Liquid–liquid equilibrium in binary systems of isomeric C_8 aliphatic monoethers with nitromethane

Tadeusz Hofman*, Mateusz Reda, Marek Gliński

Department of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

A B S T R A C T

New apparatus to measure liquid–liquid or solid–liquid equilibria by a synthetic method has been built and described. It was used to determine the liquid–liquid equilibrium curves for four binary mixtures of nitromethane + {heptyl methyl ether–$CH_3O^nC_7H_{15}$, or ethyl hexyl ether–$C_2H_5O^nC_6H_{13}$, or pentyl propyl ether $^nC_3H_7O^nC_5H_{11}$, or dibutyl ether $^nC_4H_9O^nC_4H_9$}. The influence of position of the ethereal group on the solubility curve has been discussed.

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1. Introduction

Among fluid-phase equilibria, that of liquid–liquid seems to be one among most important and simultaneously probably the most difficult to describe. Practical importance is due to the extraction processes which take an advantage from different solubilities of a component in a liquid biphasic system. Numerous papers and monographs were published dealing with practical and theoretical problems but a satisfactory model description for the liquid–liquid equilibrium has not been achieved yet [1–3].

This difficulty is usually explained by a temperature dependence of activity coefficients which plays a crucial role for the equations binding parameters in the equilibrium state and generally is not well described by any thermodynamic model. This is common to relate some, usually energetic parameters, to temperature using strictly empirical equations, i.e. power expansion.

Another problem which we underline is an ambiguity in the group definition when a group-contribution approach is applied [4]. In the most general approach, group contribution models equate isomers having the same groups but differing as to their localization in a molecule. This is a serious shortcoming which, at least partly, can be overcome by a definition of numerous subgroups taking into account a character of neighboring ones. Such an approach makes the model more flexible but considerably increases the number of model parameters what simultaneously

deprives the model its predictive abilities and may be applied with some restrictions only. Majority of group contribution models, as that of modified UNIFAC [5], combine polar groups with a short aliphatic adjacent neighbor thus forming a few complex groups as CH_3X, CH_2X, CHX and CX, where X denotes a polar part.

This paper begins our systematic study on thermodynamic properties of binary systems in a series of isomeric compounds dissolved in a common solvent. Its aim is to determine how a position of a polar group influences thermodynamic properties. The liquid–liquid-equilibrium was selected for this purpose as even small changes of thermodynamic parameters has a considerable impact on this property.

Aliphatic monoethers is a group of compounds for which such a study can be easily performed. If an ethereal group is being shifted from the middle position into periphery of a molecule, a family of positional isomers can be formed. On the other hand, changes in the aliphatic chain length of an ether makes possible to induce a miscibility gap for a well-defined polar solvent.

According to Sazonov et al. compilation [6], the miscibility gap in systems of aliphatic monoethers with nitromethane is observed for the C_{12} ethers, with the UCST located between 328 and 351 K. From the observed tendency it is clear that the liquid–liquid equilibrium appears for lower ethers, too. It must be underlined that the thermodynamic data of the nitromethane with lower aliphatic monoethers are extremely scarce and apart from a separate data point of the activity coefficient at infinite dilution for the dibutyl ether + nitromethane system, they concern mixtures with diethyl ether only.

* Corresponding author. Tel.: +48 22 234 7475.
  E-mail address: hof@ch.pw.edu.pl (T. Hofman).

a_{ij}	parameter of Eq. (2)
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g_{ij}	energy interaction between i–j molecules
G^E	excess Gibbs energy
HR	heating rate
x_i	mole fraction of component (i)
T	temperature
u	standard uncertainty

Greek letters

α	nonrandomness parameter in the NRTL equation
Δg_{ij}	energy parameters in the NRTL equation
ϕ_1	volume fraction
σ	standard deviation

Fig. 1. Schematic drawing of the cloud-point apparatus. (1) Equilibrium cell; (2) thermostated vessel; (3), magnetic stirrer; (4) main thermostat; (5) autotransformer; (6) cooler; (7) LED; (8) light detector; (9) unit measuring light intensity; (10) temperature probe; (11) temperature measuring unit.
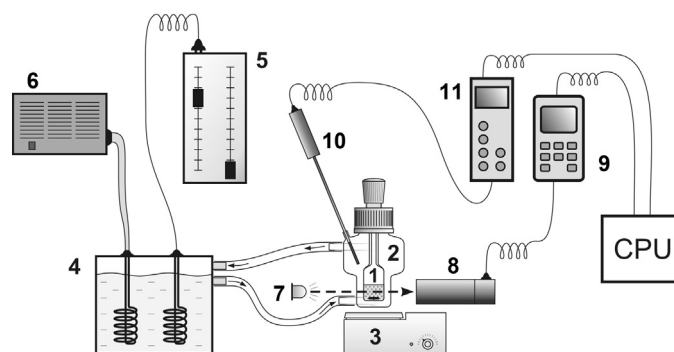
The preliminary examination of the nitromethane + a symmetric ether mixture at approximately equimolar composition showed that a limited miscibility appears for dibutyl ether at the room temperature.

2. Experimental

2.1. Apparatus and method

The liquid–liquid-equilibrium was determined using a synthetic method or a cloud-point technique. A biphasic sample of known composition stirred rigorously was slowly heated and disappearance of turbidity was taken as the solubility temperature. The extent of turbidity was measured by intensity of light beam crossing the measuring cell. The breakdown on the intensity *versus* temperature dependence corresponded to the solubility temperature. Similar apparatuses were frequently described in the literature [7–11]. The diagram of the apparatus is given in Fig. 1.

Light and measuring of its intensity. Usually in such a measuring unit laser is used as a source of light. We found that an ordinary LED (white light, 20°, 10,000 mcd) is sufficient for this purpose. Moreover it guarantees a high beam stability while laser generators require additional systems to keep intensity of light constant. The intensity was measured by the LP 471 LUM 2 luminance measurement probe supplemented by Photo-Radiometer HD2102.1 (Delta OHM, Italy). The probe measured luminance in 0.1–2×10^6 cd/m^2 range. The stability of a signal was better than 0.3%.

Data processing. Measured temperatures and light intensities were acquired independently and transformed into the light intensity *versus* temperature dependence. This dependence was correlated by two straight lines and filtered. Its character modeled by the Lambert-Beer law is shown in Fig. 2a. The discontinuity of the first derivative is distinct and the slope of the dependence preceding the equilibrium point depends on the amount of phase which disappears. A typical observed dependence noted for the nitromethane + ethyl hexyl ether system is drawn in Fig. 2b.

Temperature. The temperature was measured by Pt100 resistance probe P 650 (DOSTMANN electronic, Germany) with an accuracy of ±0.03 K and stability of ±0.01 K. The probe was immersed in thermostating medium (water or water solution of ethylene glycol) and located approximately in a distance of 2 mm from the outer wall of the equilibrium cell. An experiment showed that the difference between temperature of the medium and an actual temperature of the solution in the equilibrium cell did not exceed 0.02 K. The heating rate was controlled manually and varied between 5 and 40 mK min^{-1}. It was checked that reducing of heating rate from 15 mK min^{-1} down to 5 mK min^{-1} did not influence significantly the determined solubility temperature (observed change in the determined equilibrium temperature was about 0.02 K). It was already reported that detecting of equilibrium temperature during heating was more credible than while cooling because of possible overcooling for the latter case [12]. Our observation for the system nitromethane + dibutyl ether showed that both temperatures were almost identical with the differences
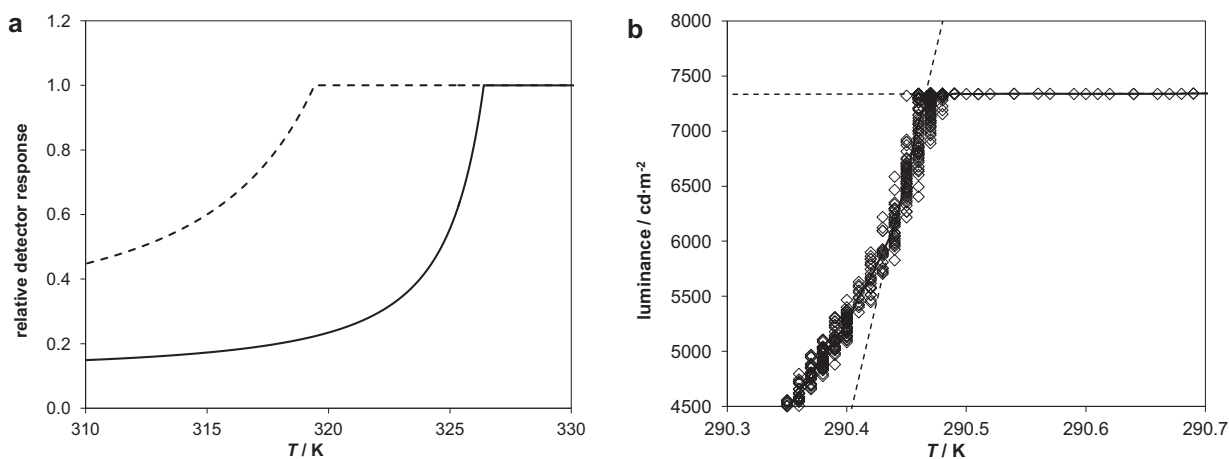
Fig. 2. Luminance as s function of temperature. (a) Theoretical dependence based on the Lambert-Beer law for solid-liquid equilibrium for the octadecan-1-ol (1) + n-heptane (2) system modeled by the ideal solubility equation and two concentrations: solid line, $x_1 = 0.7$; dashed line, $x_1 = 0.4$. (b) Actual dependence for the nitromethane (1) + ethyl hexyl ether (2) system for $x_1 = 0.61336$.