Experimental vapour–liquid equilibrium data and modeling for binary mixtures of 1-butene with 1,1,2,3,3,3-hexafluoro-1-propene, 2,2,3-trifluoro-3-(trifluoromethyl)oxirane, or difluoromethane

Shalendra Clinton Subramoney [a], Alain Valtz [b], Christophe Coquelet [a,b], Dominique Richon [a], Paramespri Naidoo [a], Deresh Ramjugernath [a,*]

[a] Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, Durban, South Africa
[b] MINES ParisTech, CTP–Centre Thermodynamique des Procedes, 35 Rue Saint Honoré, 77305 Fontainebleau Cedex, France

ABSTRACT

Novel isothermal (P–x–y) vapour–liquid equilibrium data are reported at three temperatures for each of the (1,1,2,3,3,3-hexafluoro-1-propene + 1-butene), (2,2,3-trifluoro-3-(trifluoromethyl)oxirane + 1-butene), and (difluoromethane + 1-butene) binary systems. The experimental values were measured on a "static–analytic" type apparatus which utilized two electromagnetic ROLSI™ capillary samplers for repeatable and reliable equilibrium phase sampling and handling. The VLE results are correlated with in-house thermodynamic software based on the "PR–MC–WS–NRTL" model which comprises the Mathias–Copeman alpha function, Wong–Sandler mixing rule, and non-random two-liquid local composition activity model introduced in the Peng–Robinson equation of state. A maximum pressure azeotrope is observed at all temperatures studied for the (2,2,3-trifluoro-3-(trifluoromethyl)oxirane + 1-butene), and (difluoromethane + 1-butene systems), but not for the 1,1,2,3,3,3-hexafluoro-1-propene system. Liquid–liquid immiscibility is not observed for any of the systems studied over the range of temperatures investigated.

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1. Introduction

This study is part of a continuing research programme on the thermodynamic properties of fluorocarbons and their mixtures. The objective of this programme is the development of an experimental property database for the investigation of novel fluorocarbon technologies. We have previously reported pure component saturated vapour pressures and densities for a perfluoroolefin and a perfluoroepoxide [1,2], and vapour–liquid equilibria for binary mixtures involving perfluoroalkanes or perfluoroolefins [3–6]. In the present work, vapour–liquid equilibrium values are reported for binary mixtures of an olefin with three fluorocarbons, *viz.* a perfluoroolefin, a perfluoroepoxide, and a hydrofluorocarbon.

The olefin 1-butene is commonly sourced as a by-product of refinery cracking processes and used in the production of gasoline and higher value chemicals such as butanol, butadiene, and maleic anhydride [7]. The perfluoroolefin 1,1,2,3,3,3-hexafluoro-1-propene or hexafluoropropylene (R-1216) is used in the manufacture of high value fluoroethers and as a precursor for the preparation

of 2,2,3-trifluoro-3-(trifluoromethyl)oxirane [8,9]. In the context of refrigerants, binary mixtures of R-1216 with chlorodifluoromethane (R22) or low molar mass hydrocarbons are known to form effective blends comparable to dichlorodifluoromethane (R12) and 1,1,1,2-tetrafluoroethane (R134a) [10,11]. 2,2,3-Trifluoro-3-(trifluoromethyl)oxirane or hexafluoropropylene oxide (HFPO) is considered a key intermediate in organofluorine chemistry that provides readily accessible synthetic routes to higher value fluoropolymers, lubricants, and fluoro-intermediates [9]. The hydrofluorocarbon difluoromethane (R-32) is a non-ozone depleting refrigerant commonly used in low temperature refrigeration, air conditioning, and heat pump applications [12]. However, the high global warming potential of hydrofluorocarbons has led to the phase out and investigation of alternative refrigerants, in some instances blends of fluorocarbons with hydrocarbons and other natural refrigerants [13–15].

To the best of our knowledge, vapour–liquid equilibrium (VLE) results for binary mixtures of 1-butene with R-1216, HFPO, or R-32 have not been previously reported in the open literature. In general, bibliographic studies reveal a scarcity of published VLE data involving olefins and the fluorochemicals considered in this work. As a result, group contribution methods, for example the

* Corresponding author. Tel.: +27 31 2603128; fax: +27 31 2601118.
  E-mail address: ramjuger@ukzn.ac.za (D. Ramjugernath).

Nomenclature

AAD	average absolute deviation (%)
c_i	Mathias–Copeman coefficients
k_{ij}	mixing rule binary interaction parameter
k	coverage factor for statement of expanded uncertainty
n_i	mole number
N	number of experimental points
P	pressure (MPa)
ROLSI[TM]	Rapid-On-Line-Sampler-Injector
T	temperature (K)
U	generic property
$\bar{U}$	expanded uncertainty
V	volume (cm^3, μL, mL)
x	liquid mole fraction
y	vapor mole fraction

Greek letter

α	NRTL non-randomness parameter
α_{ij}	relative volatility
ω	acentric factor
Φ	fugacity coefficient
τ_{ij}	NRTL binary interaction parameter

Subscripts

c	critical property
cal	calculated property
exp	experimental property

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semi-empirical Predictive Soave–Redlich–Kwong equation of state (PSRK) [16], are unable to describe the phase equilibrium behaviour of such mixtures. The experimental VLE data reported in this work, combined with previously reported data for mixtures of R-1216 or R-32 with olefins [6,17], are of great interest for the fitting of interaction parameters for fluorocarbon/alkene main groups for the PSRK group contribution method. Moreover, the reported data are useful for fitting the interaction parameters for correlative thermodynamic models, for example the cubic Peng–Robinson equation of state [18], that are extensively used for process design purposes [19].

The experimental measurements have been conducted on a VLE apparatus based on the "static–analytic" method which utilizes two electromagnetic ROLSI[TM] capillary samplers [20] for repeatable and reliable equilibrium phase sampling and handling. The experimental data are correlated using the "PR–MC–WS–NRTL" model constituted by the Mathias–Copeman alpha function [21], Wong–Sandler mixing rule [22], and non-random two-liquid local composition model [23] introduced in the Peng–Robinson equation of state [18].

2. Experimental

2.1. Materials

Table 1 contains the list of chemicals used in this study, along with the details of the suppliers and the supplier stated purities and CAS numbers. The purity of the chemicals was checked using gas chromatography during the various runs in the development of the gas chromatographic method for the equilibrium phase composition analysis. No impurities were found in concentrations higher than those stated by the suppliers. Consequently, the chemicals were used without further purification.

TABLE 1
Suppliers, stated purities, and CAS numbers of chemicals used in this study.

Component	Supplier	Purity[a,b]	CAS Number
1-Butene	Alrich	>0.99	106-98-9
1,1,2,3,3,3-Hexafluoro-1-propene	Pelchem	>0.999	116-15-4
2,2,3-Trifluoro-3-(trifluoromethyl)oxirane	Pelchem	>0.995	428-59-1
Difluoromethane	DEHON	>0.9995	75-10-5

[a] Supplier stated purity in volume fraction.
[b] Supplier stated purity checked using gas chromatograpy.

2.2. Apparatus

The VLE still used in this work is similar in concept to that of Laugier and Richon [24] and identical to that of Valtz *et al.* [25]. The apparatus has been well described in previous works [3,25], and only a brief description is given here. VLE conditions are produced inside a thermo-regulated equilibrium cell (V = 34 cm^3). The equilibrium cell consists of a sapphire tube held between two stainless steel flanges. Each flange contains valves and fittings for loading, discharging, degassing, and evacuation operations, and provisions for temperature and pressure measurement. The equilibrium chamber contains an efficient stirring rod assembly, driven by an external magnet attached to a stirring device. The cell is placed in a thermo-regulated liquid bath and maintained at a desired operating temperature. Two 100 Ω platinum resistance thermometer probes (Actifa, France) are inserted into wells on the top and bottom stainless steel flanges. The apparatus is equipped with two pressure transducers (Druck, U.S.A., PTX611): a high pressure transducer (0 to 6 MPa) that is always connected, and a low pressure transducer (0 to 0.6 MPa) that can be bypassed by an isolation valve. Only the high pressure transducer is used in the present work. The pressure transducers are maintained at a constant temperature above the temperature of the measurements through a PID regulator (WEST, U.S.A., Model 6100) connected to a heating resistance. The signals from the temperature and pressure sensors are transmitted to a data acquisition unit (Agilent, U.S.A., HP34970A) connected to a personal computer system for real time data logging. Two Monel capillary tubes extend into the equilibrium cell from the top stainless steel flange, and are positioned to allow independent sampling of the vapour and liquid phases. The capillaries are connected to two electromagnetic ROLSI[TM] samplers supplied by ARMINES-Transvalor. A helium carrier gas line is connected to each ROLSI[TM] sampler for carrying the equilibrium samples to a gas chromatograph (Perichrom, France, PR-2100) for analyses. The GC unit is equipped with a thermal conductivity detector (TCD) and fitted with a packed column (Restek, France). All transfer lines are insulated and heated to ensure that the analysed samples are representative of the equilibrium cell contents. The electromagnetic ROLSI[TM] samplers are actuated using a dedicated control box that allows monitoring of the ROLSI[TM] sampler opening time with a 0.01 s resolution. For a given equilibrium cell pressure, the mass of sample withdrawn by the ROLSI[TM] samplers can be adjusted through specifying the opening time. GC peak area analyses and integrations are performed with the data acquisition software WINILAB III (Perichrom, France, Ver. 4.6).