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Vapor–liquid equilibrium data for the dimethyl ether (RE170) + decafluorobutane (R3-1-10) system at temperatures from 313.28 to 392.83 K and pressures up to 4.9 MPa

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ABSTRACT

Isothermal vapour–liquid equilibrium data have been measured for the RE170 + R3-1-10 binary system at nine temperatures between 313.28 and 392.83 K, and pressures between 0.57 and 4.9 MPa. The experimental method used in this work is of the static-analytic type, taking advantage of two pneumatic capillary samplers (ROLSI^{TM}, Armines' patent) developed in the CEP/TEP laboratory. The data were obtained with accuracies within ±0.02 K, ±0.0006 MPa and ±0.009 for molar compositions. The particularity of this system is to present an azeotrope. The isothermal *P*, *x*, *y* data are well represented with the Peng and Robinson equation of state using the Mathias Copeman alpha function and the Wong–Sandler mixing rules involving the NRTL g^E model.

1. Introduction

In the recent year, organic Rankine cycle (ORC) has become a promising technology for the conversion of low or medium temperature heat to electricity. The heat source can be of various origins but one interesting source is the waste stream of industrial processes. The temperature is below 200 °C. Initially, the working fluids used in Rankine cycle engines was steam but is generally apply for higher temperature Rankine Engines. Steam is not very expensive and chemically stable. But concerning low grade energy application [1], steam is not the best choice of working fluid. Moreover, the selection of the working fluids is very important for the use of ROC process. A bad choice leads to a low thermodynamic efficiency and technico-economy [2]. The thermodynamic properties for a good fluid are [1,2]:

- Critical temperature value must be above the highest temperature of the cycle
- Not excessive vapour pressure but it must be above atmospheric pressure at the minimum temperature of the cycle (condensing pressure)
- Triple point value is below the minimum ambient temperature to avoid solidification
- Small specific volume, low viscosity at the liquid phase,
- No ozone depletion potential (ODP) and law global warming potential (GWP)
- Non corrosivity and compatibility with common system materials
- The fluid should be chemical stable (no thermal decomposition)
- Non toxicity, non flammability
- Good lubrification properties
- Low cost and available in large quantity

In this communication we propose to determine the thermodynamic properties (phase equilibria) of the possible candidate which is a mixture of dimethyl ether (RE170) and perfluorobutane (R3-1-10). The critical properties and CAS numbers of the two fluids are presented in Table 1. We can see that the values of their critical temperature can be adequate for ORC. The GWP (100 years) of the R3-1-10 is 7000 [4] or [5]. The GWP of RE170 is equal to 1 [5]. Otherwise, the R3-1-10 is non flammable which is not the case of the RE170.

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Table 1
Critical parameters and acentric factors [3].

Compound	Name	CAS number	Purity	T_C (K)	P_C (MPa)	ω
R3-1-10	Decafluorobutane	355-25-9	98 vol.%	386.33	2.323	0.374
RE170	Dimethylether	115-10-6	99.9 vol.%	400.3	5.3405	0.197

The new enclosed experimental results are fitted using the Peng and Robinson equation of state (PR EoS). This work reveals that the binary system can be classified as type I according to Scott and van Konynenburg classification [6] with a positive deviation to ideality involving an azeotrope. At the knowledge of the authors, it exists not data in the open literature.

2. Experimental

2.1. Materials

RE170 was obtained from Arkema (France) with a certified purity higher than 99.9 vol.%. R3-1-10 was purchased from Pelchem (South Africa) and has a certified purity higher than 98 vol.%. RE170 was carefully degassed before use to remove uncondensed gases.

2.2. Apparatus

The apparatus used in this work is based on a static-analytic method with liquid and vapour phase sampling. This apparatus is similar to that described by Valtz et al. [7–10].

The equilibrium cell is contained in a liquid thermostatic bath. Temperatures are measured with two platinum resistance thermometer probes (Pt100) inserted inside the walls of the equilibrium cell. These Pt100 probes are calibrated against a 25-Ω reference probe (TINSLEY Precision Instrument) calibrated by the Laboratoire National d'Essais (Paris) following the 1990 International Temperature Scale protocol.

Pressures are measured using two pressure transducers (Druck, type PTX611, range: 0–1 MPa and 0–6 MPa). The first one is used for pure component vapour pressure measurements and the second one for vapor liquid equilibria (VLE) measurements. These sensors are calibrated against a dead weight pressure balance (5202S model from Desgranges & Huot) for pressure above 0.3 MPa and digital standard (Desgranges et Huot modèle 24610) for the low pressure (below 0.3 MPa).

Pressure and temperature data acquisitions are performed with a computer linked to an Hewlett–Packard unit (HP34970A) connected to a computer. The resulting accuracies in this work are not higher than ±0.02 K, ±0.0002 MPa (vapour pressure) and ±0.0006 MPa (VLE).

The analytical work was carried out using a gas chromatograph (VARIAN model CP-3800) equipped with a thermal conductivity detector (TCD) connected to a data acquisition unit. The analytical column is 5% Krytox Carboblack B model, 60/80 Mesh (1/8″ silcosteel tube, 2 m length, from Resteck, France). The TCD was repeatedly calibrated by introducing known amounts of each pure compound through a syringe in the injector of the gas chromatograph. Taking into account the uncertainties due to calibrations and dispersions of analyses (five at least for each sample), resulting uncertainties on vapour and liquid mole fractions are estimated to be less than ±0.009.

2.3. Experimental procedure

At room temperature, the equilibrium cell and its loading lines are evacuated down to 0.1 Pa. The cell is first loaded under a vacuum with liquid RE170 (about 5 cm^3). Equilibrium temperature is assumed to be reached when the two Pt100 probes give equivalent temperature values within their temperature uncertainty for at the least 10 min. After recording the vapour pressure of the RE170 (the heavier component) at equilibrium temperature, the two-phase envelopes are described with about eight P, x, y points (liquid and vapour). R3-1-10 (the lighter component) is introduced step by step, leading to successive equilibrium mixtures of increasing overall R3-1-10 content. Equilibrium is assumed when the total pressure remains unchanged within ±1.0 kPa during a period of 10 min under efficient stirring.

For each equilibrium condition, at least five samples of both vapour and liquid phases are withdrawn using the pneumatic samplers ROLSI$^{\text{TM}}$ [11] and analyzed in order to check for the measurement repeatability.

2.4. Correlations

The critical temperatures (T_C), critical pressures (P_C), and acentric factors (ω), for each of the two pure components are provided in Table 1. Our experimental VLE data are correlated by means of homemade software developed by Armines, Mines Paristech. We have used the PR EoS [12] to correlate the data. To have accurate representation of vapour pressures of each component, we use the Mathias-Copeman alpha function [13] given below with three adjustable parameters, which was especially developed for polar compounds.

$$\alpha(T) = \left[1 + c_1\left(1 - \sqrt{\frac{T}{T_C}}\right) + c_2\left(1 - \sqrt{\frac{T}{T_C}}\right)^2 + c_3\left(1 - \sqrt{\frac{T}{T_C}}\right)^3\right]^2 \quad (1)$$

For $T > T_C$, Eq. (1) must be replaced by Eq. (2),

$$\alpha(T) = \left[1 + c_1\left(1 - \sqrt{\frac{T}{T_C}}\right)\right]^2 \quad (2)$$

c_1, c_2 and c_3 are adjustable parameters.

To have good representation of VLE, we chose the Wong–Sandler [14] mixing rules.

$$b = \frac{\sum_i \sum_j x_i x_j (b - (a/RT))_{ij}}{1 - \left(\sum_i x_i (a_i/b_i)/RT + g^E(T, P = \infty, x_i)/CRT\right)} \quad (3)$$

$$b - \frac{a}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij} \quad (4)$$

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{1}{2}\left[\left(b - \frac{a}{RT}\right)_i + \left(b - \frac{a}{RT}\right)_j\right](1 - k_{ij}) \quad (5)$$

k_{ij} is a binary interaction parameter. C is a numerical constant which depends on the EoS.

The excess Gibbs energy function is based on the NRTL [15] local composition model.

$$\frac{g^E(T, P, x_i)}{RT} = \sum_i x_i \sum_j \frac{x_j \exp(-\alpha_{ji}(\tau_{ji}/RT))}{\sum_k x_k \exp(-\alpha_{ki}(\tau_{ki}/RT))}\tau_{ji} \quad (6)$$

$\tau_{ii} = 0$ and $\alpha_{ij} = 0$.