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Thermodynamic properties of 1,1,1,2-tetrafluoroethane (R-134a) + 2,3,3,3-tetrafluoropropene (R-1234yf) mixtures: Measurements of the critical parameters and a mixture model based on the multi-fluid approximation

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ABSTRACT

Thermodynamic properties are discussed for 1,1,1,2-tetrafluoroethane (R-134a) + 2,3,3,3-tetrafluoropropene (R-1234yf) mixtures. The critical temperatures, densities, and pressures experimentally determined are first presented with their uncertainties. Subsequently a mixture model for calculations of thermodynamic properties is formulated using the multi-fluid approximation. Comparisons to experimental data show that the mixture model calculates the vapor–liquid equilibrium and densities of the mixtures with reasonable accuracies. The critical parameters are also well represented by the mixture model.

Propriétés thermodynamiques des mélanges de 1,1,1,2-tetrafluoroethane (R-134a) + 2,3,3,3-tetrafluoropropene (R-1234yf) : Mesures des paramètres critiques et un modèle de mélange basé sur l'approximation multi-fluide

Mots clés : Densité critique ; Pression critique ; Température critique ; Modèle de mélange ; Mélange de R-134 + R-1234yf

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Nomenclature

a	molar Helmholtz energy (J mol^{-1})
c_p	isobaric heat capacity (J mol^{-1} K^{-1})
F_{12}	adjustable parameter for the departure function (–)
N	number of data points (–)
M	molar mass (g mol^{-1})
p	pressure (Pa)
p_b	bubble-point pressure (Pa)
p_c	critical pressure of pure fluids (Pa)
p_{cm}	critical pressure of mixtures (Pa)
p_d	dew-point pressure (Pa)
R	universal gas constant (8.3144621 J mol^{-1} K^{-1})
S	objective function (–)
T	temperature (K)
T_c	critical temperature of pure fluids (K)
T_{cm}	critical temperature of mixtures (K)
T_{red}	reducing temperature (K)
v	molar volume (m^3 mol^{-1})
v_c	critical molar volume of pure fluids (m^3 mol^{-1})
v_{cm}	critical molar volume of mixtures (m^3 mol^{-1})
v_{red}	reducing volume (m^3 mol^{-1})
W	weighting factor (–)
x	mole fraction of R-134a

Superscripts

○	ideal gas part
E	contribution from mixing
idmix	ideal mixture contribution
r	residual part/departure function

Subscripts

1	R-134a
2	R-1234yf
12	crossover term
c	critical point
cal	calculated value
exp	experimental value
i	component i
L	liquid
red	reducing function
V	vapor

Greek symbols

α	dimensionless Helmholtz energy (–)
α^r_{12}	departure function (–)
β_T	adjustable parameter for the reducing temperature
β_v	adjustable parameter for the reducing volume
γ_T	adjustable parameter for the reducing temperature
γ_v	adjustable parameter for the reducing volume
Δ_T	adjustable parameter for the mixture critical temperature
Δ_p	adjustable parameter for the mixture critical pressure
Δ_v	adjustable parameter for the mixture critical volume
ΔX	relative deviation for property X
δ	reduced volume (–)
θ	surface fraction (–)
ρ	density (kg m^{-3})
τ	inverse reduced temperature (–)

1. Introduction

2,3,3,3-Tetrafluoropropene (CF_3 $CF{=}CH_2$, R-1234yf) is a potential next generation refrigerant due to its very low global warming potential (GWP) and preferable vapor pressures. Mobile air conditioners and beverage coolers designed for this novel refrigerant are now available. However, more R & D effort is required for the use of R-1234yf in large-scale air conditioners. The most significant problem is that R-1234yf is mildly flammable (classified as A2L); therefore, comprehensive risk assessments are needed for centrifugal chillers or other stationary applications. Lewandowski (2012) demonstrated a fault tree analysis (FTA) to estimate the overall risk of R-1234yf for residential heat pumps. Another concern is that pure R-1234yf is generally less advantageous in performance over conventional hydrofluorocarbon (HFC) refrigerants. Minor et al. (2010) showed that the volumetric cooling capacity of R-1234yf is slightly smaller as compared to 1,1,1,2-tetrafluoroethane (R-134a), although the vapor pressures of both refrigerants are very similar. Piao et al. (2012) performed drop-in tests in a residential and small commercial unitary system, and found that the performance of pure R-1234yf is considerably less than those of difluoromethane (R-32) and R-410A.

Mixing of R-1234yf with R-134a is one solution to reduce the risk and shortcomings of pure R-1234yf. ASHRAE approved a 44/56 wt% blend of the R-134a/1234yf mixture as R-513A. As shown later, the mixture shows azeotropic behavior with very narrow gaps between the bubble- and dew-point curves. This indicates strong nonideality in the mixture, and therefore ordinary cubic equations of state and the van der Waals mixing rules are not adequate for reasonable modeling. A mixture model specially formulated for this mixture is needed for accurate property calculations.

This work first measured the critical parameters of R-134a/1234yf mixtures. The critical parameters are some of the most important fundamental properties, and a prerequisite for reliable property formulations. Subsequently this work developed a mixture model using the multi-fluid approximation. The mixture model calculates the vapor–liquid equilibrium (VLE), densities, and critical parameters with sufficient accuracies for most technical applications.

2. Critical points of R-134a/1234yf mixtures

2.1. *Saturated vapor and liquid densities near the critical point*

Fig. 1 shows an experimental apparatus to measure the saturated vapor and liquid densities near the critical point. Over the last two decades, this apparatus has been employed