

# **THERMAL EXPANSIVITIES OF *n*-HEXANE, *n*-HEXANOL AND THEIR MIXTURES OVER THE TEMPERATURE RANGE FROM 303 K TO 503 K AT PRESSURES UP TO 400 MPa**

*S. L. Randzio, J.-P. E. Grolier\* and J. R. Quint\**

POLISH ACADEMY OF SCIENCES, INSTITUTE OF PHYSICAL CHEMISTRY, UL.  
KASPRZAKA 44/52, 01-224 WARSAW, POLAND

\*LABORATOIRE DE THERMODYNAMIQUE ET CINÉTIQUE CHIMIQUE, UNIVERSITÉ  
BLAISE-PASCAL, B. P. 45, 63179 AUBIÈRE, FRANCE

The isobaric thermal expansivities of *n*-hexanol and of its binary mixtures with *n*-hexane have been measured in a pressure-controlled scanning calorimeter at 303 K, 353 K, 403 K, 453 K and 503 K under pressures up to 400 MPa. In both the *n*-hexanol and its mixtures with *n*-hexane a regular crossing point of isotherms of thermal expansivities was observed. The value of pressure at which the crossing appeared increased with the increasing amount of *n*-hexane.

**Keywords:** pressure-controlled scanning calorimeter, thermal expansivity

## **Introduction**

The coefficient of isobaric thermal expansivity is an interesting parameter to be measured in investigations of dense liquids. First of all its measurements can be performed by pressure-controlled scanning calorimetry over large pressure and temperature intervals [1]. Secondly, thermal expansivity can be related to the effective intermolecular potential of a dense liquid and its structure [2]. In the present communication we present first results of measurements of isobaric thermal expansivity for *n*-hexanol and its binary mixtures with *n*-hexane. It is known that for *n*-hexane a regular crossing point of isotherms of thermal expansivities is observed [3-5]. It would be interesting to investigate how this behaviour is influenced by an addition of molecules with the same chain length but different chemical nature, like *n*-hexanol.

*John Wiley & Sons, Limited, Chichester*  
*Akadémiai Kiadó, Budapest*

## Materials

*n*-Hexanol 52830 Fluka, puriss, 99%, *n*-hexane 52765 Fluka, puriss. 99.5%, used without further purification.

## Experimental

The thermodynamic bases for pressure-controlled scanning calorimetry, which permits determination of thermal expansivities, were presented elsewhere [1] and will not be recalled here. The pressure-controlled scanning calorimeter used in this study was constructed at the Blaise-Pascal University in Clermont-Ferrand in cooperation with the Institute of Physical Chemistry in Warsaw. It is similar to that described earlier [4], except that it is fully automated on the basis of an 8255 I/O card and a PC. The pressure steps at high-pressure region were 20 MPa and at lower pressures 10 MPa. The steps were realized always with the same rate of 0.05 MPa/s. The temperature of the system was changed with the rate of 0.05 K/s. After the system gained the set temperature it was pressurized and left for 12000 s to reach both thermal and mechanical equilibria. The isothermal measurements were always performed with the reduction of pressure by steps. After the last pressure step at a given temperature was realized, the procedure was repeated automatically for the next higher temperature. The integration of curves was also automated. In case of base line drifting the thermograms were corrected with an assumption that the equilibration of the calorimeter was completed after a period of 6 calorimetric time constants.

## Results and discussion

Thermal expansivities of *n*-hexanol measured as a function of pressure at five temperatures are presented graphically in Fig. 1. Similar results of measurements for mixtures of *n*-hexanol with *n*-hexane are presented in Figs 2, 3 and 4 for 0.8, 0.5 and 0.1 mole fraction of *n*-hexanol respectively. It was previously demonstrated [3-5] that for *n*-hexane a regular crossing point of isotherms of thermal expansivities appeared at about 70 MPa. It is worth noting from the results presented that a similar crossing point is observed for mixtures with *n*-hexanol and for *n*-hexanol itself. However the value of pressure at which the crossing appears is shifted to higher pressures with the increasing amount of *n*-hexanol. It is not a typical result for associated liquids and is most probably connected with the type of associates formed by *n*-hexanol and their behaviour under high pressures.

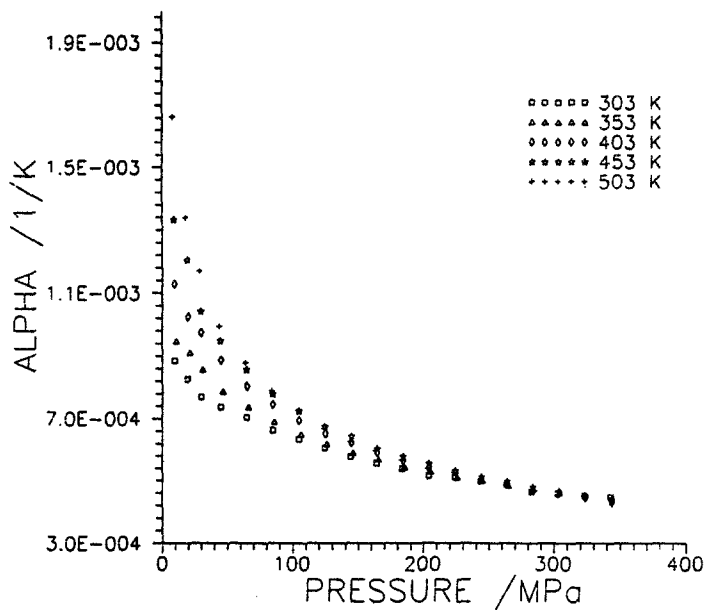


Fig. 1 Isobaric thermal expansivities of *n*-hexanol

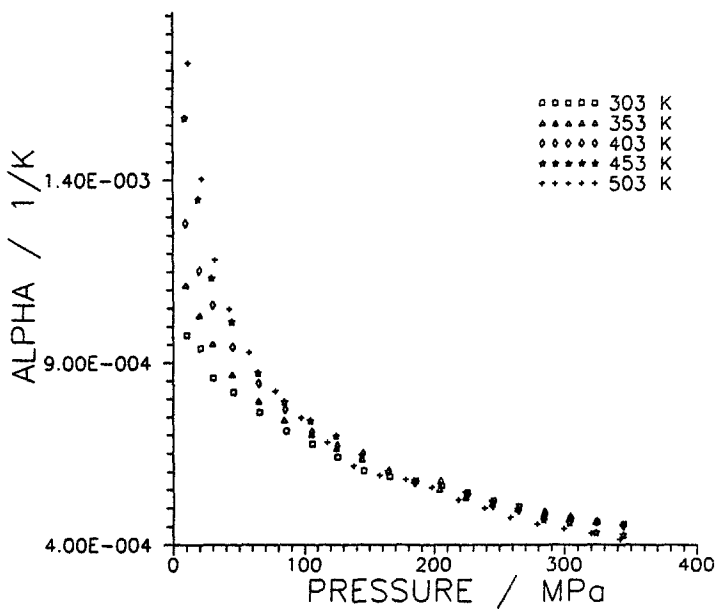


Fig. 2 Isobaric thermal expansivities of {0.8 *n*-hexanol - 0.2 *n*-hexane} mixture

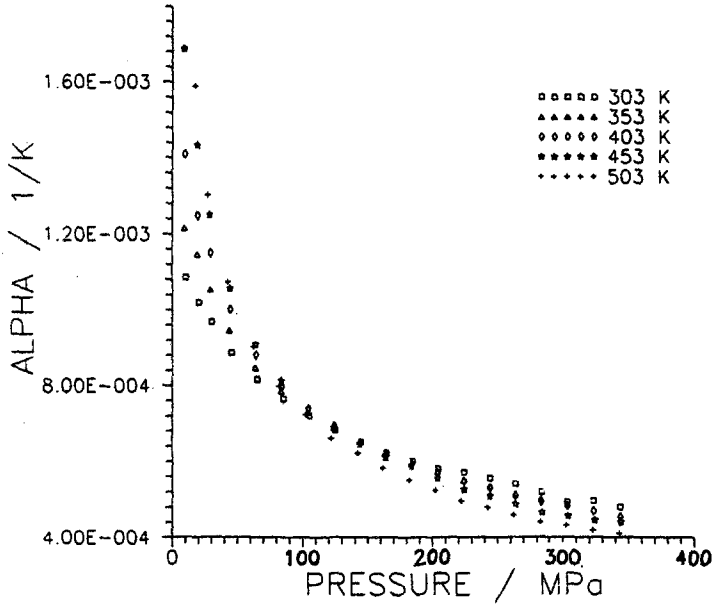


Fig. 3 Isobaric thermal expansivities of {0.5 *n*-hexanol-0.5 *n*-hexane} mixture

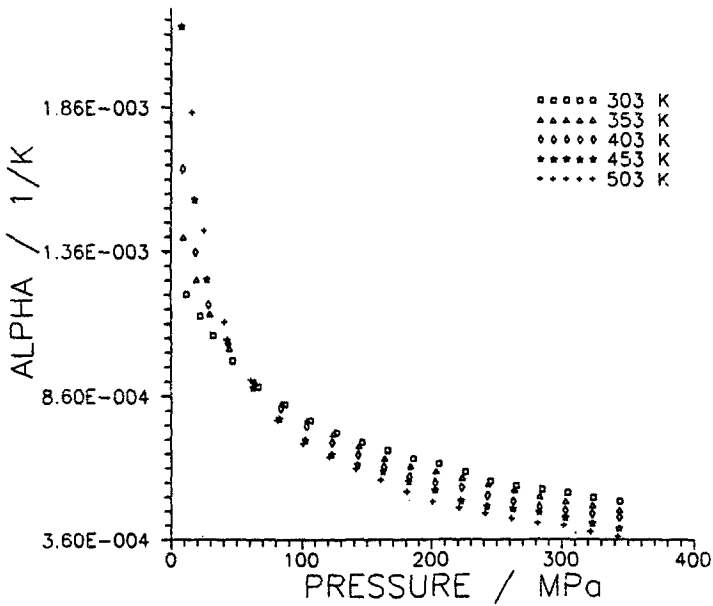


Fig. 4 Isobaric thermal expansivities of {0.1 *n*-hexanol-0.9 *n*-hexane} mixture

## References

- 1 S. L. Randzio, *Thermochim. Acta*, 89 (1985) 215.
- 2 S. L. Randzio, *Phys. Lett. A* 117 (1986) 1473.
- 3 Ph. Pruzan, *J. Phys. Lett., (Paris)* 45 (1984) 273.
- 4 S. L. Randzio, D. J. Eatough, E. A. Lewis and L. D. Hansen, *J. Chem. Thermodyn.*, 20 (1988) 937.
- 5 Ph. Pruzan, *J. Chem. Thermodyn.*, 23 (1991) 274.

**Zusammenfassung** — In einem druckkontrollierten Scanning-Kalorimeter wurden bei Drücken bis zu 400 MPa bei 303 K, 353 K, 403 K, 453 K und 503 K die isobare Wärmeausdehnung von *n*-Hexanol und seiner binären Gemische mit *n*-Hexan gemessen. Sowohl bei *n*-Hexanol als auch bei seinen Gemischen mit *n*-Hexan wurde ein regulärer Schnittpunkt der Isothermen der Wärmeausdehnung gefunden. Der Druck, bei dem der Schnittpunkt auftritt, steigt mit zunehmenden Gehalt an *n*-Hexanol.