

THERMAL EXPANSIVITY, VOLUME AND THE EFFECT OF PRESSURE ON THE ISOBARIC HEAT CAPACITY OF 1-HEXANAMINE FROM 0.1 TO 400 MPa AT 303, 353, 403 AND 453 K

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The thermal expansivity of 1-hexanamine has been determined as a function of pressure up to 400 MPa over the temperature range from 303 to 453 K. Measurements were performed in a pressure-scanning calorimeter by the stepwise technique. The compressibility as a function of pressure at 303 K was determined using the technique described before. The molar volume under atmospheric pressure was determined from the density measurements with a Paar instrument. From both the molar volume as a function of pressure at 303 K and the thermal expansivities the effects of pressure on the isobaric heat capacity were determined over the whole pressure and temperature range under study.

Keywords: 1-hexanamine, isobaric heat capacity, pressure-controlled scanning calorimeter (PCSC), thermal expansivity, thermodynamics

Introduction

The increasing interest in thermodynamic properties of systems formed by alkane-alkanol-amine mixtures can be observed in recent publications [1-3]. However, the thermodynamic description of those systems is still incomplete because of lack of data over larger pressure intervals. In previous papers we have presented first results of measurements performed under pressures up to 400 MPa over large temperature intervals for 1-hexanol [4] and for {1-hexanol-1-hexanamine} mixtures [5]. In the present communication we present first results of a high-pressure investigation of pure 1-hexanamine.

Materials

1-Hexanamine 53131 Fluka, purum; about 99%, used without further purification.

Experimental

The measurements have been carried out in a pressure-controlled scanning calorimeter (PCSC) presented elsewhere [6, 7]. The PCSC allows to determine the isobaric thermal expansivity of a substance over large pressure and temperature intervals [8, 9]. The automated hydraulic system of the instrument was used to determine the isothermal compressibility of the substance under investigation at the reference temperature [10]. The density under atmospheric pressure at the reference temperature was measured with a Paar instrument. From such measurements the molar volume as a function of both pressure and temperature could be obtained and the effects of pressure on thermodynamic functions could be determined with the use of known thermodynamic relations [11]. As an example of such procedure the pressure effect on the isobaric heat capacity of 1-hexanamine will be presented.

Results and discussion

The results of measurements of the isobaric thermal expansivities for 1-hexanamine are presented as smoothed lines in Fig. 1. The results for its molar volume determined

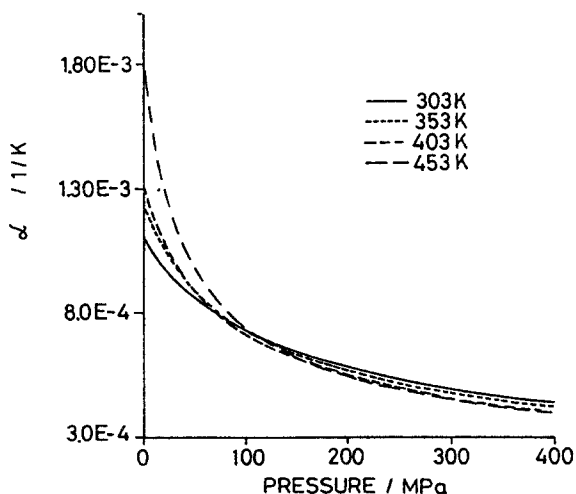


Fig. 1 Thermal expansivity of 1-hexanamine

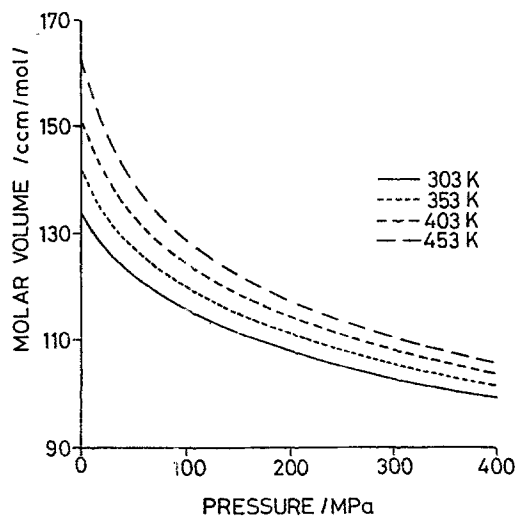


Fig. 2 Molar volume of 1-hexanamine

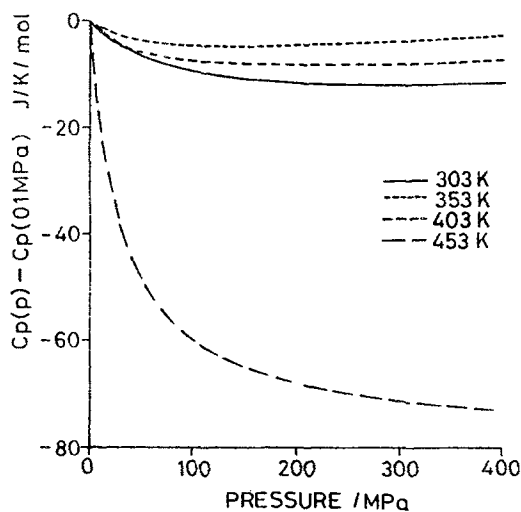


Fig. 3 Effects of pressure on the isobaric heat capacity of 1-hexanamine

at four temperatures are presented also as smoothed lines in Fig. 2. The detailed experimental results will be presented elsewhere. The results of calculations of the pressure effect on the isobaric heat capacity are presented in Fig. 3. The results obtained can be interpreted with the help of results obtained for other liquids. It is known that for simple liquids without specific intermolecular interactions a regular crossing point of

isotherms of isobaric thermal expansivities is observed and the value of pressure at which the crossing appears depends on the liquid [12]. As a result of such behaviour of thermal expansivity, minimums on the isotherms of the isobaric heat capacity appear and the heat capacity isotherms never cross. When the temperature of the liquid is increased, the value of the minimum pressure is shifted to higher pressures. For associated liquids the situation can be different because any change of pressure or temperature is connected also with a shift of chemical equilibrium in the system. 1-hexanamine is known as an associated liquid. [13]. The most probable reason for this is the effect of pressure on its isobaric heat capacity at 303 K is higher than at 353 K and 403 K. The increase of temperature causes a shift of chemical equilibrium into non-associated species and starting from 353 K 1-hexanamine demonstrates behaviour described above for non-associated liquids. The results also show that the association in 1-hexanamine is weaker than in 1-hexanol [4] and is much weaker than in {1-hexanol-1-hexanamine} mixtures [5].

References

- 1 H. Funk, M. Wetzel and A. Heintz, *Pure Appl. Chem.*, 61 (1989) 1429.
- 2 R. Reimann and A. Heintz, *J. Sol. Chem.*, 20 (1991) 29.
- 3 C. G. Panayiotou, *J. Sol. Chem.*, 20 (1991) 97.
- 4 S. L. Randzio, J.-P. E. Grolier and J. R. Quint, *J. Thermal Anal.*, (in press).
- 5 I. Tomaszkiwicz and S. L. Randzio, *J. Thermal Anal.*, (in press).
- 6 S. L. Randzio, *J. Cal. Anal. Therm.*, 20 (1990) 449.
- 7 S. L. Randzio, *Pure Appl. Chem.*, 10 (1991) 1409.
- 8 L. Ter Minassian and Ph. Pruzan, *J. Chem. Thermodyn.*, 9 (1977) 375.
- 9 S. L. Randzio, *Thermochim. Acta*, 89 (1985) 215.
- 10 S. L. Randzio, D. J. Eatough, E. A. Lewis and L. D. Hansen, *J. Chem. Thermodyn.*, 20 (1988) 937.
- 11 S. L. Randzio, *Thermochim. Acta*, 121 (1987) 463.
- 12 S. L. Randzio, *Phys. Lett.*, A117 (1986) 1473.
- 13 M. Kern, L. Abello, D. Caceres and G. Pannatier, *Bull. Soc. Chim. France*, 11 (1970) 3849.

Zusammenfassung — Im Temperaturbereich 303-453 K wurde bis zu einem Druck von 400 MPa die Wärmeausdehnung von 1-Hexanamin als eine Funktion des Druckes ermittelt. Die Messungen wurden in einem Druck-Scanning Kalorimeter durch schrittweises Vorgehen ausgeführt. Unter Anwendung derselben Technik wurde bei 303 K die Kompressibilität als eine Funktion des Druckes ermittelt. Das molare Volumen bei atmosphärischem Druck wurde aus Dichtemessungen mit einem Paar-Instrument bestimmt. Aus dem molaren Volumen als eine Funktion des Druckes bei 303 K und den Wärmeausdehnungen wurde der Einfluß des Druckes auf die isobare Wärmekapazität über den gesamten untersuchten Druck- und Temperaturbereich bestimmt.