Density, Speed of Sound, Surface Tension, and Electrical Conductivity of Sodium Dodecanoate Aqueous Solutions from $T = (293.15 \text{ to } 323.15)$ K

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Density, surface tension, electric conductivity, and speed of sound of sodium dodecanoate (sodium laurate) aqueous solutions have been determined. Also, isentropic compressibility was calculated. The influence of surfactant concentration and temperature upon these physical properties has also been studied. The experimental values of several physical properties have been employed to determine the critical micellar concentration for this system.

Introduction

Aqueous surfactant solutions that could possess a dual character (hydrophilic and hydrophobic) are employed in different industrial applications.[1] These applications (i.e., pharmaceutical, cosmetic, or cleaning products) use the special characteristics generated by the presence of this kind of substance on physical properties, such as the diminution of surface tension.[2] An important relevant characteristic of these colloidal systems, which have generated a great number of applications and research studies, is the aggregation phenomenon that is produced under certain experimental conditions. Aggregation phenomena can produce different kinds of aggregates, most importantly, micelles[3] and microemulsions.[4]

Sodium dodecanoate is present in different industrial streams such as glycerol aqueous solutions produced in the biodiesel production process.[5] In this industrial process, the production of glycerol is high, and then the presence of sodium dodecanoate in this solution could reach important concentrations taking into account that low surfactant concentration produces large effects upon certain physical properties. Also, medium chain fatty acids, such as sodium dodecanoate, have been investigated as possible candidates for an absorption enhancer for drugs and cosmetics.[6]

The aim of the present work is to analyze the influence of the presence of sodium dodecanoate in aqueous solutions upon several physical properties that allow the characterization of this kind of solutions. Sodium dodecanoate is present in aqueous solutions with other components (i.e., glycerol), but in the present work, the influence of other mixture components has been removed to analyze the influence of sodium laurate before analyzing more complex systems.

Experimental Section

Materials. The surfactant employed in the present work, sodium dodecanoate (sodium laurate, NaL, CAS number 629-25-4), was supplied by Fluka with a molar purity ≥ 98 %. Bidistilled water was used to prepare sodium dodecanoate aqueous solutions. All solutions were prepared by mass using an analytical balance (Kern 770) with a precision of 10^{-4} g. The uncertainty of the sample preparation in mole fraction was ± 0.0005.

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Density and Speed of Sound. The density and speed of sound of water and aqueous solutions of different solutes were measured with an Anton Paar DSA 5000 vibrating tube densimeter and sound analyzer. The uncertainty in the density and speed of sound measurements was $\pm\ 1.8 \cdot 10^{-4}\ \text{g} \cdot \text{cm}^{-3}$ and $\pm\ 0.23\ \text{m} \cdot \text{s}^{-1}$, respectively. In general, each value came from an average of three measurements.

Surface Tension. The surface tension was determined by employing a Krüss K-11 tensiometer using the Wilhelmy plate method. The plate employed was a commercial platinum plate supplied by Krüss. The platinum plate was cleaned and flame-dried before each measurement. The uncertainty of the measurement was $\pm\ 0.09\ \text{mN} \cdot \text{m}^{-1}$. Each surface tension value reported came from an average of five measurements. The samples were thermostatted in a closed stirring vessel before the surface tension measurements.

Electrical Conductivity. The electrical conductivity (κ) was measured with a Mettler-Toledo Sevenmulti conductimeter with a cell constant of $0.5077\ \text{cm}^{-1}$, to determine the influence of temperature and sodium dodecanoate concentration upon the value of this property. The conductivity meter was calibrated using two conductivity standard solutions supplied by Metler Toledo ($\kappa = 1413\ \mu\text{S} \cdot \text{cm}^{-1}$ and $\kappa = 12.88\ \text{mS} \cdot \text{cm}^{-1}$ at 298.15 K). The samples were thermostatted in a closed stirring vessel before the measurements were carried out. In general, each electrical conductivity value reported was an average of three measurements. The uncertainty of this measurement was 1.5 %.

Results and Discussion

This work determines different physical properties (density, electrical conductivity, surface tension, and speed of sound) to characterize aqueous solutions of sodium dodecanoate with different surfactant concentration and temperatures. Tables 1 to 5 summarize the experimental values obtained that correspond to the different physical properties analyzed in the present work.

Besides the analysis of the influence of mixture composition and temperature upon the value of the physical properties studied in the present work, these properties have been analyzed in the literature for surfactant systems due to their ability to characterize the aggregation processes on the basis of the measured experimental values (i.e., electrical conductivity and/or surface tension). For this reason, the behavior obtained about the

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Table 1. Density ρ of Water (1) + Sodium Dodecanoate (2) from T = (293.15 to 323.15) K

C_2	T/K			
mol·L^{-1}	293.15	303.15	313.15	323.15
	ρ/g·cm^{-3}			
0.00000	0.99824	0.99569	0.99225	0.98806
0.00001	0.99824	0.99569	0.99225	0.98806
0.00005	0.99824	0.99569	0.99225	0.98806
0.00010	0.99824	0.99569	0.99225	0.98806
0.00050	0.99825	0.99570	0.99226	0.98807
0.00100	0.99826	0.99571	0.99228	0.98808
0.00150	0.99828	0.99572	0.99229	0.98809
0.00250	0.99831	0.99575	0.99231	0.98811
0.00400	0.99836	0.99578	0.99234	0.98814
0.00500	0.99839	0.99581	0.99236	0.98816
0.00750	0.99847	0.99588	0.99242	0.98821
0.01000	0.99854	0.99595	0.99248	0.98825
0.01500	0.99866	0.99606	0.99257	0.98836
0.02000	0.99879	0.99616	0.99268	0.98845
0.02500	0.99893	0.99628	0.99279	0.98854
0.03000	0.99906	0.99640	0.99288	0.98864
0.03500	0.99917	0.99651	0.99297	0.98872
0.04000	0.99927	0.99658	0.99305	0.98879
0.05000	0.99943	0.99674	0.99319	0.98891
0.06000	0.99962	0.99691	0.99333	0.98903
0.07000	0.99977	0.99706	0.99346	0.98913
0.08000	0.99995	0.99722	0.99358	0.98921
0.10000	1.00019	0.99743	0.99380	0.98936

Table 2. Speed of Sound, u, of Water (1) + Sodium Dodecanoate (2) from T = (293.15 to 323.15) K

C_2	T/K			
mol·L^{-1}	293.15	303.15	313.15	323.15
	u/m·s^{-1}			
0.00000	1483.1	1509.0	1528.4	1541.8
0.00001	1483.1	1509.1	1528.4	1541.8
0.00005	1483.1	1509.1	1528.4	1541.8
0.00010	1483.2	1509.1	1528.5	1541.9
0.00050	1483.2	1509.2	1528.6	1542.1
0.00100	1483.3	1509.3	1528.7	1542.4
0.00150	1483.4	1509.5	1529.0	1542.7
0.00250	1483.6	1509.8	1529.3	1543.1
0.00400	1484.0	1510.3	1529.8	1543.6
0.00500	1484.3	1510.6	1530.2	1543.8
0.00750	1484.9	1511.3	1531.0	1544.3
0.01000	1485.6	1512.1	1531.4	1544.6
0.01500	1487.7	1513.1	1532.1	1545.4
0.02000	1487.7	1513.6	1532.6	1545.8
0.02500	1488.8	1514.3	1533.0	1546.0
0.03000	1489.5	1514.6	1533.3	1546.0
0.03500	1489.9	1514.8	1533.4	1546.1
0.04000	1490.2	1514.9	1533.4	1546.1
0.05000	1490.6	1515.1	1533.4	1546.1
0.06000	1490.9	1515.3	1533.4	1545.9
0.07000	1491.2	1515.4	1533.5	1545.8
0.08000	1491.6	1515.6	1533.4	1545.6
0.10000	1492.2	1515.9	1533.4	1545.3

Table 3. Adiabatic Compressibility, κ_s, of Water (1) + Sodium Dodecanoate (2) from T = (293.15 to 323.15) K

C_2	T/K			
mol·L^{-1}	293.15	303.15	313.15	323.15
	κ_s·10^{10}/Pa^{-1}			
0.00000	4.5541	4.4104	4.3142	4.2576
0.00001	4.5541	4.4103	4.3141	4.2575
0.00005	4.5541	4.4103	4.3141	4.2574
0.00010	4.5540	4.4101	4.3139	4.2572
0.00050	4.5537	4.4092	4.3132	4.2558
0.00100	4.5530	4.4085	4.3123	4.2540
0.00150	4.5523	4.4073	4.3109	4.2525
0.00250	4.5507	4.4054	4.3087	4.2500
0.00400	4.5483	4.4026	4.3058	4.2475
0.00500	4.5465	4.4007	4.3036	4.2463
0.00750	4.5424	4.3962	4.2991	4.2432
0.01000	4.5377	4.3917	4.2964	4.2412
0.01500	4.5307	4.3851	4.2925	4.2365
0.02000	4.5241	4.3822	4.2894	4.2344
0.02500	4.5170	4.3778	4.2866	4.2331
0.03000	4.5119	4.3755	4.2845	4.2322
0.03500	4.5093	4.3740	4.2835	4.2313
0.04000	4.5068	4.3730	4.2830	4.2309
0.05000	4.5037	4.3714	4.2825	4.2310
0.06000	4.5015	4.3697	4.2819	4.2312
0.07000	4.4990	4.3678	4.2812	4.2314
0.08000	4.4959	4.3664	4.2807	4.2319
0.10000	4.4913	4.3640	4.2803	4.2332

Table 4. Surface Tension, σ, of Water (1) + Sodium Dodecanoate (2) from T = (293.15 to 323.15) K

C_2	T/K			
mol·L^{-1}	293.15	303.15	313.15	323.15
	σ/mN·m^{-1}			
0.00000	72.7	71.3	69.3	67.9
0.00001	69.2	67.0	66.7	66.0
0.00005	61.4	59.4	58.8	56.3
0.00010	56.5	54.9	53.5	51.9
0.00050	48.4	45.8	41.1	37.9
0.00100	42.3	38.7	34.4	31.6
0.00150	38.8	34.8	30.7	28.8
0.00250	35.6	31.6	27.9	26.0
0.00400	31.4	27.6	24.8	23.3
0.00500	29.4	25.9	23.3	22.2
0.00750	26.7	24.0	22.2	21.1
0.01000	24.9	22.8	21.8	20.6
0.01500	23.7	22.2	21.4	20.6
0.02000	23.1	22.0	21.4	20.3
0.02500	22.9	22.5	21.3	20.4
0.03000	23.0	21.8	21.1	20.3
0.03500	22.8	22.6	21.3	20.4
0.04000	22.6	22.2	21.3	20.2
0.05000	22.6	22.0	21.3	20.2
0.06000	22.5	22.0	20.9	20.1
0.07000	22.3	21.9	20.9	20.0
0.08000	22.5	21.7	20.9	19.9
0.10000	22.4	21.6	21.1	19.9

influence of composition upon each physical property has been analyzed carefully with the aim of obtaining important information about this phenomenon.

In relation with the influence of sodium dodecanoate addition to the liquid phase density, a common behavior was observed. A continuous increase in the value of this physical property has been observed when the surfactant concentration also increases. The analysis of the influence of sodium dodecanoate concentration upon density reveals that a change in the behavior that could imply an aggregation process between surfactant molecules does not exist. Density has not been considered as an interesting physical property for aggregation studies.

A similar behavior was also observed for the different temperatures employed in this study. On the other hand, an increase in temperature produces a decrease in the value of density. Taking into account the values of density and the influence of composition upon this property allows us to conclude that the aggregation process has no influence upon this property. This behavior is in agreement with previous studies[7] for other systems with surfactants.

On the other hand, previous studies[8] have shown an important influence of aggregation process upon the speed of sound values. This phenomenon could produce a change in the slope of the speed of sound/composition data or a change in the sign of the slope value. These behaviors were found in the system analyzed in the present work (see Figure 1). Different authors[8] indicate that the intersection of linear fits allows the calculation of the critical micelle concentration. When an increase in the surfactant

Table 5. Electrical Conductivity, κ, of Water (1) + Sodium Dodecanoate (2) from T = (293.15 to 323.15) K

C_2	T/K			
mol·L^{-1}	293.15	303.15	313.15	323.15
	κ/μS·cm^{-1}			
0.00000	1.34	1.54	1.80	2.01
0.00001	1.69	2.22	2.34	3.41
0.00005	3.89	5.12	5.99	6.84
0.00010	5.97	7.80	9.47	12.5
0.00050	27.8	36.0	46.7	56.9
0.00100	55.7	70.3	86.9	103.5
0.00150	82.1	105.5	127.9	155.2
0.00250	132.7	170.6	208	237
0.00400	216	276	309	371
0.00500	268	338	399	471
0.00750	386	489	589	690
0.01000	516	640	755	897
0.01500	740	910	1110	1298
0.02000	956	1177	1453	1711
0.02500	1156	1407	1720	2050
0.03000	1310	1564	1920	2330
0.03500	1420	1710	2080	2580
0.04000	1552	1873	2290	2800
0.05000	1720	2120	2630	3170
0.06000	1892	2360	2945	3525
0.07000	2060	2610	3258	3886
0.08000	2240	2840	3570	4260
0.10000	2569	3350	4180	5020

concentration is produced, also an increase in the value of speed of sound is observed until critical micelle concentration is reached. A surfactant concentration higher than a critical micelle corresponding value produces a change in speed of sound/concentration plot slope. This behavior is assigned to the formation of micelles in this kind of system.[9] This change in slope value is higher when temperature is increased.

Also, the isentropic compressibility coefficient, κ_s, was calculated from speed of sound and density values, using the Laplace equation (eq 1).

$$\kappa_s = \frac{1}{u^2\rho} \tag{1}$$

where u is the speed of sound and ρ is the density of the solution. A behavior similar to the previous one for speed of sound data has been observed for the isentropic compressibility values in relation with the determination of the critical micelle concentration values. This parameter has been considered for critical micelle determination in previous works.[9]

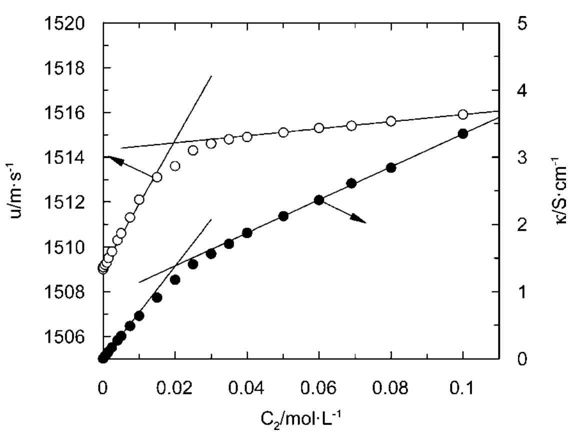

Figure 1. Physical properties of aqueous solutions of sodium dodecanoate: ○, speed of sound; ●, electrical conductivity. t = 303.15 K.

Table 6. Critical Micelle Concentration for the Water (1) + Sodium Dodecanoate (2) System

T	cmc (u)	cmc (K_s)	cmc (κ)	cmc (σ)
K	mol·L^{-1}	mol·L^{-1}	mol·L^{-1}	mol·L^{-1}
293.15	0.029	0.028	0.025	0.021
298.15	-	-	0.0244[10] 0.0281[11]	0.023[10]
303.15	0.018	0.021	0.020	0.015
313.15	0.015	0.016	0.018	0.010
323.15	0.014	0.013	0.017	0.010

Figure 1 also shows the behavior of electrical conductivity when surfactant concentration changes in solution. When sodium dodecanoate concentration increases in aqueous solution, a continuous increase in the value of electrical conductivity is observed. This behavior is due to the use of an ionic surfactant, and then, an increase in surfactant concentration produces an increase in ion concentration. A behavior similar to that previously commented for speed of sound has been obtained for electrical conductivity (see Figure 1). Then, also a change in the slope for electrical conductivity/composition data is observed, and the intercept of both linear fits corresponds with the critical micelle concentration (formation of sodium dodecanoate micelles in aqueous solutions). Figure 1 shows that the value of critical micelle concentration (intercept of linear fits) determined using these physical properties is in agreement and takes similar values. Table 6 shows the critical micelle concentration determined using different experimental techniques and a comparison with previous studies[10,11] obtained at an intermediate temperature. An agreement between experimental and literature data exists for critical micelle concentration determined by means of electrical conductivity data.

Figure 2 shows the effect of surfactant concentration upon the value of the surface tension. In this case, the presence of surfactant produces a dramatic decrease in the surface tension, but this decrease reaches a constant value at a certain surfactant concentration value. It has been shown that surface tension is a physical property highly influenced by the aggregation phenomenon, due to a change in the surface concentration of the surfactant.[12] The micellization process makes the surface surfactant concentration remain constant because the addition of new added surfactant molecules is employed in the micelle formation; however, it has no influence on the surfactant concentration in the free liquid surface, and so the surface tension remains at a constant value.

Figure 2 also shows the critical micelle concentration determination by means of surface tension values versus the surfactant concentration on a logarithmic scale. As a result, two

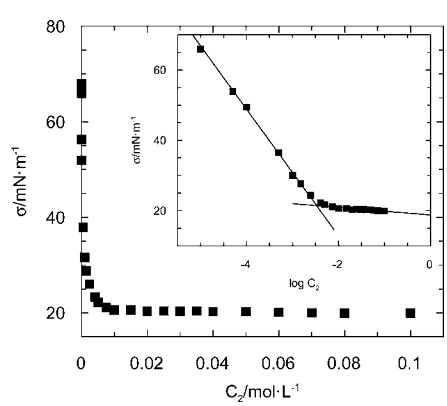

Figure 2. Influence of mixture composition upon surface tension. t = 323.15 K.

linear trends can be observed, and the intersection of the two lines allows the precritical micelle concentration determination. The critical micelle concentration has been determined using the experimental procedure developed for this system in a previous work.[13]

In relation with the influence of the physical property employed to determine the critical micelle concentration value for sodium dodecanoate, Table 6 shows that the value determined by surface tension data takes values less than the corresponding ones determined using the influence of surfactant concentration upon the other properties (speed of sound, isentropic compressibility, and electrical conductivity). Also in the present work, the critical micelle concentrations determined using surface tension values are less than the corresponding ones obtained in previous work.[10] Taking into account previous studies,[14] this difference could be due to the influence of time upon the value of surface tension. The experimental data in the present work have been obtained at 100 s and are in agreement with previous work that analyzes the influence of time[14] and the suitable experimental procedure upon surface tension data, but this dynamic behavior could influence the surface tension and then critical micelle concentration determination.

Analyzing the critical micelle concentration for another substance with similar structure but with different chain length (2.72 mM for sodium palmitate, 1.8 mM for sodium stearate, and 2.1 mM for sodium oleate),[15] the conclusion was reached that an increase in chain length produces a decrease in the value of critical micelle concentration[7,15] because a minor number of molecules are needed to form a micelle.

Table 6 shows the determined values for critical micelle concentration for the different temperatures employed in the present work and using the experimental values of physical properties that could be employed to analyze the aggregation process for the sodium dodecanoate aqueous solution. The critical micelle concentration values show that an increase in temperature produces a decrease in the surfactant concentration needed for micellization. This behavior is in agreement with previous studies that analyze the thermodynamics of the micellization process because in all cases the formation of micelles is an endothermic process at low temperatures and exothermic at higher temperatures.[16] Taking into account this previous study, a minimum in the critical micelle concentration near the temperature value of 323.15 K is commonly observed. This behavior is due mainly to two opposite effects:

(i) The increase in temperature produces a reduction in the hydration of the hydrophilic part of the surfactant that tends to favor the micellization process because the micelles are formed with a lower concentration (cmc decreases).

(ii) On the other hand, the increase in temperature also produces an increase in water molecule disorganization near the hydrophobic molecule zone that does not favor the micelle formation (cmc increases).

The experimental results shown in Table 6 are in agreement with the behavior previously reported because there is a decrease in the critical micelle concentration when temperature increases, and this reduction decreased its magnitude near 323.15 K.

Conclusions

The influence of surfactant concentration and aggregation phenomenon upon physical properties for aqueous solutions of sodium dodecanoate has been analyzed in the present work. Different behaviors have been observed for the physical properties studied; i.e., for density, electrical conductivity, and speed of sound, an increase in surfactant concentration produces an increase in these physical properties, while for surface tension a decrease is observed. The aggregation phenomenon shows great influence upon the behavior of surface tension and speed of sound. Regarding electrical conductivity data, a minor effect of aggregation is observed. Critical micelle concentration data have been determined by different methods, and the value determined by surface tension takes values lower than the corresponding ones obtained by the other physical properties. Taking into account the influence of time upon the value of this physical property, perhaps surface tension is not the best property to determine the critical micelle concentration. On the other hand, an increase in temperature produces a decrease in the value of critical micelle concentration in the studied range.

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