Vapour-liquid, Liquid-liquid and Vapour-liquid-liquid Equilibria in the System of Trifluoromethane+(2-methylpropyl)benzene

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Vapour-liquid, liquid-liquid, liquid-liquid-vapour equilibria in the asymmetric system consisting of the refrigerant, trifluoromethane and lubricant from the family of alkylbenzenes – (2-methylpropyl)benzene, were experimentally collected and presented for temperatures range 245…400 K and pressures up to 15 MPa. The investigated system exhibits type III phase behaviour according to the classification of van Konynenburg and Scott. The critical endpoint $L_2 + L_1 = V$ was found at $T = 309.34 \text{ K}$, $P = 5.615 \text{ MPa}$.

Keywords: vapour-liquid, liquid-liquid, liquid-liquid-vapour equilibria, critical endpoint

The understanding and correlation of thermophysical properties of refrigerant and lubricant oil mixtures is highly important for the design of refrigeration systems and for the proper selection of the lubricant oil. Important factors for selection of the refrigerant/oil mixture are viscosity and lubricity, which are dependent on refrigerant solubility. Furthermore, the solubility influences the heat transfer of the evaporator and condenser working fluid system. A good solubility of the refrigerant-lubricant mixtures is often required for proper oil circulation in the system [1, 2].

In order to obtain a good efficiency and good oil return in the refrigeration cycle it is very important to know the properties of the lubricant-refrigerant mixture. Among these, vapour-liquid equilibrium data are required as functions of temperature.

Nowadays, binary mixtures consisting of hydrofluorocarbon (HFC’s) refrigerant and synthetic oils like polyol esters, polyalkylene glycols or phenylalkanes are used as working fluids in the refrigeration industry. Phenylalkanes have good chemical stability, seal compatibility, high lubricity and low hygroscopic character. However, these lubricants cannot compete with the POEs or the PAGs because of their limited miscibility with HFCs. Still, they have a higher solubility in HFCs compared with aliphatic-based mineral lubricants [1-3]. In combination with trifluoromethane or other refrigerant azeotropic mixtures, these lubricants are functioning as fluids in the cascade refrigeration cycle for very low temperatures [4].

Such systems belong to the asymmetric, highly non-ideal systems with significant difference in the size of the molecule. These asymmetric systems can develop type II, III, IV or V phase behaviour [5,6] according to the classification of van Konynenburg and Scott.

Our previous [7, 8] studies have shown for the systems consisting of CHF$_3$ and different 1-phenylalkanes (1phC$_n$, $n = 3, 8, 14$) type III phase behaviour according to the classification of van Konynenburg and Scott.

This paper presents the experimental data on vapor-liquid, liquid-liquid and liquid-liquid-vapor equilibria for the system trifluoromethane - CHF$_3$ (R23) and a branched alkylbenzene: (2-methylpropyl)benzene.

The experimental data were plotted as P-T diagrams, and then the P-x, T-x cross-sections were constructed and discussed.

**Experimental part**

**Chemicals used:**
- trifluoromethane (CHF$_3$, R-23 Praxair, min. of 99.995%)
- (2-methylpropyl)benzene (phC$_4$, Fluka, with a purity of 99.8%).

Some properties of these compounds are given in table 1.

The chemicals were used without further purification.

**Procedure of measurements**

The measurements were carried out with the so-called Cailletet apparatus [11, 12]. In this apparatus phase equilibria for mixtures of known overall composition can be observed visually by adjusting the pressure and the

### Table 1

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>$T_s$/ K</th>
<th>$T_m$/ K</th>
<th>$T_e$/ K</th>
<th>$P_e$/ MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>trifluoromethane</td>
<td>CHF$_3$</td>
<td>191.7$^a$</td>
<td>117.97$^a$</td>
<td>299.3$^a$</td>
<td>4.858$^a$</td>
</tr>
<tr>
<td>(2-methylpropyl)benzene</td>
<td>C$_6$H$_5$-C$_4$H$_9$</td>
<td>445.9$^c$</td>
<td>222.15$^c$</td>
<td>650$^c$</td>
<td>3.05$^b$</td>
</tr>
</tbody>
</table>

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REV. CHIM. (Bucharest) • 61 • Nr. 8 • 2010  http://www.revistadechimie.ro 767
The mixtures are prepared by dosing the low-volatile compound (liquid at the room temperature) in the sealed end of the Cailletet tube by means of a micrometer syringe. The exact mass of the liquid component is determined by weighting.

The liquid is thoroughly degassed by successive freezing and melting under high vacuum. For every degassing step, nitrogen liquid was used as cooling agent. The gaseous component (light component) is added volumetrically using a mercury displacement method [10].

Mercury was used as a transmitting fluid between the hydraulic oil and the sample. In this way the sealing of the sample was provided. The final accuracy of the mole fraction of alkylbenzene is better than 0.001.

The measurements consist of visually observation of the phase transitions when the pressure is slowly changed at constant temperature, or the temperature is slowly varied at constant pressure.

The pressure is measured with a dead-weight pressure gauge (type De Wit, accuracy of ±0.003 MPa), or in the case of the measurements of liquid-liquid-vapour equilibria with a manometer (type Heise, uncertainty ±0.01 MPa). The manometer was calibrated against the dead weight gauge. A platinum resistance thermometer (Pt 100), previously calibrated against a standard thermometer, records the temperature of thermostat liquid near the sample with accuracy within 0.01 K [10].

**Results and discussions**

Liquid-liquid-vapour equilibria (LLVE), liquid-vapour equilibria (LVE), liquid-liquid equilibria (LLE) were measured in the system consisting of trifluoromethane and (2-methylpropyl) benzene. The data cover the whole range of compositions, for pressures \( P = 1…15 \) MPa and temperatures \( T = 245…370 \) K. The data are plotted in figure 1 and figure 2.

The liquid-liquid-vapour curve ends in an upper critical endpoint (UCEP - \( L_1 + L_2 = V \)) and goes uninterrupted to low temperatures. Between the two LL branches, liquid-vapour equilibrium line (LLV).

At the UCEP, the liquid \( L_2 \), richer in the light (volatile) component - CHF\(_3\) and the vapour phase merge in one single fluid phase. This critical fluid coexists with the second liquid phase, \( L_1 \), rich in the heavy (less volatile) component isobutyl benzene.

The coordinates of the UCEP were found to be: \( T = 309.94 \) K and \( P = 5.615 \) MPa. There are no literature data reported for the studied system so far.

The vapour pressure data (VPC, CHF\(_3\), – fig. 1) measured in this work are in accordance with the data reported in the literature. The measured critical point \( (T_c = 298.95 \pm 0.02 \) K, \( P_c = 4.79 \pm 0.005 \) MPa) agrees within the experimental uncertainty with the data given in [13 - 14], or with the more recent data [15-17].

Figure 1 and 2 show that for mixtures with composition \( x(CHF_3) = 0.100…0.400 \), only bubble points (LV points) could be measured. A liquid-liquid split occurs and liquid-liquid (LL) phase boundaries were measured, for samples with higher content of light component (trifluoromethane). Thus, for \( x(CHF_3) = 0.5000…0.5400 \), LL and LV curves for every composition meets in a point of the three-phase equilibrium line (LLV).

The LL phase boundaries are very steep curves and move towards higher temperatures and pressures when the mole fraction of trifluoromethane increases. The slope of these curves changes from negative, for concentration close to the critical composition, to positive for concentration further removed from the critical concentration.

By starting with composition \( x(CHF_3) = 0.5817 \), the LV and LL lines join in one continuous curve, positioned above the three-phase equilibrium line, showing a pressure minimum. The same trend will have the experimentally isopleths for mixtures with \( x(CHF_3) = 0.5871…0.7009 \).

Because of the limitations of the Cailletet apparatus (maximum pressure: 15 MPa) the highest in pressure located isoplet was measured in this system for a mixture with \( x(CHF_3) = 0.7009 \). Further no LL line could be observed, for compositions \( x(CHF_3) = 0.7009…0.9007 \).

In contrast, for samples with \( x(CHF_3) = 0.9007 \), LL phase boundaries were obtained. These curves move slowly to lower pressure with increasing the mole fraction of trifluoromethane. So, it can be concluded that most probably the critical line is positioned between \( x(CHF_3) = 0.7009 \) and \( x(CHF_3) = 0.90 \).

Particularly interesting is the sample with mole fraction, \( x(CHF_3) = 0.9502 \). The corresponding curve presents two LL branches: one very steep line, located at very low temperature (\( T = 245 \) K), the second, in the region of high temperatures. Between the two LL branches, liquid-vapour equilibrium points were experimentally observed. The...
resulted LV curve starts at $T = 252 \text{ K}$ and ends at $T = 302 \text{ K}$ and is positioned slightly above the three-phase LLV equilibrium line. The difference in pressure is around 0.3 MPa. So, no back turn of the LL isopleth in the LLV equilibrium line was observed. Probably, samples with compositions slightly below $x(\text{CHF}_3) = 0.9502$ will show the return of the LL in the LLV line (fig. 3). But the intersection point is located out of the temperature range of the measurements with the Cailletet apparatus.

From figure 1 and 2, isothermal P-x cross-sections and isobaric T-x cross-sections were constructed by interpolation. The results are presented in figure 3 and respectively in figure 4.

For temperatures and pressures lower than the values of critical endpoint, the three-phase line separates the L,V region from the upper two-phase regions: L,L$_2$ and L,V.$^*$ The isotherms change the character from LV curve to LL curve and show around $x(\text{CHF}_3) = 0.75$, a point of inflection.

At pressure $P < \text{PUCEP}$ the LV and LL curves join in the three-phase equilibrium line, each isobar presents two branches and two horizontal points of inflection.

According to our previously work in other similar systems [7, 15 -17], the critical composition corresponds to the point where the two horizontal inflections points are joining. Further, every isobar will detach from the LLV line and will pass through a point of inflection: maximum for the LV curves and respectively minimum for the LL branches, at higher temperatures. Similarly to the P-x cross-sections, the critical composition is estimated at $x = 0.75$ mole fraction of trifluoromethane.

The figure shows that these equilibria are not strongly depending on pressure, except the critical region.

**Conclusions**

Vapour-liquid, liquid–liquid, liquid-liquid-vapour equilibrium and the critical endpoint have been measured for the binary system consisting of trifluoromethane and (2-methylpropyl)benzene.

The measurements were carried out in the Cailletet apparatus, designed for investigation of the high pressure phase equilibria. The apparatus and the procedure of measurements were described.

According to the general classification of van Konynenburg and Scott, the system exhibits type III phase behaviour, characteristic for the asymmetric systems with a large region of immiscibility. The data obtained have no literature correspondent, so far.

Isothermal P-x diagrams and isobaric T-x diagrams have been constructed and discussed.

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REV. CHIM. (Bucharest) ● 61 ● Nr. 8 ● 2010 http://www.revistadechimie.ro 769