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THE COVOLUMES OF THE FUSED ALIPHATIC ACIDS FROM C_9 TO C_{18} AND OF C_2, FROM VISCOSITY MEASUREMENTS

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The results of measurements of the viscosities and molar volumes of the organic acids (C_9–C_{18}) as functions of the temperature are reported. They are discussed in connection with the equations of Arrhenius and Batchinski.

Results concerning viscosity measurements on the linear aliphatic acids C_9, C_{10}, C_{12}, C_{14}, C_{16} and C_{18} were discussed in a previous paper [1]. The present one deals with the covolumes (obtained from viscosity measurements by the Batchinski formula) of all the acids, odd and even, from C_9 to C_{18}, and of C_2.

Experimental

The experimental methods are described in detail in the previous paper [1].

Materials

Fluka purum hendecanoic and tridecanoic acids and puriss. pentadecanoic and margaric acids were purified as previously [1] described; C. Erba RP acetic acid was purified by distillation following the Rabinowitsch method [2].

Results and discussion

The experimental values are collected and shown in Table 1 and Fig. 1(a–b). From the graphs $\log \eta$ versus $1/T$ and φ versus V_m it is possible to obtain E_{act} and b_v from the Arrhenius and Batchinski equations. These are listed in Tables 2 and 3. As previously described [1], for the even series the covolumes of these acids can be calculated on the basis of the model reported in Fig. 4 of the preceding note [1]. Further, for the acids C_{11}, C_{13}, C_{15} and C_{17}, the covolume b_v closely corresponds to the value that can be calculated from the model under the hypothesis that the dimer rotates around the a axis, describing a cylinder; that is $b_v = 1/2(l_2/2+r_c)^2 l_1 N$. This correspondence is pointed out in Table 2. In Fig. 2, furthermore, the regular and univocal trend of b_v versus n_c (number of carbon atoms) is shown. If the dimer

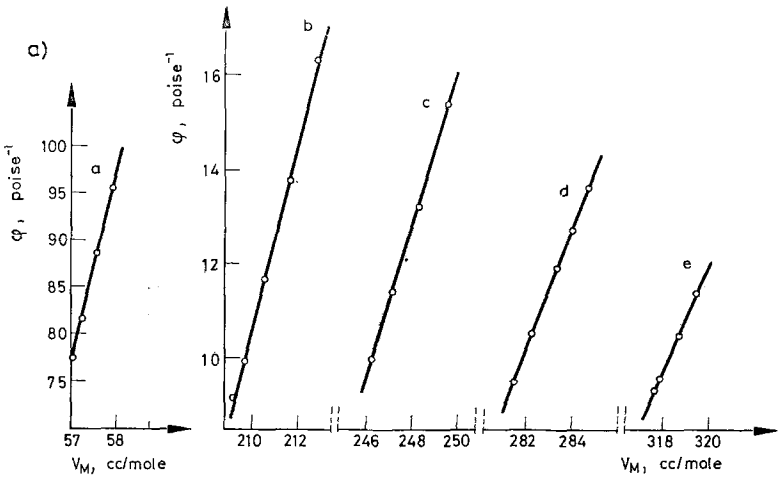

Fig. 1a. Dependence of the fluidity on the molar volume of: a: Acetic acid; b: Hendecanoic acid; c: Tridecanoic acid; d: Pentadecanoic acid; e: Margaric acid

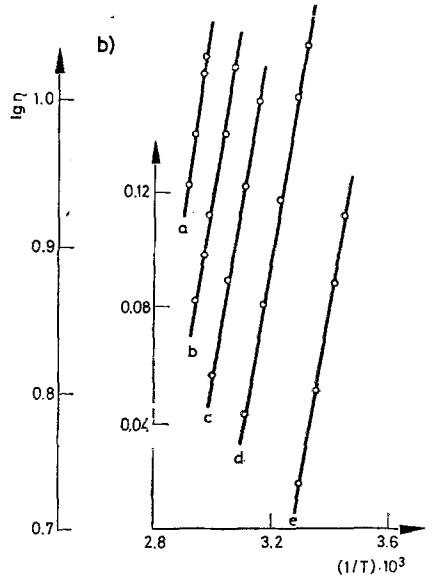

Fig. 1b. Dependence of the viscosity on the temperature of a: Margaric acid; b: Pentadecanoic acid, ordinate from 0.7 to 1.0; c: Tridecanoic acid; d: Hendecanoic acid; e: Acetic acid, ordinate from 0.04 to 0.12

at the melting point begins to rotate around the a axis, the melting entropy [3, 4] should be an univocal function of the moment of inertia $I = \Sigma mr^2$ of the dimer about the axis. This fact, that all values (reported in [3, 4]) of ΔS lie on a smooth line, is demonstrated in Fig. 3; the typical alternance of the graph ΔS versus n_c disappears or is very attenuated in the graph ΔS versus I.

Table 1

Acid	T, K	η cP	V_M, cm³/mole
Acetic	290.1	1.29	57.06
	293.4	1.23	57.27
	298.4	1.13	57.60
	303.4	1.05	57.92
Hendecanoic	301.5	10.91	209.20
	304.4	10.05	209.72
	309.5	8.58	210.62
	315.2	7.28	211.63
	321.9	6.13	212.82
Tridecanoic	317.5	10.01	246.25
	322.1	8.77	247.20
	327.5	7.56	248.30
	333.7	6.51	249.58
Pentadecanoic	325.8	10.53	281.40
	329.4	9.50	282.25
	334.2	8.38	283.38
	337.0	7.87	284.04
	339.9	7.32	284.73
Margaric	336.6	10.71	317.66
	337.5	10.45	317.90
	340.6	9.51	318.73
	343.5	8.77	319.51

Table 2

Parameters of the Batchinski formula $\eta = A/(V-b_v)$, and calculated values V_{cyl}

Acid	b_v, cm³/mole	V_{cyl}, cm³/mole	I/A, poise^{-1}cm^{-3}
Acetic	53.4	41.1	21.058
Hendecanoic	204.7	207.2	1.987
Tridecanoic	240.1	244.1	1.618
Pentadecanoic	273.8	281.0	1.247
Margaric	309.4	317.9	1.123

Table 3

Parameters of the Arrhenius equation $\eta = C \exp(E/RT)$

Acid	C, cP	E, Kcal/mole
Acetic	$1.00 \cdot 10^{-2}$	2.8
Hendecanoic	$1.08 \cdot 10^{-3}$	5.5
Tridecanoic	$1.39 \cdot 10^{-3}$	5.6
Pentadecanoic	$1.72 \cdot 10^{-3}$	5.6
Margaric	$4.68 \cdot 10^{-4}$	6.7

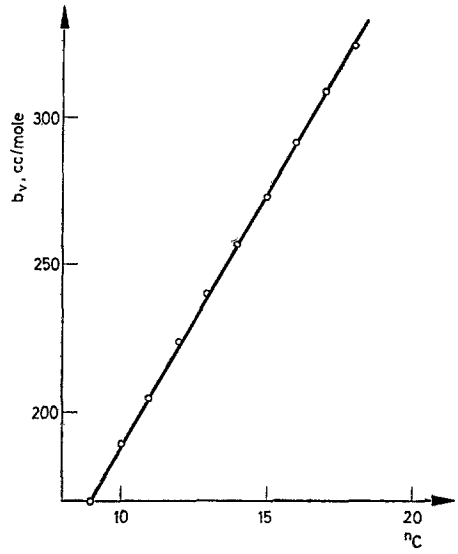

Fig. 2. Dependence of b_v on the number of carbon atoms of the acid

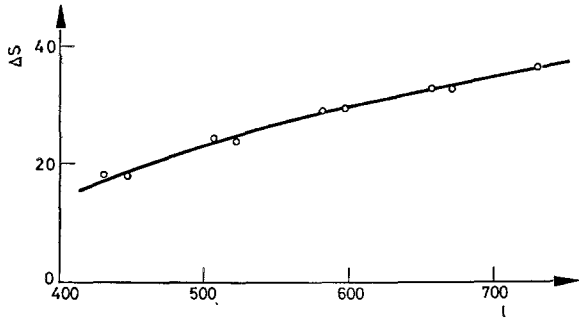

Fig. 3. Dependence of the melting entropy (e.u.) on the moment of inertia $I = \Sigma mr^2$ (m and r expressed in atomic units)

As regards acetic acid, the results are a little different; in fact $b_v > V_{cyl}$. This fact shows that the dimer probably rotates incompletely around the center of the dicarboxylic ring rather than about the *a* axis, describing a greater volume than that of the cylinder. The shortness of the chain in acetic acid probably makes the motions around the center of the dicarboxylic ring less hindered.

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