Apparent Molar Volumes and Viscosities of Lauric, Palmitic, and Stearic Acids in 2-Butanol at (20, 30, 40, and 60) °C

Erol Ayranci* and Gokcen Akgul

Department of Chemistry, Akdeniz University, P.O. Box 510, Antalya, Turkey

Apparent molar volumes ($V_\varnothing$) and viscosities of lauric, palmitic, and stearic acids as a function of concentration at (20, 30, 40, and 60) °C in 2-butanol are reported. The apparent molar volumes at infinite dilution ($V_\varnothing^\circ$) were determined by extrapolating $V_\varnothing$ values to zero concentration. The variations of both $V_\varnothing^\circ$ and viscosity values with temperature and with chain length of fatty acid were examined. $V_\varnothing^\circ$ values were found to decrease with increasing temperature for all three fatty acids and to increase with increasing chain length of fatty acid at a constant temperature. Apparent molar expansivity data at infinite dilution ($E_\varnothing^\circ$) were derived from the $V_\varnothing^\circ$ versus temperature data determined experimentally. $E_\varnothing^\circ$ values were negative, and their absolute values were found to increase with the chain length of fatty acid. The viscosities do not change appreciably with concentration at constant temperature while they do decrease considerably with temperature at a constant concentration. On the other hand, at a constant temperature and concentration, viscosities increased with increasing chain length.

Introduction

It is important to know the interactions of fatty acids with water in order to examine their function in biological media. However, limited solubilities of long chain fatty acids due to their hydrophobicity restrict the study of the aqueous solution behavior of these compounds. On the other hand, the investigation of solution behaviors of fatty acids in nonaqueous solvents may help us to understand their interaction with water. The study of fatty acid−solvent interactions may also lead us to understand the interactions of solvents with fats, which are triglycerides of fatty acids.

Apparent molar volumes and expansivities at infinite dilution and viscosities are important tools to study solute−solvent interactions and have been utilized successfully in various works from our laboratories. For example, the solution behaviors of compounds with asymmetric carbon atoms,[1] amino acids in water and in guanidine hydrochloride,[2] and proteins and their denaturation in urea[3,4] were all determined using the methods of apparent molar volumes and viscosities. These methods were proven to be sensitive to reveal the effects of structural factors on ion−solvent or in general solute−solvent interactions.[5−8] It is known that the study of the apparent molar volumes at different temperatures leads to the determination of apparent molar expansivities, which provide important supplementary information about solute−solvent interactions.

Although apparent molar volumes of biologically important compounds such as amino acids and peptides in water have been extensively studied,[9,10] there are few studies on volumes of aqueous solutions of lipids such as long chain fatty acids, probably due to their limited solubility in water. Viscosities of some long chain fatty acids and their relation to the chain length have been studied by Liew et al.[11] More recently, Valeri and Meirelley[12] studied the viscosities of fatty acids, triglycerides, and their binary mixtures. However, these studies do not provide any information on lipid−solvent interactions, since they were carried out on pure compounds in the liquid state.

The purpose of the present study is to determine the apparent molar volumes, the apparent molar expansivities, and the viscosities of lauric, palmitic, and stearic acids in 2-butanol in order to understand the solution behavior of these compounds, which are of industrial and biochemical importance.

Experimental Section

Materials. Lauric and palmitic acids were obtained from Sigma while stearic acid was from Merck. The solvent 2-butanol was from J. T. Baker. All these compounds were at least 99% pure, as stated by the manufacturer, and used without further purification.

Density Measurements. Densities were measured using pycnometers of about 10 mL. The volumes of the pycnometers were calibrated with deionized water at (20, 30, 40, and 60) °C using the densities of water reported by Kell.[13] The densities of fatty acid solutions in 2-butanol were determined from the mass of the solution in the pycnometer after reaching thermal equilibrium with a water bath at (20, 30, 40, or 60) °C. The densities of pure 2-butanol at four temperatures were also measured.

Determination of Apparent Molar Volumes. Apparent molar volumes were determined using the measured densities of solvent and solution in eq 1[14]

$$V_\varnothing = [1000(\rho_0 - \rho)/(c\rho_0)] + M_w/\rho_0 \qquad (1)$$

where $V_\varnothing$ is the apparent molar volume, c is the molarity, M_w is the molecular weight of the solute (fatty acid), and ρ_0 and ρ are the densities of the solvent (2-butanol) and the solution, respectively. In general, $V_\varnothing$ was found to vary linearly with concentration for the systems studied. Thus, $V_\varnothing$ data were fitted into eq 2

$$V_\varnothing = V_\varnothing^\circ + b_v c \qquad (2)$$

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* To whom correspondence should be addressed. Phone: 90 242 3102315. Fax: 90 242 2278911. E-mail: ayranci1@pascal.sci.akdeniz.edu.tr.

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where $V_\varnothing^\circ$ is the apparent molar volume at infinite dilution and b_v is an experimentally determined parameter.

The density measurements with the pycnometers used in this work were reproducible to 2×10^{-5} g·cm^{-3}. This leads to an uncertainty of ±2.0 cm^3·mol^{-1} in $V_\varnothing$ at $c = 0.01$ M and ±0.6 cm^3·mol^{-1} at $c = 0.3$ M. These uncertainties correspond to a relative uncertainty of (0.2 to 0.8)% in $V_\varnothing$ for an average value of 250 cm^3·mol^{-1}.

It should be recognized that the reliability and the reproducibility of $V_\varnothing$ values at low concentrations (<0.01 M) derived from density measurements using the pycnometer are rather poor. Sometimes unreasonably high or low $V_\varnothing$ values can be obtained for very dilute solutions. In the treatment of the data to obtain $V_\varnothing^\circ$ values, $V_\varnothing$ values at very low concentrations were utilized cautiously and only those which obey the general trend seen at higher concentrations were taken into consideration.

Determination of Apparent Molar Expansivities. From the apparent molar volumes determined at different temperatures, it is possible to derive the apparent molar expansivities through the thermodynamic relation given by eq 3

$$E_\varnothing = (\partial V_\varnothing / \partial t)_P \tag{3}$$

where $E_\varnothing$ is the apparent molar expansivity, t is the temperature, and P is the pressure. The slope of the $V_\varnothing$ versus t plot gives $E_\varnothing$. The linearity of the $V_\varnothing$ versus t plot over a certain temperature range indicates that $E_\varnothing$ is constant over that range and given by the slope of the line. The apparent molar expansivity at infinite dilution, $E_\varnothing^\circ$, can be obtained if $V_\varnothing^\circ$ values are used for $V_\varnothing$ in this treatment.

Viscosity Measurement. The viscosity measurements were made with Cannon-Fenske glass capillary viscometers obtained from Herzog Lauda Co. The provided calibration constants were checked with glycerin, ethanol, and water, whose viscosities are well-known.[15] Viscometers were placed in a thermostat that is equipped with a stirrer, a heater, and a lamp. The temperature was kept constant to ±0.01 °C in the thermostat. The method described in ASTM-D 2515 was followed to measure the flow time. Then the absolute viscosities of solutions, η, were calculated from

$$\eta = k\rho f \tag{4}$$

where f is the flow time and ρ is the density of the solution and k is the viscometer constant. The viscometers were selected in such a way that the total flow time for each solution is at least 200 s, as recommended in ASTM-D 2515. Since the viscometer constant k is checked against liquids such as glycerin, ethanol, and water, whose viscosities are known to 2×10^{-3} mPa·s, the uncertainty in the η values determined in the present experiments is limited to this value. The uncertainty caused by the flow time measurement is much less than this value (about 5×10^{-5} mPa·s). A linear relation was observed between η and the concentration of solutions.

Results

The densities at varying molarities, the corresponding $V_\varnothing$ values calculated according to eq 1, and the viscosities of lauric, palmitic, and stearic acids in 2-butanol at (20, 30, 40, and 60) °C are given in Tables 1−4, respectively. The densities and viscosities of pure 2-butanol at these four temperatures are also included in the first row of each table.

Table 1. Densities, Apparent Molar Volumes, and Viscosities of Lauric, Palmitic, and Stearic Acids in 2-Butanol at 20 °C

fatty acid	c mol·L^{-1}	ρ g·cm^{-3}	$V_\varnothing$ cm^3·mol^{-1}	η mPa·s
pure 2-butanol (no fatty acid)		0.806 6		3.663
lauric acid	0.0103	0.806 38	272.1	3.580
	0.0500	0.807 27	231.2	3.665
	0.1003	0.807 29	233.4	3.700
	0.1500	0.808 85	229.6	3.688
	0.2001	0.808 76	234.8	3.744
	0.3500	0.812 86	226.1	3.841
palmitic acid	0.0100	0.807 66	192.0	3.530
	0.0500	0.807 67	290.8	3.616
	0.1000	0.809 21	285.3	3.613
	0.1501	0.810 16	288.3	3.700
	0.2001	0.810 60	293.0	3.828
	0.3501	0.813 04	295.0	4.056
stearic acid	0.0100	0.806 45	368.9	3.611
	0.0500	0.806 90	344.8	3.679
	0.1000	0.813 95	261.3	3.795
	0.1500	0.810 78	317.9	3.785
	0.2000	0.811 62	321.5	3.799
	0.3501	0.814 68	324.0	4.177

Table 2. Densities, Apparent Molar Volumes, and Viscosities of Lauric, Palmitic, and Stearic Acids in 2-Butanol at 30 °C

fatty acid	c mol·L^{-1}	ρ g·cm^{-3}	$V_\varnothing$ cm^3·mol^{-1}	η mPa·s
pure 2-butanol (no fatty acid)		0.799 3		2.527
lauric acid	0.0103	0.798 71	323.6	2.547
	0.0500	0.800 23	227.8	2.548
	0.1003	0.800 56	235.0	2.573
	0.1500	0.801 14	235.3	2.585
	0.2001	0.801 85	234.7	2.624
	0.3500	0.805 19	229.6	2.704
palmitic acid	0.0100	0.799 68	275.2	2.464
	0.0500	0.800 09	301.4	2.499
	0.1000	0.801 34	295.5	2.512
	0.1501	0.802 89	291.0	2.585
	0.2001	0.802 96	298.0	2.665
	0.3501	0.806 24	296.1	2.834
stearic acid	0.0100	0.798 83	417.2	2.499
	0.0500	0.799 70	346.4	2.531
	0.1000	0.806 09	271.1	2.466
	0.1500	0.803 50	321.0	2.627
	0.2000	0.804 54	323.2	2.584
	0.3501	0.806 92	328.7	2.919

A typical $V_\varnothing$ versus concentration graph for the three fatty acids at 20 °C is given in Figure 1. The apparent molar volumes at infinite dilution, $V_\varnothing^\circ$, and the b_v parameters of eq 2 were determined by linear regression analysis of the data and are presented in Table 5.

A typical plot of viscosity data as a function of molarity for lauric acid at (20, 30, 40, and 60) °C is shown in Figure 2.

Discussion

Apparent Molar Volumes and Expansivities. Apparent molar volumes at infinite dilution are expected to provide information on solute−solvent interactions, as solute−solute interactions can be assumed to be eliminated at infinite dilution. The $V_\varnothing^\circ$ values given in Table 5 can be examined as a function of both temperature and chain length of fatty acid. The variation of $V_\varnothing^\circ$ with temperature for lauric, palmitic, and stearic acids is shown in Figure 3. It is seen that $V_\varnothing^\circ$ decreases with increasing temperature for all three fatty acids. The parameter that measures the

Table 3. Densities, Apparent Molar Volumes, and Viscosities of Lauric, Palmitic, and Stearic Acids in 2-Butanol at 40 °C

fatty acid	c / mol·L^{-1}	ρ / g·cm^{-3}	$V_\varnothing$ / cm^3·mol^{-1}	η / mPa·s
pure 2-butanol (no fatty acid)	-	0.792 2	-	1.801
lauric acid	0.0103	0.791 02	397.9	1.810
	0.0500	0.793 39	222.7	1.818
	0.1003	0.794 11	228.8	1.851
	0.1500	0.794 51	233.4	1.865
	0.2001	0.794 64	237.5	1.877
	0.3500	0.797 47	233.8	1.951
palmitic acid	0.0100	0.792 63	269.7	1.751
	0.0500	0.792 74	310.1	1.789
	0.1000	0.794 66	292.6	1.808
	0.1501	0.795 01	300.1	1.850
	0.2001	0.795 11	305.3	1.921
	0.3501	0.799 34	297.9	2.045
stearic acid	0.0100	0.792 46	326.6	1.766
	0.0500	0.792 65	347.7	1.808
	0.1000	0.796 45	305.4	1.790
	0.1500	0.796 91	319.4	1.886
	0.2000	0.79776	324.0	1.881
	0.3501	0.800 50	329.2	2.017

Table 4. Densities, Apparent Molar Volumes, and Viscosities of Lauric, Palmitic, and Stearic Acids in 2-Butanol at 60 °C

fatty acid	c / mol·L^{-1}	ρ / g·cm^{-3}	$V_\varnothing$ / cm^3·mol^{-1}	η / mPa·s
pure 2-butanol (no fatty acid)		0.778 0		1.025
lauric acid	0.0103	0.778 39	209.1	1.050
	0.0500	0.779 62	215.7	1.040
	0.1003	0.780 76	222.1	1.070
	0.1500	0.782 00	223.2	1.080
	0.2001	0.782 90	226.0	1.100
	0.3500	0.785 30	230.8	1.150
palmitic acid	0.0500	0.782 30	219.0	1.090
	0.1000	0.782 90	266.6	1.080
	0.1501	0.783 19	285.2	1.130
	0.2001	0.783 51	294.2	1.140
	0.3501	0.787 50	294.7	1.270
stearic acid	0.0500	0.782 79	242.5	1.090
	0.1000	0.783 92	289.6	1.100
	0.1500	0.784 23	312.3	1.160
	0.2000	0.785 41	318.0	1.160
	0.3501	0.788 89	325.7	1.360

Table 5. $V^\circ_\varnothing$ and b_v Parameters of Eq 2 for Lauric, Palmitic, and Stearic Acids in 2-Butanol at Four Temperatures

	LA		PA		SA	
t / °C	$V^\circ_\varnothing$ / cm^3·mol^{-1}	b_v / cm^3·mol^{-2}·L	$V^\circ_\varnothing$ / cm^3·mol^{-1}	b_v / cm^3·mol^{-2}·L	$V^\circ_\varnothing$ / cm^3·mol^{-1}	b_v / cm^3·mol^{-2}·L
20	234.0	−17.7	286.4	23.8	353.5	−119.2
30	232.9	−2.3	282.7	52.3	312.0	36.0
40	225.4	34.1	270.0	190.3	303.2	81.7
60	213.0	58.6	236.0	211.8	286.9	122.3

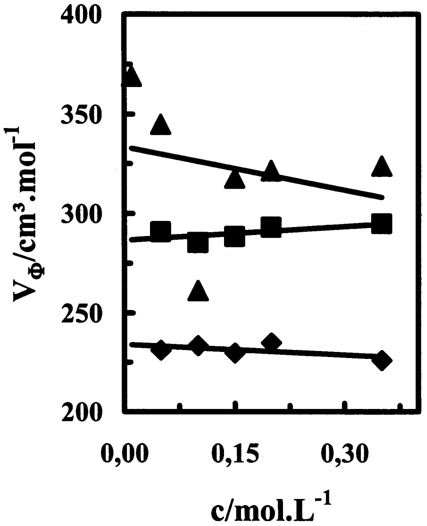

Figure 1. $V_\varnothing$ as a function of c for lauric acid (◆), palmitic acid (■), and stearic acid (▲) in 2-butanol at 20 °C.

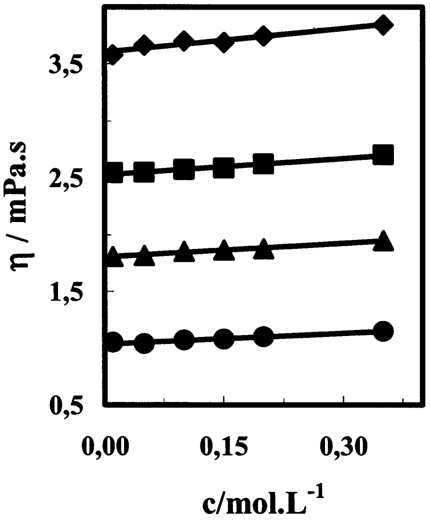

Figure 2. η as a function of c for lauric acid in 2-butanol at 20 °C (◆), 30 °C (■), 40 °C (▲), and 60 °C (●).

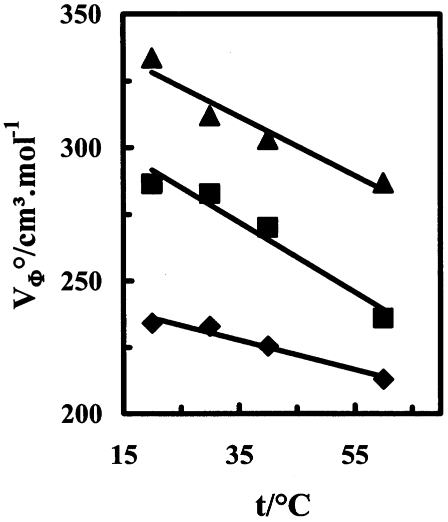

Figure 3. $V^\circ_\varnothing$ as a function of temperature for lauric acid (◆), palmitic acid (■), and stearic acid (▲) in 2-butanol.

variation of volume with temperature is the apparent molar expansivity, which was defined by eq 3. The slopes of the lines for lauric, palmitic, and stearic acids in Figure 3 give the apparent molar expansivities at infinite dilution, $E^\circ_\varnothing$, of the three fatty acids. These values were found as (−0.56, −1.31, and −1.50) cm^3·mol^{-1}·K^{-1} for lauric, palmitic, and stearic acids, respectively, by linear regression analysis of the data shown in Figure 3. Negative expansivity (i.e. decreasing volume with increasing temperature) is a characteristic property of aqueous solutions of hydrophobic solutes.[16] Although the solvent in the present systems is not water, it is still a slightly polar solvent due to the −OH group. On the other hand, the fatty acids studied have a

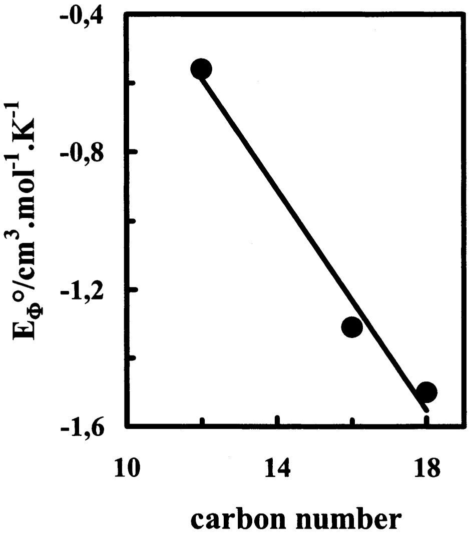

Figure 4. $E_{\varnothing}^{\circ}$ as a function of carbon number in the hydrocarbon chain of the fatty acid in 2-butanol.

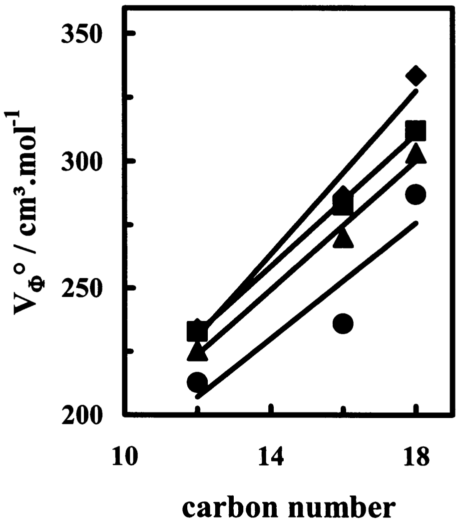

Figure 5. $V_{\varnothing}^{\circ}$ as a function of carbon number in the hydrocarbon chain of the fatty acid in 2-butanol at 20 °C (◆), 30 °C (■), 40 °C (▲), and 60 °C (●).

large hydrophobic/hydrophilic balance. So, one can say that the negative $E_{\varnothing}^{\circ}$ values originate from the highly hydrophobic characters of the fatty acids. Furthermore, $E_{\varnothing}^{\circ}$ values become more negative as the number of carbon atoms in the hydrocarbon chain of the fatty acid increases, as shown in Figure 4. It should be noted that the number of carbon atoms in the hydrocarbon chain of the fatty acid is proportional to the degree of hydrophobic/hydrophilic balance of the whole compound.

The variation of $V_{\varnothing}^{\circ}$ values with the chain length of fatty acids provides an explanation for lipid–solvent interactions. To see this variation, $V_{\varnothing}^{\circ}$ values in Table 5 are plotted as a function of carbon number in the fatty acid chain (12 for lauric acid, 16 for palmitic acid, and 18 for stearic acid) at four temperatures in Figure 5. The variation is almost linear at each temperature. The slopes of these lines, determined by the least-squares analysis, are 16.1, 13.1, 12.7, and 11.4 $\mathrm{cm^3 \cdot mol^{-1} \cdot (carbon\ number)^{-1}}$ at (20, 30, 40, and 60) °C, respectively. These slopes indicate the change in $V_{\varnothing}^{\circ}$ per $-CH_2-$ group along the chain. It is seen that these values decrease with increasing temperature, which is consistent with the above finding of negative expansivities.

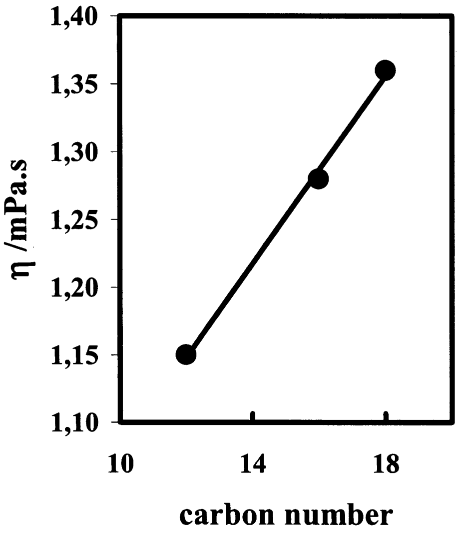

Figure 6. Typical η vs carbon number in the hydrocarbon chain of the fatty acid plot at a constant concentration of 0.35 M in 2-butanol and a temperature of 60 °C.

Beyond the infinite dilution conditions, the system becomes more complex as the concentration increases because solute–solute interactions start to gain importance in addition to solute–solvent interactions. The b_v values given in Table 5 reflect the concentration dependence of $V_{\varnothing}$ values. The b_v values increase with increasing temperature for all three fatty acids. This shows that $V_{\varnothing}$ values become more strongly dependent on concentration as the temperature increases.

Viscosities. Viscosities of lauric, palmitic, and stearic acids in 2-butanol increase slightly with concentration at all four temperatures (see Figure 2 as an example). This can be attributed to the increase in both solute–solvent and solute–solute interactions with concentration. On the other hand, at a constant temperature and concentration, viscosities are found to increase with the carbon number along the hydrocarbon chain of the fatty acid. A typical η versus carbon number plot at a constant concentration of 0.35 M and a temperature of 60 °C is given in Figure 6. The increase in η with carbon number can be explained by the increase in both molecular weight of the fatty acid and the degree of solute–solvent interactions with carbon number.

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