

ULTRASONIC VELOCITY, ISOTHERMAL COMPRESSIBILITY, FREE VOLUME AND P_i/T_f VALUES IN MOLTEN STEARIC, PALMITIC AND LAURIC ACIDS. REFLECTIONS ON FUSION

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Ultrasonic measurements on molten stearic, palmitic and lauric acids enable us to calculate the internal pressure (P_i), free volume, isoentropic compressibility, isothermal compressibility and heat capacity at constant volume as functions of the temperature. The P_i/T_f values are compared with $\Delta S_f/b - v_{\text{in}}^{\text{in}}$ values previously published and a general discussion on the fusion phenomenon is given. An equation connecting internal pressure, molar volume and temperature ($P_i V = RT + (a'/V)$) is proposed and the a' values are given.

There are various ways of studying the structure and properties of the liquid state, and recently Ubbelohde [1] has given a panoramic view of the various theories and aspects of this state of matter. One of the most visual methods of considering liquids is to study their properties near the fusion point or to measure the variations in some quantities such as volume, entropy or heat capacity during the fusion process. This method allows results to be interpreted in terms of the structure of the melts, starting from the structural model of the solid. In this note, giving ultrasonic velocity, as well as P_i , P_i/T_f , β_s , β_T , c_v and V_f values of some molten organic acids, we discuss some considerations on the link existing between fusion entropy and disorder volume on the basis of data of preceding works [2–5] or on the basis of data available in the literature on both organic and inorganic compounds. We also give an equation connecting P_i , V and T , valid in the temperature range studied.

Experimental

The ultrasonic velocities were measured with an interferometer manufactured by Metronex (Warsaw, Poland). This equipment consists of five principal assemblies:

1. A transmitting part consisting of a 2.5 MHz standard frequency generator, dividers, frequency synthesizers and multipliers, trigger and output circuit.
2. A receiving part consisting of a high-frequency amplifier, mixer, local generator accompanied by synchronization circuit, attenuator and system of reference signal amplitude regulation.

3. A minima counter circuit.
4. An oscilloscope with synchronized time base lamps feeding systems.
5. A feeder for the whole system.

The pulse method was employed: voltage as an impulse from the output circuit supplies the transmitting transducer that changes the electric vibration into a mechanical vibration of the same frequency. The mechanical vibration (i.e. ultrasonic wave) penetrates the medium in the container and reaches the receiving transducer placed in the probe, where the mechanical vibration is again transformed into an electric vibration, amplified and sent to the mixer, to which the reference signal impulse is delivered directly from the output. If the length of the route of the ultrasonic waves is changed (i.e. the delay of the signal coming from the ultrasonic channel is also changed), the phase shift between the two signals changes and the resultant signal (visible on the screen of the oscilloscope) shows minima and maxima values corresponding to the phase difference $\Delta\phi = (2n + 1) \lambda/2$ or $\Delta\phi = 2n \lambda/2$. If Δl_1 is the course of the probe required to see two neighbouring maxima signals in the oscilloscope, the ultrasonic velocity u is given by:

$$u = v\Delta l_1 \quad (1)$$

where v is the frequency employed.

In order to minimize the error in the reading of Δl_1 , the probe is shifted by a length Δl_n and formula (1) becomes:

$$u = (\Delta l_n/n) \cdot v \quad (2)$$

Table 1

Parameters of the equations of ultrasonic velocity (at 10 MHz) and the derived quantities

Acid	Stearic	Palmitic	Lauric
a (m/sec)	1280.9	1288.1	1302.4
b (m/sec K)	1.702	3.274	3.119
c (bar ⁻¹)	71.7	70.5	67.1
d (bar K) ⁻¹	0.245	0.449	0.422
e (bar ⁻¹)	84.0	81.9	77.6
f (bar K) ⁻¹	0.217	0.434	0.478
A (ml/mole)	9.370	15.362	12.840
E' (kcal/mole)	2.76	3.04	2.78
g (cal/K mole)	132.48	125.80	88.92
h (cal/K ² mole)	0.553	0.513	0.106
i (bar)	3378.7	3401.2	3244.4
l (bar/K)	1.684	9.907	5.801

Validity range of the parameters:
 from T_z to 75° (stearic acid)
 76° (palmitic acid)
 70° (lauric acid)

where n is the number of minimum points observed on the screen and registered by the minima counter (≈ 50). Δl_n was read by a cathetometer to 0.01 mm. The container is thermostated by an ultrathermostat U 10, manufactured by Pabisch. The apparatus may be employed up to a temperature of 80°. Before each measurement, the transmitting and receiving crystals were adjusted to exact parallelism as evidenced by the maximum depth of the signal produced. The calibration was reported previously [6].

The experimental values of ultrasonic velocity, and the derived quantities (isoentropic compressibility β_s , isothermal compressibility β_T , free volume V_f , heat capacity at constant volume c_v , and internal pressure P_i) are given in Table I following the equations:

$$u = a - b(T - T_f) \quad (3)$$

$$\beta_s = c + d(T - T_f) \quad (4)$$

$$\beta_T = e + f(T - T_f) \quad (5)$$

$$V_f = A \exp(-E'/RT) \quad (6)$$

$$c_v = g + h(T - T_f) \quad (7)$$

$$P_i = i + l(T - T_f) \quad (8)$$

The value P_i/T_f is also given. It represents, as previously demonstrated [5], dS/dV for the melting process.

General considerations

As far as the fusion process is concerned, it is in general difficult to establish an empirical relationship between the thermodynamic quantities and some structural parameters. It may be observed in fact that the fusion entropy is not generally a regular function of the ionic radius; obviously, it depends more widely on the structural differences between the solid and liquid states. An explanation of entropy values on a theoretical basis would require a knowledge of the partition functions of the two states, which is difficult in the case of complex chemicals. Of the various theories (Eyring [18], Kirkwood [19], Petit [20]), the latter permits easier analysis of the results, as demonstrated by Petit [20] for several salts. As in the case of salts with very low-symmetry anions [7b], the melting entropy may be interpreted on the basis of the Petit [20] equation. In fact, the fusion-invariable term is near to the value $\Delta S_f/3$ for many of these salts (Table 2), as predicted. In the remaining salts the value $\Delta S_f/3$ is so far from the fusion-invariable term that in order to explain it both the configuration integral and the functions of the rotation partition would need to be known. This method is in general difficult and cannot be applied to chemically complicated species except with considerable difficulty. In our opinion, however, there exists a simpler possibility of relating the fusion entropy to the disorder volume, introduced

Table 2
Fusion and transition entropy of some salts with low-symmetry anions

Salt	ΔS_f e.u.	$\Delta S_f/3$ e.u.	ΔS_2 e.u.	Reference
NaCNS	9.93	3.31	—	8
KCNS	6.84	2.28	0.89	7,9
RbCNS	6.67	2.22	0.89	7
CsCNS	3.20	1.07	5.23	7
LiNO ₃	12.15	4.05	—	10
NaNO ₃	6.43	2.14	1.68	7,10
KNO ₃	3.95	1.32	3.23	10,11
RbNO ₃	1.90	0.63	4.15	12
CsNO ₃	4.85	1.62	2.10	13,14
HCOONa	7.67	2.56	0.56	7
HCOOK	6.39	2.13	0.45	7
HCOORb	6.41	2.14	—	7
HCOOCs	3.01	1.00	3.46	7
CH ₃ COONa	7.32	2.44	—	15,17
CH ₃ COOK	6.27	2.09	—	16,17
CH ₃ COORb	5.14	1.71	1.04	7
CH ₃ COOCs	6.22	2.07	—	7

at the fusion point, which would produce an interesting result. A fusion process is thermodynamically reversible, and therefore, as demonstrated previously [5]:

$$dG_{T,P} = 0 \quad (9)$$

$$dH - TdS = 0 \quad (10)$$

$$dE + pdV = TdS \quad (11)$$

$$P_i dV + pdV = TdS \quad (12)$$

But since $P_i \gg P$ (13)

$$P_i dV = TdS$$

$$dS/dV = P_i/T \quad (14)$$

Therefore, thermodynamics envisages a relation between S and V in a fusion process.

Experimental considerations

The fusion ΔV is a quantity that can be related only with difficulty to the fusion ΔS [1], and while ΔS_f is always a positive quantity, this is not always true for ΔV_f , as in the case of H₂O and CH₃COOK [21]. We think that dV in eq. (2) represents the expansion effectively supported by the molecules, especially at

the expense of the "gaps" present in the solid, and that therefore it does not necessarily represent ΔV_f ; in fact, $P_1 dV$ represents the work against the forces existing in the crystal even in the gaps. That is, according to this way of thinking, the fusion process could be seen in the following way:

1. An event of acquiring energy, when the molecules or the ions with greater rotatory or translational motion come to acquire greater space and therefore to have a resultant geometric form different from or at least bigger than their real dimensions.

2. A bedding event when these new molecular volumes pack themselves in.

This second event, probably simultaneous to event 1, can in some cases lead to a contraction, but it is not impossible that in the first event there is a real "expansion" of the structural units of the system at the expense of both the internal gaps and the fusion ΔV .

We arrived at this idea from a consideration of the viscosimetric experimental results. The viscosimetric data of some organic melts [2-4], plotted according to Batschinski [23] as $n = A/(V - b)$, provide a covolume b , which is much greater with respect to the effective dimensions of the compound:

$$V_{\text{intr}} \ll b < V \quad (15)$$

Table 3

Covolume b and intrinsic volume for some organic substances

Substance	b , ml/mole	V_{intr} , ml/mole
1-Eicosene	344.1	57.3
Eicosane	351.6	57.3
Nonadecane	334.9	54.3
Octadecane	319.9	51.6
cis-Decaline	146.2	55.1
trans-Decaline	149.7	54.5
Capric acid	189.4	40.6
Undecanoic acid	204.7	44.6
Lauric acid	224.0	48.6
Tridecanoic acid	240.1	52.6
Myristic acid	257.4	56.6
Pentadecanoic acid	273.8	60.6
Palmitic acid	292.2	64.6
Margaric acid	309.4	68.6
Stearic acid	325.2	72.6
Ethyl stearate	358.2	81.6
Methyl stearate	339.7	76.4
Diphenyl ether	154.8	52.6 (35.1)*
Dihexadecyl ether	556.4	90.2

* following a planar model or not.

This suggests that the structural entities of the system, during fusion, acquire motions so rapid as to render unusable to the flux a volume much greater than the effective one of the molecule or the ion. We therefore thought that b could be a measure of the disorder volume and in Table 3 we have given the values of both b and V_{intr} . In the case of saturated fatty acids it is also surprising that b is equivalent to the rotation volume of the molecule around the axis a (Fig. 4 in [2]).

For angular structure molecules, such as organic substances, it is not very easy to calculate V_{intr} from the bond angles and lengths [24]; we chose the following method: we made an ideal choice of one or more parallelepipeds to surround the molecule tightly at every point, and calculated the volume of these geometric figures which represents V_{intr} .

According to us, $(b - V_{\text{intr}})$ represents the molar disorder the introduction of which into the system at T_f provokes the increase of entropy ΔS_f . This assumption is valid as long as the calculation of V_{intr} which we made is valid, and as long as it is true that at T_f that solid has not itself a certain molecular disorder. The application of eq. (14) to these results produces the values tabulated in Table 4. It can be seen that there is a certain constancy in the relation $\Delta S_f/V_{\text{dis}}$, which could be the consequence of a dependence of T_f on P_i , and as a result the

Table 4
Agreement between the melting entropy and the disorder volume,
evaluated as $b - V_{\text{intr}}$,

Substance	$\Delta S_f/(b - V_{\text{intr}})$, cal/K ml
1-Eicosene	0.11
Eicosane	0.17
Nonadecane	0.16
Octadecane	0.17
cis-Decaline	0.11
trans-Decaline	0.15
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
Ethyl stearate	0.18
Methyl stearate	0.18
Diphenyl ether	0.13
Dihexadecyl ether	0.13

relation P_i/T_f in a certain family of substances with molecular interactions of the same nature could be roughly constant.

In order to examine, on the basis of eq. (14), the validity of the values in Table 4, it would be necessary to know the internal pressure of the substances under examination in the solid state at the point of fusion. Since this is not a widely-known quantity, it is difficult to compare the experimental value of $\Delta S_f/(b - V_{intr})$ and the value predicted by thermodynamics, according to eq. (14).

For stearic, palmitic and lauric acids we introduce ultrasonic measurements, from which it is possible to obtain isoentropic compressibility values $\beta_s (= 1/u^2d)$. The internal pressure is given by

$$P_i = (\alpha/\beta_T)T \quad (16)$$

where β_T is the isothermal compressibility, which is deducible from the adiabatic one, β_s , once the specific heat is known ($\beta_T = \beta_s + TV\alpha^2/c_p$). The specific heat is given in the literature [25], and α , the coefficient of thermal expansion, is deduced from the preceding volumetric measurements [2, 3]. The experimental values of ultrasonic velocity and the derived quantities are given in Tables 1 and 5.

The accord can be seen to be satisfactory (in these acids) and $(b - V_{intr})$ can more or less be considered a measure of the disorder volume introduced by

Table 5

Internal pressure and P_i/T_f values at the melting point, for stearic, palmitic and lauric acids

Substance	$P_{i,fus}$, atm	T_{fus} , K	P_i/T , cal/K ml
Stearic acid	3334.4	339.3	0.23
Palmitic acid	3356.6	334.6	0.24
Lauric acid	3201.8	316.0	0.24

the fusion on the crystalline matrix. A further analysis of eq. (14) could be made on alkali metal halides and nitrates, using calorimetric data, the viscosimetric and volumetric data collected in [22] and the internal pressure data published by Bockris [26]. In Table 6 the results are given (in this case the V_{intr} calculation is very simple). As one can see, there is good agreement, even if an objection could be made about the use of the P_i of the melt at the fusion point instead of the solid at the fusion point. A better use of eq. (14) indicates, therefore, a wider knowledge of the internal pressure of the two phases at T_f . However, as both the phases under examination are condensed and at the same temperature, it is probable that P_i is not very different. For the moment, therefore, a more profound discussion on the difference between $\Delta S_f/(b - V_{intr})$ and P_i/T_f cannot be made.

Table 6

Empirical and theoretical values of the agreement between the melting entropy and the disorder volume for alkali metal chlorides, bromides, iodides and nitrates and for CH_3COOK

Salt	$\Delta S / (b - V_{\text{intr}})$, cal/K ml	$(P_i/T)_f$, cal/K ml
LiCl	0.49	0.39
NaCl	0.35	0.28
KCl	0.28	0.23
RbCl	0.20	—
CsCl	0.18	0.22
LiBr	0.42	0.31
NaBr	0.38	0.22
KBr	0.27	0.21
RbBr	0.23	—
LiI	0.38	—
NaI	0.30	0.22
KI	0.23	0.18
RbI	0.20	—
CsI	0.18	—
LiNO ₃	0.80*	—
NaNO ₃	0.35	0.45
KNO ₃	0.20	—
CH ₃ COOK	0.13	—

* LiNO₃ exhibits singular behaviour, probably due to a different mechanism of melting

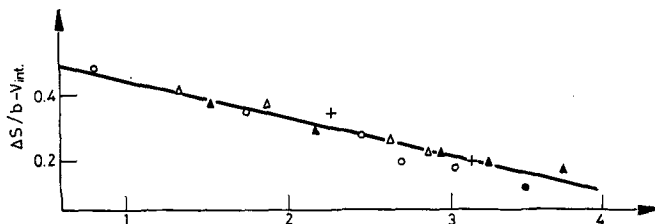


Fig. 1 Trend of the empirical values of the agreement between the melting entropy and disorder volume versus the ionic potentials: \circ chlorides; \triangle bromides; \blacktriangle iodides; $+$ nitrates; \bullet CH_3COOK

Figure 1 shows the dependence of $\Delta S_f / (b - V_{\text{intr}})$ on $1/v^+v^-$ for alkali metal halides and nitrates, where v^+ and v^- are ionic potentials as defined before [27]. For potassium acetate, furthermore, for which data on viscosity and molar volume exist [21], $\Delta S_f / (b - V_{\text{intr}})$ has been calculated; for the calculation of V_{intr} it has been assumed that the acetate ion is comparable to a cylinder of the dimensions given by Hazlewood et al. [21] and that it encloses the planar acetate ion. It is probable enough, in fact, that in the solid state there is no free rotation

along three axes, but at the most one rotation of the methyl around the C—C axis, and perhaps a head-to-tail rotation of the acetate ion [21]. The result is in good agreement with the values for the other salts, and this is reasonably significant because it makes it possible to group together this high-asymmetry anion salt with other salts with symmetrical anions (and probably a different fusion mechanism) under a single fusion law. Unfortunately, an analogous verification for other salts with asymmetrical anions (thiocyanates and formates) is not possible because of the scarcity of data in the literature, perhaps as a result of the relative thermal stability of these salts of an organic nature.

We hope to be able as soon as possible to initiate viscosity, internal pressure and volumetric measurements on these low-symmetry organic anion salts in order to confirm what has been found up to now for the other compounds. From these results, the conclusion could be reached for the moment that the fusion is a phenomenon which may consist of different events, or of at least two events, which might be visualized as done previously in points 1 and 2; the melt obtained is to be considered from the structural point of view as a packing of geometric forms which are the results of translational and rotational movements of the molecules or the ions; the fusion entropy is related to the disorder volume, which is not necessarily equal to the fusion ΔV ; a quantity which can give an idea of the disorder in the liquid phase is the term b of the Batschinski equation; the "volumic entropy of fusion" dS/dV , that can be calculated as P_i/T_f or $\Delta S_f/(b - V_{intr})$, may be put into relation to the structural parameters more than the entropy of fusion.

The free volume obtained from ultrasonic measurements as $V(u_G/u_L)^3$ is much lower than that found from viscosimetric measurements [2–4] as $V - b$; this difference is not discussed here owing to the approximation in the calculation of u_G as $(RT/M)^{1/2}$. The activation energy of free volume and that of viscous flux are of the same order. The internal pressure is a linear function of the temperature in the range examined. It is interesting to note that the internal pressure P_i , molar volume V and temperature T are related in the temperature range examined, following the equation $P_i V = RT + a'/V$. The values of a' for the three acids are: 162.8 l^2 atm (lauric); 295.0 l^2 atm (palmitic); 370.9 l^2 atm (stearic).

*

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Symbols

S	entropy
ΔS_f	fusion entropy
ΔS_t	transition entropy
G	free energy of Gibbs
H	enthalpy

E	internal energy
P	external pressure
V	molar volume
V_f	free volume
V_{intr}	intrinsic volume
V_{dis}	disorder volume
P_i	internal pressure
T	temperature
η	viscosity
b	covolume following Batschinski equation
α	coefficient of thermal expansion
β_s	coefficient of adiabatic compressibility
β_T	coefficient of isothermal compressibility
v^+, v^-	ionic potentials
c_v	molar heat capacity at constant volume
u	ultrasonic velocity
ν	frequency of the ultrasonic wave
E'	activation energy for the free volume
d	density
G, L	gas and liquid, respectively
M	molecular weight
R	gas constant

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RÉSUMÉ — Le calcul de la variation de la pression interne, du volume libre, de la compressibilité isoentropique, de la compressibilité isotherme et de la chaleur spécifique à volume constant des acides stéarique, palmitique et laurique, en fonction de la température, a été effectué à partir de mesures aux ultrasons. Les valeurs P_i/T_i sont comparées à celles de $\Delta S_f/(b - V_{\text{intr}})$ déjà publiées. Une discussion générale porte sur le phénomène de fusion. Une équation reliant la pression interne, le volume molaire et la température ($P_i V = RT + (a'/V)$) est proposée et les valeurs de a' sont données.

ZUSAMMENFASSUNG — Die an geschmolzener Stearin-, Palmitin und Laurinsäure durchgeführten Ultraschallmessungen ermöglichen die Berechnung des inneren Druckes, des freien Volumens, der isoentropischen Kompressibilität, der isothermen Kompressibilität und der Wärmekapazität bei konstantem Volumen als Funktion der Temperatur. Die P_i/T_i Werte werden mit den früher veröffentlichten Werten von $\Delta S_f/(b - V_{\text{intr}})$ verglichen und eine allgemeine Beschreibung des Schmelzvorgangs wird gegeben. Eine Gleichung zur Verbindung des inneren Druckes, des Molarrolumens und der Temperatur ($P_i V = RT + (a'/V)$) wird vorgeschlagen und die a' Werte angegeben.

Резюме — Ультразвуковые измерения, выполненные на расплавленных стеариновой, пальмитиновой и лауриновой кислотах, позволили вычислить внутреннее давление, свободный объем, изоэнтропийную и изотермическую сжимаемости, также теплоемкость при постоянном объеме в зависимости от температуры. Сопоставлены значения P_i/T_i с ранее опубликованными значениями $\Delta_p S_f/(b - V_{\text{intr}})$ и проведено общее обсуждение явления плавления. Предложено уравнение, связывающее внутреннее давление, молярный объем и температуру: $P_i V = RT + (a'/V)$ и приведены значения a' .