

ENTROPY VARIATIONS IN BINARY MIXTURES OF TETRALINE WITH QUINOLINE AND *m*-CRESOL AS A FUNCTION OF PRESSURE FROM 0.1 TO 400 MPa AT TEMPERATURES 353 K, 403 K AND 453 K

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The isothermal pressure derivatives of entropy per unit volume have been measured in a pressure-controlled scanning calorimeter for tetraline and its binary mixtures with quinoline and *m*-cresol at 353 K, 403 K and 453 K over the pressure range up to 400 MPa.

Introduction

Tetraline, quinoline and *m*-cresol and their mixtures have been studied as models for coal liquids [1-5]. Temperature was the main external variable in those studies and thus the thermodynamic analysis was limited to temperature derivatives of the thermodynamic functions. In the case of enthalpimetric measurements [4] the pressure range was too small to determine accurately any of the pressure derivatives of the thermodynamic functions.

The present paper presents the first results of measurements of isothermal pressure derivatives of entropy per unit volume for tetraline and its binary mixtures with quinoline and *m*-cresol at 353 K, 403 K and 453 K performed in a pressure-controlled scanning calorimeter over the pressure range up to 400 MPa.

Materials

m-Cresol, 99%, ALDRICH C8,572-7, without further purification; quinoline, 99%, ALDRICH 24, 401-0, without further purification; tetraline (1, 2, 3, 4-Tetrahydronaphthalene), 99%, ALDRICH 10,241, without further purification.

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Akadémiai Kiadó, Budapest

Experimental

The instrument used in the present study was constructed in the Institute of Physical Chemistry and it was already presented elsewhere [6, 7]. It is similar to that described previously [8], except the calorimetric cells have been modified in order to reduce the heat exchange through the stainless steel tubings. In the actual construction reducers connect the calorimetric cells made from 304 SS tubing with o.d. 14 mm and i.d. 4.76 with an external connectors made from 304 SS tubing o.d. 6.35 and i.d. 1.59 mm. The reducers are placed in the calorimetric thermostat and the only heat exchange by conduction is through the thin external connectors fixed to a magnifold mounted on the laboratory table. The calorimetric detector is home made composed of 20 iron-constantan thermocouples and the signal is amplified by a Keithley amplifier. The instrument is automated on the basis of 8255 I/O card. The main advantage of automation is that the pressure steps of about 20 MPa were realized always with the same constant rate of 0.05 MPa/s. The calibration of the instrument was performed with *n*-hexane as a calibrating liquid.

Results

The results of measurements are presented as smoothed lines in Fig. 1 for tetraline, in Fig. 2 and Fig. 3 for {0.319 *m*-cresol–0.681 tetraline} and 0.682 *m*-cresol–0.318 tetraline} mixtures respectively, and in Fig. 4 for {0.494 quinoline–0.506 tetraline} mixture. More detailed data will be presented elsewhere [9].

The pressure derivative of entropy per unit volume corresponds in magnitude to the isobaric coefficient of thermal expansivity, thus the results obtained can be compared with the known literature data for other liquids. It is known that for liquids without strong specific interactions a crossing point of isotherms is observed at relatively low pressures, while for liquids with strong chemical interactions (e.g. water) especially low temperature isotherms can behave differently [10]. With this respect one can say that tetraline is not an associated liquid and the pressure of its crossing point of isotherms corresponds approximately to that of quinoline for which one can assume only weak, if any, chemical interactions [11]. Most probably for this reason the shape of isotherms for the mixture of tetraline with quinoline is similar to that of tetraline (Figs 1 and 4). In the case of the mixtures of tetraline with *m*-cresol (Figs 2 and 3) the situation is more complicated, because *m*-cresol is an associated liquid [12]. It is worth noting, however, that the isotherms have a tendency to cross at higher pressures than it was observed for pure *m*-cresol [13]. This behaviour is different from that of *n*-hexanol-*n*-hexane system, for which a regular increase of the pressure was observed at which the crossing appeared when the concentration of *n*-hexanol increased, but the value of pressure never ex-

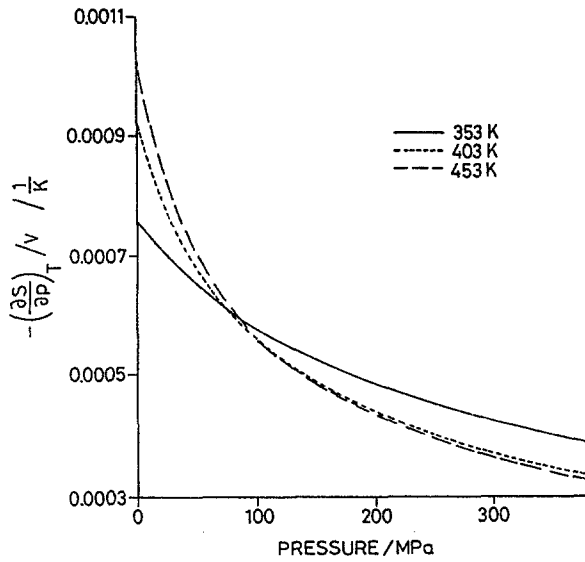


Fig. 1 $\left(\frac{\partial S_m}{\partial p}\right)_T / V_m$ for 1, 2, 3, 4-tetrahydronaphthalene as a function of pressure at various temperatures

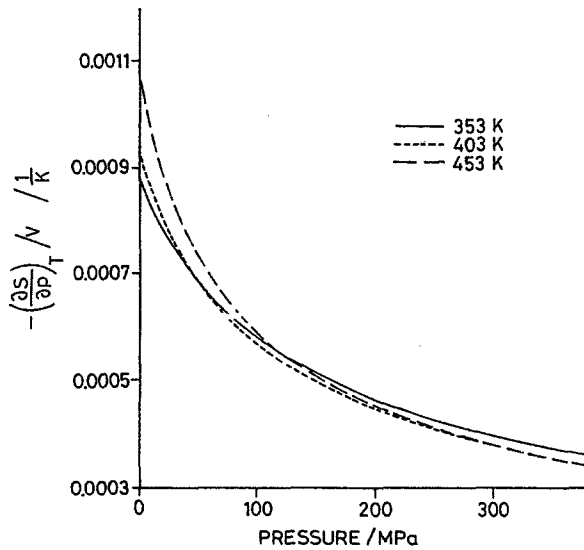


Fig. 2 $\left(\frac{\partial S_m}{\partial p}\right)_T / V_m$ for {0.319 m-cresol-0.681 1, 2, 3, 4-tetrahydronaphthalene} mixture as a function of pressure at various temperatures

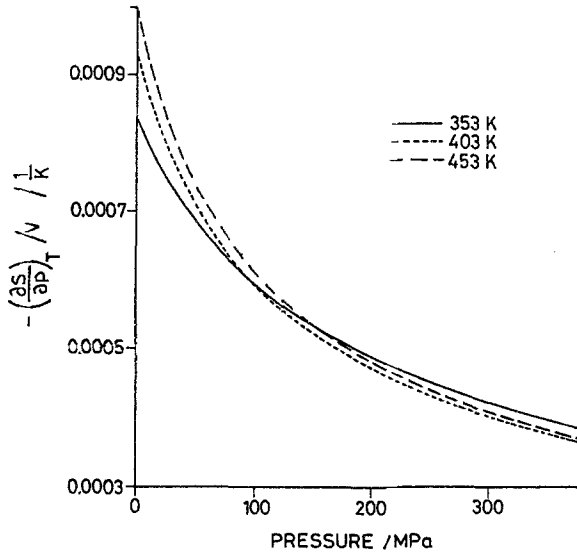


Fig. 3 $\left(\frac{\partial S_m}{\partial p}\right)_T / V_m$ for 0.682 m-cresol - 0.318 1, 2, 3, 4-tetrahydronaphthalene) mixture as a function of pressure at various temperatures

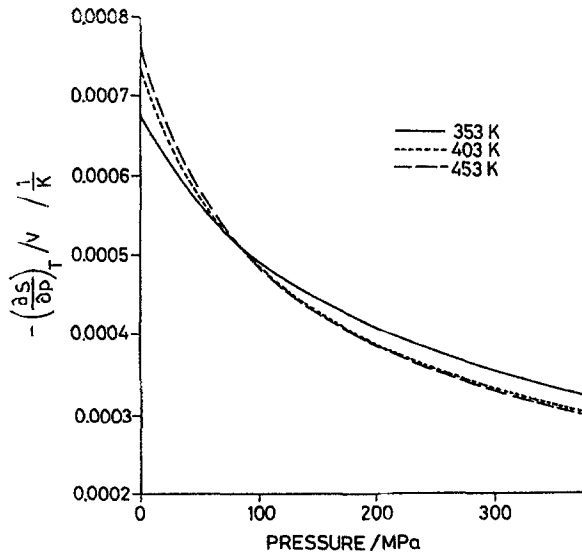


Fig. 4 $\left(\frac{\partial S_m}{\partial p}\right)_T / V_m$ for 0.494 quinoline-0.506 1, 2, 3, 4-tetrahydronaphthalene) mixture as a function of pressure at various temperatures

ceeded that of the crossing point for pure *n*-hexanol [14]. The difference in behaviour can be caused by different forms of associates in both systems.

References

- 1 C. M. White, F. K. Schweighardt and J. Schultz, *Fuel Process. Techn.*, 1 (1978) 209.
- 2 C. M. White and N. C. Li, *Anal. Chem.*, 54 (1982) 1157.
- 3 C. M. White, L. Jones and N. C. Li, *Fuel*, 62 (1983) 1397.
- 4 G. D. Mohr, M. Mohr, A. J. Kidnay and V. F. Yesevage, *J. Chem. Thermodyn.*, 15 (1983) 425.
- 5 D. J. Eatough, S. L. Wolfley, L. J. Dungan, E. A. Lewis and L. D. Hansen, *J. Energy and Fuels*, 1 (1987) 94.
- 6 S. L. Randzio, *J. Cal. Anal. Therm.*, 20-21 (1990) 449.
- 7 S. L. Randzio, *Pomiary, Automatyka, Kontrola*, 1991, 37(3) 56.
- 8 S. L. Randzio, D. J. Eatough, E. A. Lewis and L. D. Hansen, *J. Chem. Thermodyn.*, 20 (1988) 937.
- 9 S. L. Randzio, *Pure Appl. Chem.*, 1991.
- 10 S. L. Randzio, *Phys. Lett.*, 117 (1986) 1473.
- 11 S. L. Randzio, D. J. Eatough, E. A. Lewis and L. D. Hansen, *J. Chem. Thermodyn.*, (in press).
- 12 E. M. Woolley, J. G. Travers, B. O. Erno and L. G. Hepler, *J. Phys. Chem.*, 76 (1971) 3591.
- 13 S. L. Randzio, D. J. Eatough, E. A. Lewis and J. D. Hansen, *J. Chem. Thermodyn.*, (in press).
- 14 S. L. Randzio, J. P. E. Grolier, J. R. Quint, *J. Thermal Anal.*, (this volume).

Zusammenfassung — Mittels eines druckkontrollierten Scanning-Kalorimeters wurden für Drücke bis 400 MPa bei den Temperaturen 353 K, 403 K und 453 K für Tetralin und seine binären Gemische mit Quinolin und *m*-Kresol die isotherme Ableitung von Entropie/Einheitsvolumen nach dem Druck ermittelt.