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State variables in calorimetric investigations: Experimental results and their theoretical impact[1]

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Abstract

Use of state variables (p, V, T) in scanning calorimetric measurements is demonstrated by results obtained for various condensed systems, such as dense liquids of various physicochemical natures, polymers, and liquid crystals. The simultaneous determination of thermal and mechanical responses of the investigated system, perturbed by a variation of an independent thermodynamic variable while the other independent variable is kept automatically constant, allows the determination of thermodynamic derivatives over wide ranges of pressure and temperature, impossible to obtain by other known techniques. It is demonstrated that through appropriate molecular models for respective thermodynamic derivatives or models on which the respective EOS are constructed, the *pVT*-controlled scanning calorimetry is a useful means of relating microscopic molecular properties with macroscopic observations. © 1997 Elsevier Science B.V.

Keywords: Dense liquids; Equations of state; Liquid crystals; Phase transitions; Polymers; *pVT*-Controlled scanning calorimetry; Scanning transitiometry; Thermophysical properties

1. Introduction

Some time ago the present author had given thermodynamic fundamentals for scanning calorimeters controlled by an independent thermodynamic variable and demonstrated selected metrological problems of the proper use of this technique in determination of selected thermodynamic derivatives [1]. Since that time a number of new instruments have been constructed based on those principles and performing over wide ranges of pressure and temperature [2–4]. The most important advancement of this technique in recent years was an introduction of simultaneous recordings of both thermal and mechanical responses of a system perturbed by a variation of one of its independent variables (p, V or T) while the other independent variables remain constant [3,5]. A schematic presentation of four thermodynamic situations, possible to realize in such a *pVT*-controlled scanning calorimeter is given in Fig. 1:

a) simultaneous recording of both heat flow and volume changes resulting from a given pressure variation under isothermal conditions leads to simultaneous determination of both $(\partial S/\partial p)_T$ and $(\partial V/\partial p)_T$ (or isobaric thermal expansivity, α_p, see Maxwell relation, and isothermal compressibility, κ_T) as a function of pressure at a given temperature;

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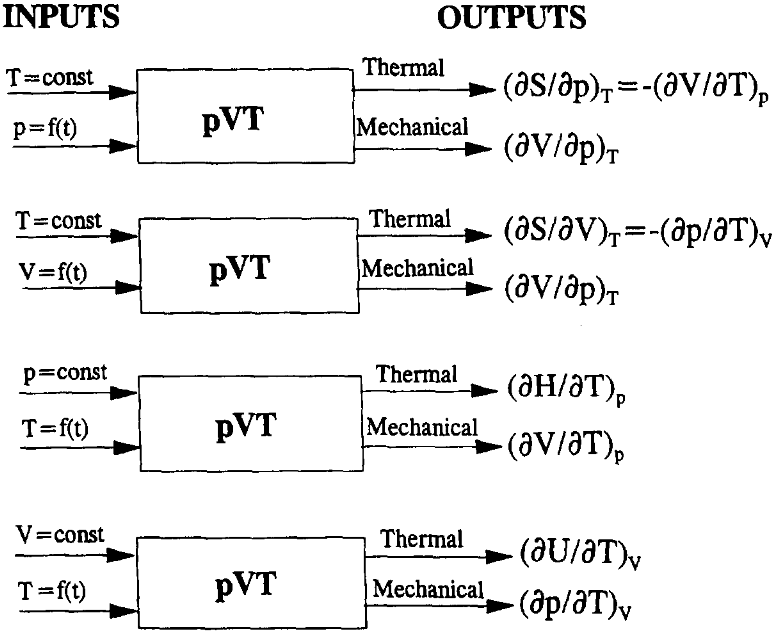

Fig. 1. A thermodynamic scheme of a *pVT*-controlled scanning calorimeter.

b) simultaneous recording of both heat flow and volume changes resulting from a given volume variation under isothermal conditions leads to simultaneous determination of both $(\partial S/\partial V)_T$ and $(\partial V/\partial p)_T$ (or temperature coefficient of pressure, β, see Maxwell relation, and isothermal compressibility, κ_T) as a function of volume at a given temperature;

c) simultaneous recording of both heat flow and volume changes resulting from a given temperature variation under isobaric conditions leads to simultaneous determination of both $(\partial H/\partial T)_p$ and $(\partial V/\partial T)_p$ (or isobaric heat capacity, C_p, and isobaric thermal expansivity, α_p) as a function of temperature at a given pressure;

d) simultaneous recording of both heat flow and volume changes resulting from a given temperature variation under isochoric conditions leads to simultaneous determination of both $(\partial U/\partial T)_V$ and $(\partial p/\partial T)_V$ (or isochoric heat capacity, C_V, and temperature coefficient of pressure, β) as a function of temperature at a given volume.

All the four situations involve closed systems, and any change in the composition results from perturbation of the thermodynamic state by a variation of the inducing independent variable.

The simultaneous determination of both thermal and mechanical contributions to the total change of thermodynamic potential, not only leads to the complete thermodynamic description of the system under study, but also permits investigation of systems with limited stability or systems with irreversible transitions. This approach is also very useful in analyzing the course of a transition. By a proper external change of the controlling variable, the transition under investigation can be accelerated, impeded or even stopped at any degree of its advancement and then taken back to the beginning, all with simultaneous recording of the heat flow and mechanical variable variations. This permits not only determination of the total changes of the thermodynamic functions for the transitions but also allows an analysis of their evolution along the advancement of the transformation. For this reason this technique was recently given the name *scanning transitiometry* [6,7], because it permits direct investigation of physico–chemical transitions of various types and a much deeper description than could be obtained from separate calorimetric and/or dilatometric analysis.

The possibility of scanning independent variables over wide ranges of temperature, pressure or volume and the determination of appropriate derivatives provides a direct and easy use of macroscopic data for the determination of microscopic molecular properties of matter through appropriate models [8]. Actually, most interesting from the point of view of both science and industry are dense physico-chemical systems, such as organic and inorganic liquids, liquid and crystalline polymers, polymers in interactions with supercritical compressed gases, etc.

The present article is mainly focused on the presentation and analysis of selected new recent results obtained with various modes of scanning transitiometry, when investigating selected dense systems. A special emphasis will be given to the uniqueness of the new results, such as the crossing point of α_p isotherms, minima on the C_p isotherms and to attempts of their molecular explanations. In order to facilitate an understanding and evaluation of these relatively new results, let us first briefly recall the experimental basis of the new technique.

2. Experimental

A schematic diagram of a typical experimental arrangement of a scanning transitiometer is given in Fig. 2. The investigated substance is placed in a calorimetric vessel constructed from type 304 stainless steel tubing with 4.76 mm i.d. The upper end was fitted with a cone plug held in place with a threaded plug. The lower end of the tubing was connected through an adapter to a stainless steel tubing with o.d. 6.35 mm and i.d. 2.4 mm, in order to reduce the heat leakage. The thin tubing was then connected to an extensiometric pressure detector and to a high-pressure pump driven by a stepping motor through an appropriate gear box. The steps of the motor can be counted and calibrated in the units of the volume change (cm^3). For example, such a calibration constant for the instrument at Warsaw was $(5.838 \pm 0.014)\ 10^{-6}\ cm^3$ per motor step [9] and for the instrument at Clermont–Ferrand was $(5.228 \pm 0.026)\ 10^{-6}\ cm^3$ per motor step [10]. The extensiometric pressure detector had a precision of 0.1% fsd. The thermostat of the calorimetric detector is of metallic block type and has a reasonable space of a homogeneous temperature field. The temperature controller of the thermostat is connected to a computer

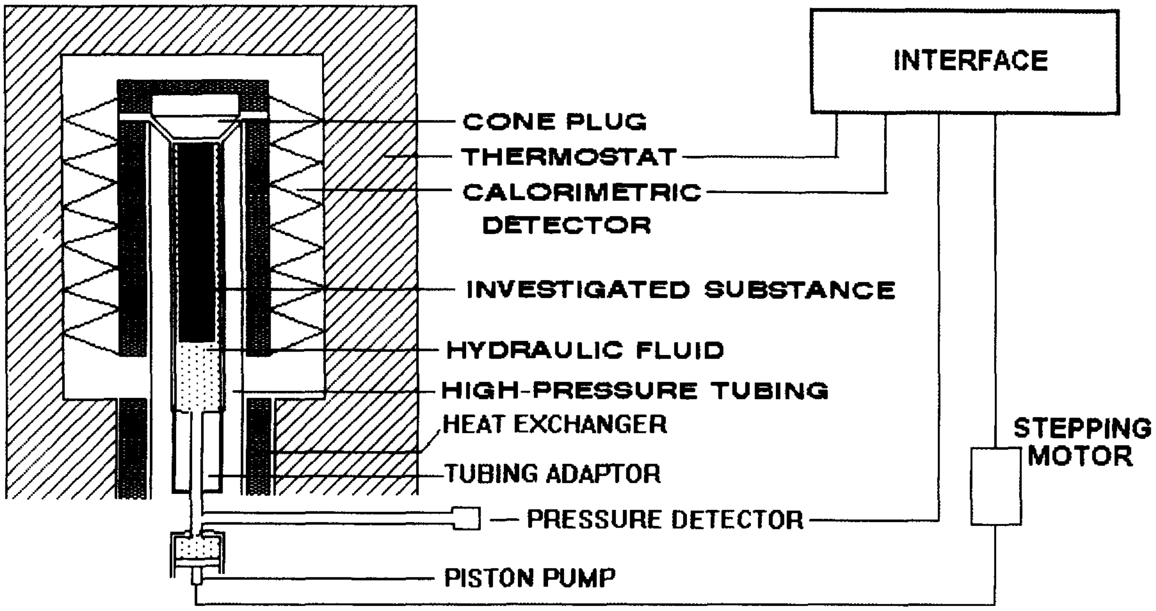

Fig. 2. A sketch diagram of a *pVT*-controlled scanning calorimeter.

interface or can be set manually. In order to keep the whole calorimetric vessel in the region of the homogeneous temperature field two sleeves, which served as heat exchangers, were fixed between the middle of the tubing and the calorimetric detector and between the middle of the tubing and the calorimetric block. Detailed descriptions of the calorimetric vessels and their mountings are given elsewhere [4,11]. The calorimetric detectors were all of the heat-flow type, connected to the computer interface through appropriate amplifiers. With the four variables (p, T, V, heat flux) selected in this way, the four thermodynamic situations presented in Fig. 1 could be easily realized with the help of an appropriate software. The low scanning rates of the respective variables were as follows: $T: 8 \times 10^{-4}\,\mathrm{K\,s^{-1}}$, $V: 2 \times 10^{-5}\,\mathrm{cm^3 s^{-1}}$, $p: 2\,\mathrm{kPa s^{-1}}$. These low rates allow measurements near equilibrium for many processes. Once the sample is loaded into the experimental vessel, the phenomenon under investigation can be observed in various thermodynamic planes. The choice of the inducing variable cannot often be arbitrary. For example, the pressure-scanning technique is advantageous at high pressure regions. However, when approaching the critical point or even the saturation line at lower temperatures, the volume changes corresponding to a given pressure variations become so large that the pressure-scanning procedure becomes less precise or even unusable. Thus, at those conditions it is more advantageous to use the volume-scanning procedure [12].

3. Dense liquids

Liquids being compressed above the atmospheric pressure or the pressure of the saturated vapour will be called dense liquids. The pressure variable has often been neglected in the thermodynamic investigation of liquids, although its practical and theoretical importance is evident. The actual practical problems where the pressure variable is important include the exploitation of geothermal energy, oil and gas recovery, high-pressure organic synthesis, etc. The role of pressure variable in testing the theories of liquids was pointed out by Bridgman [13] at the beginning of this century. Bridgman himself investigated various liquids at pressures up to several hundred MPa with the use of *pVT* techniques. On the basis of volumetric measurements and derived data, Bridgman pointed out that the isobaric heat capacity, C_p, and the thermal expansion, α_p, of liquids at high pressures exhibit unusual behaviour. Specifically, he stated that the curves for various temperatures may cross and recross in the most bewildering way [13,14]. As emphasized by Street [15], it seems possible that at least part of this unusual behaviour is not real, but is a result of errors in the measured volumes. It is known that even very small errors in such measurements can lead to large errors in the first and second derivatives of the equation of state (EOS), especially at high pressures where the pressure and temperature dependencies of these derivatives are small. Recent developments of calorimetric high-pressure techniques for investigation of liquid systems and direct measurements of these derivatives are very helpful in elucidating the problem. A number of various liquids have been already investigated by Ter Minassian and his group with the use of piezothermal technique [16,17] and of a pneumatic compensation calorimeter [18], such as benzene [19], water [20], *n*-hexane [21,22], *n*-butane [23], CO_2 [23], coal-derived liquids [24], toluene [25], and binary mixtures of acetone with CS_2 [26]. The pressure-scanning technique was used in investigations of quinoline [9], *n*-hexane [11], 1-hexanamine [27] and its binary mixtures with 1-hexanol [28], tetraline and its binary mixtures with *m*-cresol and quinoline [29], 1-hexanol and its binary mixtures with *n*-hexane [30–32], *m*-cresol [33], and its binary mixtures with quinoline [34]. A general conclusion from these investigations is that the simple liquids, without strong intermolecular interactions, exhibit a unique crossing point of α_p isotherms. For associated liquids or for liquids with strong specific intermolecular interactions the crossing of α_p isotherms is temperature dependent, and the form of this dependence is related to the nature of the specific intermolecular interactions. A number of results of calorimetric measurements of α_p for selected liquids are presented in Fig. 3 (a–f). One can see that such liquids as *n*-hexane (Fig. 3a), quinoline (Fig. 3b) and a binary mixture of *m*-cresol with quinoline near 2 : 1 molar ratio (Fig. 3c) exhibit unique crossing points of α_p isotherms. While for *n*-hexane and quinoline this observation can be considered as evident, the behaviour of 2 : 1 mixture of *m*-cresol with quinoline needs to be commented. It is

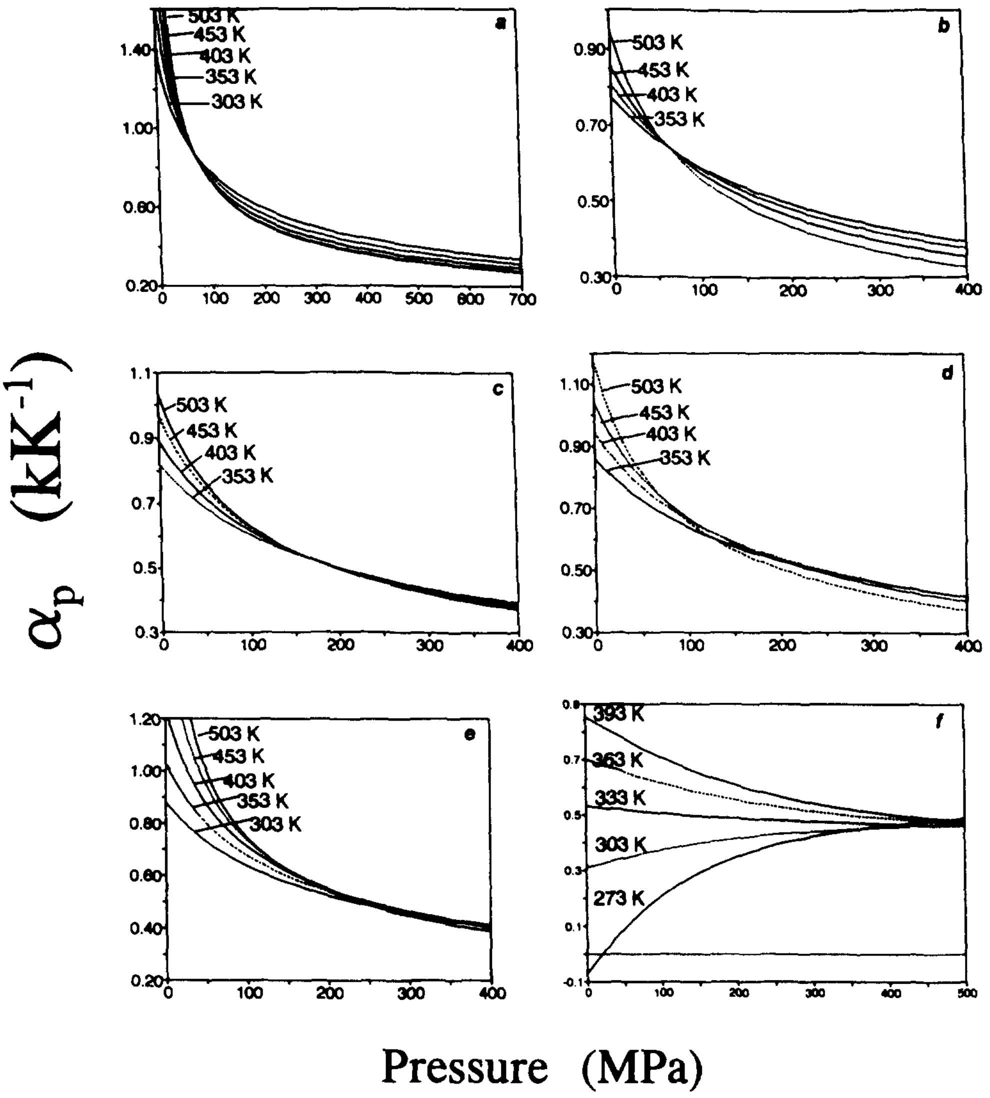

Fig. 3. Isobaric thermal expansivities: a, *n*-hexane [11]; b, quinoline [9]; *c*, \{0.6325 *m*-cresol +0.3675 quinoline\} mixture [34]; d, *m*-cresol [33]; e, 1-hexanol [32]; f, water [20].

worth recalling that, near this concentration, the excess enthalpy of mixing of *m*-cresol with quinoline is at a maximum, nearly −7.7 kJ/mol [35]. In the 2 : 1 mixture, the liquid phase is composed of strongly bound intermolecular complexes which behave like the molecules of a liquid without association. Thus, the macroscopic properties of such a phase are similar to those of non-polar liquids [34]. In the case of associated liquids, such as *m*-cresol (Fig. 3d), 1-hexanol (Fig. 3e) or water (Fig. 3f) the situation is completely different. However, it is generally observed that as the temperature increases, the association bonds are broken and the α_p isotherms demonstrate a tendency towards a unique crossing point. This was observed for *m*-cresol [33], 1-hexanol [32], and for binary mixtures of *n*-hexane with 1-hexanol [31], investigated over wide ranges of temperature and pressure.

The crossing point of α_p isotherms can be analyzed from the point of view of the hole theory and the concepts of metastable liquids which are based on the use, in the correlation equation, of the spinodal line as the stability limit for the liquid state [23,25,36–40]. This is an interesting way of correlating experimental data and creating empirical equations of state, but this approach does not significantly improve the molecular knowledge of the dense liquid state. Another approach is through molecular-based equations of state (EOS). The intermolecular interactions in dense liquids have long been of interest to many scientists. The best known van der Waals EOS is based on the attractive potential determined by London dispersion forces and the hard-sphere potential [41]. Despite many later improvements, no EOS with only the attractive part modified could reproduce the crossing point of α_p isotherms, neither for methane nor for n-hexane [42]. Although with coordinates rather far from experimental data, the crossing points of α_p isotherms for methane and n-hexane could be reproduced [42] with van der Waals–Carnahan–Starling EOS [43] which has the repulsive part softer than the original van der Waals EOS. However, the best reproduction of the experimental data was obtained with a soft-sphere EOS [44] having the repulsive part constructed on the 8-4 Lennard–Jones potential (softer than the Carnahan–Starling modification [43]) and the van der Waals attractive part. Thus, the softness of the intermolecular potential is an important molecular property determining the macroscopic properties of liquids at high densities. Similar conclusions have been drawn by the present author in an attempt to explain the macroscopic properties of liquids at high pressures by a pressure sensitive shape of the effective intermolecular potential [45].

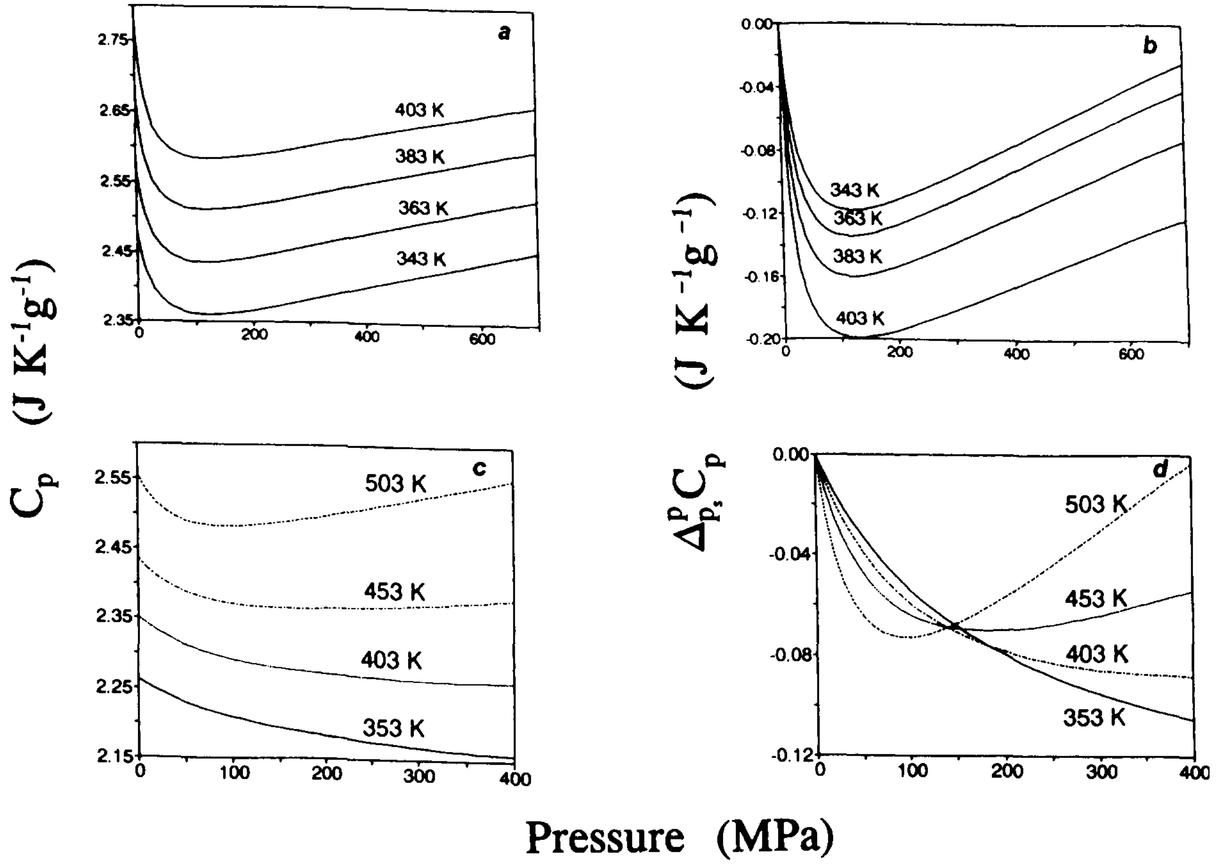

Fig. 4. Isobaric heat capacities: a – n-hexane [11]; c – m-cresol [33] and pressure effects on the isobaric heat capacities: b – n-hexane [11]; d – m-cresol [33].

When the α_p isotherms cross at a given pressure, $(\partial\alpha_p/\partial T)_p$ changes sign and this property generates minima on the isotherms of isobaric heat capacity and on the pressure effect on C_p [46] (see Eq. (1)).

$$\Delta^{p}_{ps} C_{p,T}(p) = -T \int_{ps}^{p} V(p,T)\left[\alpha^2 + \left(\frac{\partial\alpha}{\partial T}\right)_p\right] dp \qquad (1)$$

As a model behaviour for simple liquids [11] both the absolute values of selected C_p isotherms and the pressure effects on the isochoric heat capacity of *n*-hexane at pressures up to 700 MPa are presented in Fig. 4 (a) and (b) respectively. One can see that the all isotherms exhibit minima. As the temperature increases the minima are shifted to higher pressures. At higher temperatures, especially when approaching the critical temperature, the minima become shallow [11]. It is interesting to recall that the experimental C_p isotherms for methane could be also best reproduced with the soft-sphere EOS, just as in the reproduction of the α_p isotherms [44].

As an example of associated liquids, the absolute values of selected C_p isotherms and the pressure effects on the isochoric heat capacity for *m*-cresol are presented in Fig. (c) and (d). At low temperatures, where the association is strong, there are no minima, because the isotherms of α_p cross at high pressures (see Fig. 3 d) and the change of sign of $(\partial\alpha_p/\partial T)_p$ does not sufficiently compensate the positive value of α_p^2 over the pressure range under investigation. At higher temperatures, where the association bonds are broken or weakened, the minima appear and the behaviour of *m*-cresol becomes similar to the that of simple liquids.

The examples of experimental results presented here and their theoretical approach with the use of molecular based EOS demonstrate the use of varying pressure in calorimetric investigation of dense liquids and in acquiring an understanding of their molecular behaviour.

4. Polymers

Crystalline polymers are very interesting because they are examples of the stable coexistence of crystal and amorphous phases. The Pastine EOS [47] for polyethylene is composed of a crystal part constructed on the basis of precise crystallographic structural data, and an amorphous part constructed with the use of averaged structural assumptions. In a recent study [10], we have performed a series of α_p measurements for polyethylenes of various crystallinities at several temperatures as a function of pressure, up to 300 MPa, with the use of a pressure-controlled scanning transitiometer [4]. In Fig. 5 are given typical results for various polyethylenes (LDPE-A, crystallinity 0.39; LDPE-B, crystallinity 0.32; MDPE, crystallinity 0.59; MDPE annealed during 72 h at 363 K, the annealing has increased the crystallinity by 3%; cross-linked XMDPE, crystallinity 0.71; and HDPE-A, crystallinity 0.73). One can see that all α_p isotherms for various polyethylenes have a tendency to converge at high pressures, but they do not cross as was observed for simple liquids. Exceptions are only the isotherms near or above the temperature of fusion of crystalline polymers at atmospheric pressure. Of course, the aforesaid observation is valid only for the pressure range under investigation. From these measurements, it was found that α_p is a linear function of crystallinity over the whole (p, T) surface under investigation. From this property, α_p for both crystal and amorphous phases were extrapolated and compared to the values derived from the Pastine EOS. In case of crystal phase, the agreement is surprisingly good at atmospheric pressure; for the amorphous phase, the agreement is less satisfactory at the same conditions. For both phases important discrepancies appear at higher pressures. It is worth noting that the α_p isotherms for the amorphous phase extrapolated from the calorimetric measurements cross as was observed for simple liquids, but the isotherms derived from the Pastine EOS for the same phase do not cross [48]. Thus, this EOS needs to be modified in order to describe correctly the high pressure properties of crystalline polyethylenes. It is hoped that the calorimetric measurements with the pressure as an inducing variable, will serve as a guide in further search for better EOS for crystalline polymers, or improving the existing equations.

5. Phase transitions

Scanning transitiometry is an extremely useful technique in studying the phase transitions. In order

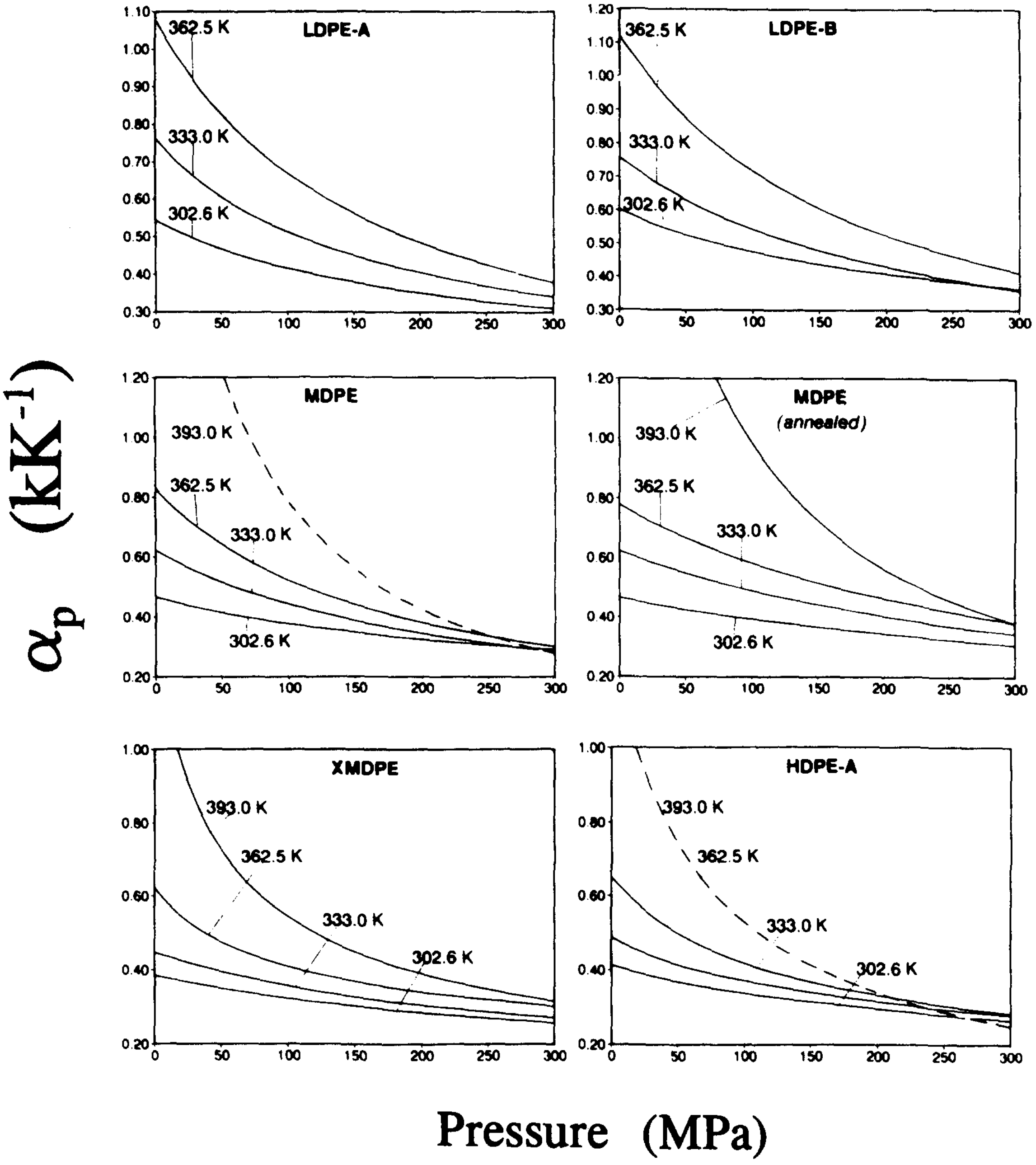

Fig. 5. Isobaric thermal expansivities of various polyethylenes determined in a pressure-controlled scanning transitiometer [10].

to demonstrate various possibilities of the new technique, benzene was taken as an example and the solid-to-liquid and liquid-to-solid transitions investigated in various thermodynamic planes. Fig. 6a shows an example of isothermal solidification, at 303.15 K, on linearly increasing the pressure at a rate of 5 kPa s^{-1} and recording both the volume and heat flux variations. Fig. 6b shows an example of isobaric fusion, at 78.2 MPa, on a linear temperature increase from 299.9 to 309.7 K at a rate of

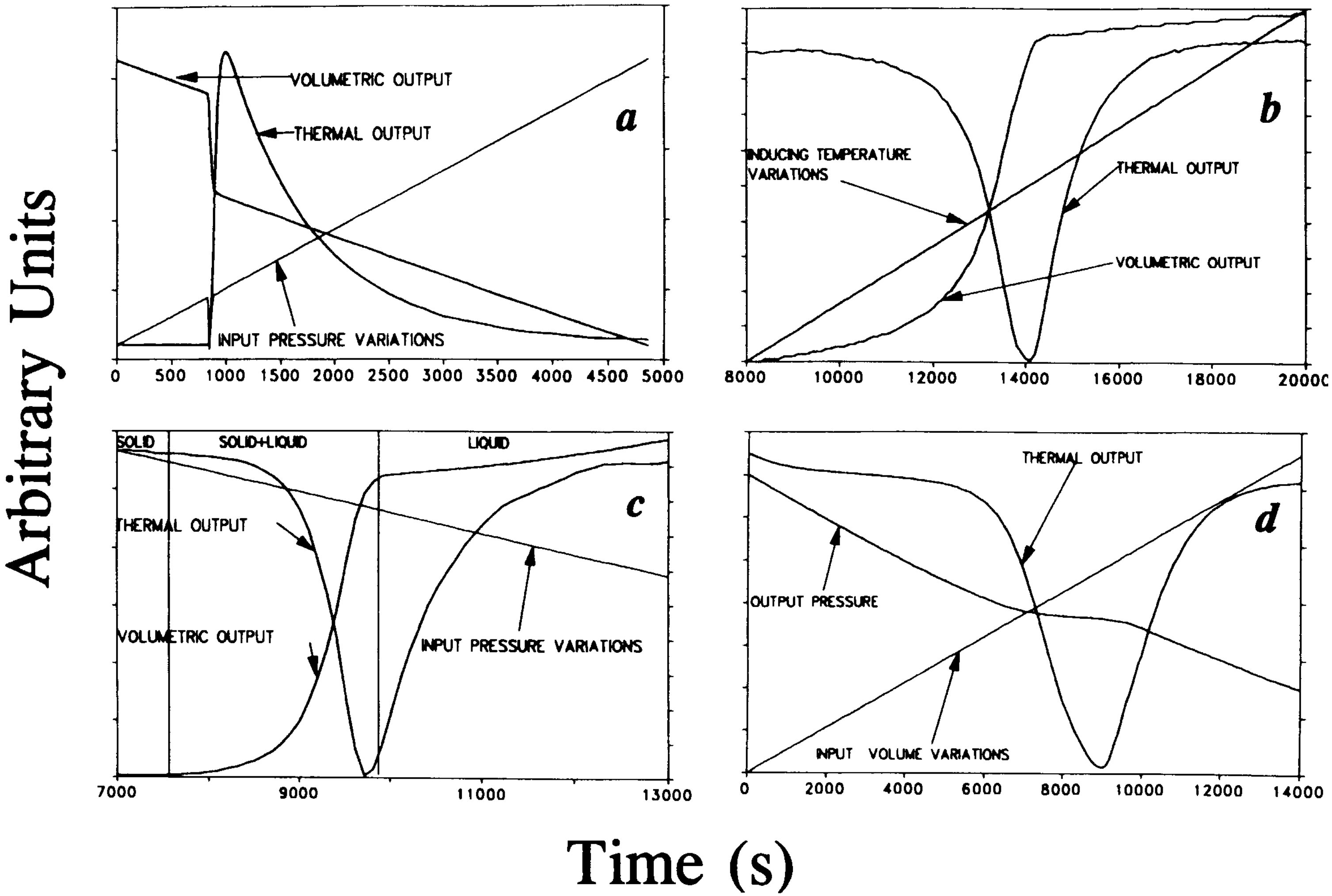

Fig. 6. Demonstration of various modes of investigating phase transitions by scanning transitiometry, taking benzene as a test substance. For explanations see the text.

8.3×10^{-4} K s^{-1} and recording both the heat flux and volume variations. Fig. 6c shows an example of isothermal fusion at, 303.15 K, induced by a linear pressure decrease at a rate of 5 kP s^{-1} and recording both the heat flux and the volume variations. Fig. 6d shows an example of isothermal fusion, at 299.15 K, induced by a linear volume increase at a rate of 1.17×10^{-4} cm^{3}s^{-1} and recording both the heat flux and the pressure variations. These are model examples of studying the phase transitions. The experiments are simple and rather easy to perform, they can be used in teaching physical chemistry, and especially in demonstrations of concepts of independent and dependent variables, relations between the thermodynamic derivatives at various phase equilibria, etc.

In order to demonstrate the possibility of scanning transitiometry in studying more complex transitions, Fig. 7 presents thermograms of compressions of 4-*n*-pentyl-phenylthiol-4'-decyloxybenzoate liquid crystal starting from various initial pressures at 370 K. This liquid crystal has three smectic phases, A, B, and C all observable only on cooling; on heating, the solid phase goes directly to the smectic-A-phase [49]. From thermodynamics, it is known that a compression of a system corresponds to cooling, and decompression to heating. At 370 K and atmospheric pressure, the liquid crystal under study is in the isotropic liquid phase. When compression begins at this point following isotropic to nematic transition, a rather complex thermogram is obtained corresponding, probably, to transitions between smectic phases and then to the solid phase. However, if decompression is stopped somewhere in equilibrium between the phases (before the isotropic phase appears) and then recompression is performed, three distinct peaks are observed. Their forms depend on the pressure at which the transition was stopped. For the recompressions given in Fig. 7, the starting pressures were 131.5, 134.4, and 136.1 MPa respectively. If the pressures of starting recompression were lower than 131.5 MPa, the obtained thermograms were similar to the thermogram of compression obtained from the isotropic liquid phase. Thus, the observed phenomena are most prob-

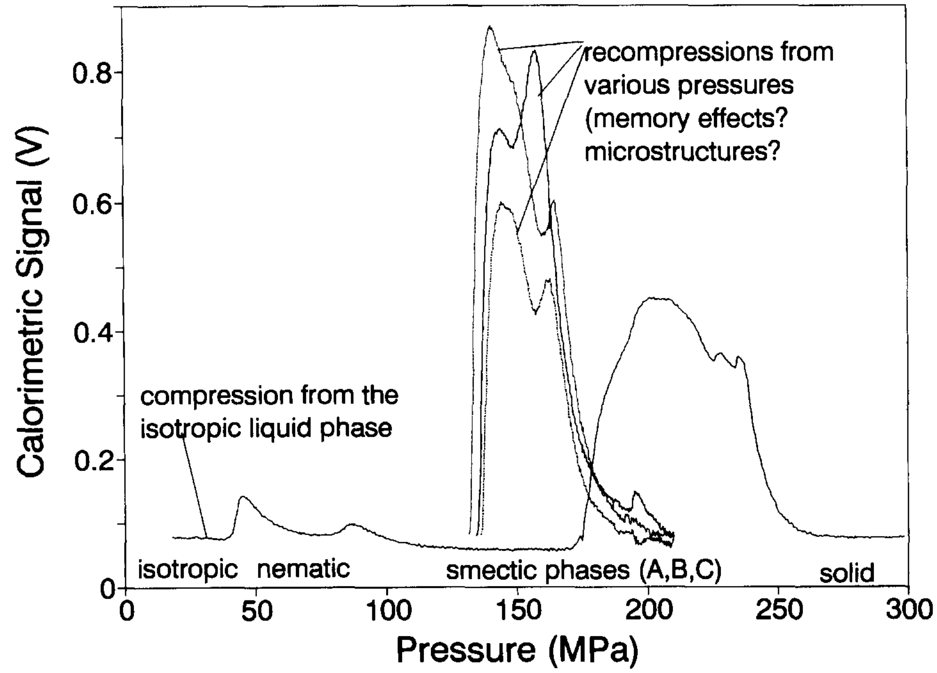

Fig. 7. Transitiometric thermograms of compressions of 4-*n*-pentyl-phenylthiol-4'-decyloxybenzoate liquid crystal starting from various initial pressures at 370 K.

ably connected to the conditions of formation of a structure in the liquid phase. More examples of studying the phase transitions by scanning transitiometry and their model interpretation are given elsewhere [6,7].

6. Derived thermophysical data

In the preceding sections, only direct experimental data and their use in modelling the molecular properties of matter were given. However, when an appropriate set of thermodynamic derivatives is determined in a scanning transitiometer, it is almost possible to derive a complete set of thermodynamic data over wide ranges of pressure and temperature, otherwise actually impossible to obtain, by proper integrations using thermodynamic formulae. Examples include sets of thermodynamic properties obtained for *n*-hexane, such as a model for simple liquids [11], 1-hexanol [32], *m*-cresol [33], quinoline [9], and a coal-derived liquid [50]. When appropriate measurements are performed both for pure components and respective mixtures, it is also possible to derive the thermodynamic excess properties over the pressure range, impossible to attain by flow calorimetry [46,51]. The pressure effects on the thermodynamic properties of liquids, especially on the excess functions, are relatively easy to obtain from the scanning transitiometric measurements [46,52]. Fig. 8 presents pressure derivatives of H^E, TS^E, G^E, and $C_p{}^E$ for {*n*-hexane + 1-hexanol} binary mixtures at 363 K. More such pressure derivatives derived from scanning transitiometric measurements are given elsewhere [52] over a much wider pressure range.

7. Conclusions

On the basis of obtained experimental results for various condensed systems, it was demonstrated that the use of state variables, such as *p*, *V*, and *T*, as inducing controlled variables in calorimetric measurements, allows direct determination of important thermodynamic derivatives over wide pressure and temperature ranges, impossible to explore by other techniques. The same derivatives can also be derived from the equations of state, thus the experimental

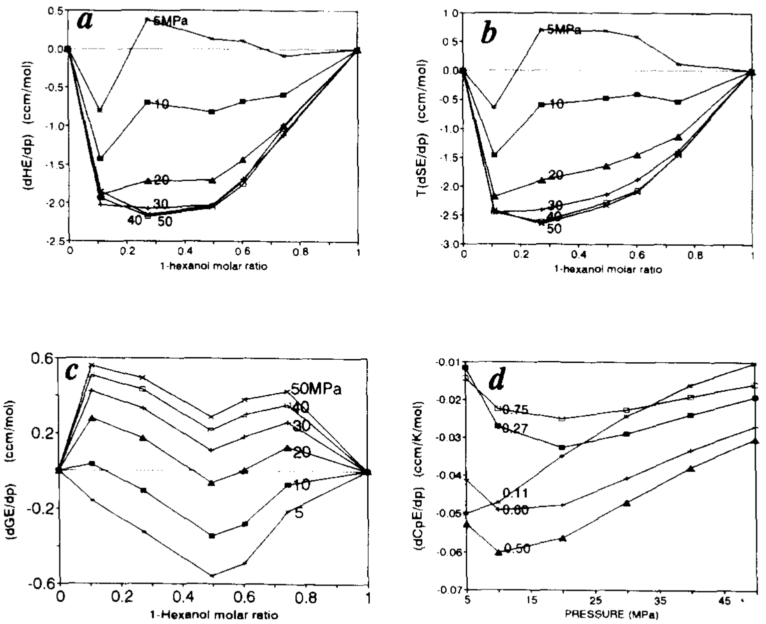

Fig. 8. Pressure derivatives of excess functions for {*n*-hexane + 1-hexanol} mixtures: a – $(\partial H^E/\partial p)_T$; b – $T(\partial S^E/\partial p)_T$; c – $(\partial G^E/\partial p)_T$; and d – $(\partial C_p{}^E/\partial p)_T$. Numbers correspond to the molar fractions of 1-hexanol.

results can be used as a verification for existing equations or can be used as a guide in further searching for better EOS, especially for dense matter. Through appropriate molecular models for respective thermodynamic derivatives or through models on which the respective EOS are constructed, the scanning transitiometry is a useful means of relating microscopic molecular properties with macroscopic observations. This can be especially explored in teaching physical chemistry, and particularly chemical thermodynamics. The determination of thermophysical properties from scanning transitiometric measurements over wide ranges of pressure and temperature is of great importance in solving immediate practical problems concerning exploitation of geothermal energy, oil and gas recovery, coal liquefaction, high-pressure organic synthesis, etc.

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