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FUSION ENTROPY AND MELT VISCOSITY IN SOME ALIPHATIC HYDROCARBONS. RELATION BETWEEN FUSION ENTROPY AND PARAMETER *b* OF THE BATCHINSKI EQUATION

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The fusion entropy, viscosity and molar volume are measured for the following hydrocarbons: $C_{18}H_{38}$, $C_{19}H_{40}$, $C_{20}H_{42}$ and $C_{20}H_{40}$. A relation between ΔS_{fus} and the parameter *b* of the Batchinski equation is given for these compounds and for others previously studied. By employing the calorimetric and viscometric data found in the literature for ionic melts, a similar relation is found to hold for molten salts.

In two previous papers [1, 2] and at a recent congress [3] it was pointed out that some organic melts follow the Batchinski equation [4]; in fact the fluidity is a linear function of the molar volume:

$$\eta = \frac{A}{(V - b)}$$

$$\phi = \frac{-b}{A} + \frac{V}{A}, \qquad (1)$$

From the experimental straight line $\phi = f(V)$ the *b* values were obtained for several acids, two esters and two ethers.

Generally *b* is higher than the intrinsic volume and lower than the molar volume. For the acids [1, 3] a geometrical form of volume *b* was found, whose packing gives the molar volume approximatively.

The hypothesis was put forward that *b* is generally not the intrinsic volume, but the volume not utilizable for the flux owing to the motions of the molecules, i.e.

$$b = V_{\text{intr}} + V_{\text{dis}} \qquad (2)$$

Therefore, $b - V_{\text{intr}}$ may be a measure of the disorder caused by the motions of the molecules and introduced at the fusion point.

In this note a relation between the fusion entropy and V_{dis} is examined for the studied compounds [1–3]; in addition, four hydrocarbons are investigated and the relation is also verified for them. Finally, the relation is extended to a wide class of molten salts (alkali metal halides and nitrates) by employing data from the literature.

Experimental

The melting enthalpy was measured with a Perkin-Elmer differential scanning calorimeter, DSC-IB, the calibration details having been reported in a previous paper [5].

The viscosity measurements were performed with a Höppler viscometer, manufactured by VEB (Freital, DDR), the details also having been given previously [1]. Thermostating within 0.1° was achieved by means of a VEB UI Ultrathermostat. The density was measured with an Ostwald pycnometer, dipped in a thermostat thermoregulated by a mercury–toluene system previously described [6].

The chemicals employed: Fluka purissimum octadecane, nonadecane, eicosane and 1-eicosene, were treated as described previously [1].

Results

The DSC curves for eicosane, 1-eicosene and octadecane exhibit a single peak, and that for nonadecane two peaks; the transition peak arises on the tail of the curve 10° below the fusion peak. The deduced values of enthalpy and entropy are reported in Table 1. In the case of eicosane and octadecane it is possible to compare our results with the previously published ones [7, 8]: $\Delta S_{\text{eicosane}} = 47$ e.u.; $\Delta S_{\text{octadecane}} = 47.8$ e.u.

Table 1

Enthalpies and entropies of fusion of octadecane, nonadecane, eicosane and 1-eicosene

Substance	ΔH, Kcal · mole^{-1}	ΔS, e.u.
$C_{18}H_{38}$	14.7	48.8
$C_{19}H_{40}$	13.8	45.4
$C_{20}H_{42}$	16.0	51.8
$C_{20}H_{40}$	8.5	31.0

The agreement is within 2% for octadecane and within 10% for eicosane. The viscosities and molar volumes are given in Table 2. In Table 3 the activation energies, obtained from the Arrhenius equation, are given with the parameters of the Batchinski equation. The activation energy increases with the chain length and is the highest for 1-eicosene; b increases with the chain length; that corresponding to eicosene is lower than that for eicosane. In the liquid state eicosene probably has a more compact structure (lower b, higher E_{act}, lower ΔS_{fus}).

Table 2

Viscosities and molar volumes of octadecane, nonadecane, eicosane and 1-eicosene

	T, K	η, cP	V, ml · mole^{-1}
$C_{18}H_{38}$	303.3	3.88	328.7
	310.0	3.29	330.6
	316.8	2.87	332.6
	324.5	2.29	334.8
$C_{19}H_{40}$	305.8	4.39	345.1
	307.7	4.17	345.7
	309.1	4.01	346.1
	311.7	3.74	346.9
$C_{20}H_{42}$	310.6	4.42	363.4
	312.2	4.23	363.9
	313.1	4.15	364.2
	314.6	4.00	364.6
	315.5	3.93	364.9
$C_{20}H_{40}$	306.4	5.37	354.8
	308.6	5.07	355.5
	310.8	4.81	356.1
	313.6	4.48	356.9
	316.7	4.18	357.8

Table 3

Arrhenius and Batchinski equation parameters for the studied alkanes and alkene and for the decalins

Parameters of the Arrhenius equation $\eta = a \exp(E/RT)$			Parameters of the Batchinski equation $\eta = A/(V - b)$		
	E, cal/mole	$a \cdot 10^4$, cP	A, poise · mlmole^{-1}	b, ml	V_{intr}, mlmole^{-1}
$C_{20}H_{40}$	5515.2	6.56	0.5734	344.1	57.3
$C_{20}H_{42}$	4450.9	32.7	0.5177	351.6	57.3
$C_{19}H_{40}$	4893.0	13.11	0.4486	334.9	54.3
$C_{18}H_{38}$	4478.0	23.54	0.3482	319.9	51.6
cis-decalin			0.2961	146.2	55.1
trans-decalin			0.2068	149.7	54.5

Discussion

As shown in Fig. 1, a plot of the fluidity versus the molar volume is linear in the temperature range studied (generally 10–20° above the melting temperature), following the Batchinski equation [4]. By the least squares method, Eq. (1) is

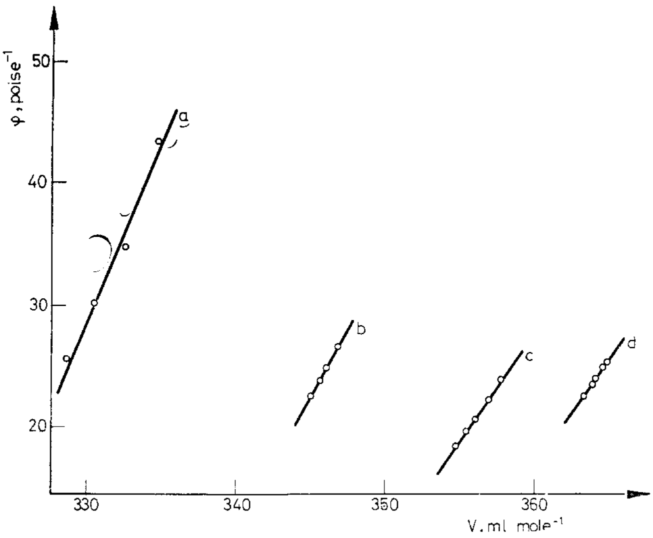

Fig. 1. Fluidity (poise^{-1}) versus molar volume, ml • mole^{-1}: (a) octadecane; (b) nonadecane; (c) 1-eicosene; (d) eicosane

Table 4

$\Delta S_{fus}/(b - V_{intr})$ values for some acids, esters, ethers, alkanes and the decalins

Compound	$\Delta S_{fus}/(b - V_{intr})$
capric acid	0.12
undecanoic acid	0.11
lauric acid	0.14
tridecanoic acid	0.13
myristic acid	0.14
pentadecanoic acid	0.14
palmitic acid	0.14
margaric acid	0.14
stearic acid	0.15
methyl stearate	0.18
ethyl stearate	0.18
diphenyl ether	0.13
dihexadecyl ether	0.13
octadecane	0.17
nonadecane	0.16
eicosane	0.17
1-eicosene	0.11
cis-decalin	0.11
trans-decalin	0.15

found. The corresponding b and A values are given in Table 3, where the V_{intr} values (calculated as the volume of the parallelepiped that tightly envelops the hydrocarbon molecules) are also reported. It is noteworthy that the function $\Delta S_{fus}'/(b - V_{intr})$ is 0.17 ± 0.01 for the alkanes, but 0.11 for the alkene. These values are within the limits relating to the studied acids, esters and ethers [3], (Table 4).

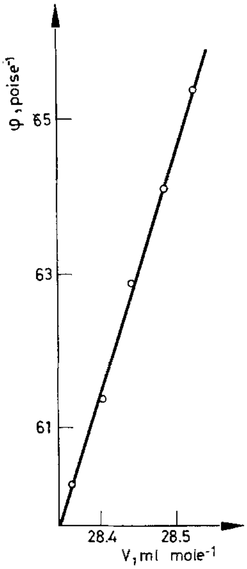

Fig. 2. Fluidity (poise^{-1}) versus molar volume, ml · mole^{-1} for LiCl

In a given class of compounds $\Delta S_{fus}/(b - V_{intr})$ is constant within ± 0.01 e.u. ml^{-1}, whereas it may change between different classes of compounds, with ± 0.03 e.u. ml^{-1} as maximum oscillation (in the substances examined).

The calorimetric measurements may be reproduced within 1 or 2%, but the inaccuracy is frequently higher because a calorimetric measurement depends mainly on the calibration and on the identity of the conditions during the calibration and the experiment.

The viscometric measurements in this note are given to 2% [1]; hence, an inaccuracy higher than 5% is to be expected in $\Delta S_{fus}/(b - V_{intr})$.

The relation $\Delta S_{fus}/(b - V_{intr})$ = constant may be considered valid with a fluctuation of 20%, but with an uncertainty lower than 20%. This fluctuation may be related with the structures of the compounds. In fact, the highest value of $\Delta S_{fus}/(b - V_{intr})$ is obtained for the hydrocarbons (except for 1-eicosene) and esters, and decreases for the acids and ethers. Apolar compounds but with more rigid structures, such as cis and trans-decalin (whose values of η, V and ΔS_{fus} are to be found in the literature [9–11], have lower $\Delta S_{fus}/(b - V_{intr})$ values.

Table 5

b and $\Delta S_{fus}/(b - V_{intr})$ values for the alkali metal halides and nitrates

Salt	b, ml·mole^{-1}	V_{intr}, ml·mole^{-1}	ΔS_{fus}, e.u.	$\Delta S_{fus}/(b - V_{intr})$, e.u. ml^{-1}
LiCl	26.6	15.5	5.39	0.49
NaCl	34.7	17.1	6.23	0.35
KCl	42.8	20.8	6.08	0.28
RbCl	51.0	23.0	5.70	0.20
CsCl	56.7	26.7	5.27	0.18
LiBr	32.0	19.8	5.13	0.42
NaBr	37.4	21.3	6.12	0.38
KBr	47.5	24.9	6.06	0.27
RbBr	52.1	27.0	5.77	0.23
LiI	40.0	27.6	4.72	0.38
NaI	49.2	29.1	6.04	0.30
KI	58.9	32.8	6.02	0.23
RbI	63.9	34.8	5.73	0.20
CsI	73.2	38.6	6.27	0.18
$LiNO_3$	37.6	23.0	11.66	0.80
$NaNO_3$	41.8	24.5	6.1	0.35
KNO_3	50.6	28.1	4.58	0.20

This relation was also examined on a wide class of ionic compounds, alkali metal halides and nitrates, via data given in the literature [12]. For these compounds, too, the relation $\phi = f(V)$ is linear, as shown in Fig. 2 for LiCl.

b and V_{intr}, calculated from the data reported in [12], are given in Table 5, together with $\Delta S_{fus}/(b - V_{intr})$ values; these fluctuate widely between 0.50 and 0.18 e.u. ml^{-1} (except for $LiNO_3$, that behaves exceptionally). V_{intr} is calculated as $4/3\pi\ (r_c^3 + r_a^3)N$ for salts with spherical ions; for the NO_3^- ion the volume is calculated as that of a cylinder, with the dimensions given by Ubbelohde [13]. The function $\Delta S_{fus}/(b - V_{intr})$ seems to be dependent on the dimensions of the ions; in fact the anion being equal, it decreases in the sense Li → Cs; the cation being equal, it decreases in the sense Cl → I. The dimensions of the ions, i.e. the "ionic potential" v, previously defined by Sinistri et al. [14], can be related to

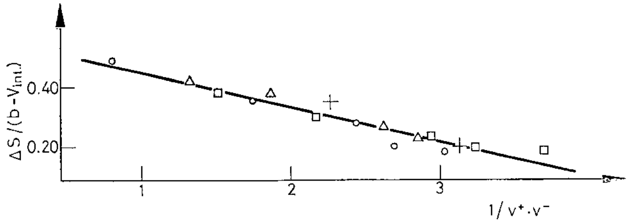

Fig. 3. $\Delta S/(b - V_{intr})$ versus $(v^+v^-)^{-1}$ for the alkali metal halides and nitrates; ○ chlorides; △ bromides; □ iodides; + nitrates

$\Delta S_{fus}/(b - V_{intr})$ as shown in Fig. 3. All the salts obey the equation $\Delta S_{fus}/(b - V_{intr}) = f(v^+ \cdot v^-)$, with a maximum difference of 20% for RbCl, $NaNO_3$ and CsI. $LiNO_3$ exhibits exceptional behaviour. The relation between ΔS_{fus} and the parameter b of the Batchinski equation seems to hold for a wide number of substances:

$$\text{for organic melts} \frac{\Delta S_{fus}}{(b - V_{intr})} = 0.14 \pm 0.03 \tag{3}$$

$$\text{for ionic melts} \frac{\Delta S_{fus}}{(b - V_{intr})} = 0.52 - 0.118/v^+v^- \tag{4}$$

The first and second principles of thermodynamics may be written in the form $T\mathrm{d}S = \mathrm{d}E' + P_e\mathrm{d}V$, and by substituting $\mathrm{d}E'$ by the total-differential with respect to V and T, the following equations are obtained:

$$T\mathrm{d}S = (\partial E/\partial V)_T\mathrm{d}V + (\partial E/\partial T)_V\mathrm{d}T + P_e\mathrm{d}V$$

$$T\mathrm{d}S = P_i\mathrm{d}V + c_v\mathrm{d}T + P_e\mathrm{d}V$$

$$T\mathrm{d}S = c_v\mathrm{d}T + (P_i + P_e)\mathrm{d}V$$

Generally, at atmospheric pressure, $P_i \gg P_e$, and therefore

$$T\mathrm{d}S = c_v\mathrm{d}T + P_i\mathrm{d}V \tag{5}$$

A melting process is an isothermal one, and for this reason Eq. (5) simplifies to

$$T\mathrm{d}S = P_i\mathrm{d}V$$

With assumption that P_i does not vary during the melting process, the following integration is possible:

$$T\Delta S = P_i \int_{V'}^{V''} \mathrm{d}V$$

where $V'' - V'$ is the disorder volume gained by the molecules during the melting process. Thus:

$$T\Delta S = P_i\Delta V$$

$$\Delta S/\Delta V = P_i/T \tag{6}$$

That is the relation between the melting entropy and the disorder volume depends on the internal pressure and on the fusion temperature. In a class of similar substances P_i and T_{fus} are probably dependent, and P_i/T may be roughly constant as shown by Eq. (3). In order to compare Eqs (6) and (4) or (5), it is necessary to know the P_i values.

By means of an ultrasonic interferometer, already described [15], we are currently performing measurements of the ultrasonic velocity and of the derived isoentropic compressibility β_s. At the moment only the results on pelargonic acid are available:

T (°C)	u(m/sec)	β_s(bar^{-1})	α (K^{-1})
26	1319.2	$63.8 \cdot 10_{-6}$	0.000879

For the other compounds analogous measurements will be performed in the near future; the thermal coefficient of expansion α is derived from the published data [1]. The internal pressure is $P_i = T \cdot \alpha/\beta_T$. The isothermal compressibility β_T is derivable from β_s via the specific heats ($\beta_T = c_p\beta_s/c_v$). Since the specific heat is not reported in the literature, β_s is used in order to calculate P_i; this results in 4046 atm (a little higher than the true value). Similar substances (homologous acids, esters, etc.) probably have P_i values of the same order; in fact, in other organic substances this value represents the order of P_i [16].

This value, substituted in formula (6), together with the relation 1 atm = = 0.0234 cal $\cdot$ cm^{-3}, gives $\Delta S/\Delta V$ values varying between 0.30 and 0.26 for the organic acids.

With a certain approximation (owing to the uncertainty in P_i), the theoretical relation (given by Eq. (6) and the experimental one (Eq. (3)) are of the same order. Via the Bockris data [17] for P_i for the alkali metal halides the term P_i/T is calculated (the melting temperatures are taken from Janz [12]). The following values are obtained: LiCl 0.39; NaCl 0.28; KCl 0.23; CsCl 0.22; LiBr 0.31; NaBr 0.22; KBr 0.21; NaI 0.22; KI 0.18; $NaNO_3$ 0.45. These agree satisfactorily with the $\Delta S/(b - V_{\text{intr}})$ values.

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Résumé — L'entropie de fusion, la viscosité et le volume molaire des hydrocarbures $C_{18}H_{38}$, $C_{19}H_{40}$, $C_{20}H_{42}$ et $C_{20}H_{40}$ ont été mesurés. Une relation entre l'entropie de fusion, ΔH_{fus}, et le paramètre b de l'équation de Batchinski est proposée pour ces composés et pour d'autres, précédemment étudiés. En utilisant les données calorimétriques et viscosimétriques trouvées dans la littérature pour les produits ioniques fondus, une relation analogue est proposée pour les sels fondus.

Zusammenfassung — Die Schmelzentropie, die Viskosität und das Molvolumen wurden für folgende Kohlenwasserstoffe gemessen: $C_{18}H_{38}$, $C_{19}H_{40}$, $C_{20}H_{42}$, $C_{20}H_{40}$. Eine Korrelation zwischen ΔS_{fus} und dem Parameter b der Gleichung von Batchinski wird für diese sowie für andere früher untersuchte Verbindungen vorgeschlagen. Durch Verwendung der kalorimetrischen und viskosimetrischen Literaturangaben für geschmolzene ionische Produkte wurde eine analoge Korrelation für geschmolzene Salze vorgeschlagen.

Резюме — Измерены энтропия плавления, вязкость и молярный объем следующих углеводородов: $C_{18}H_{38}$, $C_{19}H_{40}$ $C_{20}H_{42}$ и $C_{20}H_{40}$. Для этих соединений, а также для ранее изученных, приведено соотношение между ΔSпл. и b параметром уравнения Бачинского. Используя калориметрические и вискозиметрические данные, найденные в литературе для расплавов ионных солей, было установлено, что найденное соотношение справедливо и для них.

Symbols

η = viscosity
ϕ = fluidity $(1/\eta)$
V = molar volume
b = covolume, following the Batchinski equation
V_{intr} = intrinsic volume
V_{dis} = disorder volume
E = activation energy for the viscous flux
ΔH_{fus} = fusion enthalpy
ΔS_{fus} = fusion entropy
r_c = cation radius
r_a = anion radius
N = Avogadro's number
v^+ = cationic potential = $(1/r_c)$
v^- = anionic potential = $(1/r_a)$
E' = internal energy
P_e = external pressure
P_i = internal pressure = $(\partial E'/\partial V)_T$
c_v = specific heat at constant volume
c_p = specific heat at constant pressure
u = ultrasonic velocity
β_S = isoentropic compressibility
β_T = isothermal compressibility
α = thermal expansion coefficient