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

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Thermal expansivities of liquid mixtures of 1-hexanol and 1-hexanamine have 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. Compressibilities of the mixtures under study were determined at 303 K using the technique described before. Molar volumes under atmospheric pressure were determined for each mixture 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: isobaric heat capacity, liquid mixtures, pressure-scanning calorimeter, thermal expansivities

Introduction

The use of isothermal pressure-controlled scanning calorimetry in investigations of compressed liquid mixtures was described recently [1, 2]. The method is based on the isothermal measurements for a given mixture of the heat of compression, which is directly related through the Maxwell relation to the isobaric expansivity. The measurements are performed over large pressure intervals at several temperatures, thus the thermal expansivity α (p, T) is determined as a function of both pressure and temperature. From such data the molar volume $V(p, T)$ can be determined with the use of Eq. (1):

$$V(p,T) = V(p,T_r)\exp\int_{T_r}^{T} \alpha(p,T)\,\mathrm{d}T \qquad (1)$$

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if the molar volume $V(p, T_r)$ is known as a function of pressure at a given reference temperature T_r. It can be determined from density measurements at normal pressure and from isothermal compressibility as a function of pressure. The isothermal compressibility can be measured in an automated pressure-controlled scanning calorimeter with the use of a technique described before [3]. The technique is based on counting the number of motor steps as a function of pressure and calibrating them in units of volume change with the use of a proper calibrating liquid.

When the thermal expansivity and the molar volume are known then the influence of pressure on thermodynamic functions can be found.

An example is the heat capacity at constant pressure, for which the influence of pressure can be determined from Eq. (2):

$$\overset{p}{\underset{p_r}{\Delta}} C_{p,T} = -T \int_{p_r}^{p} V(p, T_r) \left[\alpha^2 + \left(\frac{\partial \alpha}{\partial T}\right)_p\right] \mathrm{d}p \qquad (2)$$

In the present paper the method is applied for investigations of binary mixtures of *n*-hexanamine with *n*-hexanol.

Materials

1-Hexanol 52830 Fluka, puriss.; 99% and 1-hexanamine 53131 Fluka, purum; about 99%, were used without further purification.

Experimental

The calorimetric measurements of thermal expansivities have been carried out in a pressure-scanning calorimeter, constructed in the Institute of Physical Chemistry in Warsaw. The calorimetric system, presented in details elsewhere [4], was composed from the following main parts: – a calorimetric detector placed in a metallic block, a pair of twin calorimetric vessels, a high pressure piston pump driven by a stepper motor, a UNIPAN type 655 temperature controller, and an interface which connected the pressure gauge, stepper motor, Keithley nanovoltmeter and IBM PC computer.

The calorimetric detector is formed by 20 iron-constantan thermocouples mounted in series and arranged in the metallic block. Outside the block the heating and cooling jackets are mounted. The whole construction of the calorimetric detector can be moved up and down over the calorimetric vessels connected through the special tubing system to the pressure detector and to the high pressure pump.

In operation, the pump, pressure detector and the part of connecting system were filled with a pressure transmitting fluid. The pressure transmitting fluid and the investigated sample were separated by mercury, located in a special U-shape connection.

The important advantages of this design are that the calorimetric vessel can easily be filled with the investigated liquid from the top by moving the pump piston and no convections current can occur in the sample placed in the vessel, because its warmer part is always at higher position than the colder one.

The experimental determination of thermal expansivity is based on equation (3):

$$\alpha-\alpha_{ss}=-\frac{k}{V}\left(\frac{I}{\Delta pT}\right) \tag{3}$$

where: $\alpha_{ss}=5.1\cdot10^{-5}\,\mathrm{K}^{-1}$ is the expansivity of the stainless steel from which the vessel is made, k/V is the calibration constant, determined at various temperatures when the cell was filled with n-hexane, for which expansivity is known, T is the absolute temperature and I is the integral of the thermogram resulting from the calorimeter response to the change of pressure.

The pressure variations for each step at about 20 MPa were always performed with a constant rate at 0.05 MPa/s.

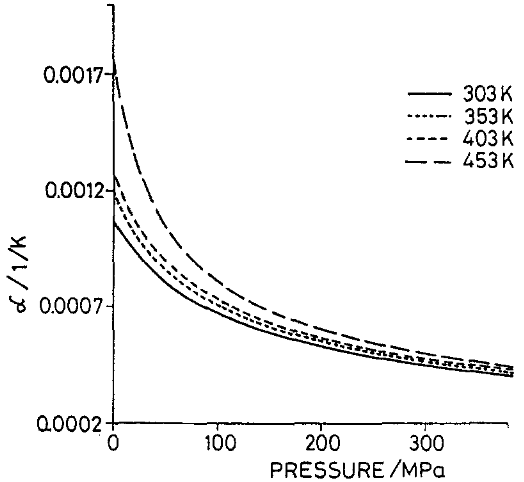

Fig. 1 Thermal expansivity of {0.5024 1-hexanamine + 0.4976 1-hexanol} mixture

The isothermal compressibilities have been determined at 303.15 K from a function of the number of motor steps versus pressure with the use of *n*-hexane as a calibrating fluid [3].

The densities at 303.15 K at atmospheric pressure were measured with the use of a Paar instrument.

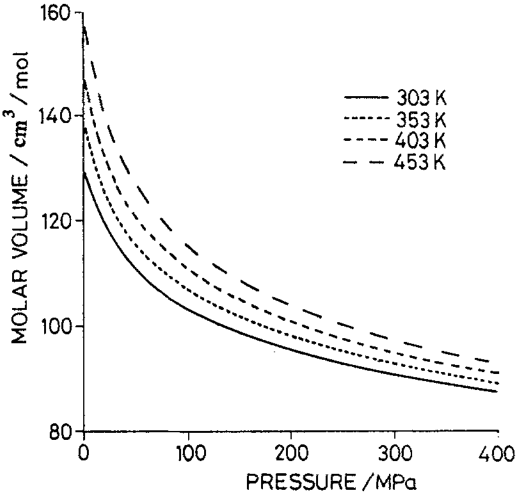

Fig. 2 Molar volume of {0.5024 1-hexanamine + 0.4976 1-hexanol} mixture

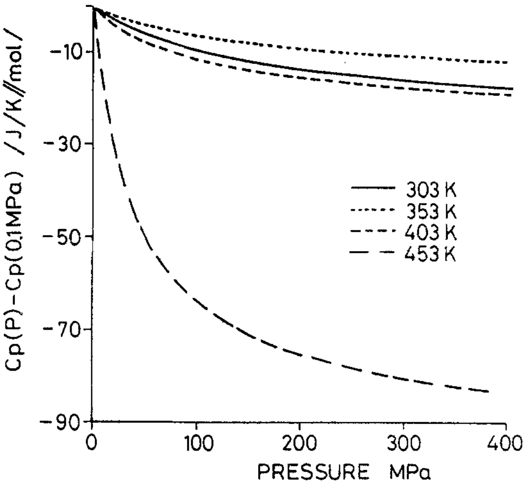

Fig. 3 Effects of pressure on isobaric heat capacity of {0.5024 1-hexanamine + 0.4976 1-hexanol} mixture

Results

The results of investigations of {0.5024 1-hexanamine + 0.4966 1-hexanol} mixture are presented as smoothed lines in Fig. 1 for isobaric thermal expansivities, in Fig. 2 for molar volumes and in Fig. 3 for effects of pressure on the isobaric heat capacity at various temperatures. In Fig. 4 are presented results of measurements of isobaric thermal expansivities for {0.2948 1-hexanamine + 0.7052 1-hexanol} mixtures. More detailed description of the results obtained will be presented elsewhere.

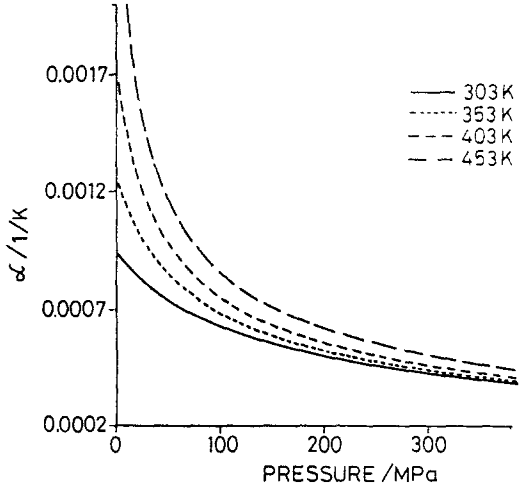

Fig. 4 Thermal expansivity of {0.2948 1-hexanamine + 0.7052 1-hexanol} mixture

The most characteristic feature of the behaviour of isotherms of thermal expansivities for both mixtures is the lack of crossing point what can be interpreted as the presence of strong intermolecular interactions in these mixtures, announced previously in the literature for alcohol-amine systems [6, 9]. It is worth noting that such crossing point of isotherms of thermal expansivities is observed for 1-hexanol at about 300 MPa [10], for 1-hexanamine [11] at 120 MPa and for n-hexane at about 70 MPa only [3, 12].

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Zusammenfassung —Im Temperaturbereich 303-453 K wurde der thermische Ausdehungskoeffizient flüssiger Gemische aus 1-Hexanol und 1-Aminohexan als Funktion des Druckes bis 400 MPa bestimmt. Die Messungen wurden in einem Druck-Scanningkalorimeter nach der Schritt-für-Schritt-Methode ausgeführt. Die Kompressibilität der untersuchten Gemische wurde bei 303 K mittels der bereits beschriebenen Methode bestimmt. Mittels Dichtemessungen in einem Paar-Gerät wurde für jedes Gemisch das molare Volumen bei Atmosphärendruck ermittelt. Anhand der Druckabhängigkeit des molaren Volumens bei 303 K sowie der thermischen Ausdehnungskoeffizienten wurde der Einfluß des Druckes auf die isobare Wärmekapazität im gesamten untersuchten Druck- und Temperaturintervall bestimmt.