,
 0.01 m and 0.001 m NaCl at 20° and 30° C,
 0.17158 m (1 percent) and 0.0858 m (0.5 percent) NaCl at 30° C,
 5 percent n-butanol at 20° and 25° C, and
 5 percent i-propanol at 20° and 30° C.

EXPERIMENTAL

Strategy

A measurable heat effect occurs when a solution of micellar material is diluted. This heat effect (enthalpy change) results from the change of the structure of the solution due to dilution and demicellization. The magnitude of these heat changes is small, and their significance is not in the temperature change that a surfactant slug would experience on dilution, but rather these effects give a measure of the stability of the micellar material in thermodynamic terms. The aggregation of the long-chain surfactant ions in solution to form micelles is a reaction which increases rapidly over a narrow concentration range (the critical micelle concentration). Nearly all measured properties of micellar solutions show an abrupt change in this concentration region. The calorimetric measurements of heat effects were also expected to show this change in solution structure. The strategy adopted for the calorimetric studies was to determine dilution enthalpies above and below the critical micelle concentration (cmc). Construction of a curve showing the interrelationship of each of the measured dilutions allows calculation of the heat-of-micelle formation. For each dilution, the measured heat effect is given by equation 1,

$$\Delta H(\text{measured}) = H_{\phi}(\text{final}) - H_{\phi}(\text{initial}), \quad (1)$$

where the H_{ϕ} are apparent molar enthalpies.

For solutions with electrolyte background, the observed reaction may be written as:

where NaX is the electrolyte. The reaction of interest, the change of enthalpy for the sodium dodecyl sulfate,

$$\text{NaC}_{12}\text{H}_{25}\text{SO}_4 \cdot r(\text{nH}_2\text{O}) + x(\text{nH}_2\text{O}) =$$

$$\text{NaC}_{12}\text{H}_{25}\text{SO}_4 \cdot (r+x)(\text{nH}_2\text{O}), \quad (3)$$

does not include the dilution enthalpy terms for the salt background. Therefore "correction" terms for the dilution of the electrolyte are subtracted from the measured heat change to give the reaction of equation 3. The correction equations are

$$r(\text{NaX} \cdot \infty \text{H}_2\text{O}) = r(\text{NaX} \cdot \text{nH}_2\text{O}) \quad (4)$$

$$x(\text{NaX} \cdot \infty \text{H}_2\text{O}) = x(\text{NaX} \cdot \text{nH}_2\text{O}) \quad (5)$$

$$(r+x)(\text{NaX} \cdot \text{nH}_2\text{O}) = (r+x)(\text{NaX} \cdot \infty \text{H}_2\text{O}) \quad (6)$$

The values for reactions 4 through 6 were taken from the literature (13,21) and are largely compensatory. The sum of the correction terms is generally less than 4 cal mol⁻¹. The enthalpy change for equation 3 is given by

$$\Delta H = \Delta H(\text{measured}) + \Sigma \quad (7)$$

where Σ is the sum of the correction terms arising from the dilution of the electrolyte.

No corrections have been made for the measurements in alcohol backgrounds. To make such corrections requires enthalpy-of-unmixing data for the alcohol at constant molality as a function of background ionic strength. It would be necessary to assume a model for the background electrolyte and to measure mixing enthalpies for the alcohol and the model electrolyte. The author believes these quantities would be small and largely compensatory as in the salt background case.

For any solution,

$$H_\phi = H_\phi^\circ + L_\phi, \quad (8)$$

where L_ϕ is the relative apparent molar enthalpy and H_ϕ° is the apparent molar enthalpy of the reference state of infinite dilution. The use of equation 8 to give L_ϕ values is essentially a scaling operation to give L_ϕ at zero concentration a value of zero.

For convenience in assembling and interrelating the ΔH terms, H_ϕ for an initial stock solution was arbitrarily assigned a value of zero, and a segment of the curve of H_ϕ versus molality was constructed into which other series of values were fitted by interpolation and scaling. A value for H_ϕ° was determined by extrapolation of measurements below the cmc to infinite dilution using a plot of H_ϕ versus $m^{\frac{1}{2}}$. Equations, such as the Debye-Huckel equations (9,19), were also used for fitting the data below the cmc.

The general equation for the calorimeter process is

$$\Delta H(\text{measured}) = \epsilon \times S/n, \quad (9)$$

where ϵ is a calibration constant, S the measured signal, and n the amount of material diluted. The convention of giving a negative sign to the enthalpy change for an exothermal reaction is followed throughout this work. Throughout this report $1 \text{ cal} = 4.184 \text{ J}$.

Apparatus

The experimental measurements were performed with a commercial microcalorimeter (LKB)³ which is operated as a heat-conduction flow instrument (15). The calorimeter system is shown in figure 1. A baseline steady state is established by pumping water through both injection pumps. The reaction is initiated by introducing reactant through one of the pumps into the mixing zone of the flow cell.

A steady-state heat effect is maintained as long as the pumping rates and ratio are constant. A change in the pump ratio gives a different final concentration and, therefore, a different heat effect. The heat effect measured is the heat transfer across the surrounding thermopiles. The calibration constant for the instrument was determined by passing a measured electrical current through a 50-ohm heater mounted in the base of the mixing cell. The calibration constant is considered accurate to 0.5 percent.

³ Reference to specific brand of equipment is made for identification only and does not imply endorsement by ERDA.

FIGURE 1. Flow Microcalorimeter System.

Several modifications were made on the commercial instrument. The calorimeter block was placed within a "submarine," of the type designed by R. Biltonen (11), in a Tronac water bath with a Tronac-40 temperature controller. The water bath provides a more stable thermal environment for the calorimeter. A platinum resistance thermometer placed inside the submarine indicated a stability of better than 0.0005°C . The thermal environment of the calorimeter cells should be of even greater temperature stability. The resistance thermometer,

calibrated at the National Bureau of Standards, was also used to determine the absolute temperature of the calorimeter. Measurements were carried out at 20°, 25°, 30°, and 35° C $\pm 0.005^\circ$ C.

Initial measurements with sodium dodecyl sulfate using the LKB peristaltic pumps with silicone tubing indicated an adsorption of the surfactant on the silicone creating a concentration gradient. This problem was avoided by use of the Picker design (23) all-Teflon axial rotary piston pump. These pumps give stable flow rates and very little pulsation. The pumps were calibrated by measuring the mass of water pumped in a given time period. The molar flow rates were calculated by use of density values obtained from interpolation of measured densities. The scanning mode was not used with the pumps, but the programmed steps for flow ratios have been used extensively in this work. The overall flow rate for the work reported here was approximately $0.5 \text{ cm}^3 \text{ min}^{-1}$. Entering solutions were thermostated in an external heat exchanger consisting of several coils of gold tubing within the submarine before they were allowed to enter the internal heat exchangers of the calorimeter block. Use of water temperature 10° to 15° C different from the bath temperature gave no deflection of the baseline. This would indicate that the thermostating by the heat exchangers of incoming solutions to calorimeter temperature is complete.

The detection system consists of two pairs of thermopiles wired in opposition. For the 25° and 35° C measurements, the thermopile output was sent into a Keithley 150B microvolt amplifier. The amplifier analog output was directed to a strip chart recorder.

For the 20° and 30° C measurements, a major modification of the amplifier system was made. An operational amplifier was mounted on the wall of the calorimeter block, and the output from the operational amplifier was sent to a Dana 5000 digital voltmeter, then to a recorder and to an interface for data

handling and storage in a digital form. The use of the operational amplifier circuit shown in figure 2 gives a gain of approximately 25,000. This gives increased sensitivity with reduced noise since the signal coming out of the calorimeter to the digital voltmeter has a magnitude of volts or millivolts rather than the microvolt or nanovolt signal with the original system. The operational amplifier is a Analog Devices module, 261K, which has an extremely low

FIGURE 2. Modified Amplification System.

temperature drift, less than 0.1 microvolt per degree, which is not observed at the stability level of the water bath. This amplification system is of the type in use on microcalorimeters designed by E. J. Prosen at the National Bureau of Standards (24).

For the 20° C measurements, an additional modification was made on the instrument. The flow-through cell, shown on the right-hand side of the calorimeter in figure 1, was replaced with a second mixing cell. A set of paired pumps was used on that side of the calorimeter, thereby canceling some viscosity heating effects between the two calorimeter cells and giving a more stable baseline.

The calorimeter performance was checked with sodium chloride solutions and with sucrose solutions. The measured enthalpy changes were in excellent agreement with the literature values (7,21). The minimum detectable signal with the modified instrument is approximately 0.2 microwatt and reproducibility is 0.2 percent. It is believed that by use of a statistical treatment of the digital output greater reproducibility may be obtained.

Materials

The sodium dodecyl sulfate was prepared by E. J. Eisenbraun of Oklahoma State University, who used a modification of the procedure of Dreger (2). The starting material was commercial dodecanoic acid. The acid was esterified with diazomethane, and the resulting ester was fractionally distilled through a 1-inch by 14-inch packed column containing perforated 1/4-inch steel saddles. A Teflon spinning band column was also tried, but it was found that the results were comparable. Gas chromatographic analysis using a Carbowax 20M column, 1/4 inch by 10 feet, showed the ester to be free of impurities. It was then reduced with diisobutylaluminum hydride in toluene. The resulting alcohol was distilled and then treated with chlorosulfonic acid to give the half ester. The half ester was neutralized to the sodium salt using the calculated amount of sodium carbonate. It was filtered, recrystallized repeatedly from isopropyl alcohol, filtered again, and then dried overnight at reduced pressure (0.2 mm Hg) at 100° C.

Elemental analysis gave the following results (with the theoretical values in parentheses): carbon, 49.99 (49.98); hydrogen, 8.58 (8.74); sulfur, 10.92 (11.12); and sodium, 8.02 (7.97). The observed critical micelle concentrations from the enthalpy measurements are in excellent agreement with those reported in the literature (16) and indicate a high purity for the sample.

All measurements on a solution were made the same day that the solution was prepared since early experiments showed a change in enthalpy values after 24 hours. This change is believed to result from the reported hydrolysis of the

dodecyl sulfate (10). Any surface water was removed by drying by pumping at room temperature (pressure less than 2×10^{-3} mm Hg) for at least 3 hours. All solutions were made with water distilled from alkaline permanganate solution and were prepared on a mass basis with appropriate corrections for buoyancy. The water was boiled shortly before use in order to remove any dissolved gases which would cause bubbles in the pumping system or calorimeter cells.

The sodium chloride solutions were prepared from Fisher Certified Reagent, Lot 753783, which was dried at 100° C for 4 hours or longer before use. The sodium bromide solutions were prepared from Fisher Certified Reagent, Lot 764930, dried at 110° C for 4 hours before use. Isopropanol solutions were prepared from Fisher Certified A.C.S., Lot 754537, 2-propanol, and n-butanol solutions from Fisher Certified A.C.S., Lot 751188, 1-butanol. Concentrations of all solution prepared for use as background media are considered accurate to at least 0.1 percent.

RESULTS

Tables 1 through 13 present the experimentally determined enthalpies for the dilution of sodium dodecyl sulfate at the conditions listed. In all cases, at least one additional non-significant figure is carried in the tabulated terms to avoid rounding errors. The L_{ϕ} terms are based on equation 8 where at infinite dilution the L_{ϕ} is assigned the value of zero. Tables 14 and 15 include experimental enthalpies for dilutions in higher sodium chloride concentration. A 1-percent NaCl solution corresponds to 0.17158 m and 0.5 percent to 0.0858 m. Measurements below the cmc have not been made owing to the extremely low concentration, so the H_{ϕ} terms are not referenced to the infinitely dilute state but only to a convenient reference point. These dilution measurements are of interest in demonstrating the change in shape of the dilution curve with increasing salt concentration. Values for the cmc at various background conditions are given in table 16. Smoothed values for the L_{ϕ} terms in water at selected molalities are given in table 17. A graphical presentation of the results is given in figures 3 through 9. A dilution which occurs endothermally corresponds to an increase on the ordinate.

TABLE 1. Experimental values of relative apparent molar enthalpies, L_ϕ ,
for sodium dodecyl sulfate in H_2O at $20^\circ C$

Initial molality, $\text{mol (kg } H_2O)^{-1} \times 10^2$	L_ϕ , cal mol^{-1}	Final molality, $\text{mol (kg } H_2O)^{-1} \times 10^2$	L_ϕ , cal mol^{-1}	$\Delta H(\text{measured})$, cal mol^{-1}
8.3978	436.0	4.9637	499.8	63.8
8.3978	436.0	4.1224	514.3	78.3
8.3978	436.0	3.7031	519.2	83.2
7.5677	453.0	4.5068	512.6	59.6
7.5677	453.0	3.7487	516.1	63.1
7.4628	455.0	4.4074	511.3	56.3
7.4628	455.0	4.0333	515.5	60.5
7.4628	455.0	3.6600	517.6	62.6
7.4628	455.0	3.2873	520.4	65.4
7.4628	455.0	2.9153	519.2	64.2
6.8351	469.0	3.3890	521.2	52.2
3.5365	518.0	1.7818	460.3	-57.7
3.5365	518.0	1.6051	438.0	-80.0
3.4948	519.0	2.0722	491.1	-27.9
3.4948	519.0	1.7225	450.4	-68.6
3.4948	519.0	1.5478	429.2	-89.8
3.4948	519.0	1.3733	398.6	-120.4
2.9818	521.0	1.7838	473.7	-47.3
2.9818	521.0	1.4855	420.7	-100.3
2.9818	521.0	1.1875	346.8	-174.2
2.2903	504.0	1.3712	399.2	-104.8
2.2903	504.0	1.1420	328.9	-175.1
2.2903	504.0	1.0275	294.7	-209.3
1.9081	475.0	1.1333	327.9	-147.1
1.9081	475.0	0.9424	256.1	-218.9
1.9081	475.0	0.8470	218.5	-256.5
1.9081	475.0	0.7517	187.1	-287.9
1.7452	455.0	1.0454	296.7	-158.3
1.6908	449.0	1.0128	277.5	-171.5
1.6908	449.0	0.8436	202.2	-246.8
1.3942	404.0	0.8354	207.8	-196.2
0.9854	271.0	0.5858	154.8	-116.2
0.9854	271.0	0.5365	136.1	-134.9
0.9854	271.0	0.4872	128.4	-142.6
0.9854	271.0	0.3887	98.3	-172.7

TABLE 2. Experimental values of relative apparent molar enthalpies, L_ϕ ,
for sodium dodecyl sulfate in H_2O at $25^\circ C$

Initial molality, $\text{mol (kg } H_2O)^{-1} \times 10^2$	L_ϕ , cal mol^{-1}	Final molality, $\text{mol (kg } H_2O)^{-1} \times 10^2$	L_ϕ , cal mol^{-1}	$\Delta H(\text{measured})$, cal mol^{-1}
14.3135	-242.0	8.5446	-133.4	108.6
14.3135	-242.0	7.8244	-116.0	126.0
14.3135	-242.0	7.1076	-95.4	146.6
14.3135	-242.0	6.3924	-76.4	165.6
14.3135	-242.0	5.6805	-48.0	194.0
5.9558	-60.0	2.9592	+72.6	132.6
5.9558	-60.0	1.7687	139.7	199.7
3.2568	+55.0	1.7812	136.7	81.7
3.2568	55.0	1.6209	147.6	92.6
3.2568	55.0	1.4558	156.7	101.7
3.2568	55.0	1.2930	167.4	112.4
3.2568	55.0	1.1306	176.7	121.7
2.5503	93.0	1.2687	167.8	74.8
2.5503	93.0	1.1412	178.0	85.0
2.5503	93.0	1.0140	176.8	83.8
2.5503	93.0	0.7593	170.8	77.8
2.5503	93.0	0.6322	155.0	62.0
2.0835	121.0	1.0432	181.9	60.9
2.0835	121.0	0.9392	176.8	55.8
2.0039	124.0	1.0094	183.2	59.2
2.0039	124.0	0.9092	182.4	58.4
2.0039	124.0	0.8092	176.1	52.1
1.9353	129.0	1.1494	179.4	50.4
1.9353	129.0	1.0527	181.7	52.7
1.9353	129.0	0.9558	180.6	51.6
1.9353	129.0	0.8591	175.2	46.2
1.9353	129.0	0.7625	165.8	36.8
1.5176	154.0	0.9183	179.9	25.9
1.5176	154.0	0.8425	177.2	23.2
1.5176	154.0	0.7666	167.1	13.1
1.5176	154.0	0.6907	160.9	6.9
1.5176	154.0	0.6147	151.0	-3.0
1.0923	176.0	0.6499	149.0	-27.0
1.0923	176.0	0.5406	135.5	-40.5
1.0923	176.0	0.4311	119.1	-56.9

TABLE 3. Experimental values of relative apparent molar enthalpies, L_ϕ ,
for sodium dodecyl sulfate in H_2O at $30^\circ C$

Initial molality, $\text{mol (kg } H_2O)^{-1} \times 10^2$	$-L_\phi$, cal mol^{-1}	Final molality, $\text{mol (kg } H_2O)^{-1} \times 10^2$	$-L_\phi$, cal mol^{-1}	$\Delta H(\text{measured})$, cal mol^{-1}
16.0186	848.0	9.4312	724.2	123.8
16.0186	848.0	8.6262	703.1	144.9
16.0186	848.0	7.8231	678.5	169.5
16.0186	848.0	6.2292	621.4	226.6
10.0113	740.0	5.9079	608.4	131.6
10.0113	740.0	4.9049	556.2	183.8
10.0113	740.0	3.9065	487.6	252.4
5.9850	611.0	3.6056	457.6	153.4
5.9850	611.0	3.0064	398.5	212.5
5.9850	611.0	2.7074	363.2	247.8
5.9850	611.0	2.4085	315.8	295.2
4.1520	503.0	2.4645	327.7	175.3
4.1520	503.0	2.2566	298.4	204.6
4.1520	503.0	2.0491	260.8	242.2
4.1520	503.0	1.8414	217.1	285.9
3.0390	402.0	1.8366	206.3	195.7
3.0390	402.0	1.5322	124.6	277.4
3.0390	402.0	1.3802	76.8	325.2
3.0390	402.0	1.2281	26.9	375.1
1.9947	235.0	1.1883	-1.0	234.0
1.9947	235.0	0.9888	-97.2	332.2
1.9947	235.0	0.8892	-147.2	382.2
1.9947	235.0	0.7895	-168.7	403.7
1.7241	171.0	1.0430	-59.6	230.6
1.7241	171.0	0.9568	-97.6	268.6
1.5185	125.0	0.9189	-139.7	264.7
1.5185	125.0	0.8430	-169.2	294.2
1.5185	125.0	0.7670	-178.1	303.1
1.5185	125.0	0.6911	-172.2	297.2
1.5185	125.0	0.6152	-164.1	289.1
0.9547	-122.0	0.5694	-156.4	34.4
0.9547	-122.0	0.4739	-139.3	17.3
0.9547	-122.0	0.3785	-122.0	0.0
0.7775	-177.0	0.4708	-136.4	-40.6
0.7775	-177.0	0.3931	-124.2	-52.8
0.5489	-153.0	0.2775	-106.8	-46.2
0.5489	-153.0	0.2501	-98.1	-54.9

TABLE 4. Experimental values of relative apparent molar enthalpies, L_ϕ ,
for sodium dodecyl sulfate in H_2O at $35^\circ C$

Initial molality, $\text{mol (kg } H_2O)^{-1} \times 10^2$	$-L_\phi$, cal mol^{-1}	Final molality, $\text{mol (kg } H_2O)^{-1} \times 10^2$	$-L_\phi$, cal mol^{-1}	$\Delta H(\text{measured})$, cal mol^{-1}
17.4625	1422.0	10.3733	1287.1	134.9
17.4625	1422.0	8.6200	1236.4	185.6
17.4625	1422.0	6.8807	1167.0	255.0
7.5743	1196.0	4.5412	1012.8	183.2
7.5743	1196.0	3.7825	936.8	259.2
7.5743	1196.0	3.0262	828.6	367.4
4.5478	1013.0	2.7233	772.5	240.5
4.5478	1013.0	2.5064	723.8	289.2
4.5478	1013.0	2.2795	662.7	350.3
4.5478	1013.0	1.8256	517.0	496.0
2.1332	613.0	1.2752	205.7	407.3
2.1332	613.0	1.0618	36.3	576.7
2.1332	613.0	0.8485	-186.1	799.1
1.6057	402.0	0.9602	-77.0	479.0
1.6057	402.0	0.8799	-154.2	556.2
1.6057	402.0	0.7996	-197.4	599.4
1.6057	402.0	0.7193	-183.8	585.8
1.6057	402.0	0.6392	-177.0	579.0
1.1059	83.0	0.6616	-179.3	262.3
1.1059	83.0	0.5510	-163.5	246.5
1.1059	83.0	0.4404	-144.2	227.2
0.8185	-197.0	0.4941	-153.9	-43.1
0.8185	-197.0	0.4122	-143.2	-53.8
0.7434	-189.0	0.4451	-149.0	-40.0
0.7434	-189.0	0.3706	-131.3	-57.7

TABLE 5. Experimental values of relative apparent molar enthalpies, L_{ϕ} ,
for sodium dodecyl sulfate in 0.001 m NaCl at 20° C

Initial molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	L_{ϕ} , cal mol^{-1}	Final molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	L_{ϕ} , cal mol^{-1}	$\Delta H(\text{measured})$, cal mol^{-1}	$-\Sigma$, cal mol^{-1}
5.7825	523.0	3.4209	556.5	-33.9	0.4
5.7825	523.0	2.8419	553.0	-30.5	0.5
5.7825	523.0	2.2646	539.2	-16.9	0.7
2.9442	555.0	1.7467	503.5	+51.0	0.5
2.9442	555.0	1.4521	453.5	100.9	0.6
2.9442	555.0	1.3049	424.2	130.0	0.8
2.9442	555.0	1.1579	384.5	169.6	0.9
2.9370	552.0	1.7513	510.8	40.7	0.5
2.9370	552.0	1.4574	453.6	97.8	0.6
2.9370	552.0	1.3106	431.1	120.2	0.7
2.9370	552.0	1.1639	387.3	163.8	0.9
1.8731	519.0	1.1125	360.8	157.7	0.5
1.8731	519.0	0.9251	267.7	250.6	0.7
1.8731	519.0	0.8315	218.5	299.7	0.8
1.8731	519.0	0.7379	173.3	344.7	1.0
1.1407	382.0	0.6780	171.2	210.2	0.6
1.1407	382.0	0.5639	141.4	239.8	0.8
1.1407	382.0	0.5069	119.5	261.6	0.9
1.1407	382.0	0.4499	103.7	277.3	1.0
0.7717	202.0	0.3453	85.0	116.1	0.9
0.7717	202.0	0.3068	65.5	135.5	1.0

TABLE 6. Experimental values of relative apparent molar enthalpies, L_ϕ ,
for sodium dodecyl sulfate in 0.01 m NaCl at 20° C

Initial molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	L_ϕ , cal mol^{-1}	Final molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	L_ϕ , cal mol^{-1}	$\Delta H(\text{measured})$, cal mol^{-1}	$-\Sigma$, cal mol^{-1}
7.4891	363.0	4.4497	412.7	-51.4	1.7
7.4891	363.0	3.6700	417.9	-57.3	2.4
7.4891	363.0	3.3256	422.0	-61.7	2.7
4.6008	406.0	2.3166	418.1	-14.4	2.3
4.6008	406.0	2.0867	411.9	-8.5	2.6
4.6008	406.0	1.8570	407.6	-4.6	3.0
2.2417	417.0	1.3559	373.1	42.4	1.5
2.2417	417.0	1.2437	353.3	61.9	1.8
2.2417	417.0	1.1316	338.4	76.6	2.0
2.2417	417.0	1.0195	317.0	97.7	2.3
2.2417	417.0	0.9075	298.5	115.9	2.6
2.0865	412.0	1.2392	358.3	52.2	1.5
2.0865	412.0	1.0305	321.4	88.6	2.0
2.0865	412.0	0.9262	295.5	114.2	2.3
2.0865	412.0	0.8219	267.7	141.7	2.6
1.5064	384.0	0.8243	271.4	111.0	1.6
1.5064	384.0	0.7490	243.9	138.3	1.8
1.5064	384.0	0.6737	211.1	170.9	2.0
1.5064	384.0	0.5984	181.1	200.7	2.2
1.1233	337.0	0.6801	209.3	126.5	1.2
1.1233	337.0	0.5677	159.2	176.3	1.5
1.1233	337.0	0.4554	108.9	226.2	1.9
1.0252	320.0	0.6094	161.0	157.8	1.2
1.0252	320.0	0.5582	126.8	191.9	1.3
0.9918	312.0	0.6005	166.7	144.2	1.1
0.9918	312.0	0.5013	129.7	180.9	1.4
0.9918	312.0	0.4517	96.7	213.7	1.6
0.9918	312.0	0.4022	83.3	226.9	1.8
0.7334	221.0	0.4359	114.4	105.6	1.0
0.7334	221.0	0.3993	95.9	124.0	1.1
0.7334	221.0	0.3626	76.1	143.7	1.2
0.7334	221.0	0.2893	50.4	169.1	1.5
0.5339	130.0	0.3175	88.2	41.0	0.8
0.5339	130.0	0.2641	50.1	78.9	1.0

TABLE 7. Experimental values of relative apparent molar enthalpies, L_ϕ ,
for sodium dodecyl sulfate in 0.001 m NaCl at 30° C

Initial molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	$-L_\phi$, cal mol^{-1}	Final molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	L_ϕ , cal mol^{-1}	$\Delta H(\text{measured})$, cal mol^{-1}	$-\Sigma$, cal mol^{-1}
8.1913	608.0	4.9330	-479.5	128.9	0.4
8.1913	608.0	4.1121	-430.0	178.6	0.6
8.1913	608.0	3.2944	-367.2	241.7	0.9
8.1913	608.0	2.8868	-326.9	282.1	1.0
5.7949	522.0	2.9173	-329.1	193.6	0.7
5.7949	522.0	2.3389	-252.7	270.2	0.9
3.9501	419.0	2.3886	-262.3	157.2	0.5
3.9501	419.0	1.9932	-193.3	226.4	0.7
3.9501	419.0	1.5985	-108.5	311.4	0.9
3.9501	419.0	1.4014	-60.2	359.9	1.1
3.4245	378.0	1.7291	-135.2	243.5	0.7
3.4245	378.0	1.3869	-41.3	337.6	0.9
1.8480	165.0	1.1197	+54.6	220.2	0.6
1.8480	165.0	0.9349	140.4	306.2	0.8
1.6932	134.0	1.0262	93.2	227.7	0.5
1.6932	134.0	0.9415	130.6	265.2	0.6
1.6932	134.0	0.8568	173.3	308.0	0.7
1.6932	134.0	0.6875	218.0	352.9	0.9
1.5214	86.0	0.7700	201.1	287.7	0.6
1.5214	86.0	0.6179	196.0	282.8	0.8
1.4280	67.0	0.8651	175.1	242.6	0.5
1.4280	67.0	0.7937	192.2	259.8	0.6
1.4280	67.0	0.7228	214.0	281.7	0.7
1.4280	67.0	0.6514	209.1	276.8	0.7
1.4280	67.0	0.5801	192.2	260.1	0.9
1.4280	67.0	0.5087	190.6	258.6	1.0

TABLE 8. Experimental values of relative apparent molar enthalpies, L_ϕ ,
for sodium dodecyl sulfate in 0.01 m NaCl at 30° C

Initial molality, mol (kg H ₂ O) ⁻¹ × 10 ²	- L_ϕ , cal mol ⁻¹	Final molality, mol (kg H ₂ O) ⁻¹ × 10 ²	- L_ϕ , cal mol ⁻¹	ΔH (measured), cal mol ⁻¹	- Σ , cal mol ⁻¹
8.6855	740.0	5.6178	663.2	78.5	1.7
8.6855	740.0	5.1815	647.0	95.0	2.0
8.6855	740.0	4.3114	612.2	130.5	2.7
7.3724	717.0	4.3436	613.8	105.3	2.1
7.3724	717.0	3.9742	593.9	125.5	2.4
7.3724	717.0	3.6053	575.2	144.6	2.8
7.3724	717.0	3.2372	552.0	168.3	3.3
7.3724	717.0	2.8696	522.7	198.0	3.7
4.3008	613.0	2.5408	495.0	120.1	2.1
4.3008	613.0	2.1104	444.7	171.1	2.8
4.3008	613.0	1.6808	378.1	238.5	3.6
3.1180	544.0	1.8687	408.3	137.6	1.9
3.1180	544.0	1.5568	347.5	199.1	2.6
3.1180	544.0	1.4008	315.3	231.6	2.9
3.1180	544.0	1.2451	267.3	280.0	3.3
2.6733	507.0	1.6858	375.7	133.0	1.7
2.6733	507.0	1.4183	319.6	189.7	2.3
2.6733	507.0	1.1511	238.2	271.8	3.0
1.5779	358.0	0.9344	155.3	204.4	1.7
1.5779	358.0	0.8554	109.0	250.9	1.9
1.5779	358.0	0.7765	73.0	287.1	2.1
1.5779	358.0	0.6976	19.5	340.9	2.4
1.5779	358.0	0.6188	-30.0	390.7	2.7
1.2051	257.0	0.7235	+31.1	227.3	1.4
1.2051	257.0	0.6030	-48.8	307.7	1.9
1.2051	257.0	0.4825	-102.5	361.8	2.3
1.2051	257.0	0.4223	-102.1	361.7	2.6
1.2051	257.0	0.3621	-88.7	348.5	2.8
1.0409	203.0	0.5209	-67.6	272.3	1.7
1.0409	203.0	0.4689	-99.9	304.8	1.9
1.0409	203.0	0.4169	-100.1	305.3	2.2
1.0409	203.0	0.3648	-110.5	315.9	2.4

TABLE 9. Experimental values of relative apparent molar enthalpies, L_ϕ ,
for sodium dodecyl sulfate in 0.01 m NaBr at 30° C

Initial molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	$-L_\phi$, cal mol^{-1}	Final molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	$-L_\phi$, cal mol^{-1}	$\Delta H(\text{measured})$, cal mol^{-1}	$-\Sigma$, cal mol^{-1}
8.1459	732.0	4.9402	642.7	91.6	2.3
8.1459	732.0	4.1238	602.9	132.4	3.3
8.1459	732.0	3.3106	555.3	181.2	4.5
5.1204	645.0	3.1139	541.2	106.6	2.8
5.1204	645.0	2.6012	496.7	152.1	3.8
5.1204	645.0	2.0897	438.5	211.5	5.0
3.3011	556.0	2.0043	433.6	125.2	2.8
3.3011	556.0	1.6737	373.6	186.2	3.8
3.3011	556.0	1.3440	291.4	269.4	4.8
2.7091	510.0	1.6512	377.9	134.8	2.7
2.7091	510.0	1.3801	309.2	204.3	3.5
2.7091	510.0	1.1093	224.0	290.5	4.5
2.2380	463.0	1.3646	317.2	148.2	2.4
2.2380	463.0	1.1407	240.8	225.5	3.3
2.2380	463.0	0.9170	136.7	330.4	4.1
1.6951	382.0	0.8611	115.4	269.2	2.6
1.6951	382.0	0.6917	17.1	368.4	3.5
1.6951	382.0	0.6070	-5.9	392.0	4.1
1.2024	257.0	0.6112	-28.5	287.9	2.4
1.2024	257.0	0.4910	-86.0	345.5	2.5
1.2024	257.0	0.4309	-106.6	367.1	3.5

TABLE 10. Experimental values of relative apparent molar enthalpies, L_ϕ ,
for sodium dodecyl sulfate in 5 percent n-butanol at 20° C

Initial molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	$-L_\phi$, cal mol^{-1}	Final molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	$-L_\phi$, cal mol^{-1}	$\Delta H(\text{measured})$, cal mol^{-1}
6.8692	3330.0	4.1540	2471.2	858.8
6.8692	3330.0	3.4664	2181.9	1148.1
6.8692	3330.0	3.1230	2045.3	1284.7
6.8692	3330.0	2.7800	1849.5	1480.5
2.8245	1884.0	1.7117	1089.6	794.4
2.8245	1884.0	1.4292	862.6	1021.4
2.8245	1884.0	1.1468	588.7	1295.3
2.2322	1500.0	1.3533	779.6	720.4
2.2322	1500.0	1.1300	558.0	942.0
2.2322	1500.0	1.0184	451.9	1048.1
2.2322	1500.0	0.9068	314.7	1185.3
1.0412	515.0	0.6316	-3.0	518.0
1.0412	515.0	0.5275	-123.3	638.3
1.0412	515.0	0.4754	-187.3	702.3
1.0412	515.0	0.4234	-259.0	774.0
0.8726	240.0	0.5294	-172.9	412.9
0.8726	240.0	0.4421	-249.5	489.5
0.8726	240.0	0.3985	-295.3	535.3
0.8726	240.0	0.3549	-321.8	561.8
0.4851	-170.0	0.2944	-270.8	100.8
0.4851	-170.0	0.2459	-225.3	55.3
0.4851	-170.0	0.2216	-170.0	0.0

TABLE 11. Experimental values of relative apparent molar enthalpies, L_{ϕ} ,
for sodium dodecyl sulfate in 5 percent n-butanol at 25° C

Initial molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	$-L_{\phi}$, cal mol^{-1}	Final molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	$-L_{\phi}$, cal mol^{-1}	$\Delta H(\text{measured})$, cal mol^{-1}
7.3073	3757.0	4.1035	2850.2	906.8
7.3073	3757.0	3.7379	2712.2	1044.8
7.3073	3757.0	3.3726	2571.1	1185.9
7.3073	3757.0	3.0077	2389.8	1367.2
6.2772	3528.0	3.8352	2756.3	771.7
6.2772	3528.0	3.2068	2500.1	1027.9
6.2772	3528.0	2.5795	2185.6	1342.4
5.7031	3408.0	3.4855	2615.4	792.6
5.7031	3408.0	2.9146	2363.2	1044.8
5.7031	3408.0	2.3447	2018.4	1389.6
2.5006	2124.0	1.5308	1395.3	728.7
2.5006	2124.0	1.4057	1262.8	861.2
2.5006	2124.0	1.2807	1170.5	953.5
2.5006	2124.0	1.0307	880.0	1244.0
1.4246	1300.0	0.8726	679.8	620.2
1.4246	1300.0	0.7301	487.4	812.6
1.4246	1300.0	0.5877	294.6	1005.4
1.3387	1218.0	0.8200	592.7	625.3
1.3387	1218.0	0.6861	438.4	779.6
1.3387	1218.0	0.5523	201.0	1017.0
1.1210	990.0	0.6868	440.2	549.8
1.1210	990.0	0.6307	363.4	626.6
1.1210	990.0	0.5747	295.7	694.3
1.1210	990.0	0.5186	207.4	782.6
1.1210	990.0	0.4626	77.8	912.2
0.9845	822.0	0.6032	306.8	515.2
0.9845	822.0	0.5540	225.0	597.0
0.9845	822.0	0.5048	166.8	655.2
0.9845	822.0	0.4555	96.1	725.9
0.9845	822.0	0.4063	-6.9	828.9
0.4541	80.0	0.2783	-171.4	251.4
0.4541	80.0	0.2556	-184.1	264.1
0.4541	80.0	0.2329	-209.8	289.8
0.4541	80.0	0.2102	-207.6	287.6
0.4541	80.0	0.1875	-173.6	253.6

TABLE 12. Experimental values of relative apparent molar enthalpies, L_{ϕ} ,
for sodium dodecyl sulfate in 5 percent i-propanol at 20° C

Initial molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	L_{ϕ} , cal mol^{-1}	Final molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	L_{ϕ} , cal mol^{-1}	$\Delta H(\text{measured})$, cal mol^{-1}
5.5623	25.0	3.3662	291.2	266.2
5.5623	25.0	2.8095	370.0	345.0
5.5623	25.0	2.5315	415.4	390.4
3.1917	303.0	1.9340	530.9	227.9
3.1917	303.0	1.6147	581.1	278.1
3.1917	303.0	1.4552	599.8	296.8
3.1917	303.0	1.2957	636.2	333.2
2.6804	390.0	1.6246	589.4	199.4
2.6804	390.0	1.3565	622.8	232.8
2.6804	390.0	1.2225	635.6	245.6
2.6804	390.0	1.0885	637.9	247.9
1.3406	627.0	0.8132	590.9	-36.1
1.3406	627.0	0.6791	473.5	-153.5
1.3406	627.0	0.6120	414.8	-212.2
1.3406	627.0	0.5450	320.6	-306.4
1.0593	635.0	0.6425	421.8	-213.2
1.0593	635.0	0.5367	286.4	-348.6
1.0593	635.0	0.4837	211.8	-423.2
1.0593	635.0	0.4307	146.9	-488.1
0.9402	625.0	0.4764	183.7	-441.3
0.9402	625.0	0.4294	142.6	-482.4
0.9402	625.0	0.3824	111.7	-513.3
0.8397	605.0	0.5094	249.3	-355.7
0.8397	605.0	0.4674	185.0	-420.0
0.8397	605.0	0.4255	118.1	-486.9
0.8397	605.0	0.3835	108.4	-496.6
0.8397	605.0	0.3415	89.0	-516.0

TABLE 13. Experimental values of relative apparent molar enthalpies, L_{ϕ} ,
for sodium dodecyl sulfate in 5 percent i-propanol at 30° C

Initial molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	$-L_{\phi}$, cal mol^{-1}	Final molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	$-L_{\phi}$, cal mol^{-1}	$\Delta H(\text{measured})$, cal mol^{-1}
10.8810	1746.0	6.4898	1441.3	304.7
10.8810	1746.0	5.4001	1326.7	419.3
10.8810	1746.0	4.8564	1259.1	486.9
10.8810	1746.0	4.3138	1183.0	563.0
5.3492	1322.0	3.7073	1084.4	237.6
5.3492	1322.0	2.6355	837.4	484.6
5.3492	1322.0	2.1011	667.5	654.5
5.3492	1322.0	1.5679	454.2	867.8
2.7709	875.0	1.6467	495.0	380.0
2.7709	875.0	1.3689	358.4	516.6
2.7709	875.0	1.0920	199.0	676.0
2.7709	875.0	0.8151	13.9	861.1
2.4921	797.0	1.4926	408.6	388.4
2.4921	797.0	1.2434	273.1	523.9
2.4921	797.0	0.9942	114.6	682.4
2.4921	797.0	0.7454	-73.0	870.0
1.9182	602.0	0.9479	+82.8	519.2
1.9182	602.0	0.7562	-43.4	645.4
1.2952	320.0	0.6404	-118.9	438.9
1.2952	320.0	0.5109	-139.1	459.1
1.2952	320.0	0.3815	-88.1	408.1
1.1955	253.0	0.7107	-94.2	347.2
1.1955	253.0	0.5912	-137.9	390.9
1.1955	253.0	0.4716	-125.2	378.2
1.1955	253.0	0.3522	-61.7	314.7
1.1124	200.0	0.4445	-129.5	329.5
1.1124	200.0	0.3333	-87.0	287.0
1.0202	144.0	0.6117	-128.3	272.3
1.0202	144.0	0.5097	-147.2	291.2
1.0202	144.0	0.4076	-97.4	241.4
1.0202	144.0	0.3566	-83.7	227.7

TABLE 14. Experimental values of apparent molar enthalpies, H_{ϕ} , for sodium dodecyl sulfate in 0.0858 m NaCl at 30° C

Initial molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	$-H_{\phi}$, cal mol^{-1}	Final molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	$-H_{\phi}$, cal mol^{-1}	$\Delta H(\text{measured})$, cal mol^{-1}	$-\Sigma$, cal mol^{-1}
11.0138	493.0	7.1261	459.4	36.7	3.1
11.0138	493.0	6.5723	452.2	44.4	3.6
11.0138	493.0	5.4687	436.2	61.5	4.7
11.0138	493.0	4.3696	413.9	85.0	5.9
6.4875	450.0	3.8723	399.7	53.1	2.8
6.4875	450.0	3.2227	379.4	74.2	3.6
6.4875	450.0	2.5749	355.0	99.5	4.5
6.4875	450.0	1.9286	321.2	134.2	5.4
5.3764	434.0	3.2498	387.3	49.2	2.5
5.3764	434.0	2.7116	368.0	69.2	3.2
5.3764	434.0	2.1745	342.3	95.6	3.9
3.4225	390.0	2.0545	331.9	59.9	1.8
3.4225	390.0	1.7121	304.7	87.6	2.3
3.4225	390.0	1.3701	268.6	124.3	2.9
3.4225	390.0	1.1993	240.1	153.0	3.1
3.2604	387.0	1.6248	307.4	81.9	2.3
3.2604	387.0	1.2989	271.2	118.6	2.8
2.4005	349.0	1.4375	278.4	72.0	1.4
2.4005	349.0	1.1974	247.5	103.3	1.8
2.4005	349.0	0.9574	210.9	140.3	2.2
1.5992	290.0	0.9551	196.5	94.5	1.0
1.5992	290.0	0.7951	154.3	137.0	1.3
1.2080	255.0	0.7217	147.2	108.6	0.8
1.2080	255.0	0.6008	99.8	156.2	1.0
1.2080	255.0	0.4801	23.9	232.3	1.2

TABLE 15. Experimental values of apparent molar enthalpies, H_{ϕ} , for sodium dodecyl sulfate in 0.17158 m NaCl at 30° C

Initial molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	$-H_{\phi}$, cal mol^{-1}	Final molality, $\text{mol (kg H}_2\text{O)}^{-1} \times 10^2$	$-H_{\phi}$, cal mol^{-1}	$\Delta H(\text{measured})$, cal mol^{-1}	$-\Sigma$, cal mol^{-1}
9.4616	1020.0	6.7131	997.9	24.1	2.0
9.4616	1020.0	5.7608	989.0	33.7	2.7
9.4616	1020.0	4.8118	974.4	49.1	3.5
9.4616	1020.0	3.8669	956.1	68.2	4.3
9.4616	1020.0	2.9266	935.2	90.0	5.2
5.9112	991.0	3.5156	954.7	38.3	2.0
5.9112	991.0	2.9236	935.2	58.4	2.6
5.9112	991.0	2.6282	923.7	70.2	2.9
5.9112	991.0	2.3332	915.2	79.0	3.2
3.1335	942.0	1.5454	867.9	75.7	1.6
3.1335	942.0	1.2323	836.7	107.2	1.9
3.1335	942.0	0.9197	790.9	153.3	2.2
2.7522	929.0	1.6859	871.5	58.5	1.0
2.7522	929.0	1.4103	856.1	74.2	1.3
2.7522	929.0	1.1352	821.0	109.6	1.6
2.7522	929.0	0.8604	776.9	154.0	1.9
1.8890	883.0	1.3471	847.6	36.0	0.6
1.8890	883.0	1.1579	827.7	56.1	0.8
1.8890	883.0	0.9689	797.4	86.6	1.0
1.8890	883.0	0.7801	752.7	131.5	1.2
1.8890	883.0	0.5914	693.6	190.8	1.4
0.9709	800.0	0.4801	639.9	160.6	0.5
0.9709	800.0	0.3830	562.2	238.4	0.6
0.9709	800.0	0.2860	445.1	355.6	0.7
0.5134	660.0	0.3053	514.1	146.1	0.2
0.5134	660.0	0.2540	377.2	283.1	0.3
0.5134	660.0	0.1513	88.4	572.0	0.4
0.4000	580.0	0.1979	224.3	355.9	0.2
0.4000	580.0	0.1179	4.3	576.0	0.3
0.4000	580.0	0.0979	-6.9	587.2	0.3

TABLE 16. Critical micelle concentrations for sodium dodecyl sulfate

<u>Background</u>	<u>cmc, mol (kg H₂O)⁻¹ × 10³, ±0.5</u>			
	<u>20° C</u>	<u>25° C</u>	<u>30° C</u>	<u>35° C</u>
H ₂ O	8.1	8.3	8.4	8.3
0.001 m NaCl	7.4	-	7.8	-
0.01 m NaCl	4.4	-	4.9	-
0.01 m NaBr	-	-	4.8	-
5% i-Propanol	4.4	-	5.2	-
5% n-Butanol	3.6	2.5	-	-

TABLE 17. Selected values for sodium dodecyl sulfate

<u>Molality,</u> <u>mol kg⁻¹</u>	<u>L_φ, cal mol⁻¹</u>			
	<u>20° C</u>	<u>25° C</u>	<u>30° C</u>	<u>35° C</u>
0.0	0	0	0	0
0.005	130	141	154	158
cmc	199	169	195	197
0.010	279	182	101	31
0.015	421	154	-99	-327
0.020	484	125	-224	-574
0.025	511	97	-317	-724
0.030	520	72	-387	-827
0.035	520	46	-437	-904
0.040	516	22	-479	-964
0.045	507	0	-515	-1011
0.050	501	-18	-548	-1053
0.055	493	-41	-574	-1089
0.060	484	-62	-600	-1121
0.065	474	-79	-620	-1149
0.070	465	-92	-639	-1174
0.075	454	-106	-656	-1194
0.080	444	-119	-671	-1214

FIGURE 3. Sodium Dodecyl Sulfate Enthalpy Curves at Various Temperatures.

FIGURE 4. Sodium Dodecyl Sulfate Enthalpy Curves in Salt Background.

FIGURE 5. Sodium Dodecyl Sulfate Enthalpy Curves in High Salt Concentration Background.

FIGURE 6. Sodium Dodecyl Sulfate Enthalpy Curves in 5 Percent n-Butanol.

FIGURE 7. Sodium Dodecyl Sulfate Enthalpy Curves in 5 Percent i-Propanol.

FIGURE 8. Sodium Dodecyl Sulfate Below the CMC.

FIGURE 9. Sodium Dodecyl Sulfate Enthalpy Curve at 20° C.

DISCUSSION

Observations

Figure 3 shows the strong temperature dependence of the enthalpy of micellization of sodium dodecyl sulfate. Although the cmc is only slightly temperature dependent, the enthalpy terms demonstrate a strong dependence on temperature for the formation of the sodium dodecyl sulfate micelle. There is a slight temperature dependence below the cmc as the results of table 17 demonstrate. Figure 8 shows at 25° C that there is a slight increase in the slope of the $L\phi$ curve at the cmc. This increase is more evident in the 20° C results shown in figure 9. At higher temperatures, 30° and 35° C, the curves fall off sharply at the cmc.

A salt background has considerable effect on the dilution enthalpy curves as shown in figures 4 and 5. The cmc is lowered, and the curves are changed. In higher salt concentrations (figure 5), the curves drop off over a narrow concentration range and level off, whereas in lower salt concentrations the falloff is more gradual and leveling off occurs at higher concentrations of surfactant. This seems to indicate a higher degree of stability in high salt concentration which would be expected because of the additional cation ability to neutralize the charge environment of the micelle. Measurements with 0.01 m NaBr background give a congruent curve with the 0.01 m NaCl results indicating that the anion has little influence on the interactions of the micelle.

Alcohols as cosurfactants have considerable effect on the enthalpy terms. The phenomena of solubilization of the micelle and its monomers is still poorly understood. Qualitatively it is observed that the longer chain alcohols increase the solubility of the surfactant more so than the shorter chain alcohols. This is most likely owing to an increased ability to shield the hydrocarbon tail of the surfactant from water molecules. Work on sodium dodecyl sulfonate currently in progress shows similar results with those in figures 6 and 7.

The results for the premicellar region have raised several questions regarding the possible existence of a dimer below the cmc. The results seem to indicate that below the cmc a dimer is present rather than a monomer. The slopes of the dilution enthalpy curve, shown in figure 8, do not approach the Debye-Huckel limiting law slope for 1:1 charge

type electrolytes. Additional terms associated with ion size parameters in extended fitting equations give an even larger discrepancy since the larger the ion, the smaller the slope of the theoretical L_ϕ curve. It is of considerable interest that the measured terms approach the slope of a 1:2 electrolyte. If the L_ϕ terms are plotted against $(m/2)^{\frac{1}{2}}$, assuming complete dimerization, the results lie on the 1:2 electrolyte curve. The formation of a dimer below the cmc has been speculated numerous times in the literature. These speculations have considered the possibility of a monomer-dimer equilibrium. The results reported here would suggest an irreversible dimer being the only species below the cmc. Such a species would not be detectable using conventional methods used for study below the cmc since the dimer would give a linear relationship for properties such as conductivity, surface tension, and viscosity. While calorimetric measurements in the low concentration region are difficult, the uncertainties are not large enough to allow the data to be forced into fitting the 1:1 electrolyte pattern. If the dimer does exist it is most likely a hydrocarbon tail overlap with the polar head groups having a maximum charge separation. Many questions regarding the monomer (or dimer) equilibria with the micelle remain unanswered. The hypothesis of a dimer is one possible answer to problems raised by several other investigations. Additional work in the premicellar region is being carried out with other anionic surfactants.

Earlier Measurements

One of the major difficulties in comparing thermodynamic measurements of micellization enthalpies results from the lack of data reported in the literature. Numerous calorimetric studies have been made; however, in many cases, the measured enthalpies have been mathematically manipulated to give a value for the enthalpy of micellization. Such manipulation, while valuable in testing theories, obscures the fact that the researchers may have used different methods to treat their data. As a result, each method may produce a different value. The methods briefly summarized are:

$$\begin{aligned} L_\phi (\text{above cmc}) - L_\phi (\text{below cmc}) &, \\ L_\phi (\text{above cmc}) - L_\phi^\circ &, \\ L_\phi (\text{above cmc}) - \Delta H (\text{ion-pairing}) - L_\phi (\text{dilution}) &, \\ \bar{L} (\text{above cmc}) - \bar{L} (\text{below cmc}) &, \\ \bar{L} (\text{above cmc}) - \bar{L}^\circ &, \\ \bar{L} (\text{above cmc}) - \Delta H (\text{ion-pairing}) &, \end{aligned}$$

where $\bar{L}$ terms are partial molal enthalpies, and another method which calculates the enthalpy for adding 1 mole of monomer to the micelle.

The results reported here for the premicellar region are in good agreement with the results presented graphically by Birch and Hall (1). Since they report no experimental values,

it is not possible to make direct numerical comparisons of the values for the L_ϕ terms. The large deviation from the Debye-Huckel limiting law observed in their results is also seen in the results reported here.

The work of Skewis and Zettlemoyer (25-26) on sodium dodecyl sulfate adsorption on graphon surfaces includes several measurements of dilution enthalpies for the surfactant. The results are in agreement with our results, but their measurements have a larger uncertainty associated with them.

The work of Pilcher (22) includes measurements of the enthalpies of dilution and mixing of sodium dodecyl sulfate. He reports a value of $-(55 \pm 2)$ cal mol⁻¹ for the dilution below the cmc to infinite dilution at 23° C. This value is in disagreement with our values below the cmc; however, we obtain a value of -50 cal mol⁻¹ for dilution from below the cmc to a concentration equal to half the cmc. His notation for micellization

$$2\{0, 1\} = \{1, 1\} + \{0, 0\} \quad (10)$$

converts to

for which he obtains -609 cal mol⁻¹ at 30° C. The results reported here give -630 cal mol⁻¹ for the same reaction. At 25° C the agreement is much poorer. He reports +87 cal mol⁻¹ versus -40 cal mol⁻¹ using table 17. In Pilcher's work, the sample was recovered from solution, and at the end of the series of measurements a purity check did indicate a minimum in the surface tension versus concentration curve. The investigators did not feel that this produced a significant error in the results. No attempts to avoid hydrolysis are mentioned.

The value of Eatough and Rehfeld (3) for the enthalpy of micellization at the cmc is 0.52 ± 0.04 kcal mol⁻¹ at 25° C. They have separated their calorimetric titration heat effect into an enthalpy of micellization and an enthalpy of ion pairing and have derived an ion-pairing equilibrium constant. No correction for dilution of the monomer below the cmc is used in their work. The separation of the micellization from the ion pairing is dependent on activity coefficients and micelle number. For the present, we prefer to report enthalpy of micellization values without correction for the ion pairing. It is obvious that ion pairing does occur since the presence of a clump of 50 to 60 charge units (3) existing freely in solution is electrostatically highly unfavorable. The question of how the charge is neutralized and to what extent is still unanswered. Eatough and Rehfeld's graphical presentation of measurements by "conventional" calorimetry are in good agreement with the values reported in table 2.

The calorimetric study of Paredes (20) gives a value of 162 cal mol⁻¹ for the enthalpy of micellization at 25° C. This value is obtained after considerable mathematical treatment to separate dilution terms for the monomer and the micelle. The general shape of their enthalpy measurement curve is in agreement with our results. However, an exact

comparison is not possible because of uncertainty in the interpretation of their graphs. Their mathematical determination of enthalpies of dilution is open to question, particularly since the equation which they describe as "Owen's equation" cannot be obtained from the equations given by Owen (19).

The 1956 work of Goddard and Benson (5) on enthalpies of solution of sodium dodecyl sulfate to give final solutions of different concentrations was re-examined by the original authors (5) in 1957. They state that the work should be repeated to eliminate several errors in the measurements; however, no later measurements have been located in the literature.

Comparison of the average heat capacities calculated here with the measured values of Musbally, Perron, and Desnoyers (17) shows good agreement in the shape of the heat capacity versus concentration curve. A small shift of $-11 \text{ cal K}^{-1} \text{ mol}^{-1}$ in their C_{ϕ}° brings the results into excellent agreement. In a 1976 paper by the same authors (18), a value of $-126.7 \text{ cal K}^{-1} \text{ mol}^{-1}$ is given in contrast to the value of $-123.3 \text{ cal K}^{-1} \text{ mol}^{-1}$ in the original work. The $-112 \text{ cal K}^{-1} \text{ mol}^{-1}$ calculated here is in good agreement with their value of $-110 \text{ cal K}^{-1} \text{ mol}^{-1}$ from a recalculation of their results with a shift of C_{ϕ}° . The value is strongly dependent on the method of calculating ΔC_m , whether from differences in

$$C_{\phi} \text{ (above cmc)} - C_{\phi}^{\circ}, \quad (12)$$

$$C_{\phi} \text{ (above cmc)} - C_{\phi} \text{ (below cmc)}, \quad (13)$$

$$\bar{C} \text{ (above cmc)} - \bar{C}^{\circ}, \text{ or} \quad (14)$$

$$\bar{C} \text{ (above cmc)} - \bar{C} \text{ (below cmc)} \quad (15)$$

where $\bar{C}$'s are partial molal heat capacities and C_{ϕ} 's are apparent heat capacities.

The value for the change in heat capacity of micellization of $-134 \text{ cal K}^{-1} \text{ mol}^{-1}$ reported by Kresheck and Hargraves (12) using a titration calorimeter is in excellent agreement with the results reported here using relationship 15. Use of their method of calculating the enthalpy of micellization ($\bar{H} \text{ (above cmc)} - \bar{H}^{\circ}$) on the results reported here gives values of $-0.46 \text{ kcal mol}^{-1}$ at 25° C , $-0.92 \text{ kcal mol}^{-1}$ at 30° C , $-1.58 \text{ kcal mol}^{-1}$ at 35° C in excellent agreement with their values of -0.51 , -0.96 , and -1.69 . Their solutions were pH adjusted, and no mention is made of attempts to avoid hydrolysis (8).

PLANNED STUDIES

Future work in the area of thermodynamics of surfactant systems will concentrate on alkyl and alkyl aromatic sulfonates of the type commonly found in petroleum sulfonates. The effects of cosurfactant and brine backgrounds will be explored. Studies are planned with mixed micellar systems and with micelles in hydrocarbon backgrounds. Work on adsorption of surfactants on clay and sand surfaces is in progress.

SUMMARY

A microcalorimeter system has been assembled and put into operation for a study of micellar systems. Dilution enthalpy measurements on sodium dodecyl sulfate over a temperature range of 20° to 35° C in several background media are reported. Questions regarding the behavior of the dilution curves have been raised and possible qualitative explanations given.

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