MEASUREMENT OF THE SPECIFIC AND THE APPARENT MOLAR VOLUMES OF SOME EVEN CHAIN LENGTH FATTY ACIDS IN ETHANOL

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ABSTRACT

The specific and the apparent molar volumes of some fatty acids of even chain length from decanoic to octadecanoic acid were determined in ethanol. The objective was to understand the extent to which the acids can disturb the structure of the solvent as well as affect the micellar characteristics. The specific volumes were obtained by fitting the measured viscosity data to the Einstein equation while the apparent molar volumes were obtained using the pycnometric method. The specific volumes of the acids increased with the increase in the carbon chain length of the acids but were fairly constant within a narrow concentration and temperature ranges. Both the apparent molar volumes and apparent molar volumes at infinite dilution were temperature and carbon chain length dependent. The activation enthalpies for the viscous flows were independent of the carbon chain length suggesting little dissociation/association. The dissolution enthalpies were positive in conformity with the endothermicity of the process. The negative expansivity values were interpreted to originate from the dominant hydrophobic characters of the fatty acids. The combined analysis of $\Delta\mu_2^0$ (energy contribution of the solute to the free energy of the solution) and the Hepler constant dictated the classification of the acids as anomalous structure makers.

Keywords: Viscosity, Specific Volume, Apparent Molar Volume, Activation Energy, Expansivity, Hepler Constant

INTRODUCTION

The solution properties of some metal carboxylates in many organic solvents have been studied in our laboratory (Akanni *et al*, 1984, Akanni and Abass, 1989). The usefulness of the solutions of metal carboxylates that makes them the subject of intense research interest was discussed in these articles. The articles presented arguments for the existence of micelles and the model or mechanism of surfactant aggregation in non-aqueous media. The specific volume (volume occupied by one gram of a matrix) is perhaps the building block for the micellar formations in solution. The specific volume is a parameter of intensive quantity but has additivity characteristics. It is useful in the thermodynamic analysis of fluids since the mass can be eliminated in the computation of data.

The specific volumes of some solutes in solution had been measured. For instance, the specific volumes of some concentrations of sugar and sulphur suspensions were reported to be constant and agreed with the actual specific volumes of these solutes in the dry state (Kunitz, 1926, Einstein 1906). These articles further reported

that the specific volumes of glycogen, casein and rubber in various solvents were higher than the values in the dry state, indicating that these substances are intimately associated with a portion of the solvents. Berchiesi et al (Nat. Burr. Stand. Bull., 1917) used viscosity measurements to present data on the co-volumes of the molten aliphatic acids, ethanoic acid (C_2) and the acids containing nine (C_9) to eighteen (C_{18}) carbon atom chain length. The co-volume, designated in the article as b_v was calculated from the Batchinski formular, $\eta = A(v - b_v)$ As expected, the co-volumes (in $cm^3\ mol^{-1}$) were heavily carbon chain length dependent. It was however not clear, how the co-volumes measured by Berchiesi in the molten state, could affect the specific and apparent molar volumes in binary systems.

The literature survey shows that there is little or no information on the specific and apparent molar volumes of metal carboxylates in solvents. In fact the study in this area cited as references were studies carried out a long time ago. It is our desire to undertake a systematic evaluation of the specific volumes of metal carboxylates in some solvents. Prior to this, it was reasoned that data on

the specific or apparent molar volumes of metal carboxylates will only be meaningful, in terms of deep interpretation, when information on the volume parameters of the precursors (the fatty acids) is known. This is needful to enable the influence of substituting metal ions for the hydrogen ions of the acids, to be brought into focus. The current study thus evaluates the specific volumes and the apparent molar volumes of the even chain length fatty acids from decanoic (C_{10}) acid to octadecanoic (C_{18}) acid in ethanol.

EXPERIMENTAL

Materials

All the fatty acids used were from British Drug House (B.D.H) and were stated to have a minimum of 99% assay. They were used without further purification. The ethanol was 96% pure and was distilled twice to improve the state of purity.

Calibration

The Oswald type viscometer used is that of 1 mm capillary and was calibrated by determining the time of flow of 40% sucrose solution within the temperature range of 303 – 313 K using a stopwatch. About 15 cm^3 of the solution of the sugar in alcohol was introduced into the viscometer through the wider arm. The loaded viscometer was immersed in the water bath and the solution was allowed to equilibrate with the temperature of the bath before the time of flow (time for the loaded amount of solution to fall under its weight from one mark of the capillary tube to another mark) was determined. A standard pycnometer was used to determine the density of the 40% sucrose solution in the same 303 – 313 K temperature range.

The actual viscosity of 40% sucrose solution was obtained using the data from the National Bureau of Standards (Nat. Burr. Stand, Bull.,.1917). The

data had been used in our previous articles (Ekpe and Sime, 1976, Adeosun and Akanni, 1980) and the data fitted the equation,

$$\log_{10} \eta = -3.8089 + \frac{1.3513 \times 10^3}{T}$$

Thus at each temperature at which the time of flow was determined, the viscosity, η was calculated. Viscosity is related to the density and the time of flow by the equation, $\eta = k\varrho t$, where k is a proportionality or viscometer constant. The average value of k obtained for the viscometer used is 1.516×10^{-2}. The calculated standard deviation in the k-value is less than 3%.

EVIDENCE FOR ACCURACY OF VISCOSITY METHOD

The viscosities of certain concentrations of glucose in water were measured. The relative viscosities (ratio of viscosity of solution to that of the solvent) of the solutions were calculated. The data were fitted to the Einstein equation (Einstein, 1906),

$$\eta = \frac{1 + 0.5\theta}{(1 - \theta)^4}$$

where η is the relative viscosity and θ is the volume fraction of the solute. The Einstein equation was solved using Mathcad and Excel solvers. Initial guesses of both η and θ were input to the equation to ensure that Mathcad senses the problem to be solved. Then the experimental values of η were plugged in to give the corresponding θ values. Four values of θ are expected because the equation is a quartet (fourth power) but only one value of θ was displayed. Microsoft Excel solver was used to cross-check in order to validate the answer. This program gave four solutions and all the four are equal and the same with the single θ-value displayed by the Mathcad program.. The data obtained are

Table 1: Relative Viscosity and Specific Volume of Some Concentrations of Glucose in Water at 307 K

Percent solution	Density$\times 10^3$ (kg m^{-3})	Relative viscosity	Specific volume (cm^3 kg^{-1})
5	1.019	1.136	0.567
10	1.165	1.328	0.621
15	1.269	1.575	0.639
20	1.459	1.900	0.654
25	1.572	2.108	0.630

Viscosity is a measure of the resistance of one part of a fluid to move relative to another one. Therefore, viscosity must be closely correlated with the structural parameters of the fluid particles. In pursuance of this objective, the accuracy of the technique needs to be ascertained to ensure the reliability of data. The accuracy and precision of this study were monitored by measuring the viscosity of certain concentrations of glucose in water. The data obtained were used to calculate the specific volume of glucose presented in Table 1. The table shows that the average specific volume of glucose in water is 0.621 ± 0.036. This value is in good agreement with the previously reported value of 0.64 (Kunitz, 1926). This high accuracy provided the confidence to use the viscosity method to determine the specific volumes of fatty acids in ethanol, a solvent in which the acids are soluble even at room temperature.

RESULTS AND DISCUSSION

The time for the viscous flows of solutions of the acids decanoic (C_{10}), dodecanoic (C_{12}), tetradecanoic (C_{14}) and octadecanoic (C_{18}) acids) in ethanol was measured within the temperature range of $298 - 323$ K. Table 2 shows the example of the data obtained for different concentrations of decanoic acid at three different temperatures.

Table 2: Viscosities and Specific Volumes of Some Concentrations of Decanoic Acid in Ethanol at Three Temperatures

Concentration (mol dm^{-3})	Viscosity (mPas)			Specific volume cm^3 g^{-1}		
	298 K	313 K	328 K	298 K	313 K	328 K
0.000	1.360	1.013	1.000	--	--	--
0.029	1.370	1.021	1.006	0.33	0.34	0.31
0.058	1.379	1.028	1.015	0.31	0.33	0.34
0.087	1.389	1.034	1.023	0.31	0.31	0.33
0.116	1.402	1.036	1.031	0.34	0.35	0.33

The data for 0.050 mol dm^{-3} solutions of the four acids at three temperatures are presented in Table 3.

Table 3: Densities, Viscosities and Specific Volumes of the Acids at Three Different Temperatures

Acid	Density$\times 10^3$ (kg m^{-3})			Viscosity (mPas)			Specific Volume (cm^3 g^{-1}		
	298 K	313 K	328 K	298 K	313 K	328 K	298 K	313 K	328 K
Decanoic	0.805	0.795	0.785	1.379	1.028	0.794	0.31	0.33	0.34
Dodecanoic	0.805	0.795	0.785	1.382	1.034	0.795	0.37	0.41	0.36
Tetradecanoic	0.805	0.795	0.785	1.384	1.041	0.801	0.45	0.59	0.47
Octadecanoic	0.806	0.796	0.786	1.423	1.055	0.804	0.63	0.61	0.60

The activation energies for the viscous flows of the acid solutions were obtained from the equation,

$$\log_{10} \eta = \log_{10} A + \frac{E_\eta}{2.303RT}$$

(Ekpe and Sime, 1976) where A is the pre-exponential factor in the Arrhenius equation, E_η is

the activation energy and T is the absolute temperature. The data obtained are presented in Table 4. A typical plot of log η against 1/T for 2g of decanoic acid in 100 cm³ ethanol is shown in Fig 1. The regression coefficient of the plot, R^2 = 0.9999 and the slope is

$$\frac{E_\eta}{2.303R}$$

From this the value of 15.04 kJ mol⁻¹ for E_η was obtained for 2g of decanoic acid in 100 cm³ ethanol. Table 4 shows the activation energies for the acid solutions.

Table 4   Activation Energy for the viscous flows of Solutions of Fatty Acids in Ethanol

Concentration (g)/ 100 cm³	Activation energy (kJ mol⁻¹)			
	C_{10} Acid	C_{12} Acid	C_{14} Acid	C_{18} Acid
0.5	15.04	15.02	14.99	15.03
1.0	15.01	15.03	14.90	15.17
1.5	14.99	15.10	14.93	15.30
2.0	15.01	15.04	15.00	15.17
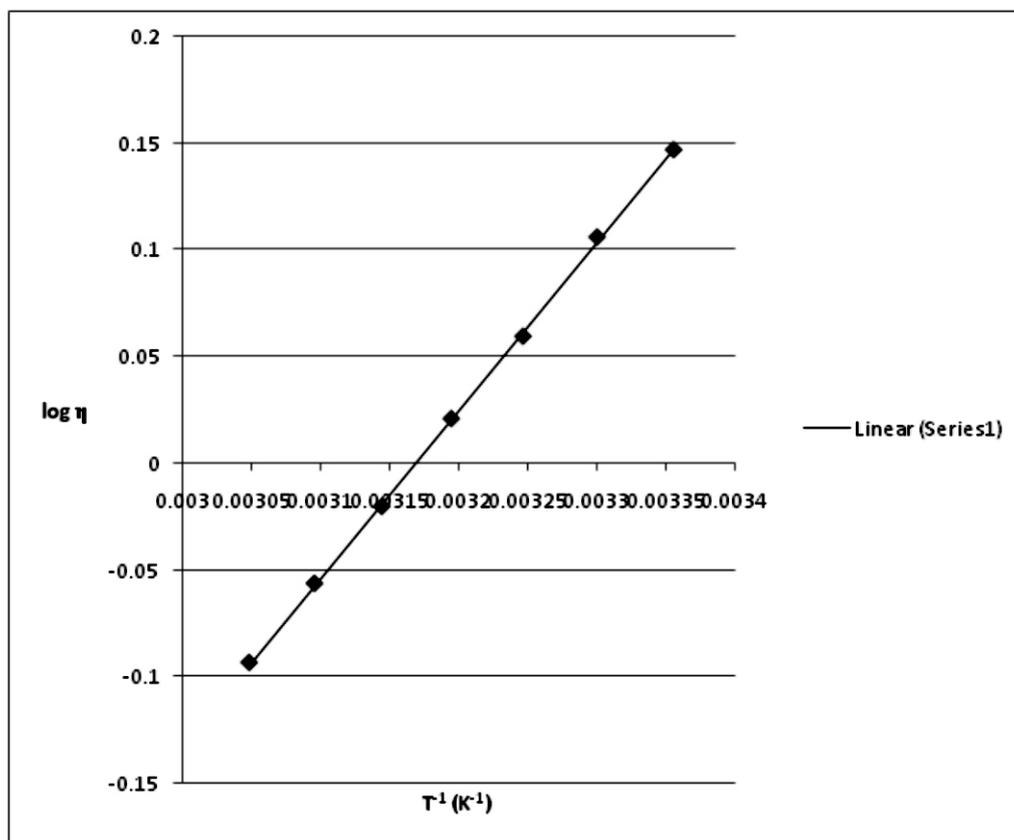
Fig. 1 Plot of Log(Viscosity) Against Inverse Temperature

The apparent molar volume of the acids in ethanol was calculated from the equation,

$$V_0 = \left[1000\frac{(\rho_0 - \rho)}{c\rho_0}\right] + \frac{M_s}{\rho_0}$$

ϱ_o and ϱ in the above equation are the densities of the pure solvent and solution respectively, c is the molarity of the solution and M_s is the molar weight of the solute. The data accumulated at two temperatures are presented in Table 5

Table 5 Apparent Molar Volumes of Fatty Acids in Ethanol at Two Temperatures

Temperature (K)	Apparent Molar Volumes of Acids (cm^3)			
	Decanoic	Dodecanoic	Tetradecanoic	Octadecanoic
303	153.3	176.6	212.5	303.4
318	194.7	228.7	267.0	345.1

Ayranci (Ayranci and Gokcen, 2003) observed that the apparent molar volume, V_o of a fatty acid varies linearly with concentration as shown by the equation,

$$V_0 = V_0^0 + b_V C$$

V_o^o is the apparent molar volume at infinite dilution, b_v denotes a measure of ion-ion interaction similar to the A-coefficient in the Jones-Dole equation. The V_o^o and the b_v data obtained by the plots of V_o against concentration at three different temperatures are presented in Table 6.

Table 6 Apparent Molar Volume at Infinite Dilution, V_0^0 (cm^3 mol^{-1}) and b_v of the Acids

Temperature (K)	Decanoic (C$_{10}$)		Dodecanoic (C$_{12}$)		Tetradecanoic (C$_{14}$)		Octadecanoic (C$_{18}$)	
	V_0^0	b_v	V_0^0	b_v	V_0^0	b_v	V_0^0	b_v
303	124.2	361.8	162.8	185.8	179.1	508.4	268.1	670.5
313	204.9	- 71.1	235.9	- 49.4	272.1	- 125.1	318.7	59.5
318	215.0	- 87.3	240.2	- 86.7	318.5	- 166.7	367.2	- 70.3

The concept of transition state theory was employed to analyse the dissolution process as suggested by Feakins (Feakins *et all,* 1986). The B-coefficient (Akanni and Adebajo, 1989) in terms of this theory is given by the equation,

$$B = \frac{\left(\overline{V}_1^0 - \overline{V}_2^0\right)}{1000} + \vec{V}_1^0 \frac{\left(\Delta\mu_2^0 - \Delta\mu_1^0\right)}{1000RT} \quad \text{where}$$

$\overline{V}_1^0$ *and* $\overline{V}_2^0$ are the partial molar volumes of the solvent and solute respectively, $\Delta\mu_2^0$ is the free energy contributed per mole of the solute to the energy of dissolution and $\Delta\mu_1^0$ is that contributed by the solvent. $V_1^0 = \frac{M_0}{\rho_0}$. M_o is the molecular weight of the pure solvent and ϱ_o is the density of the pure solvent. Therefore, V_1^0 is equivalent to V_0^0, the apparent molar volume at infinite dilution. The values of μ_1^0 are calculated from the expression,

$$\Delta\mu_1^0 = RT \ln\left(\frac{\eta_0 V_1^0}{hN}\right) \text{ while those of}$$

$$\Delta\mu_2^0 = \Delta\mu_1^0 + \left(RT/\overline{V}_1^0\right)\left[1000B - \left(\overline{V}_1^0 - \overline{V}_2^0\right)\right]$$

where R, h and N are the molar gas, Planck's and Avogadro's constants respectively. The calculated values of $\Delta\mu_1^0$ *and* $\Delta\mu_2^0$ at various temperatures are presented in Table 7.

Table 7 Solvent Energy ($\Delta\mu_1^0$) and Solute energy ($\Delta\mu_2^0$) at Some Temperatures

T (K)	$\Delta\mu_1^0$ (kJ mol^{-1}) Ethanol	$\Delta\mu_2^0$ (kJ mol^{-1}) Acids			
		C$_{10}$	C$_{12}$	C$_{14}$	C$_{18}$
298	64.41	78.94	86.76	89.38	102.75
303	65.25	80.98	87.91	94.44	104.34
308	66.09	83.57	90.23	96.65	105.95
313	66.92	86.78	92.15	101.23	107.42
318	67.76	87.46	93.32	103.10	109.33
323	68.61	90.32	94.05	104.71	111.96

The dissolution entropies, ΔS_2 for the acids were obtained by plotting $\Delta\mu_2^0$ values against T from the relationship,

$$\frac{d\Delta\mu_2^0}{dT} = -\Delta S_2$$

(Feakins, 1974). The entropy values obtained are,

decanoic acid = 454.6, dodecanoic acid = 352.2, tetradecanoic acid = 612.6 and octadecanoic acid = 342.1 J mol^{-1}.K^{-1}. A typical plot of $\Delta\mu_2^0$ against temperature for octadecanoic acid is shown in Fig. 2 with R^2 = 0.9854
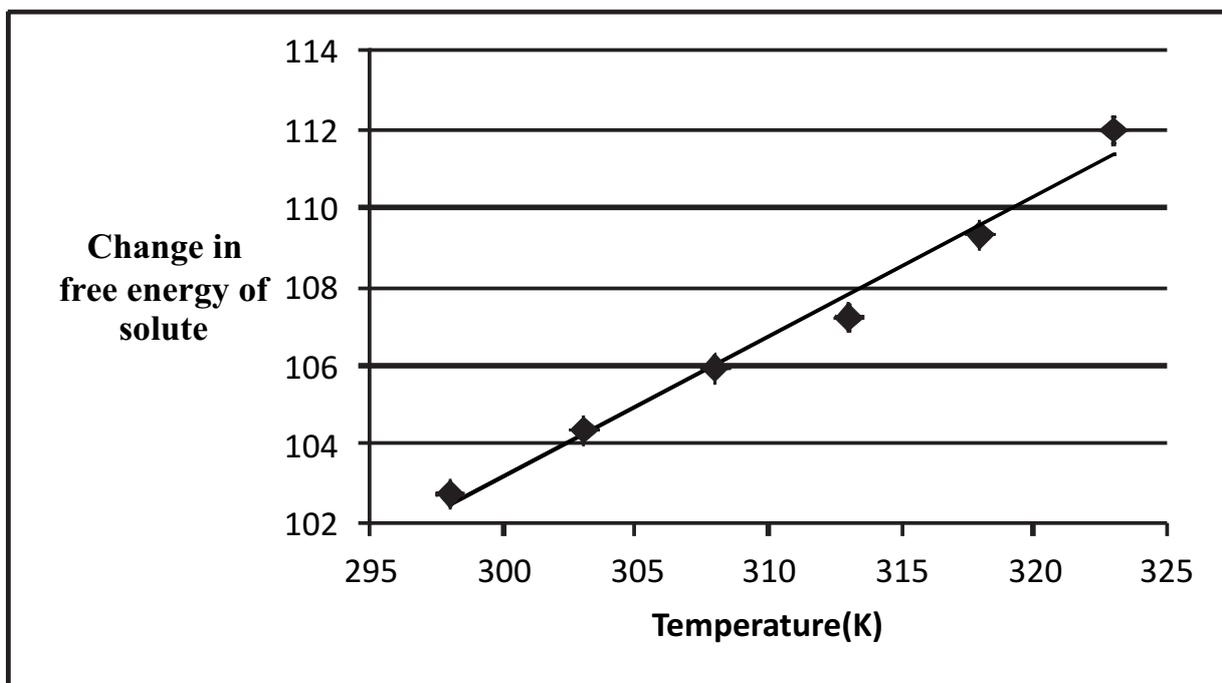
Fig. 2 Plot of Change in the Free Energy of Solute Against Temperature

The dissolution enthalpies were calculated from the equation, $\Delta H_2^0 = \Delta\mu_2^0 + T\Delta S_2^0$ and the values are shown in Table 8.

The temperature dependence of the limiting apparent molar volume at infinite dilution, V_0^0 is

fitted to the Virial type of equation (Franks, 1978) in the form, $V_0^0 = a + bT + cT^2$ where a, b and c are constants. These coefficients were obtained from the non-linear least squares analysis. The values are presented in Table 9.

Table 8   Enthalpy Changes for the Dissolution of the Acids in Ethanol

T (K)	Enthalpy Change (ΔH_2^0) kJ mol^{-1} for the Acids			
	Decanoic	Dodecanoic	Tetradecanoic	Octadecanoic
298	214.4	192.9	271.9	204.7
303	218,7	195.8	280.1	208.0
308	223.6	199.8	285.3	211.3
313	229.1	203.6	293.0	214.5
318	232.0	206.5	297.9	218.1
323	237.2	209.1	302.6	222.4

Table 9   Coefficients a, b and c from the Virial Equation

Acid	a (cm^3 mol^{-1})	b (cm^3 mol^{-1} K^{-1})	c (cm^3 mol^{-1} K^{-2})
Decanoic	- 236.3	19.5	- 0.21
Dodecanoic	- 128.0	16.0	- 0.17
Tetradecanoic	- 87.2	12.8	- 0.10
Octadecanoic	202.0	6.7	- 0.08

The partial molar expansivity or limiting molar expansivity, ϕ_E^0 for the acids are obtained at different temperatures by differentiating the equation, $V_0^0 = a + bT + cT^2$ with respect to temperature to give,

$$\phi_E^0 = \left(\frac{\partial V_0^0}{\partial T}\right)_P = b + 2cT.$$

The expansivity values for the acids are presented in table 10. Hepler (Hepler L., 1969) proposed that qualitative information on the hydration of solutes could be obtained from the thermal expansion of solutions using the identity,

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -\left(\frac{\partial^2 V_0^0}{\partial T^2}\right)_P$$

where C_p is the heat capacity at constant pressure. The Hepler's constant is obtained from the derivative of the partial molar expansivity and so,

$$\left(\frac{\partial^2 V_0^0}{\partial T^2}\right)_P = \frac{d\phi_E^0}{dT} = 2c.$$

Table 10   Expansivity Values of Fatty Acids at Different Temperatures

T (K)	Expansivity of Acid (cm^3 K^{-1} mol^{-1}			
	Decanoic	Dodecanoic	Tetradecanoic	Octadecanoic
298	- 105.7	- 85.3	- 46.8	- 41.0
303	- 107.8	- 87.0	- 47.9	- 41.8
308	- 109.9	- 88.7	- 48.6	- 42.6
313	- 112.0	- 90.4	- 49.8	- 43.4
318	- 114.1	- 92.1	- 50.7	- 44.2
323	- 116.2	- 93.8	- 51.8	- 45.0

Using the c-values in Table 9, the Hepler constants for the acids are, decanoic = - 0.42, dodecanoic = - 0.34, tetradecanoic = - 0.20 and octadecanoic = - 0.16.

Table 2 shows the example of the values obtained for decanoic acid at three different temperatures. Within the limit of experimental error, the specific volume values are constant over the temperature range covered. To gain insight to the variation of specific volume with the number of the carbon chain length, the specific volumes of 0.050 mol dm^{-3} solutions of decanoic (C_{10}), dodecanoic (C_{12}), tetradecanoic (C_{14}) and octadecanoic (C_{18}) acids were determined at three different temperatures (table 3). The table shows that the density is highly insensitive to small temperature changes whereas the specific volume shows a gradual increase in value with increase in the carbon chain length of the acids at each temperature. This suggests that the longer the chain length, the more the space one gram of an acid carves out of the solution. The specific volumes of C_{10} and C_{12} are about half of those obtained for saccharose, glucose, galactose and lactose solutions (Kunitz, 1926) while those obtained for C_{18} are almost of the same order as the values for some sugars and sulphur particles in sodium chloride but are about half of the values for glycogen solutions. The values reported (Kunitz, 1926) for casein solutions were about thirteen times greater than the fatty acids values in Table 3. The specific volumes reported for Indian rubber by the same worker in various solvents are in the 21.8 – 39.2 cm^3 g^{-1} range. These values are much higher than the values obtained in this work for the fatty acids. The activation energies for the viscous flows of the acid solutions (Table 4) show fairly constant values at different concentrations and are independent of the carbon chain length. This suggests that the mobile unit in each acid solution is the acid entity and that there is little or no dissociation/association that could have

significantly affected the streamline macroscopic flows within the concentration range in Table 4.

The apparent molar volume (V_o) is a parameter that presumably represents the sum of the geometric volume of the solute molecules and the changes that may occur in the solution due to the interaction of the solute with the solvent. In effect, the apparent molar volume and the expansivity are important tools used in the study of the solute – solvent interactions. Table 5 shows that V_o increases both with the increase in temperature and the carbon chain length. Of more interpretative significance than the V_o is the apparent molar volume at infinite dilution, V_0^0. This parameter provides information solely on the solute – solvent interaction as the solute – solute interaction is eliminated or at worst reduced to the barest minimum at infinite dilution. The trend of V_0^0 in table 6 is similar to that of V_o. The positive V_0^0 values show the extent of the solute – solvent interaction which in physical terms measures the degree to which the fatty acids disturb the structure of the solvent (ethanol). The b_v values in the table are positive at low temperatures but become negative as the temperature rises. The b_v obtained in this study is not synonymous with the Berchiesi co-volume (Nat Burr. Stand. Bull., 1917) as high positive co-volume values cannot vanish rapidly through zero to negative within a few degree rise in temperature. The trend of b_v in Table 6 is thus interpreted to be due to the weaker solute – solute or ion – ion interactions with the rise in temperature as the species in solution move past each other very fast on the account of increased thermal or kinetic agitation.

It has been suggested that dissolution can be interpreted in terms of the activation process (Feakins *et al*, 1986). Thus some thermodynamic parameters are obtained from the dissolution process analysed on the basis of the transition state theory. The B-coefficient obtained from the Jone-Dole's plot (Akanni and Adebajo, 1989) was used to calculate $\Delta\mu_2^0$ (Table 7). The values of $\Delta\mu_2^0$ for all the fatty acids are higher than those of $\Delta\mu_1^0$ for the solvent at the temperature range shown in Table 7. Both $\Delta\mu_1^0$ and $\Delta\mu_2^0$ are temperature dependent while in addition, $\Delta\mu_2^0$ is carbon chain length dependent. The higher $\Delta\mu_2^0$ values indicate the higher contribution of the solute (acids) to the

solution energy. Thus the formation of the transition state to dislodge the intermolecular bonds of the solvent structure by the solute is less favourable. Feakins *et al* (Feakins *et al*, 1974) had earlier suggested that the greater the $\Delta\mu_2^0$ value, the greater the structure making power of the solute, that is, $\Delta\mu_2^0 > \Delta\mu_1^0$ implies that the solute is a structure maker while $\Delta\mu_2^0 < \Delta\mu_1^0$ implies that the solute is a structure breaker. It is therefore tempting, on the magnitude of $\Delta\mu_2^0$ alone, to classify the fatty acids as structure maker in ethanol. The entropy of dissolution of the acids, C_{10} of 454.6, C_{12} of 352.2, C_{14} of 612.6 and C_{18} of 342.1 J mol^{-1} K^{-1} varies erratically with the chain length and the reason for the abnormal high value for the C_{14} that truncates the expected decrease of entropy with increasing molecular complexity, is not immediately clear. The entropy values are used to calculate the enthalpies of the dissolution of the solutes. Again, the data obtained (Table 8) show erratic trend with carbon chain length. The high entropy change obtained for the C_{14} is reflected in the enthalpy for the dissolution of the acid as its enthalpy values at all the working temperatures are much higher than even the higher carbon chain length, C_{18}. However, there is a general increase in the dissolution enthalpy as the temperature increases. All the enthalpy data are positive suggesting that the dissolution process is endothermic. The higher enthalpy values for the lower chain length acids may be suggestive of the relatively small dissociation upon dissolution. Such small ions in solution are just insufficient to affect the macroscopic viscous flows as observed from the approximately constancy of the activation energies for the viscous flows of the acid solutions (Table 4). The obtained coefficients from the Virial equation (Table 9) show that coefficients a and c increase with increase in the carbon chain length whereas the reverse is the case for coefficient b. The values of molar expansivities calculated from coefficients b and c (Table 10) increase with increase in the number of carbon atoms but decrease with the rise in temperature. It is possible that the solvation of the acids is affected by temperature changes. It has been argued that negative expansivity is a characteristic property of aqueous solutions of hydrophobic solutes (Franks, 1975). Although the solvent used in this

study is not water, the ethanol organic solvent is slightly polar due to the OH group and hence, the negative expansivities originate from the dominant hydrophobic characters of the fatty acids.

The Hepler constants obtained for the fatty acids are negative. Negative Hepler constant had been associated with a structure breaking property of a solute (Hepler, 1969). However, anomalous structure maker had been used to describe a solute that is not an outright structure maker or an outright structure breaker (Nightingale, 1959). Even though the $\Delta\mu_2^0$ values suggest that the fatty acids could be classified as structure makers in ethanol, it is reasonable to also lean on the Hepler constant and combine both parameters to tentatively classify the fatty acids as anomalous structure makers in ethanol and as the Hepler constant becomes more positive with the increase in the carbon chain length, the degree of structure making capacity increases correspondingly.

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