Vapor–liquid equilibrium at high temperature

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Abstract: A flow apparatus to carry out vapor-liquid equilibrium measurements at temperatures and pressures up to 623.15 K and 10 MPa, respectively, is described. The equipment was used to study binary mixtures involving methanol, ethanol and water as components and coal model compounds, such as m-cresol, quinoline and tetralin. Some of these binary systems present an azeotrope which disappears with the increase of temperature.

1 - Introduction

In the last 20 years a great effort has been spent in experimental programs to measure the vapor-liquid equilibrium (VLE) of binary mixtures. There are plenty of these experimental studies at low and room temperature (1,2). However, at high temperature experimental data are scarce and when available the desired accuracy is not present.

High temperature vapor liquid equilibrium measurements of binary mixtures involving m-cresol, quinoline and tetralin (coal model compounds) and methanol, ethanol and water are important to design chemical processes related to the production of alternative fuels, such as coal derived liquids and alcohols, respectively.

Some of these mixtures present an azeotrope which disappears with the increase of temperature. Therefore, these measurements are also relevant for the theoreticians, since the interpretation of this phenomena might improve their current knowledge on intermolecular forces.

2 - Experimental

Several experimental methods have been used in phase equilibria measurements (3,4,5). A flow method is preferable for high temperature vapor-liquid equilibrium studies. In fact, the thermal degradation of the fluids is minimized by reducing the residence time of the compounds at elevated temperature. Another advantage of this method is that it can generate relatively large liquid and vapor samples required for analysis in studies of complex systems, such as the coal derived liquids.

An apparatus, based on this method, built at Chemical Engineering Department of Colorado School of Mines, is presented in Fig. 1, which is capable to operate at temperatures and pressures up to 623.15 K and 10 MPa, respectively (6).

A liquid sample from the surge tank is pumped into a fluidized bed sand bath (preheater), where it is preheated gradually through a 6 m coil to minimize the thermal degradation. Afterwards, the sample flows through a heat exchanger for a final adjustment of temperature and then into a windowed equilibrium cell, which is inside an oven. At the present, the high pressure cell has a saphire window sealed with a gold O-ring (7).

Inside the cell, the vapor and the liquid separate, being the interface easily seen, because the oven has also a window.

The vapor and the liquid are removed from the top and the bottom of the cell, respectively. By regulating the vapor and liquid flow through the operation of two micrometering values, it is possible a fine control of the position of the interface.

Vapor and liquid streams pass through cooling heat exchangers and return to the surge tank. When the steady state is achieved, the temperature and pressure are measured and the condensed gas and liquid streams are sampled.

The temperature measurement is carried out with a platinum resistance thermometer (PRT), placed inside the equilibrium cell, and a digital multimeter. On the other hand, the pressure is measured using a differential pressure indicator (DPI), a null indicator, three Bourdon gauges, with different
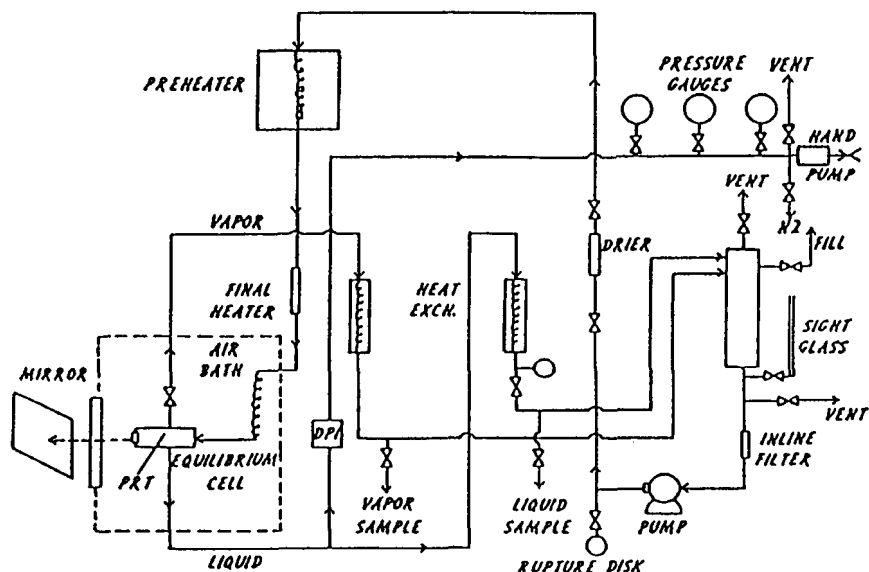
Fig. 1 - Diagram of a vapor-liquid equilibrium apparatus at Colorado School of
Mines (Golden, U.S.A.). (Reproduced, with permission, from ref.6)

pressure ranges, and nitrogen as the balancing gas. Furthermore, the compositions of vapor and
liquid samples are determined with a gas chromatograph with a flame ionization detector for binary
mixtures.

A new version of this apparatus was recently constructed at the Chemistry Department of the Faculty
of Sciences, University of Lisbon, which allows to carry out vapor-liquid equilibrium studies up to
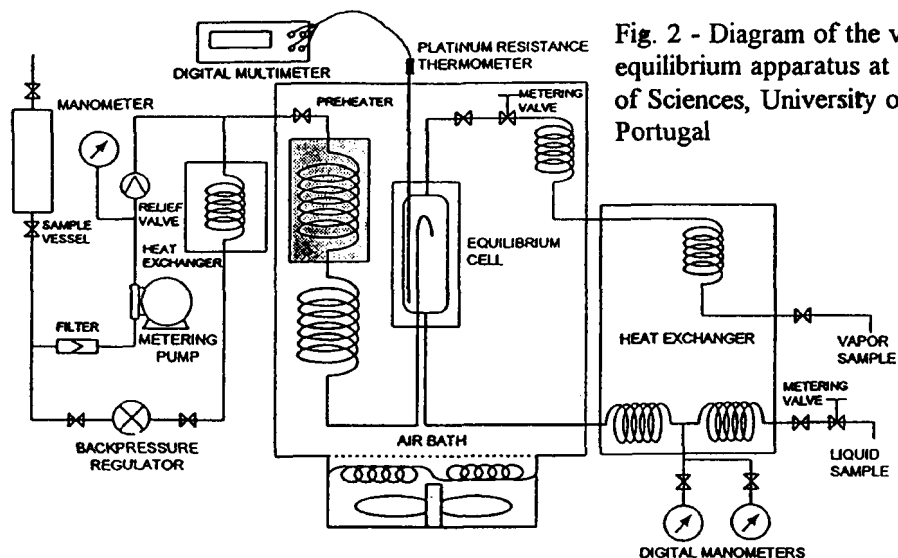473.15 K and 14 MPa (8). This equipment is depicted in Fig. 2.

Fig. 2 - Diagram of the vapor-liquid
equilibrium apparatus at the Faculty
of Sciences, University of Lisbon,
Portugal

In this version, the diaphragm pump, the fluidized bed sand bath and the pressure measurement
system were replaced by a metering pump, a simple preheater and two digital manometers,
respectively.

3 - Results and Discussion

The first flow apparatus has been used to carry out vapor-liquid equilibrium measurements at high
temperatures on binary mixtures involving alcohol and water as components and model coal
compounds.

3.1 - Vapor-liquid equilibrium with alcohol +water systems

To test the flow apparatus the ethanol+water system was chosen. Therefore, another analysis method
was used based on density measurements carried out at 303.15 K with a picnometer (6) and density
tables (9) obtained from NIST-NBS data (10).

In Fig. 3 vapor pressure data for water are presented, which are compared with the interpolated values from Kennan et al (11). The agreement is within the experimental error.

Vapor liquid equilibrium measurements on the ethanol+water system at the temperatures of 423.15, 473.15 and 523.15 K (6) are shown in the Figs 4 and 5. The system presents an azeotrope at the two lowest temperatures which disappears at the highest.

In these figures our data are compared with those obtained by Barr-David and Dodge (12). Significant differences occur at 423.15 and 473.15 K, near azeotrope, which are shown in more detail in Fig. 6.
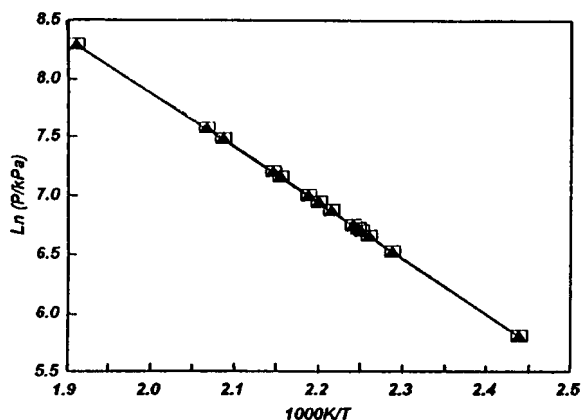
Fig. 3 - Vapor pressure of water as a function of temperature. □ - our work; ▲ - Kennan et al

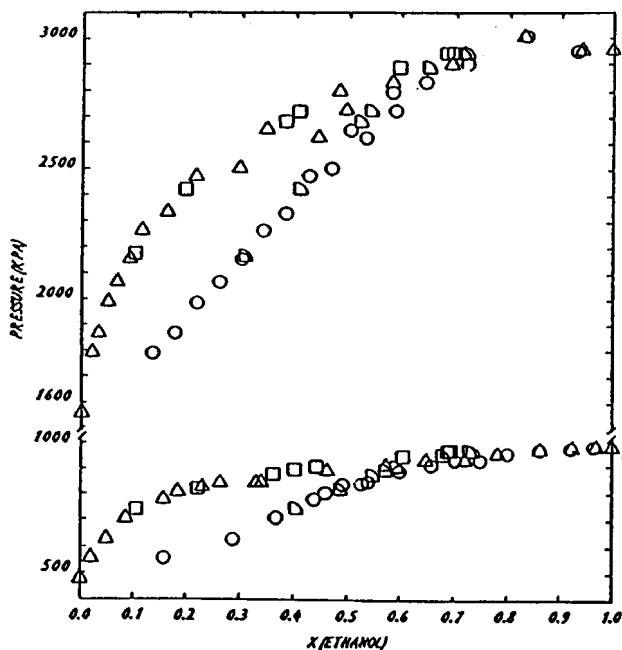Fig. 4 - Ethanol+water VLE data at 423.15 and 473.15 K. □ - Liquid, ◠- vapor - our work; △-Liquid, O-vapor- Barr -David and Dodge. (Reproduced, with permission, from ref. 6)

Fig. 5 - Ethanol+water VLE data at 523.15 K □ - Liquid,◠- vapor - our work; △- Liquid, O - vapor - Barr-David and Dodge. (Reproduced, with permission, from ref. 6)
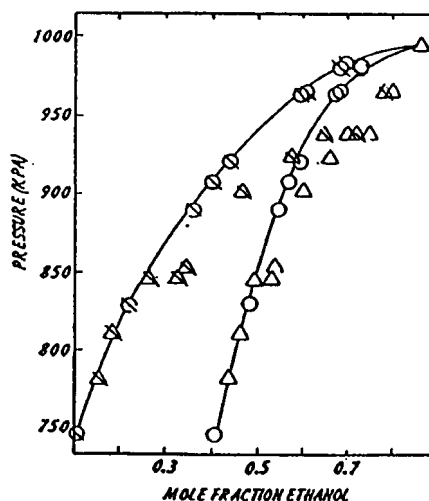
Fig. 6 - Ethanol+water VLE data at 423.15 K (near azeotrope). ◐ - liquid, O- vapor - our work; ◮ - liquid, △ - vapor - Barr David and Dodge; — Kolbe and Gmehling. (Reproduced, with permission, from ref. 6)

Our data are more accurate, because the azeotrope must be a maximum in the P(x) and P(y) curves for the ethanol+water system. On the other hand, there is an excellent agreement between our data and the calculated values at 423.65 K, obtained by fitting of those reported by Kolbe and Gmehling (13) with an empirical equation.

The ethanol-water system was chosen to test the apparatus, because it was believed that the V.L.E. data obtained by Barr-David and Dodge (12) presented high accuracy. Due to discrepancies with our data, the equipment was used to carry out vapor-liquid-equilibrium measurements on the methanol+ethanol system at 373.15 and 413.15 K to compare with data reported by Butcher and Robinson (14) at the same temperatures.

There is a good agreement between the data at the lowest temperature, while at the highest one the vapor pressures obtained by Butcher and Robinson are consistently lower by 3.5 KPa. An analysis of the vapor pressure measurements of the pure components, which are compared with those reported by Ambrose et al (15) and Skaates and Kay (16), allows to conclude that the V.L.E data obtained at Colorado School of Mines are more accurate and can be used in the future to test high temperature vapor-liquid equilibrium apparatus.

Furthermore, recent vapor liquid equilibrium measurements on the ethanol+water system at 423.15 K (8), carried out at the Chemistry Department of the Faculty of Sciences, University of Lisbon, confirm that those obtained by Barr-David and Dodge (12) show some inconsistencies near the azeotrope (Fig. 7).
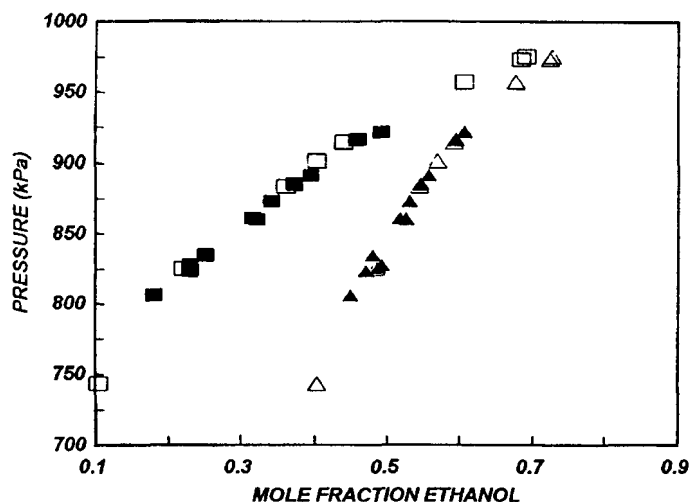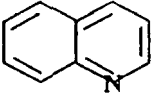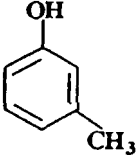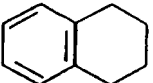

Fig. 7 - Ethanol+water VLE data at 423.15 K (near azeotrope)
□ - Liquid, △ - vapor - our data (School of Mines)
■ - Liquid, ▲ - vapor - our data (Faculty of Sciences)

TABLE 1. Model coal compounds studied at Chemical Engineering Department of Colorado School of Mines.

quinoline

m-cresol

tetralin

3.2 - Vapor-Liquid Equilibrium with Model Coal Compounds

In order to design equipment for the production of coal derived liquids, better thermodynamic correlations than those used for petroleum (17) are required. To achieve this goal, it is necessary to carry out vapor-liquid equilibrium measurements involving binary mixtures of model coal compounds. In Table I three of these compounds are shown.

Since the quinoline is a typical basic compound, the m-cresol is a typical organic acid and the tetralin is a naphthenic compound, experimental studies carried out by Niesen and Yesavage (18,19) on binary mixtures at high temperatures can improve the knowledge on the interactions occuring in coal derived liquids.

Figs. 8 and 9 represent vapor-liquid equilibrium data for the quinoline+m-cresol system, as an example. Due to the intermolecular interactions this system, at very low concentrations of m-cresol, appears to present a high boiling azeotrope at 523.15 K, which disappears at higher temperatures. The presence of an azeotrope was also detected for the same system by Leekhova et al (20) at the temperatures of 461.85 and 511.20 K.
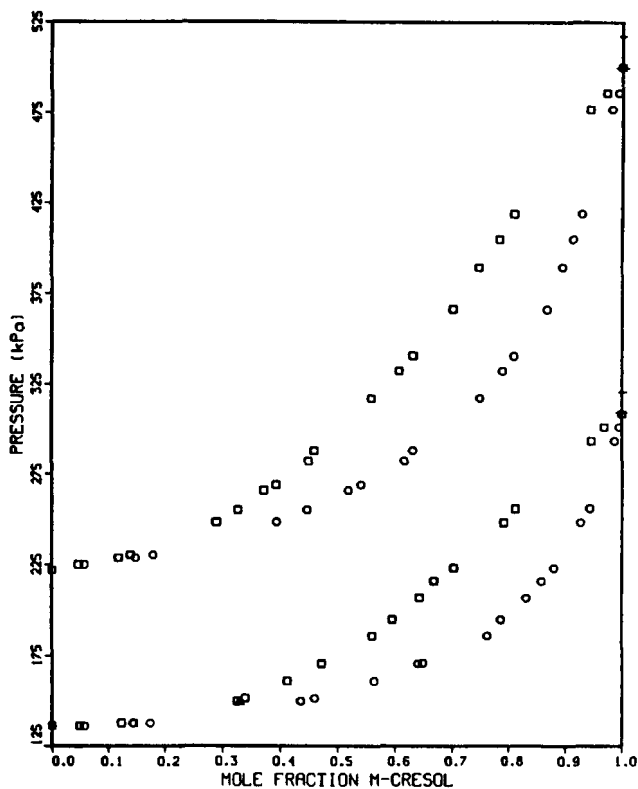
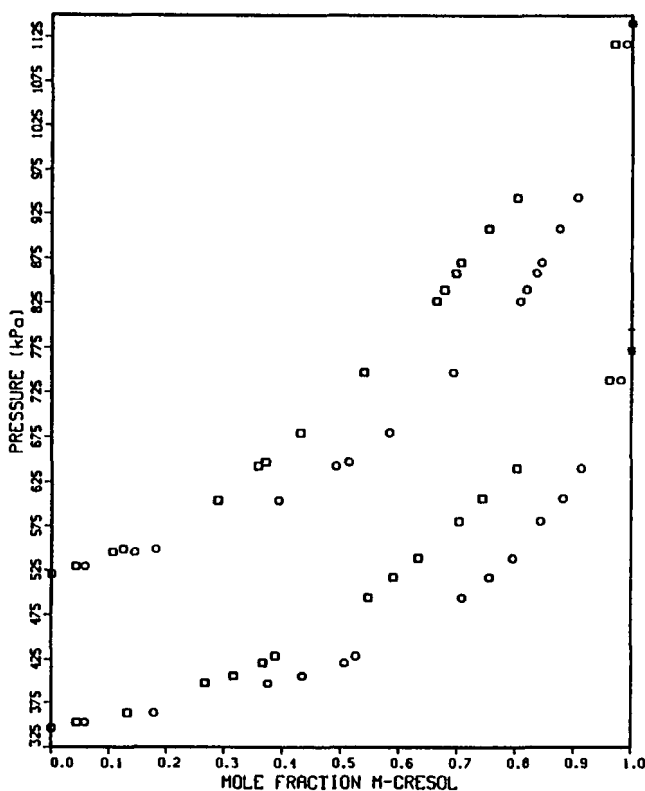Fig. 8 - m-Cresol+quinoline VLE data at 523.15 and 548.15 K □ - liquid, O - vapor (Reproduced, with permission, from ref. 18)

Fig. 9 - m-Cresol+quinoline VLE data at 573.15 and 598.15 K □ - liquid, O - vapor (Reproduced, with permission, from ref. 18)

The azeotrope is due to the hydrogen bonding involving not only the m-cresol molecules, but also those of quinoline and m-cresol . With the increase of temperature, this type of interaction becomes less important and a point is reached for which the azeotrope disappears.

The m-cresol+tetralin system presents a low-boiling azeotrope which also disappears upon increasing of temperature. In contrast, the tetralin+quinoline system only presents small departures from ideal behavior (19).

Previous measurements of vapor-liquid equilibrium of binary mixtures involving quinoline and tetralin with hidrogen, carbon dioxide and methane were carried out by Chao et al (21, 22, 23, 24) using also a flow apparatus. More recently, the same experimental technique was used by Paulaitis et al (25) to study the quinoline+methanol and tetralin+methanol systems and by Thies et al (26) for the tetralin+toluene system. These last vapor-liquid equilibrium studies at high temperature are important for the development of coal conversion processes that use dense fluids as extractive solvents.

Recently, DiGiacinto and Yesavage carried out V.L.E. measurements on the ternary system m-cresol+quinoline+tetralin (27) at high temperature, with the apparatus represented in Fig.1, completing, thus, the experimental study involving these three compounds.

4 - Conclusion

Vapor-liquid equilibrium data at high temperature are not only rare, but frequently don't present high accuracy. For binary mixtures involving m-cresol, quinoline, ethanol and methanol, the accuracy of experimental studies can be affected, because these compounds are hygroscopic (6, 18, 19).

Another problem to take into account is the thermal degradation which is minimized with the use of a flow apparatus. However, the tetralin suffers decomposition even at room temperature. Therefore, special care must be taken to carry out the measurements with this compound (19).

The Chemical Industry needs accurate VLE data of binary mixtures at high temperature. Considering the scarceness of these data, new programs must be implemented in this scientific area. In recent years two projects have been developed in Portugal. The first project is on "Vapor Liquid

Equilibrium Measurements of Binary Mixtures of Terpenes" and has involved the collaboration of Professor C.A. Nieto de Castro from Faculty of Sciences, University of Lisbon. This experimental study aims to develop the Portuguese pine rosin industry which is loosing competitivity during the last 20 years.

The second project is on "Vapor Liquid Equilibrium Measurements on Alcohol+Water Systems" which has been implemented with the collaboration of Professors V. Yesavage and A. Kidnay from Chemical Engineering Department of Colorado School of Mines. This project represents a development of the experimental study on these systems initiated in this University.

Furthermore, the binary systems ethanol+water, m-cresol+quinoline and m-cresol+tetralin present an azeotrope which disappears with the increase of temperature. This behavior suggests that the distillation at high temperature could provide a good strategy to separate the components of a system that presents an azeotrope.

Acknowledgement

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