A combined determination of phase diagrams of asymmetric binary mixtures by equations of state and transitiometry

Ulrich K. Deiters [a],*, Stanisław L. Randzio [b]

[a] Institute of Physical Chemistry, University of Cologne, Luxemburger Strasse 116, D-50939 Köln, Germany
[b] Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland

Abstract

Transitiometric investigations of the pure compounds tetracosane and anhydrous caffeine as well as of the mixtures (methane + tetracosane) and (carbon dioxide + caffeine) are reported for pressures up to 180 MPa. The results are compared with calculations from equations of state; the selection of reference data and the fitting of parameters is explicitly discussed. It is demonstrated how the calculations can aid the interpretation of transitiometric signals, and how the combination of transitiometry and thermodynamic modelling can be used to construct and understand high-pressure phase diagrams of asymmetric mixtures.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Combined technique; Transitiometry; Equation of state; Asymmetric systems; Supercritical phase diagram; Prediction; Caffeine; Tetracosane

1. Introduction

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have been used for decades to detect and to investigate phase transitions and chemical reactions in materials. Both methods subject a sample and a reference to temperature changes at constant, controlled rates. DTA records the temperature difference between sample and reference with very sensitive electronic amplifiers; DSC uses an electronic feedback circuit to obtain directly the (differential) heat flow. Both methods have been used at ambient pressure as well as under static pressures up to several 100 MPa, although seldomly directly controlled. Scanning transitiometry can be regarded as the logical extension of the two older methods. The method has been described in detail elsewhere [1,2], but for the readers' convenience a short summary of the operating principles will be given here.

The fundamental idea of scanning transitiometry consists in systematically varying one of the three variables pressure, volume or temperature, while keeping another one of the three strictly constant. During the scanning the variations of both the dependent variable and the associated calorimetric signal are simultaneously recorded. From these two quantities and the value of the scanning variable two thermodynamic derivatives, thermal and mechanic, are simultaneously determined for the system under study. The proper choice of the scanning variable and the constant property depends on the application and the desired thermodynamic information.

The transitiometer consists of a calorimeter equipped with high-pressure vessels, a pressure control system and LabView™ virtual instrument (VI) software. Two cylindrical calorimetric detectors ($\varnothing$ 17 mm, $l = 80$ mm), made from 622 thermocouples (chromel–alumel) each, are mounted differentially and connected to a nanovolt amplifier. The calorimetric detectors are placed in a metallic block, the temperature of which is directly controlled with a 22 bit digital feedback loop ($\approx 10^{-4}$ K), which is part of the transitiometer software. The calorimeter block is surrounded by a heating–cooling shield. The temperature difference between the block and the shield is set constant and is controlled by an analogue controller. The temperature measurements, both absolute and differential, are made with calibrated Pt100 sensors. The heaters are embedded in the outer surfaces of both the calorimeter block and the shield. The whole assembly is thermally insulated and enclosed in a stainless steel body fixed on a mobile stand, which allows the calorimeter to be moved up and down over the calorimetric

---

* Corresponding author. Tel.: +49 221 470 4543; fax: +49 221 470 4900.
E-mail address: ulrich.deiters@uni-koeln.de (U.K. Deiters).

vessels. When performing measurements near 273 K or below, dry air is pumped through the apparatus to prevent water condensation.

The calorimetric vessels are made from 0.8 cm internal diameter 316 SS tubing and are fixed on a mounting table attached to the mobile stand. Only the sample vessel is connected to the pressure control system. The reference vessel acts as a thermal reference only; a stainless steel bar of appropriate dimensions is placed in it to balance the baseline of the differential calorimetric signal. The tubings of both sample and reference vessels are connected to reducers, placed inside the calorimeter when it is in the lowered (measuring) position. The connections from the reducers to the manifold are made with thin stainless steel capillaries in order to reduce heat losses to the environment. The vessels are closed with a cone plug fixed in place by an internally threaded cover, which also acts as a heat exchanger between the calorimetric vessel tubing and the calorimetric detector. Two sleeves are also fixed on the calorimetric vessel tubing below the cover in order to help the control of the heat exchange between the calorimetric vessel tubing and both the calorimeter block and the shield. For further information on the functioning of the instrument the reader is referred to http://www.transitiometry.com.

Scanning transitiometry has already been used before in investigations of asymmetric systems involving supercritical fluids [2–4]. The main improvement in the present study is the use of a special device to quantitatively dose a given amount of the supercritial fluid into the sample vessel. The investigated mixture is then heated at a low scanning rate (1 or 2.5 mK/s) under strictly isobaric or isochoric conditions. The isochoric conditions are advantageous in investigations of systems where much of the supercritical fluid dissolves in the condensed phases during phase transitions (such as CO_2 in caffeine), abnormal decrease of pressure on heating appears, and the control of pressure becomes difficult.

Scanning transitiometry can be performed over wide pressure and temperature ranges and thus is particularly suited for investigating phase transitions and determining phase diagrams of asymmetric systems. However, an important disadvantage still exists: the sample in the transitiometer cannot be visually observed during a transition, and thus the exact interpretation or the identification of a recorded signal can be difficult, especially when multiple transitions are recorded. The main objective of the present study is to combine transitiometric measurements with *ThermoC*, a thermodynamic modelling package for the calculation of thermodynamic properties from arbitrary equations of state [5,6]. In such a combined technique the rôle 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 phase 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 – with due caution – 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 of transitiometry with Monte Carlo simulations has recently been successfully used for the determination of the Joule–Thomson inversion curve [7].

In this work we present combined transitiometric and computational studies of high-pressure phase diagrams of two asymmetric binary systems, namely (methane + tetracosane) and (carbon dioxide + caffeine).

2. Materials

Tetracosane was obtained from Acros Organics, mass fraction purity 0.99, caffeine (form II, low temperature melting form) was obtained from Merck; both chemicals were used without further purification. Hundred percent CO_2 was from Boc Gazy, methane was from Messer, mass fraction purity 0.999 and water content less than 10 ppm. No traces of water were observed when passing the methane through a cold trap.

3. Thermodynamics

3.1. Fluid phases

While the modelling of fluid phase equilibria with equations of state has been described in many publications and textbooks, the modelling of phase transitions involving solid phases has not been treated very often. Furthermore, the handling of caloric properties deserves some special attention.

The molar Gibbs energy of an *N*-component fluid mixture can be written as the sum of three contributions, namely the chemical potentials of the pure components in the ideal gas state, the Gibbs energy of mixing in the ideal gas state, and the Gibbs energy of compression to the final state:

$$G_m(p, T, \vec{x}) = \sum_i^N x_i \mu_i(p^{id}, T) + RT \sum_i^N x_i \ln x_i + \int_{p^{id}}^p V_m(p, T, \vec{x}) \, dp \quad (1)$$

Here p^{id} denotes a reference pressure which is assumed to be so low that all mixture compounds obey the ideal gas law. The $\mu_i(p^{id}, T)$ are the intrinsic (ideal gas) chemical potentials of the mixture components. $\vec{x}$ represents the mole fractions of all mixture components. Partial integration and conversion to Helmholtz energy then leads to

$$A_m(V_m, T, \vec{x}) = \sum_i^N x_i \mu_i(p^{id}, T) - RT + RT \sum_i^N x_i \ln x_i - \int_{V_m^{id}}^{V_m} p(V_m, T, \vec{x}) \, dV_m \quad (2)$$