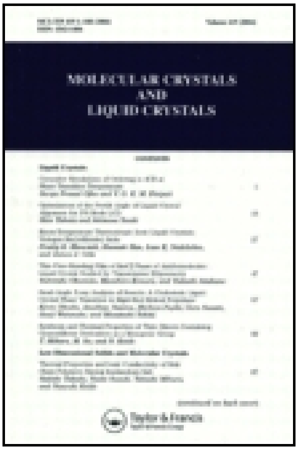

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Thermodynamic Study of Some Neopentane Derivated by Thermobarometric Analysis

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Thermodynamic Study of Some Neopentane Derivated by Thermobarometric Analysis

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By using a metabolemeter, the phase behaviour under pressure of five plastic crystals derivated from Neopentane have been studied. The analysed compounds have been: 2,2-dimethyl, 1,3 propanediol (NPG), 2-hydroxymethyl-2 methyl, 1,3 propanediol (PG), 2-amino, 2-methyl, 1,3 propanediol (AMP), tris(hydroxymethyl-aminomethane (TRIS) and 2-methyl, 2-nitro, 1-propanol (MNP). The pressure–temperature phase diagrams have been established. The molar volume changes for both solid to plastic and plastic to liquid first order phase transitions have been determined.

1. INTRODUCTION

There are very few data relating to the molar volume changes at atmospheric pressure and pressure-temperature dependence for the phase transitions of compounds formed by tetrahedral molecules characterized by orientationally disordered phases (ODIC) or plastic phases [1]. Such disorder is most readly observed with globular compounds (as tetrahedral molecules) or cyclic compounds—so-called "Plastic Crystals"—, because of their relative ease of reorientational motion. In the last decade an extensive and systematic work has been developed over basically the cyclic compounds by A. Würflinger and G. M. Schneider [2–12] in order to characterize thermodynamically the compounds and to study the dielectric behaviour, both as a function of temperature and pressure parameters.

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In the present work we report on the pressure dependence of the phase behaviour of some Plastic Crystals established with the aid of a thermobarometric method, which has been recently used to study the phase behaviour under pressure of "Liquid Crystals" i.e., disk-like mesogens [13], pyramidic mesogens [14] and rodlike mesogens (pures [15,16] or in binary mixtures [17]).

For compounds derived from Neopentane $C(CH_3)_4$, (plastic crystals studied in this work), the high symmetry of the molecular shape enables an interesting comparison with other related compounds for which some pressure-temperature data have been given recently [18–21].

The molar volume change associated to the first order phase transitions determined by the thermobarometric method will be compared to the calculated values by the extrapolation of the volume expected for the related phases at the transition temperature, from X-ray diffraction measurements, when available literature data are known.

2. EXPERIMENTAL DEVICE

The thermobarometric measurements have been performed by means of an automatic metabolemeter [22]. The details of the method (simultaneous recording of pressure of a small sample enclosed in a metallic cell as a function of temperature) interpretation and exploitation of thermobarograms and experimental procedures have been described elsewhere [15, 23].

The first order phase transitions are accompanied by a sudden increase in pressure as a function of the temperature; the slope $(dP/dT)_e$ at the transition given by the Clausius–Clapeyron relation

$$\left(\frac{dP}{dT}\right)_e = \frac{\Delta H}{T \cdot \Delta V}$$

enables us to calculate the associated molar volume change ΔV at atmospheric pressure, where the enthalpy variation ΔH and the temperature T of the transformation are well established. Outside of the transition domain, the slope of the thermobarogram $(dP/dT)_v$ is [23]

$$\left(\frac{dP}{dT}\right)_v = \frac{\alpha}{\chi}$$

where α is the isobaric thermal expansion coefficient and χ is the isothermal compressibility coefficient of the analysed phase.

The working range of the equipment used is 273–490 K and 0–120 MPa in temperature and pressure respectively. The heating and cooling rates used in this work have been $2\,K\cdot min^{-1}$. The extrapolated temperatures of the phase transitions at atmospheric pressure, match up within the experimental (± 2 K) error with those determined previously by thermal analysis.

3. SUBSTANCES

The studied compounds have been some members of the Neopentane ($C(CH_3)_4$) derivated series. From this compound, four series are typically well known, giving plastic crystal compounds. The first series can be obtained from the substitution of —CH_3 group by —CH_2OH group. That is to say, $(CH_3)_{4-n1}C(CH_2OH)_{n1}$. For this series, the members $n_1 = 2$, NPG (2,2-dimethyl, 1,3 propanediol) and $n_1 = 3$, PG (2-hydroxymethyl-2 methyl, 1,3 propanediol) have been studied and will be compared to the compound $n_1 = 1$, NPA (2,2-dimethyl, 1-propanol) studied previously [24]. The temperatures of transition and melting processes of the last member of this series $n_1 = 4$, PE (2,2-Bis(hydroxymethyl), 1,3-propanediol) are outside of the working range. All members of this series show a plastic (face centered cubic [25]) phase before the melting process.

The second series is obtained from the substitution of a —CH_3 group by the —NH_2 group, and the successive substitution of methyl groups by hydroxymethyl group. Then, the series is $(NH_2)(CH_3)_{3-n2}C(CH_2OH)_{n2}$; the two first members, $n_2 = 0$ and $n_2 = 1$, do not show a plastic phase [26]. The two next members studied in this work, are $n_2 = 2$, AMP (2-Amino, 2-methyl, 1,3 propanediol) and $n_2 = 3$, TRIS (Tris(hydroxymethyl-aminomethane), which plastic phases are known to be body centered cubic [25, 27].

The next series is generated in a similar way, but by the substitution of a —NO_2 group, giving $(NO_2)(CH_3)_{3-n3}(CH_2OH)_{n3}$ series; in this case the compound studied has been $n_3 = 1$, MNP (2-methyl,2-nitro,1-propanol), and can be compared to the compound corresponding to $n_3 = 0$, MN (2-methyl, 2-nitro propane), which phase behaviour under pressure has been described previously [18]. The last series can be obtained by the introduction of a carboxyl group (COOH), i.e., $(COOH)(CH_3)_{3-n4}C(CH_2OH)_{n4}$. Any member of this series has been analysed, but the results obtained by Chihara and co. [19] for the compound corresponding to $n_4 = 0$, PA (2,2-dimethyl propanoic acid), will be used in order to include more information.

Obviously, additional substitutions of the —CH_3 group can be performed using other different groups as —C_2H_5 (e.g., Neohexanol $(C_2H_5)(CH_3)_2C(CH_2OH)$ [28] or 1,1,1 Tris(hydroxymethyl)propane $(C_2H_5)C(CH_2OH)_3$, [29]. Only in some cases [28] the thermodynamic PVT data are reported in the literature.

The compounds have been purchased from Aldrich Chemical Company with purities of NPG 99%, PG 99%, MNP 99%, AMP 99% and TRIS 99,9 + %. In order to eliminate the residual humidity, the compounds have been dried by vacuum sublimation at different temperatures.

4. RESULTS

4.1. Thermobarograms

In Figures 1a and 1b are given examples of thermobarograms obtained for the solid II (monoclinic structure [30]) to plastic I (fcc lattice [31]) and for the plastic I to liquid L phase transitions, respectively, for NPG compound. Figure 1a shows clearly the

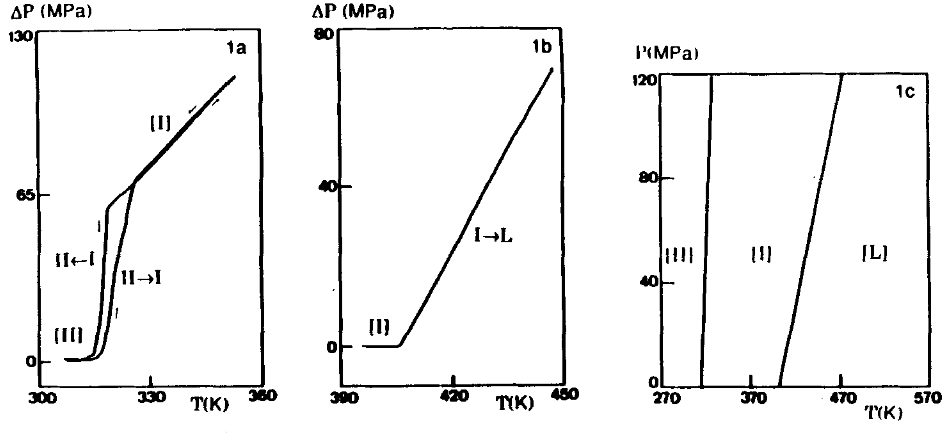

FIGURE 1 Experimental thermobarograms showing for NPG, $n_1 = 2$, $(CH_3)_2C(CH_2OH)_2$ the solid II to plastic I phase transition (on heating and cooling (a)) and the plastic I to liquid L process (b) and Pressure–Temperature phase diagram (c).

reversibility of the solid state transformation but with a weak undercooling under pressure. In both cases, very clear pressure changes (characteristic of the first order phase transitions [23]) are shown.

Figures 2a and 2b show two typical thermobarograms obtained for PG and corresponding respectively to the solid II (body centered tetragonal [32] to plastic *I* (fcc lattice [33]) and I to L transitions.

For AMP, three characteristic thermobarograms obtained experimentally are presented in Figures 3a (solid–plastic phase transition on heating and cooling) and 3b (melting process). From Figure 3a, on heating, the solid state transformation is clearly

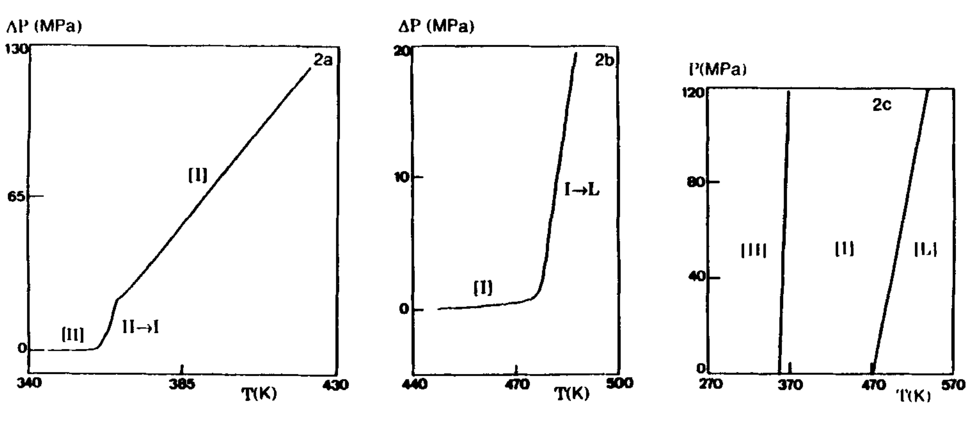

FIGURE 2 Experimental thermobarograms showing for PG, $n_1 = 3(CH_3)C(CH_2OH)_3$ the solid II to plastic I phase transition (a) and the plastic I to liquid L process (b) and Pressure–Temperature phase diagram (c).

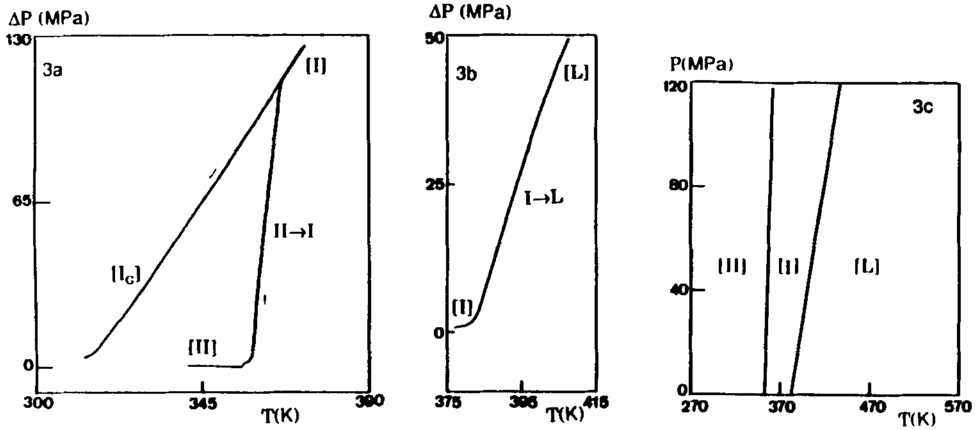

FIGURE 3 Experimental thermobarograms for AMP, $n_2 = 2$, $(NH_2)(CH_3)C(CH_2OH)_2$ on heating (solid II to plastic I phase transition) and cooling (the reversible transition is absent in the range of temperature studied) (a) and the plastic I to liquid L process (b) and Pressure–Temperature phase diagram (c).

of first order. However, on cooling, no reversible transition is obtained. This fact is due to undercooling of the plastic phase that leads to a glassy plastic phase I at low temperatures [34, 35]. More work (outside of the scope of this paper) must be performed in order to determine the glassy temperature transition at different pressures.

Figures 4a and 4b are representative of typical thermobarograms for TRIS in the solid state transition (orthorhombic to bcc) and in the melting process.

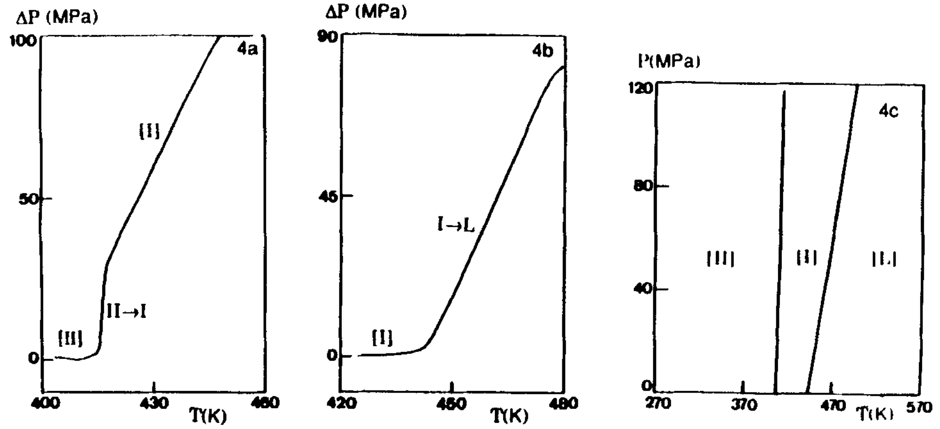

FIGURE 4 Experimental thermobarograms showing for TRIS, $n_2 = 3$, $(NH_2)C(CH_2OH)_3$ the solid II to plastic I phase transition (a) and the plastic I to liquid L process (b) and Pressure–Temperature phase diagram (c).

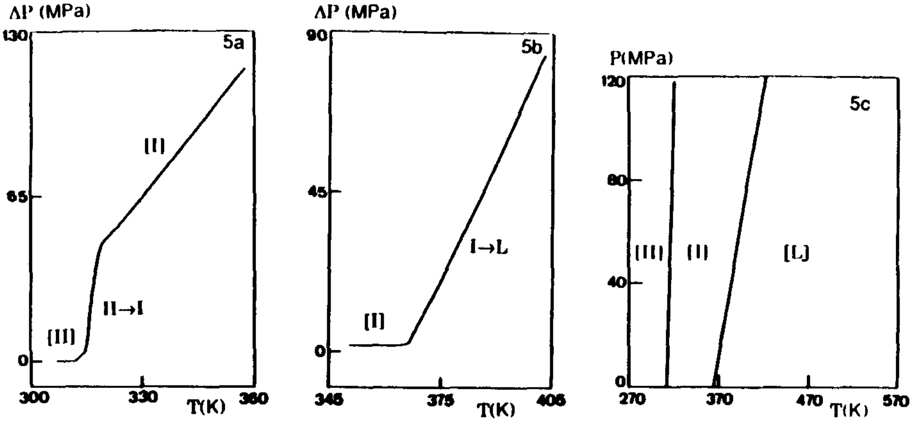

FIGURE 5 Experimental thermobarograms showing for MNP, $n_3 = 1$, $(NO_2)(CH_3)_2C(CH_2OH)$ the solid II to plastic I phase transition (a) and the plastic I to liquid L process (b) and Pressure–Temperature phase diagram (c).

Characteristic curves related to the solid–plastic transition and to the melting process for MNP compound are given in Figures 5a and 5b respectively.

4.2. Phase Diagrams

For each studied compound, the pressure-temperature phase diagram, deduced from the thermobarograms, has been given. It is interesting to note that, for all the compounds, the application of pressure displaces the region of the existence of the plastic phase to a higher and a wider temperature range, because of the difference between the data of the slopes of the P–T phase diagram for the solid–plastic and plastic–liquid equilibria. On the other hand, in not one of the studied compounds, an additional intermediate phase generated by the pressure (as in other plastic compounds [2, 9, 20, 21, 28]) has been found.

4.3. Thermodynamic Data

Literature data for the temperature, entropy and enthalpy changes at the II–I and I–L transitions are reported in Table 1 for the studied compounds, i.e., NPG, PG, AMP, TRIS and MNP and for the compounds used for comparison, i.e., NPA, MN and PA. Experimental data for the equilibrium curves $(dP/dT)_e$ of the P–T phase diagrams and molar volume changes for both transitions (calculated from Clausius–Clapeyron relation) are given in Table 1.

From the slope of the thermobarogram in the plastic domain, the ratio (α/χ) can be deduced (see Table 2). Using literature data of the isobaric thermal expansion coefficient, the isothermal compressibility coefficient (χ) has been calculated and is given in Table 2.

TABLE I

Literature data for the temperature T(K), enthalpy ΔH(kJ·mol^{-1}) and entropy variations ΔS(J·mol^{-1}·K^{-1}) at the solid–plastic (II–I) and plastic–liquid (I–L) phase transitions measured by thermal analysis; experimental data for the equilibrium curves (dP/dT) (MPa·K^{-1}) of the pressure–temperature phase diagrams and molar volume changes (cm^3·mol^{-1}) for the transitions calculated from Clausius Clapeyron relation (ΔV) and from X-Ray diffraction literature data extrapolated at the transition temperature (ΔV^+)

NPA ($n_1 = 1$)	II–I	I–L	Reference
T(K)	236.5	331.4	[24]
ΔH(kJ·mol^{-1})	4.0	3.9	[24]
ΔS(J·mol^{-1}·K^{-1})	16.9	11.8	[24]
$(dP/dT)_\theta$ (MPa·K^{-1})	4.22	1.49	[24]
ΔV(cm^3·mol^{-1})	4.01	7.90	[24]

NPG ($n_1 = 2$)	II–I	I–L	Reference
T(K)	314.6	401.3	[25]
ΔH(kJ·mol^{-1})	12.8	4.4	[25]
ΔS(J·mol^{-1}·K^{-1})	40.6	10.8	[25]
$(dP/dT)_\theta$ (MPa·K^{-1})	8.36	1.63	
ΔV(cm^3·mol^{-1})	4.86	6.63	
ΔV^+(cm^3·mol^{-1})	4.89	–	

PG ($n_1 = 3$)	II–I	I–L	Reference
T(K)	357.5	471.7	[36]
ΔH(kJ·mol^{-1})	21.3	5.1	[36]
ΔS(J·mol^{-1}.K^{-1})	59.5	10.8	[36]
$(dP/dT)_\theta$ (MPa·K^{-1})	9.71	1.79	
ΔV (cm^3·mol^{-1})	6.13	6.03	
ΔV^+(cm^3·mol^{-1})	6.09	–	

AMP ($n_2 = 2$)	II–I	I–L	Reference
T(K)	352.6	382.4	[25]
ΔH(kJ·mol^{-1})	23.3	2.83	[25]
ΔS(J·mol^{-1}.K^{-1})	66.2	7.40	[25]
$(dP/dT)_\theta$ (MPa·K^{-1})	13.08	2.18	
ΔV (cm^3·mol^{-1})	5.06	3.39	
ΔV^+(cm^3·mol^{-1})	4.87	–	

TRIS ($n_2 = 3$)	II–I	I–L	Reference
T(K)	406.8	442.7	[36]
ΔH(kJ·mol^{-1})	34.0	3.15	[36]
ΔS(J·mol^{-1}.K^{-1})	83.7	7.12	[36]
$(dP/dT)_\theta$ (MPa·K^{-1})	16.50	2.27	
ΔV(cm^3·mol^{-1})	5.07	3.14	
ΔV^+(cm^3·mol^{-1})	4.47	–	[27]

MN ($n_3 = 0$)	II–I	I–L	Reference
T(K)	260.1	299.2	[18]
ΔH(kJ·mol^{-1})	4.66	2.59	[18]
ΔS(J·mol^{-1}.K^{-1})	17.9	8.66	[18]
$(dP/dT)_\theta$ (MPa·K^{-1})	7.65	2.5	[18]
ΔV (cm^3·mol^{-1})	2.34	3.46	[18]

MNP ($n_3 = 1$)	II–I	I–L	Reference
T(K)	312.0	364.1	[25]
ΔH(kJ·mol^{-1})	15.0	3.28	[25]
ΔS(J·mol^{-1}.K^{-1})	48.1	9.00	[25]
$(dP/dT)_\theta$ (MPa·K^{-1})	12.30	2.02	
ΔV(cm^3·mol^{-1})	3.90	4.46	

TABLE I (*Continued*)

PA ($n_4 = 0$)	II–I	I–L	Reference
T(K)	≈279	309.7	[19]
ΔH(kJ·mol^{-1})	–	2.0	[19]
ΔS(J·mol^{-1}·K^{-1})	25.5	6.5	[19]
$(dP/dT)_\theta$ (MPa·K^{-1})	3.26	2.22	[19]
ΔV (cm^3·mol^{-1})	7.82	2.93	[19]

TABLE II

Literature Data of the Isobaric Thermal Expansion Coefficient (α), (a:[37], b:[25], c:[27]) Experimental Ratio (α/χ) and Calculated Isothermal Compressibility Coefficient (χ) in the Plastic Phase.

Compound	α(10^3 K^{-1})	(α/χ) (MPa·K^{-1})	χ(10^9 Pa^{-1})
NPG ($n_1 = 2$)	1.91^a	1.51	1.265
PG ($n_1 = 3$)	1.50^b	1.65	0.91
AMP ($n_2 = 2$)	1.28^b	2.06	0.62
TRIS ($n_2 = 3$)	1.23^c	2.13	0.58
MNP ($n_3 = 1$)	0.975^b	1.65	0.59

5. DISCUSSION

5.1 $(CH_3)_{4-m}C(CH_2OH)_m$ Series.

For NPG the knowledge of the structure at the low temperature solid phase [25] and the mentioned thermal expansion of the high temperature plastic phase [37], enables us to calculate the molar volume change at the solid to plastic phase transition (at atmospheric pressure) by extrapolation of the lattice volume at the transformation temperature. As we can see in Table 1, this extrapolated value and the corresponding to the thermobarometric method used in this work match up satisfactorily.

For the PG ($n_1 = 3$) the solid (body centered tetragonal [32]) and the plastic (fcc lattice [33]) phases of PG have been studied by X-ray powder diffraction at different temperatures by Barrio [25], and then, the molar volume change at the transition temperatures can be easily calculated. The agreement between this extrapolated value at the transition temperature and the calculated from the Clausius–Clapeyron relation in this work is again very good.

The literature values of NPA ($n_1 = 1$) compound [24] are included in Table 1 in order to compare to the other compounds of this series. As we can easily observe from that table, the values of the temperature, enthalpy, entropy and volume variations, and the equilibrium slopes $(dP/dT)_e$ increase when the methyl (—CH_3) groups are substituted by the hydroxyl (—CH_2OH) group. The increasing of the temperature and ΔH values (and consequently ΔS) are explained taking into account that the solid low temperature phase is characterized by a hydrogen bonded network produced by the —CH_2OH groups [38]. Then, the higher number of n_1, i.e., the number of the hydrogen bonds, the higher energy and temperature is required to enable the reorientational motion in the high temperature plastic phase. Moreover, for the next member PE ($n_1 = 4$) which

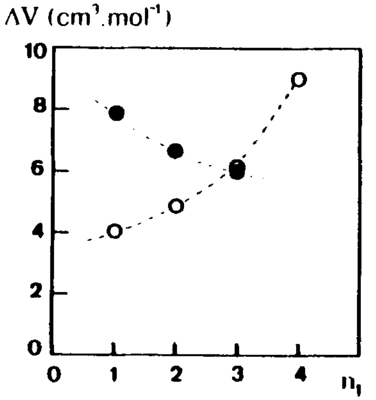

FIGURE 6 Volume change ΔV values for the solid to plastic phase transition (○) and plastic to liquid process (●) versus the number of hydroxyl —CH_2OH groups (n_1) corresponding to the $(CH_3)_{4-n1}C(CH_2OH)_{n1}$ series.

transition temperatures are outside of the working range, the molar volume change at the solid to plastic phase transition, can be obtained from the available X-ray powder diffraction reported data [25]. The calculated value is about $9.0\,cm^3 \cdot mol^{-1}$. For this series the volume changes at the solid state transition and at the melting process are plotted versus of the number of hydroxyl groups (n_1) in Figure 6. As we can clearly see, the similarity between the molar volume of the plastic and liquid phases increases when n_1 does; on the contrary, the molar volumes of the solid and plastic phases are, when n_1 increases, more different.

On the basis of the extended Pople and Karasz theory [39, 40] by Amzel and Becka [41] for rotational phase transitions and fusion of molecular crystals with orientational degrees of freedom, the volume changes on melting and for the solid–solid transition can be discussed as a function of the key parameter v. This parameter is a measure of the relative energy barriers for the rotation of the molecule and for its diffusion to an interestitial site. According to the preceding theory, the relative volume change on melting decreases, whereas for the solid–solid transition increases with v. Moreover, another interesting feature of the extended theory is that the volume changes at the solid–solid transition become larger than that on melting when $v > 0.28$. For the present series, a similar behaviour (see Figure 6) is found when analysing the volume changes as a function of n_1. Thus, on the basis of the same behaviour, n_1 may be correlated with v, and then the barrier to reorientation increases more than the barrier to diffusion for an increase in n_1. This assumption would yield high values of the reorientation barrier of the molecules with a higher number of groups with possibility of the formation of the hydrogen bond (CH_2OH group). Unfortunately, nuclear magnetic resonance studies, yielding experimental values for the energies of the reorientation and for the self-diffusion barriers, have not been performed in this series. However, we want to point out that in the case of the pivalic acid PA ($n_4 = 0$), the high values of the volume and the enthalpy of activation for molecular reorientation have been rationalized by the assumption of the formation of dimers (by hydrogen bond) in the plastic phase [19].

5.2. $(NH_2)(CH_3)_{3-n2}C(CH_2OH)_{n2}$ Series

For AMP ($n_2 = 2$), the lattice structure of the low temperature phase II was earlier determined as monoclinic [34]. The parameters at different temperatures of this phase, together with those of the high temperature bcc plastic phase have been also determined [25]. These results allow to calculate, by extrapolation, the molar volume change at the transition temperature and at atmospheric pressure; the obtained value ($4.87\ cm^3 \cdot mol^{-1}$) approaches the value obtained by the thermobarometric method in this work ($5.06 cm^3 \cdot mol^{-1}$).

For TRIS ($n_2 = 3$), the high values of the entropy change and the slope of the low temperature (orthorhombic [27]) phase and plastic equilibrium curve (the higher of the studied compounds), provide a value of the molar volume change ($5.07\ cm^3 \cdot mol^{-1}$) very similar to the previous compound of this series (AMP). The lattice parameter-temperature dependence has been well determined by X-ray single crystal diffraction by Elierman and co. [27]. The same authors have calculated, also by extrapolation at the transition temperature, the volume change associated, reporting a value of $4.47\ cm^3 \cdot mol^{-1}$ (see Table 1). In this case, a disagreement (12%) is found between this reported value and the determined here. However, the same authors [27] pointed out that in order to obtain reliable values of ΔV, using X-ray diffraction techniques, by extrapolation to the values expected at the transition temperature, more measurements should be performed; so that, the reported values has to be considered with a 30% of uncertainty.

In this series, a similar behaviour with the previous one is found when the temperatures, enthalpy changes and slope equilibria are compared. However, the volume changes are very close, being nearly independent of the hydroxyl group number (n_2).

As Table 2 presents, the values of (α/χ), α and χ are very similar for the compounds of this amino series, although in this case the lattice of the plastic phases are bcc, with regard to the previous one where are know to be fcc.

5.3. $(NO_2)(CH_3)_{3-n3}C(CH_2OH)_{n3}$ Series

For MNP, the structure of the low temperature solid phase is not known and, then the molar volume change at the solid to plastic phase transition determined in the present work can not be compared.

The literature reported values of MN ($n_3 = 0$) (see Table 1), when compared with those obtained for MNP, show a similiar behaviour that in the other series. However, the molar volume changes associated to the II–I phase transition are lower. Different crystal interactions in the two solid phases of MN and MNP must be reflected in the latter difference of the molar volume change.

5.4. $(COOH)(CH_3)_{3-n4}C(CH_2OH)_{n4}$ Series

Although any member of this series has been studied here, the previously reported values for the PA compound ($n_4 = 0$) [19] have been included in order to compare them with our results. The characteristic thermodynamic values for PA, which are included in Table 1, show that the slope of the equilibrium transition is low as compared to the previously given for the other compounds. This fact also produces a very high volume change at the transition ($7.82\,\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$, i.e., about 8.4% of the molar volume of the low temperature phase). On the contrary, the slope at the melting equilibrium is not so different from the others, although the associated volume change in this process is low.

6. CONCLUSION

The metabolemeter, previously used to determine phase changes under pressure on liquid crystals, has been used, for the first time, to study the first order phase transformations on plastic crystals.

Five compounds belonging to three series derivated from the Neopentane have been studied. The extrapolation at atmospheric pressure of the phase transition temperatures (solid to plastic and plastic to liquid) gives satisfactory values when compared to the determined values by thermal analysis.

Data for the isothermal compressibility coefficients have been calculated for the plastic phases. Values ranged from 1.265 to $0.58\,(\mathrm{GPa})^{-1}$ have been found. Similar values have been previously reported for other plastic phases [18, 42, 43].

The molar volume changes of the transitions at atmospheric pressure have been calculated by means of the Clausius Clapeyron relation. When the literature reported values of the lattice volumes for both solid and plastic phases are known, the calculation by extrapolation at the transition temperature of the volume change and our results agree, in general, satisfactorily. We would like to emphasize the point that in order to obtain reliable values of volume change by means X-ray diffraction techniques, one should know the molecular volume at several temperatures and with a good accuracy, in order to be able to extrapolate to the volumes expected at the transformation point.

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