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DEPENDENCE OF THE VISCOSITIES OF SOME ORGANIC ALIPHATIC ACIDS ON TEMPERATURE AND MOLAR VOLUME

G. Berchiesi, D. Leonesi and A. Cingolani

Istituto Chimico dell'Università—62032 Camerino, Italy

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The viscosities of some aliphatic acids were measured in the vicinity of the melting point with a Höppler viscosimeter. The dependence of the viscosity on the molar volume permitted calculation of the covolume, which is compared to that obtained from structural data.

The thermodynamic properties of fusion of organic aliphatic acids from C_{10} to C_{18} were dealt with in two preceding notes [1, 2], in which two stages were distinguished in the fusion process: prefusion and actual fusion. The prefusion enthalpy for stearic acid represents a value of about 10% of the fusion enthalpy; this value decreases from stearic acid to the acids with lower molecular weights. Such an energetic value, according to Barr et al. [3], is involved in the rocking motions of the methylene groups in the chain.

The fusion entropies of these acids were related to those of the analogous paraffins; the average fusion entropy is slightly lower in the acids, thus revealing, in comparison with the paraffins, a certain inertia induced by the dicarboxylic ring (of the dimer) on the chain.

It was hypothesized that such an entropy was working to increase the width of the twisting motion of the methylene groups on the chain. The present note examines the viscosities of these acids in the vicinity of the melting point in an attempt to elucidate the structure of the melt, the viscosity being dependent on the free volume through Batschinski's formula [4], and thus to ascribe the ΔS_{fus} at a precise variation of structure.

Experimental

Methods

The viscosity measurements were made on a Höppler viscosimeter manufactured by VEB Freital, DDR.

The fall tube was on a 10° slope with respect to the vertical of the base plane and was enclosed in a jacket through which circulated warm water, originating from an ultrathermostat with exterior circulation. The viscometer was thermostated to ±0.05°.

The fall time was measured with a chronometer to a tenth of a second. Each measurement was repeated several times and the fall times agreed within 0.1 sec. The fall tube and the balls were washed with boiling Na_2CO_3 solution and rinsed with bidistilled water and afterwards with puriss. CH_3OH. The balls were always handled with plastic tongs. Density was measured with an Ostwald pycnometer. The fill-up was carried out in a stove heated at the experimental temperature; the pycnometer was then immersed in a warm bath of about 100 l. The temperature was controlled within $\pm 0.01°$ until 40°, and within $\pm 0.03°$ at the highest temperature. The excess substance in the capillary, over the level of the bath, was kept in the liquid state with the aid of an electrically-heated resistence wire, and was then sucked off after an hour of thermostating.

Materials

The substances used weie: Schuchardt stearic, palmitic, myristic, lauric, decanoic, and pelargonic acids, whose purities were not less than 99.8%. They were recrystallized from alcohol, dried and then filtered before use, by the method described in a preceding note [5]. For each substance, from 5 to 8 density measurements were made and a linear equation was calculated by the least squares method (Fig. 1c). The lining-up of the viscometric system was controlled by measuring the fall time in bidistilled and deaerated water and in some oils of guaranteed viscosity, furnished by the same manufacturing firm, in order to check the value of the constant k.

Results

The viscosities, densities and temperatures are listed in Tables 1 and 2. The viscosity values comply with the Arrhenius equation:

$$\log \eta = a + b\frac{1}{T},$$

and parameters a and b for each compound are given in Table 3. The fluidity $\varphi = \frac{1}{\eta}$ is linear, in accordance with Batschinski's equation [4]:

$$\eta = \frac{A}{V - b_v}$$

$$\varphi = \frac{1}{A}V - \frac{b_v}{A}$$

A = constant for each substance in the studied range of temperature
V = molar volume
b_v = covolume.

Table 1

Substance	T, K	η, cP
Pelargonic acid		
	289.7	9.04
	291.7	8.48
	295.9	7.44
	303.0	6.06
	308.4	5.24
	313.9	4.59
	318.4	4.11
	323.3	3.69
Capric acid		
	308.3	6.76
	312.5	6.07
	317.6	5.31
	323.1	4.70
	333.8	3.71
Lauric acid		
	323.4	6.89
	325.5	6.51
	330.0	5.87
	330.2	5.82
	335.6	5.15
	336.4	5.02
	345.0	4.13
	347.5	3.95
Myristic acid		
	334.0	7.40
	339.1	6.53
	343.7	5.82
	348.0	5.33
Palmitic acid		
	338.3	8.89
	340.8	8.31
	343.5	7.76
	348.1	6.97
Stearic acid		
	340.7	10.54
	341.9	10.17
	344.2	9.59
	345.6	9.22
	348.0	8.70

Table 2

Substance	T, K	V_M, ml mole^{-1}
Pelargonic acid		
	292.1	174.71
	296.9	175.45
	301.1	176.08
	308.6	177.26
	314.2	178.15
	320.1	179.05
	323.2	179.50
Capric acid		
	308.2	194.08
	314.4	195.08
	322.7	196.30
	328.1	197.13
	333.6	198.07
Lauric acid		
	323.2	229.94
	328.1	230.83
	336.7	232.45
	345.1	234.00
Myristic acid		
	333.8	265.66
	338.2	266.27
	343.2	267.78
	348.1	268.80
Palmitic acid		
	336.7	300.62
	339.5	301.34
	343.2	302.29
	345.2	302.78
	348.2	303.48
Stearic acid		
	341.2	335.11
	343.2	335.58
	345.4	336.09
	348.2	337.08

Parameters $1/A$ and b_v for every studied substance are given in Table 4. It can be observed that A is not constant in the entire series studied, but, with the exception of C_9, varies regularly from C_{10} to C_{18}, perhaps due to the temperature variation.

Graphs of $\log \eta$ vs. $1/T$ and φ vs. V are reported in Figure 1; Figure 2 shows the course of the activation energy ($E_{act.}$) of the viscous flow with the number of

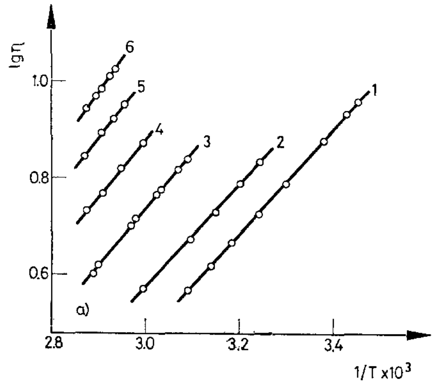


Fig. 1a. log η versus $\frac{1}{T}$. 1: pelargonic acid; 2: capric acid; 3: lauric acid; 4: myristic acid; 5: palmitic acid; 6: stearic acid

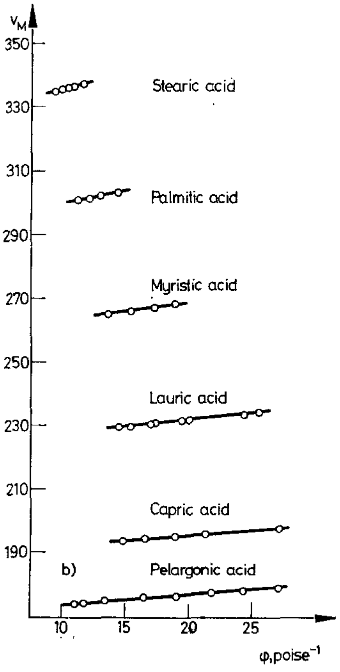


Fig. 1b. φ versus V

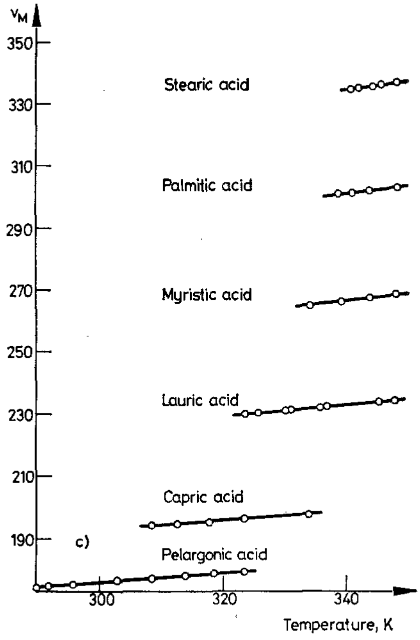


Fig. 1c. V versus T

carbon atoms of the acids examined. The activation energy was calculated from the equation $\ln \eta = A' + \frac{E}{RT}$.

Table 3

Parameters of the Arrhenius equation (η in cP)

Substance	$-a$	b
Pelargonic acid	2.8069	1089.079
Capric acid	2.6950	1086.921
Lauric acid	3.0033	1246.980
Myristic acid	2.7557	1214.870
Palmitic acid	2.7026	1229.087
Stearic acid	2.9608	1352.340

Table 4

Parameters of Batchinski's formula (η in poise)

Substance	$\frac{1}{A}$, poise ml^{-1}	b_V, ml
Pelargonic acid	2.7030	170.3
Capric acid	3.0889	189.4
Lauric acid	2.4008	224.0
Myristic acid	1.6557	257.4
Palmitic acid	1.2662	292.2
Stearic acid	0.9832	325.2

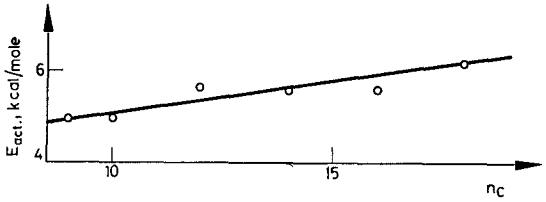
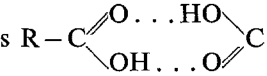


Fig. 2. Activation energy versus the number of carbon atoms in the acids

Discussion

An attempt was made to give a structural meaning to the covolume: Figure 3 shows the structure of dimers  $R-C\begin{smallmatrix}\diagup O...HO \diagdown \\ \diagdown OH...O \diagup\end{smallmatrix}C-R$ which, as demonstrated in preceding papers [1, 2] is the structural entity of the fusion. The length [6] l_2 is calculated in the following way: [2 C−C + O . . . O + 2 C−O cos (122/2)] cos (109/2) = 4.03 Å; the length l_1 is: l_3 + (2 C−C sin 109/2) (n − 2) = (2 C−C + + O . . . O + 2 C−O cos 122/2) sin 109/2 + (2 C−C sin 109/2) (n − 2), where

C–C, O . . . O and C–O represent the relative bond lengths and n the number of carbon atoms of the acid.

A cylinder with volume $\pi\left(\frac{l_2}{2}+r_c\right)^2\cdot\frac{l_1}{2}$ should represent a reliable limit for the monomer, considering the rotational motions around the axis a which, as hypothesized in preceding studies, should take place on fusion.

Table 5 shows the value thus calculated which can be observed to be slightly greater than the b_v values representing the covolumes. Such agreement further confirms the cryoscopic result that in the fused state the dimer is still the structural entity, and leads to the supposition that if an asymmetrical molecule is provided with a rapid rotating motion, the covolume b_v is: $b_v = V_{\text{intr.}} + V_{\text{dis.}}$, that is, it is

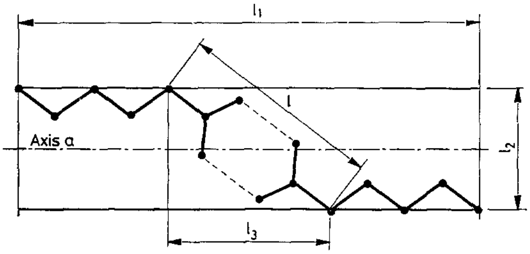


Fig. 3. Structure of the dimer

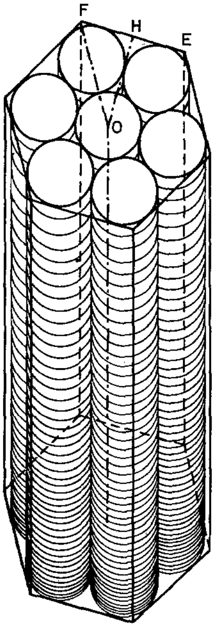


Fig. 4. Cylinders packed in a hexagonal prism

Table 5

Volumes of the acids calculated as cylinders and as parallelepipeds, and molar volumes of the molecules packed as hexagonal prisms

Substance	$V_{\mathrm{cyl.}}$, ml mole^{-1}	$V_{\mathrm{par.}}$, ml mole^{-1}	$V_{\mathrm{hex.prism}}$
Pelargonic acid	169.9	59.8	180.8
Capric acid	188.7	66.3	200.3
Lauric acid	225.6	79.2	239.5
Myristic acid	262.5	92.2	278.7
Palmitic acid	299.4	105.1	317.9
Stearic acid	336.3	118.1	357.0

the sum of the intrinsic volume and the disorder volume because the volume of the cylinder cannot be occupied by other molecules due precisely to the rotating motion. The intrinsic volume in this case could be equalized to that of a parallelepiped of dimensions $\frac{l_1}{2}$, l_2, $2r_c$.

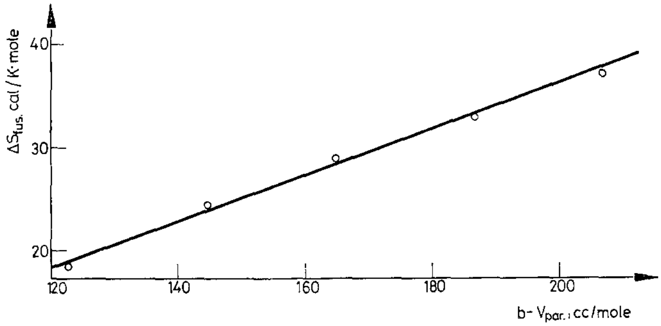


Fig. 5. ΔS_{fus} versus $(b - V_{\mathrm{paral}})$

If such cylinders should be packed as tightly as possible as shown in Figure 4, the molar volume V_{M} could be calculated as follows:

$$V_{\mathrm{M\ calculated}} = V_{\mathrm{hexagonal\ prism}} = \frac{6\overline{\mathrm{FE}}\cdot\overline{\mathrm{OH}}}{2}\,\frac{l_1}{2}\cdot\frac{N}{7}$$

$$\overline{\mathrm{FE}} = 2\overline{\mathrm{OF}}\sin 30^\circ \simeq 2\,(4.03 + 2.02 + 3r_c)\sin 30^\circ$$

$$\overline{\mathrm{OH}} = \overline{\mathrm{OF}}\cos 30^\circ \simeq (4.03 + 2.02 + 3r_c)\cos 30^\circ$$

where N is Avogadro's number and 7 represents the number of cylinders contained in each hexagonal prism. Table 5 gives the values thus calculated; these are slightly greater than the experimental V_{M} in the T interval studied, probably because the dimers do not rotate completely and thus the packing at these temperatures is greater.

The activation energy barely varies by 1 Kcal between C_9 and C_{18}, with a mean value of 5.5 Kcal/mole, which the paraffins [7] reach at about C_{30}. This can be an effect of the dimerization, which would make the term conventionally indicated as C_n really C_{2n}.

The fusion entropies of these acids [1, 2] are a linear function of the parameter $(b - V_{\text{paral.}})$, i.e. of $V_{\text{di3.}}$, as shown in Figure 5.

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Résumé — On a, à l'aide d'un viscosimètre de Höppler mesuré la viscosité de quelques acides organiques au voisinage du point de fusion. Le covolume déduit de la formule de Batschinski a été comparé à celui calculé à partir du modèle structural.

Zusammenfassung — Mit Hilfe eines Viskosimeters nach Höppler wurde die Viskosität einiger organischer Säuren in der Nähe ihres Schmelzpunktes gemessen. Das aus der Formel von Batschinski abgeleitete Kovolumen wurde mit dem aus dem Strukturmodell berechneten verglichen.

Резюме — С помощью вискозиметра Хёпплера была измерена вязкость некоторых алифатических кислот в области точки плавления. Зависимость вязкости от молярного объема позволяет вычислить кообъем, который сравнивали с тем, что был получен из структурных данных.