

# Vapor–liquid equilibrium data for the difluoromethane (R32)–dimethyl ether (RE170) system at temperatures from 283.03 to 363.21 K and pressures up to 5.5 MPa

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## Abstract

Isothermal vapour–liquid equilibrium data have been measured for the R32 + RE170 binary system at seven temperatures between 283.03 and 363.21 K, and pressures between 0.5 and 5.5 MPa. The experimental method used in this work is of the static-analytic type, taking advantage of two pneumatic capillary samplers (Rolsi™, Armines' patent) developed in the CEP/TEP laboratory. The data were obtained with uncertainties within  $\pm 0.02$  K,  $\pm 0.0002$  MPa and  $\pm 1\%$  for molar compositions.

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.

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## 1. Introduction

Industry needs new fluids to replace ozone-destroying refrigerants like chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). Their use, production and distribution are ruled by the modification of the 1987 Montreal Protocol. CFCs are prohibited since 1996 for countries-members and the deadline for HCFCs which have lower ozone depletion potential is 2030.

A new system is studied in this paper. It contains R32 and RE170 that was proposed in the past by Charles Tellier (1828–1913). RE170 has been extensively used in industrial refrigeration, as much as ammonia, it has zero ozone depletion potential and can be associated to HFCs. R134a–RE170 system was previously investigated in our laboratory [1]. R32 being an alternative refrigerant used in air conditioning and refrigeration, it was interesting to study it with RE170 in order to verify if this new system

could be an advantageous new candidate for refrigeration industry. This system belongs to the type II of the Scott and van Konynenburg classification [2].

Accurate knowledge of thermophysical properties of alternative refrigerants, like HFCs containing mixtures, is necessary to evaluate the performance of refrigeration cycles. As an answer to this request, the TEP laboratory has already published many experimental data concerning refrigerant mixtures, the most recent can be found in [1,3–8].

The new enclosed experimental results are fitted using the Peng and Robinson equation of state (PR EoS). Our data are compared to those of Fedele et al. [9] that were measured at three temperatures: 258.15, 273.15 and 293.15 K.

## 2. Experimental

### 2.1. Materials

RE170 was obtained from Atofina (France) with a certified purity higher than 99.9 vol.%. R32 was purchased

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from Dehon (France) and has a certified purity higher than 99.95 vol.%. RE170 was carefully degassed before use to remove incondensable 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 Laugier and Richon [10] and Valtz et al. [1].

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- $\Omega$  reference probe (TINSLEY Precision Instrument) calibrated by the Laboratoire National d'Essais (Paris) following the 1990 International Temperature Scale protocol.

Pressures are measured using a pressure transducer (Druck, type PTX611, range: 0–4 MPa). This sensor is calibrated against a dead weight pressure balance (5202S model from Desgranges & Huot).

Pressure and temperature data acquisitions are performed with a computer linked to a Hewlett-Packard unit (HP34970A). The resulting uncertainties in this work are not higher than  $\pm 0.02$  K and  $\pm 0.0002$  MPa.

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 system using the BORWIN ver 1.5 software, from JMBS, France. The analytical column is PORAPAK N model, 80/100 mesh (1/8 ft 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  $\pm 1\%$ .

## 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<sup>3</sup>). 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). R32 (the lighter component) is introduced step by step, leading to successive equilibrium mixtures of increasing overall R32 content. Equilibrium is assumed when the total pressure remains unchanged within  $\pm 1.0$  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<sup>TM</sup> [11] and analyzed in order to check for the measurement repeatability.

## 3. Correlations

The critical temperatures ( $T_C$ ), critical pressures ( $P_C$ ), and acentric factors ( $\omega$ ), for each of the two pure components are provided in Table 1. Our experimental VLE data are correlated by means of homemade software TepThermosoft [12], developed by Armines, Ecole des Mines de Paris. We have used the PR EoS [13] to correlate the data.

To have accurate representation of vapour pressures of each component, we use the Mathias–Copeman alpha function [14] 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 [15] mixing rules.

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

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

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

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

Table 1  
Critical parameters and acentric factors [17]

Compound	$T_c$ (K)	$P_c$ (MPa)	$\omega$
R32	351.6	5.83	0.27100
RE170	400.1	5.37	0.20022

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