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Density and vapor-liquid equilibria of binary mixtures containing ethyl acetate and a branched naphthenic compound: experimental data and modeling

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1 - Introduction and objectives

- Ethyl acetate is a common solvent and diluent used in many sectors to produce lacquers, synthetic resins for surface coatings, adhesives and perfumes
- For complex mixtures separation purposes, it is essential to improve the thermodynamic understanding of non-ideal mixtures containing ethyl acetate, paraffins and naphthenes (cycloalkanes)
- Density and VLE of pure components and mixtures are fundamental thermodynamic properties
- A lack of data can be noticed for certain kinds of mixtures: few data are available for binary systems containing ethyl acetate and a branched naphthene (alkyl cycloalkane such as methylcyclopentane)
- The aim of this work is to report new experimental densities and isobaric VLE data (at $P = 25, 50$ and 101.3 kPa) for the following binary systems : methylcyclopentane (mC5) + ethyl acetate (EA) methylcyclohexane (mC6) + ethyl acetate (EA)

2 - Experimental section

- EA (CAS 141-78-6) and mC5 (CAS 96-37-7) were supplied by *Sigma Aldrich* with a mass fraction purity of 0.999 and 0.993, respectively
- mC6 (CAS 108-87-2) was supplied by *Alfa Aesar* with a mass fraction purity of 0.992

Density measurement apparatus and method

Densities were measured at atmospheric pressure ($P = 101 \pm 2$ kPa) using a vibrating tube density meter (DMA 4500 M, Anton Paar), regularly calibrated using pure and degassed water and dry air, with a standard uncertainty $u(\rho) = 0.00005$ g·cm⁻³. Densities were measured from 288.15 K to 308.15 K with a step of 5 K

Binary mixtures were prepared using a precision balance in glass vials with appropriate volumes to minimize the gaseous space between the liquid and the stopper. The standard uncertainty of the mixture's composition was $u(x_1) = 0.0001$

Density measurements were then used to calculate the excess molar volumes of the studied binary liquid mixtures at each temperature

VLE measurement equipment

Isobaric VLE measurements were performed using a recirculation ebulliometer (Labodest VLE 602, Iludest) equipped with a Cottrell pump, allowing measurements from 5 kPa to 400 kPa ($u(P) = 0.1$ kPa). The equilibrium temperature was measured by a Pt-100 platinum probe with a standard uncertainty $u(T) = 0.05$ K. The vapor pressures of the pure components were measured beforehand, from 20 to 200 kPa, to check the accuracy of the apparatus

For the VLE measurements of the mixtures, the compositions of the liquid and condensed vapor phases collected from the ebulliometer were obtained indirectly from density measurements at 298.15 K using a polynomial fit of the previously measured density–composition data. A standard uncertainty $u(x_1) = u(y_1) = 0.001$ was estimated

3 - Experimental results and modeling

a - Density and excess molar volumes

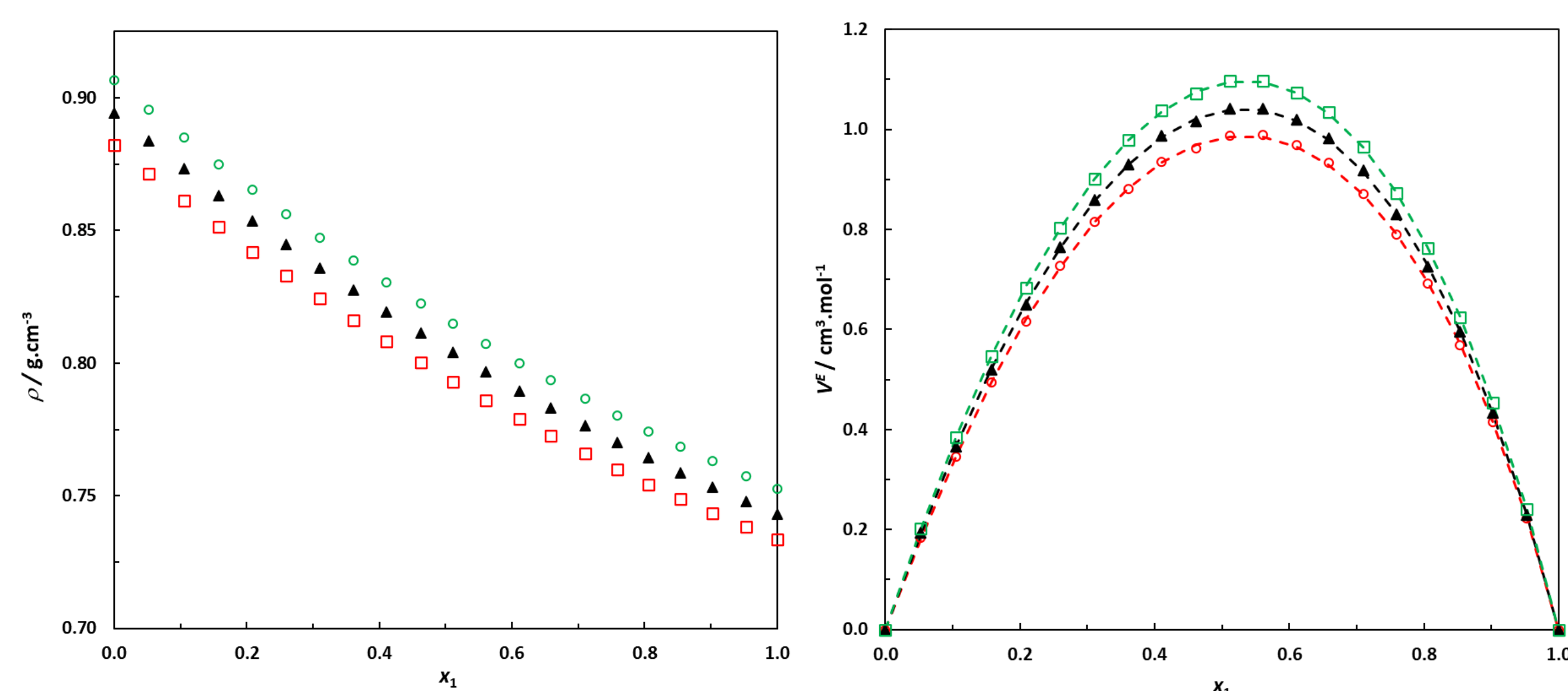


Figure 1. Densities (ρ) and excess molar volumes (V^E) for the binary system methylcyclopentane (1) + ethyl acetate (2) at 101 kPa measured in this work at 288.15 K, 298.15 K and 308.15 K. Dotted lines: correlation curves using a Redlich–Kister expression

- Densities and excess molar volumes of the system mC5 (1) + EA (2) under atmospheric pressure are reported for the first time in this work
- The binary system mC5 + EA presents pronounced positive excess molar volumes (see *Figure 1*) with a maximum value of V^E near a mC5 molar fraction of 0.55, indicating a volume expansion induced by the mixing process
- Similar results were obtained for the binary system mC6 + EA, for which excess molar volumes were published in the past at 298.15 K and 303.15 K. Results obtained in this work are consistent with previously published data
- Excess molar volumes at constant temperature were correlated against molar composition with a Redlich–Kister-type function

3 - Experimental results and modeling

b - VLE data and consistency checks

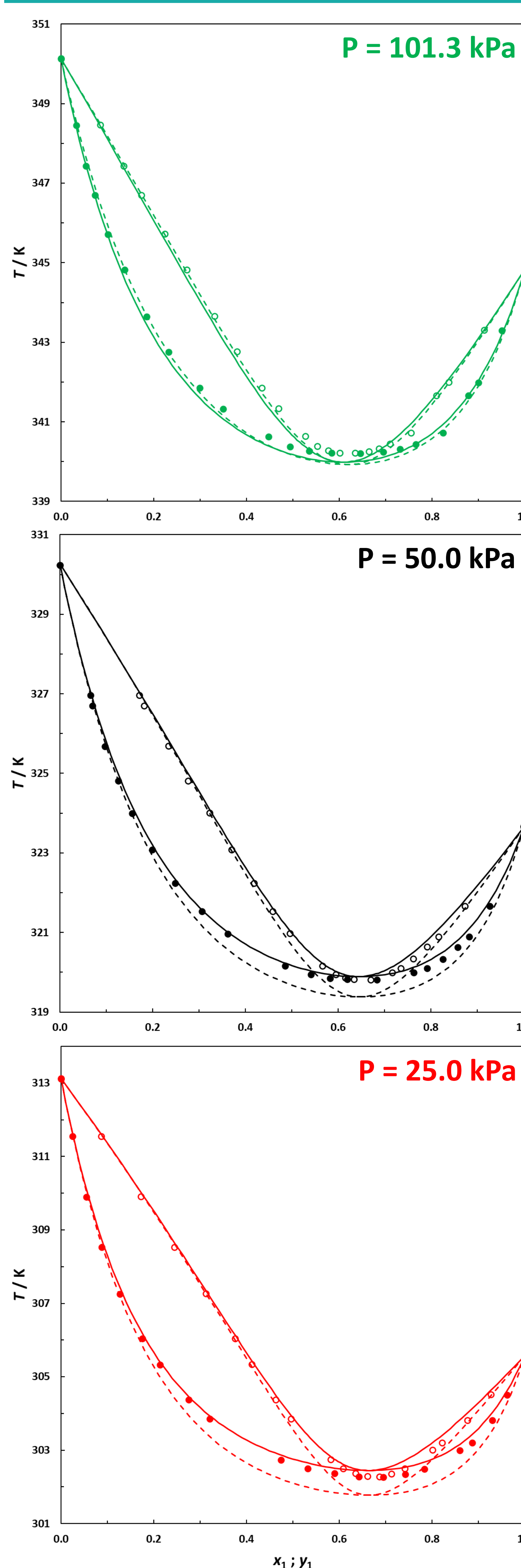


Figure 2. Isobaric phase diagrams for the binary system mC5 (1) + EA (2). Filled symbols: experimental bubble points, empty symbols: dew points. Solid lines: calculated bubble and dew curves using the NRTL model. Dashed lines: curves predicted using UNIFAC (Do)

- VLE data are available in the literature for the binary system mC6 + EA
- The phase equilibrium of the binary mixture mC5 (1) + EA (2) was measured for the first time in this work
- Isobaric VLE data were measured at 25, 50 and 101.3 kPa. Experimental data are depicted in *Figure 2* with calculated bubble and dew curves
- At the studied pressures, the mixture mC5 + EA exhibits positive deviations from ideality (see *Figure 3*) and a minimum boiling azeotrope. The experimental azeotropic composition $x_{1,az}$ slightly decreases with pressure: $x_{1,az}$ (25 kPa) = 0.68 ; $x_{1,az}$ (101.3 kPa) = 0.62
- The experimental data were checked for consistency by means of the Fredenslund test and the Wisniak (L-W) test
- The experimental VLE data were correlated using the NRTL model. The predictive UNIFAC (Do) model was also employed for comparison

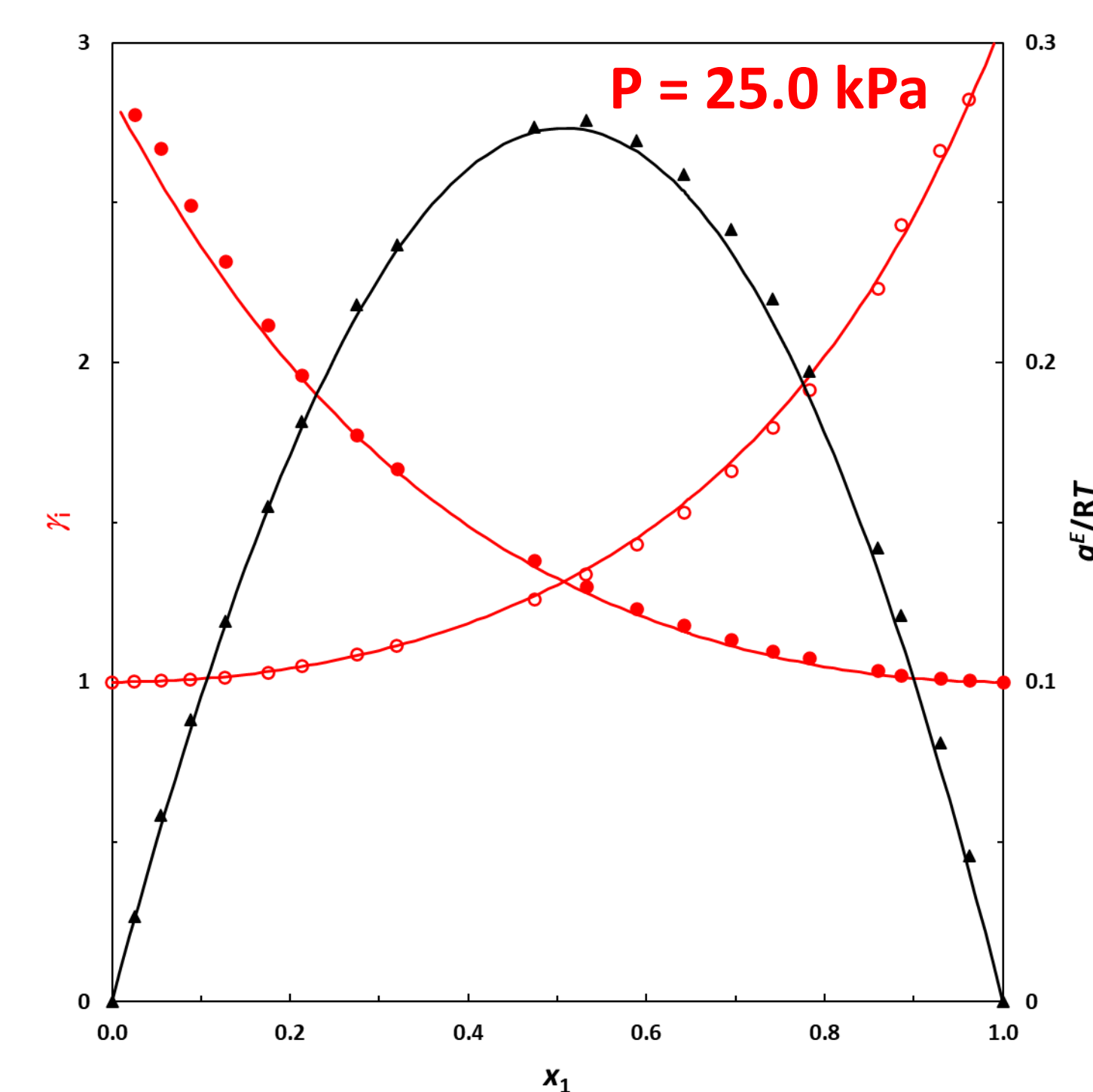


Figure 3. Experimental activity coefficients (γ_i) and excess Gibbs energy as a function of the mC5 mole fraction for the binary mC5 (1) + EA (2) at 25 kPa. Filled symbols: γ_1 ; empty symbols: γ_2 Solid lines: calculated curves using the NRTL model

4 - Conclusions

- The binary system mC5 (1) + EA (2) was studied for the first time in this work
- Densities and excess molar volumes were obtained for the systems mC5 + EA and mC6 + EA. Both mixtures present positive excess molar volumes
- The isobaric VLE of the mC5 + EA binary system was measured at 25, 50 and 101.3 kPa, revealing the presence of an azeotrope in the mC5-rich region
- The experimental VLE data were successfully correlated using the NRTL model. Furthermore, the predictive model UNIFAC gave a satisfactory prediction of the VLE at 101.3 kPa but a less accurate description at low pressures (25 & 50 kPa)

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