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SCANNING TRANSITIOMETRY AND ITS APPLICATIONS

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Scanning transitiometry combines three state variables (P,V,T) with a heat effect measured in strictly defined thermodynamic conditions. By slowly scanning one of the state variables when the other one is kept constant, the transitiometer permits to determine simultaneously two thermodynamic derivatives, always one is thermal and the other one mechanical. This study presents a number of applications of scanning transitiometry in various fields (dense liquids, supercritical systems, polymers, food systems) and presents results, often impossible to obtain with other known techniques.

Keywords: *combined techniques, dense liquids, phase transitions, polymers, starch, supercritical systems, transitiometry*

Introduction

Scanning transitiometry is a further development of PVT controlled scanning calorimetry [1], which was devoted to measurements of heat effects associated with variations of the state variables. An addition of a simultaneous recording of the mechanical dependent variable [2] permitted to create a new technique and call it scanning transitiometry [3], because it allows simultaneous measurements of the two contributions (thermal and mechanical) to the thermodynamic potential change occurring during a transition, performed in precisely defined conditions and thus describe the transition under investigation in a single experiment.

A close collaboration with Grolier started with a construction of a pressure-controlled scanning calorimeter, which performed linear and stepwise pressure variations over the pressure range up to 400 MPa [4]. The instrument was based on a Setaram C80 microcalorimeter, available already in the laboratory. Exploitation of this instrument, its adaptation to the requirements of the basic principles of transitiometry, and own elaboration of miniature calorimetric detectors placed in a precise wide temperature range thermostat, created new ideas and new possibilities, which resulted in common patents [5, 6], and production of a series of scanning transitiometers, world-wide original instruments [7].

From the physicochemical point of view, collection of precise data over large pressure and temperature ranges created new problems and challenges in their verification and interpretation, especially for dense liquids. Thus, the first task was to establish a set of thermophysical data for a simple liquid, which could serve as a model. On the basis of international cooperation of three laboratories such a set of data was established for *n*-hexane [8, 9]. Next, *n*-hexanol [10] and its mixtures with *n*-hexane [11] were investigated. On the basis of the measurements performed over wide pressure and temperature ranges, a detailed description of pressure effects on the thermodynamic properties of this binary system was presented [12].

Further most important applications of transitiometry resulted mainly from innovative initiatives of Grolier and concerned supercritical systems, thermodynamic properties of food products in the extruder processing, and thermodynamic properties of petroleum fluids from deep reservoir sources.

In the field of supercritical fluids it was first demonstrated, how a transitiometer can be used in the investigation of the specific behaviour of thermomechanical coefficients in the vicinity of the critical point [13]. Further activities were mainly concerned with the interaction of supercritical fluids with polymers [14–18]. A kind of a review on the use of scanning transitiometry to investigate thermodynamic properties of polymeric systems over extended *T* and *P* ranges can be found in [19].

Detailed studies on the starch gelatinization [20–22] were performed in large part in order to answer difficult questions encountered during common participation in a French programme Aliment pour demain.

Transitiometric investigation of asphaltenic fluids under in-well *P* and *T* conditions [23] was a real technical challenge, followed by attempts to understand them on the basis of model systems [24, 25].

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The most recent advancements are concerned with a combination of transitiometric measurements with simulation techniques such as Monte Carlo [26] or equations of state [27] in order not only to detect and measure, but also to understand various transitions and transformations even in complex systems.

The aim of the present contribution to this special edition is to present concisely the transitiometric technique and its most important applications developed in great part with Grolier, the present jubilee.

Scanning transitiometry

Scanning transitiometry is a technique, which performs simultaneous measurements of a heat effect induced by a variation of an independent state variable, *p*, *V* or *T*, while the second independent variable is kept constant, and of variations of the dependent variable [3].

The thermodynamic significance of the heat effect evolved due to a controlled variation of a thermodynamic state variable is presented in Fig. 1 [1]. When analysing the heat component of the scanning transitiometry it is important to notice that with temperature as inducing variable the heat effect is proportional to the heat capacity of the sample either in isobaric or isochoric conditions. When pressure is used as inducing variable the heat effect is proportional to the thermal expansion and with volume as inducing variable the heat effect is proportional to the isochoric temperature coefficient of pressure (thermal pressure) of the sample under investigation.

The interplay between the state variables in scanning transitiometry depending on the choice of the pair of independent variables is presented in Fig. 2. The controlled variations of the inducing variable must be sufficiently slow and performed in strictly defined conditions in order to determine appropriate thermodynamic derivatives.

When combining the relations from Fig. 1, describing the thermodynamic significance of the heat component, with the interplay between the state variables from Fig. 2, one obtains four thermodynamic situations presented in Fig. 3, each of them permits to determine simultaneously two thermodynamic derivatives, always one is thermal and another is mechanical. It is very important to notice, that the four situations from Fig. 3 are the only possible with respect to the basic thermodynamic correctness. For example, simultaneous variations of pressure and temperature in order to determine simultaneously thermal expansion and isobaric heat capacity from the recorded heat response [28, 29] is not correct, because in such conditions the thermodynamic requirements for the relations:

$$\left(\frac{\partial Q}{\partial p}\right)_{\mathrm{T}} = -\left(\frac{\partial V}{\partial T}\right)_{\mathrm{p}} \text{ and } \left(\frac{\partial Q}{\partial T}\right)_{\mathrm{p}} = C_{\mathrm{p}}$$

are not fulfilled. In the following the importance of each of the four possibilities of the scanning transitiometry will be exemplified with studies of various physicochemical properties over wide intervals of state variables.

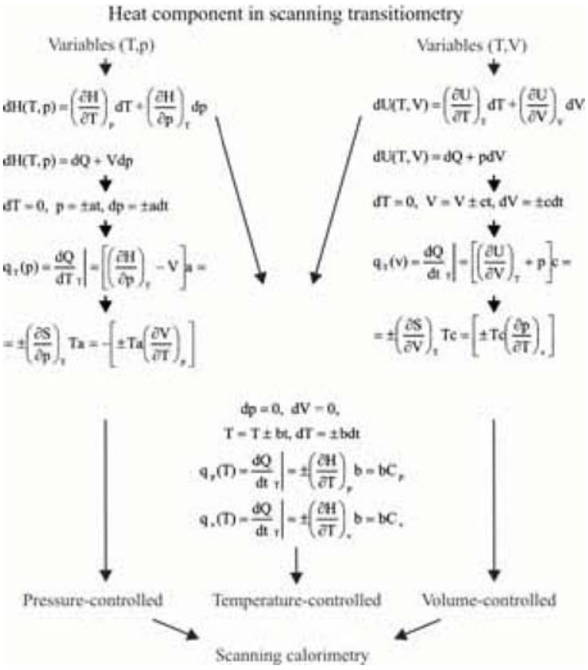

Fig. 1 Thermodynamic significance of the heat component in scanning transitiometry

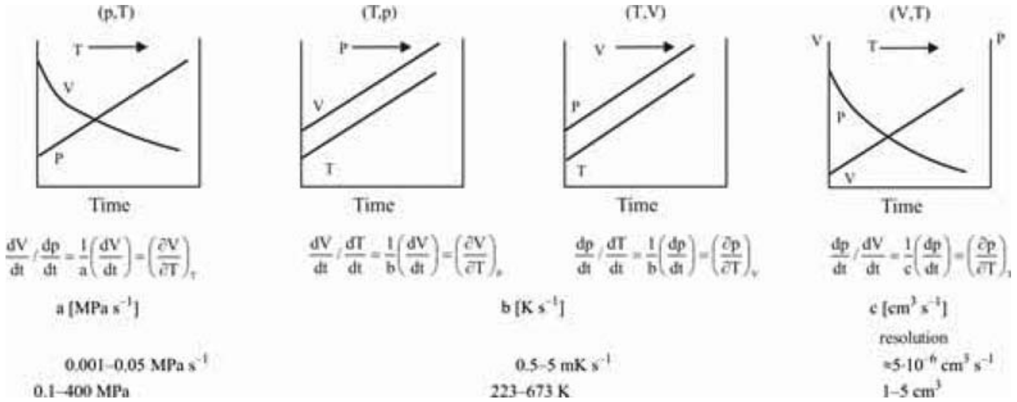

Fig. 2 Interplay of state variables (*P*, *V*, *T*) in scanning transitiometry

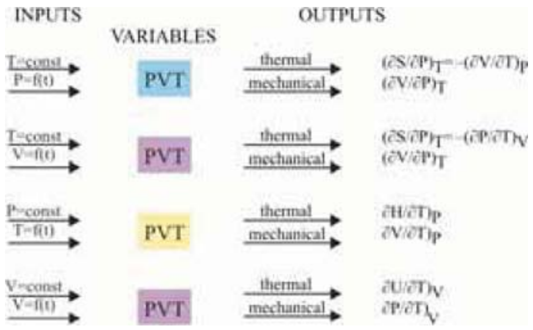

Fig. 3 Four thermodynamic situations of scanning transitiometry

Dense liquids

The possibility of directly measuring thermal expansion, the second order derivative of the thermodynamic potential, by an isothermal pressure scanning is the unique property of scanning transitiometry. It is especially useful for investigations of dense liquids, because experimental arrangements permit to determine directly the coefficient of thermal expansion, $\alpha=1/V(\partial V/\partial T)_p$, and to study its properties over wide pressure and temperature ranges for a variety of liquids. Figure 4 presents the crossing point of isotherms of α for *n*-hexane, what is a model behaviour for all simple liquids [9]. Figure 5 shows, how the behaviour of α isotherms for *n*-hexane changes with an addition of *n*-hexanol, an associated liquid [10, 11]. On the basis of transitiometric measurements for pure components and for their mixtures it is possible to determine the pressure influence on excess functions, otherwise difficult to obtain. Figure 6 presents the pressure derivative C_p^E of for selected mixtures of *n*-hexane with *n*-hexanol under various pressures over a wide temperature range, up to near the critical temperature of *n*-hexane (507.8 K) [12].

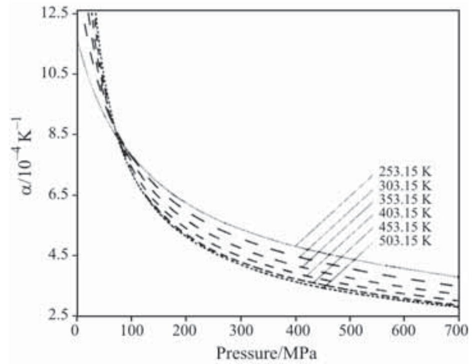

Fig. 4 Thermodynamic behaviour of the volume expansion coefficient for *n*-hexane exhibiting a net crossing point of isotherms

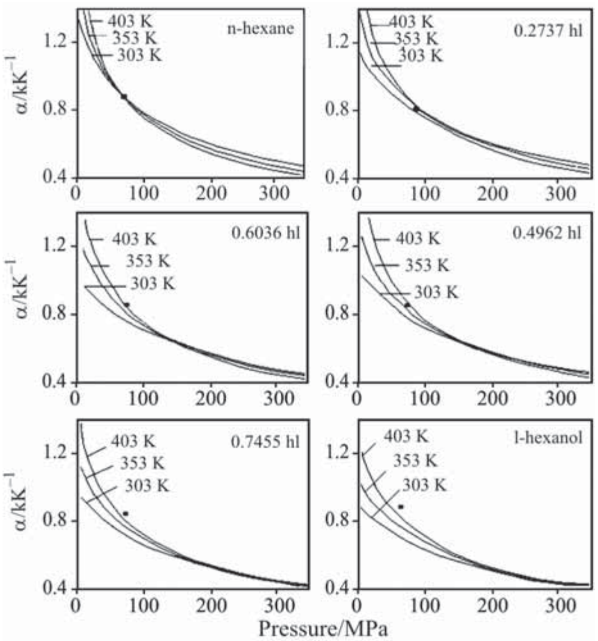

Fig. 5 Thermodynamic behaviour of the volume expansion coefficient for the binary system (*n*-hexane+1-hexanol); ■ – crossing point of α isotherms for *n*-hexane

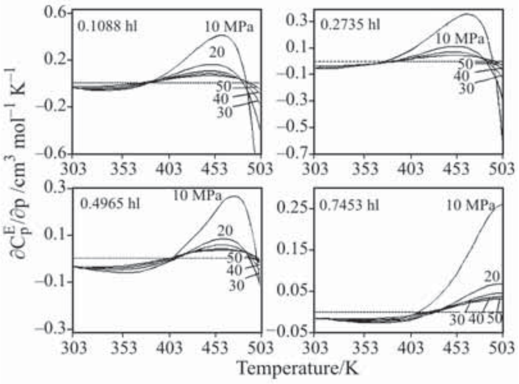

Fig. 6 Thermodynamic behaviour of the pressure derivative of C_p^E for selected mixtures of *n*-hexane with 1-hexanol

Near- and super-critical systems

In investigation of near- and super-critical systems the most interesting scanning variable is volume, because on approaching the critical point, the temperature coefficient of pressure (Fig. 3) tends to have a constant value, while thermal expansion and compressibility go to infinity, which is difficult to measure. Figure 7 presents transitiometric traces obtained during determination of thermomechanical coefficients for *n*-hexane near its critical temperature with the use of an isothermal step-wise volume scanning [13]. The derived coefficients are presented in Fig. 8 [13]. It is interesting to note, that near the critical point (507.8 K; 3.09 MPa) a variation of volume does not cause any observable pressure change, because of infinite compressibility, but causes a development of a measurable heat effect, because the temperature coefficient of pressure has a finite value (Fig. 7d). These features of scanning transitiometry can be easily used in teaching difficult problems of chemical thermodynamics.

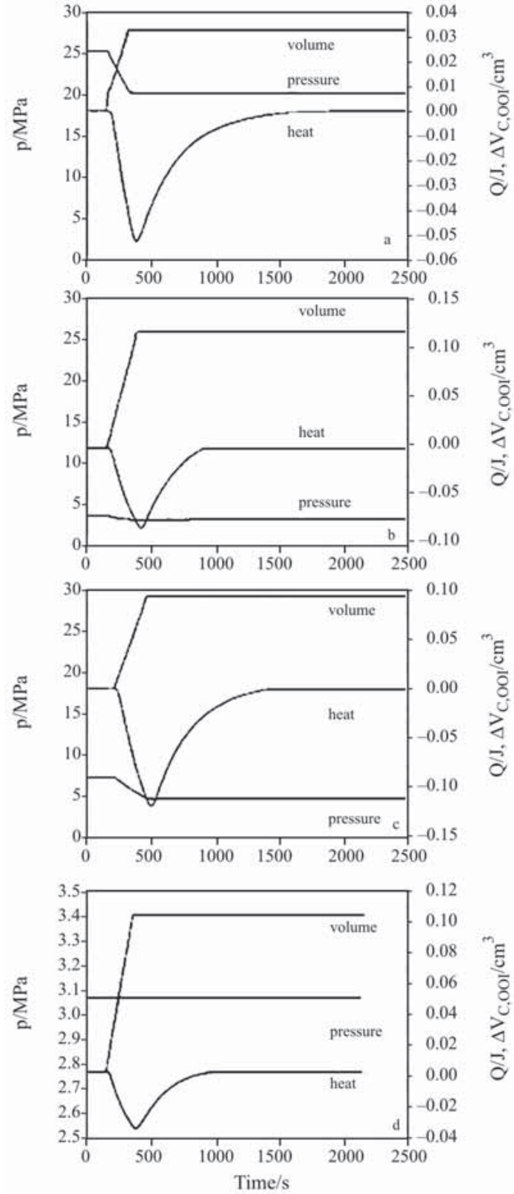

Fig. 7 Transitiometric volume scanning measurements at 507.2 K with *n*-hexane near its critical point (T_{cr}=507.8 K, p_{cr}=3.09 MPa)

Another problem of great importance from both scientific and practical point of view are the interactions of high pressure gases and supercritical fluids with polymers. The polymers are now widely used in petroleum industry, especially for making pipelines. The exploitation/production of deeper oil wells typically deals with petroleum fluids at higher *T* and *p*, which may contain important amounts of dissolved gases and supercritical fluids. The supercritical fluids or gases in contact with the plastic pipeline can induce a number of changes in properties of polymers from which the pipeline is made. One of the results of such induced changes is the blistering phenomenon, usually termed as ‘explosive decompression failure’ (XDF), which is actually very dramatic for the material. Most of the known studies on polymer-gas interactions have been devoted to sorption properties of glassy polymers. In semicrystalline polymers it was widely accepted that the sorption of gases takes place only in the amorphous phase according to the Henry law, the crystalliltes were considered as impenetrable barriers which may even impede diffusion in the amorphous phase. However, most of the known studies have been performed at rather low pressures of a few MPa. The supercritical transitiometric technique [14–16] can be used at much higher pressures. Figure 9 presents transitiometric traces of compression and decompression in the systems (MDPE+CO_2) and (PVDF+CO_2) at 352.4 K, obtained in a recent study [18]. Cubic expansion coefficients of polymers, MDPE and PVDF, in presence of two fluids, CO_2 or Hg, as a function of pressure at 352.4 K, derived from

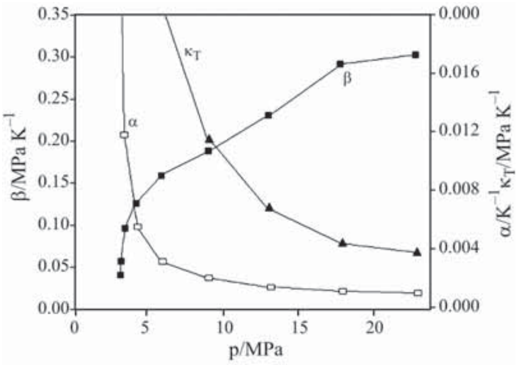

Fig. 8 Thermomechanical coefficients of *n*-hexane near its critical point determined from transitiometric volume scanning measurements (Fig. 7)

the data in Fig. 9, are presented in Fig. 10 [18]. On the basis of obtained results it can be concluded that at lower pressures (up to ~15 MPa) the main interactions correspond to the exothermic sorption of CO_2 by the surface and amorphous phases, and possibly by some voids, gaps or interstitial sites of the polymer samples in the crystal phase. At higher pressures the CO_2 is forced to enter deep inside the interstitial or other voids in the polymer and cause their mechanical distension, which is associated with an endothermic thermal effect. The sum of those effects gives minima near 20 MPa on the isotherms of both d*Q*/d*p* and of the cubic thermal expansion coefficient for the two polymers under investigation saturated with supercritical CO_2. At high pressures (above 30 MPa) the polymers saturated with CO_2 behave already as a pseudo-homogeneous phase and their cubic thermal expansion coefficient is only slightly higher (because of the presence of incorporated CO_2) than for pure polymers (pressurised with liquid mercury).

Precipitation/floculation of asphalthenes has a lot of common with the phase transitions in supercritical systems containing solid phases. The petroleum fluids from deep reservoirs contain very often heavy fractions (asphalthenes, waxes) and high concentration of dissolved gases and supercritical fluids. At high native pressures all the components make a homogeneous phase. However, during expansion, even without loss of volatile components, the heavy fractions can precipitate, because their solubility is lowered by the pressure reduction. In order to study such phenomena a special device was constructed (Fig. 11), which permits to transfer the original petroleum fluid from a bottle charged under in-well conditions to the transitiometric vessel under constant *p*, *T* conditions [23]. Such an isobaric-isothermal transfer prevents from an accidental deposition of heavy fractions. Next, by a controlled lowering of the level of mercury present in the transitiometric vessel (Fig. 11), an isothermal controlled expansion can be performed. Figure 12 presents calorimetric traces of three successive expansions of a petroleum fluid provided by TOTAL [23]. One can see

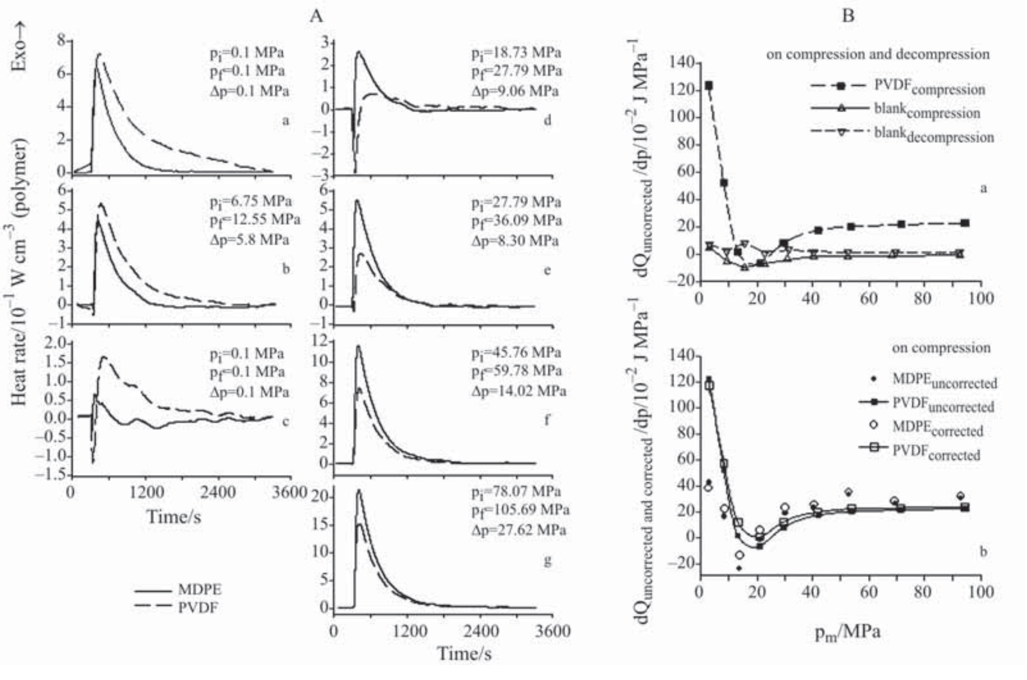

Fig. 9 Results of isothermal pressure-controlled scanning calorimetric measurements in binary systems {MDPE-CO_2} and {PVDF-CO_2} at 352.4 K. A – (a–g) – Examples of calorimetric responses to CO_2 pressure variations obtained for MDPE and PVDF; B – a – results of blank experiments performed with stainless steel rods placed in both measuring and reference vessels and results obtained with a PVDF sample placed in the measuring vessel; B – b – results obtained with the two polymers under investigation, corrected and not corrected for a small asymmetry effect

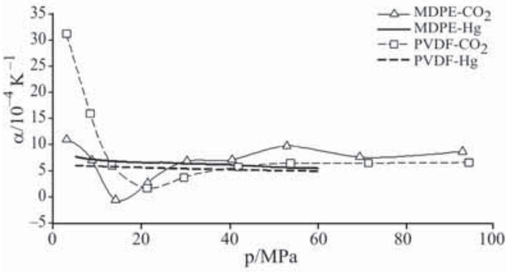

Fig. 10 Cubic expansion coefficients of polymers, MDPE and PVDF, in presence of two fluids, CO_2 or Hg, as a function of pressure at 352.4 K

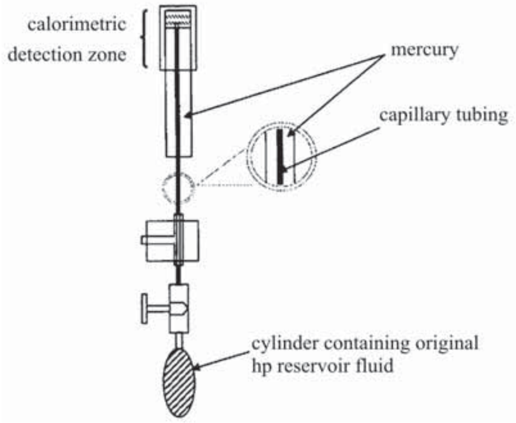

Fig. 11 A transitiometric vessel for investigation of high pressure reservoir fluids under in well pressure, temperature and composition

that the first expansion of the original fluid results in a shallow exothermic effect, what can associate with precipitation of a structured phase. After the first expansion the system was recompressed and left for 12 h for rest. The second decompression reflects a rather small effect of such flocculation/precipitation. The third and the fourth compressions/decompressions were performed in the same conditions. In Fig. 12 one can see that the 4th decompression does not show any more such exothermic phenomenon, indicating that re-compression has not re-dissolved the precipitated asphaltenes; the calorimetric response signal corresponds to the one usually observed for simple liquids [9]. It is important to notice that the technique presented above can be used only to study the precipitation/flocculation to structured phases, where a net enthalpic effect appears. To study also precipitation to amorphous phases one should use rather spectro-transitiometry, where a spectroscopic signal is recorded simultaneously with the calorimetric one [19].

Polymers

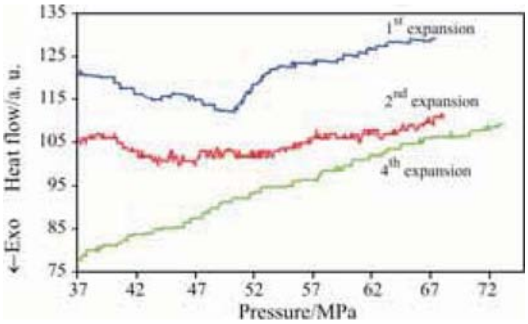

Fig. 12 Successive volume expansions of a native high pressure reservoir fluid at 420.7 K at a rate of 5.6E-5 cm^3 s^{-1}

The use of scanning transitiometry to investigate thermodynamic properties of polymeric systems over extended *T* and *P* ranges is reviewed in [19]. An interesting application is a thermodynamic description of the solid phase of polymers. An example is given in Fig. 13. From direct experimental measurements of the coefficient of thermal expansion performed over wide pressure and temperature ranges for polyethylenes of various crystallinities (Figs 13a–c) it was possible do determine the coefficient of thermal expansion for intermediate crystallinities, including the completely crystal and amorphous phases (Figs 13d and e). The obtained results can be used to verify existing equations of state or create the new ones valid over wide pressure and temperature ranges [17].

Food systems

In modern food technologies extrusion processes are widely used. The food materials introduced to an extruder are usually submitted to elevated temperatures and pressures. In order to be able to optimise the extrusion process with respect to the desired quality of produced food products, a detailed knowledge of the properties of starting materials as a function of temperature and pressure is required [30]. Starch is one of the major components of food systems and its properties must be accurately known [20–22]. Figure 14 presents an example of transitiometric investigation of 50% water suspension of wheat starch, with the use of temperature as the scanning variable at various pressures [31]. On the simultaneously recorded output signals (heat flux and thermal expansion) one can see that the process of transformation of a native globular starch to a homogenous ZOL phase is not ended at the main transition around 320–330 K (as it was usually reported [20]), but continues up to near 400 K and depends on pressure. It is also interesting to note that the endothermic main phase transition (positive enthalpy) is associated with a negative volume change. Thus, it is evident that this transition has a negative slope over the investigated pressure and temperature ranges and its temperature decreases slightly with pressure. This property can be an

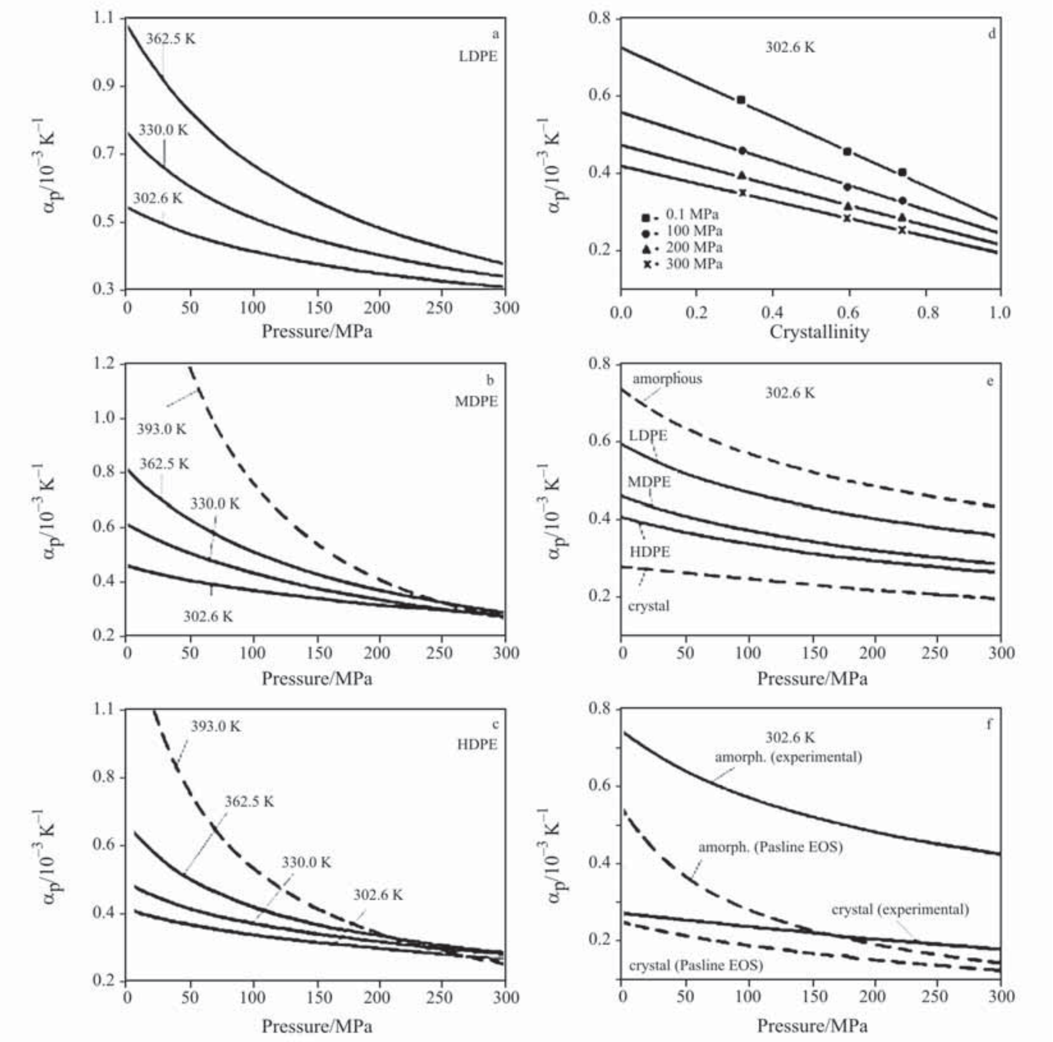

Fig. 13 Experimental coefficients of thermal expansion over wide pressure and temperature ranges for polyethylenes of various crystallinities (a–c), approximated coefficients of thermal expansion for intermediate crystallinities, including the completely crystal and amorphous phases of polyethylene (d, e) and derived from an equation of state (f) [17]

element of so called elliptic phase diagram observed for some biological systems [32].

Combined techniques

The transitiometric data can be sometimes difficult to understand or to interpret, especially for complex systems. Fortunately, the thermodynamic properties determined transitiometrically can be also modelled with equations of state or with molecular simulation techniques. Thus, there is a reason to combine the two approaches. An example of the use of such a combined technique was demonstrated for the determination of the Joule–Thompson inversion curve [26]. The Joule–Thompson inversion curve is the locus of points, where $(\partial T/\partial P)_H=0$. With the use of thermodynamic relations it can be proved, that this condition holds, when $\alpha T=1$. Thus, by making transitiometric measurements of α (see the section on dense liquids) over wide pressure and temperature ranges it is possible to determine exactly the inversion curve. However, making a large number of transitiometric measurements can be a difficult task. On the other hand the inversion curve can be determined much faster with the use of molecular modelling, e.g. Monte Carlo simulations (MCS), but the simulation results depend on the molecular parameters used for the calculations. The transitiometric data can be used to check the MCS data at selected regions of pressure and temperature and to verify the molecular parameters taken for the calculations. Such a combined procedure was used for determination of the Joule–Thompson inversion curve for methane with a high precision, impossible to get with other techniques [26].

Another example of such combined techniques are studies of phase transitions in supercritical asymmetric binary systems with appearance of solid

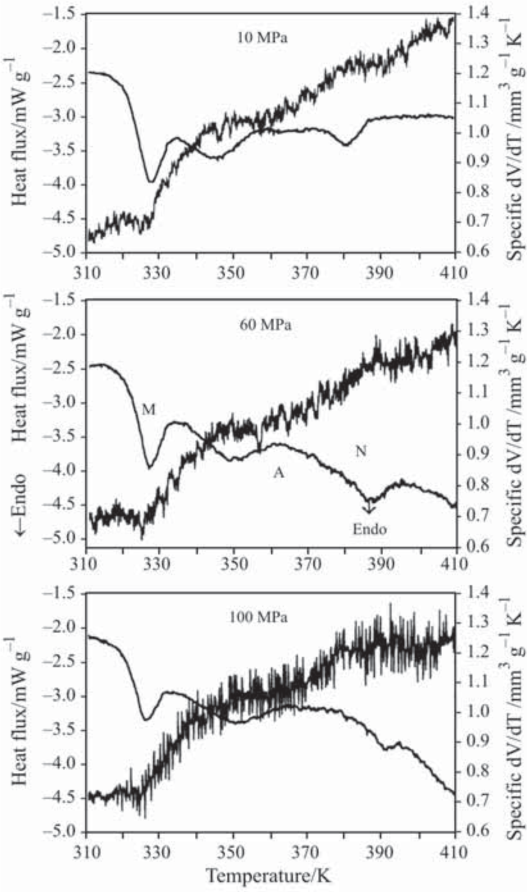

Fig. 14 Transitiometric traces (per gram of dry starch) obtained simultaneously and in situ by scanning temperature at a rate of 2.5 mK s^{-1} at various pressures for a starch-water suspension (56 mass% total water)

phases [27]. The solid sample in the transitiometer cannot be actually observed during a transition, and thus the exact interpretation or the identification of recorded signals can be difficult, especially when multiple transitions are recorded. Thus, a combination of transitiometric measurements with thermodynamic modelling is of great importance. In such a combined technique the role of the transitiometer is mainly to show the most probable path of thermodynamic behaviour in selected regions of thermodynamic parameters of the system under investigation. Then the parameters of the modelling package are carefully adjusted in such a manner as to reproduce the experimentally observed behaviour. When the transitions are correctly reproduced, the model provides possible, thermodynamically consistent identifications. Furthermore, it can be expected that the model will also work reliably under different thermodynamic conditions; it might eventually be used to replace time consuming transitiometric experiments or predict data for regions, where the transitiometric experiments are difficult or even impossible to perform. Such a combined technique was used recently in a study of high pressure phase diagrams of two asymmetric binary systems: (methane+tetracosane) and (carbon dioxide+caffeine) [27].

Acknowledgements

Grolier a été le premier à reconnaître l’importance de la transitiométrie et c’est lui qui a contribué beaucoup à son développement et surtout aux nombreuses applications dans des domaines scientifiques et techniques divers, qu’il accepte l’expression de ma profonde reconnaissance pour les travaux déjà réalisés ensemble.

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