Contents lists available at ScienceDirect

J. Chem. Thermodynamics

Experimental determination of the critical loci for R-23 + (n-propane or n-hexane) and R-116 + n-propane binary mixtures

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A R T I C L E   I N F O

A B S T R A C T

Isothermal VLE for the (R-23 + n-propane) system was measured using a static-analytic apparatus at temperatures between $T = (293.18$ and $353.15)$ K. The critical loci for the systems {R-23 + (n-propane or n-hexane)} and (R-116 + n-propane) were measured using a critical point determination apparatus. The method of Ungerer et al. was used to extrapolate the isothermal VLE data to the isothermal critical locus. These extrapolated critical loci were compared with experimental data. The Redlich-Kister type correlations were used to correlate the critical loci of the systems. A critical locus curve for the (R-23 + n-hexane) system which was calculated by the method of Heidemann and Khalil was compared with the experimental critical loci. The systems were classified according to the van Konynenburg and Scott classification system.

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1. Introduction

Supercritical fluids exhibit a number of physical properties that give them an advantage over conventional liquid solvents [1]. Most importantly, supercritical fluids have densities that are of a similar magnitude to conventional solvents. However, these densities can be varied substantially by altering the pressure and temperature of the fluid [2]. Carbon dioxide (CO_2) is by far the most commonly used supercritical solvent [1].

CO_2 is essentially a non-polar solvent, with a dipole moment of zero Debye [3]. This inhibits the ability of CO_2 to dissolve polar components to any useful extent [2]. In addition to this, CO_2 does not exhibit very large capacities for solutes, translating into larger volumes of solvent being required to perform a separation. In order to overcome these problems, an alternative solvent or mixture of solvents must be used. The more commonly applied method is the addition of co-solvents to the CO_2, in order to improve its ability to dissolve polar components [3]. Alternatively, the solvent can be replaced with a more polar solvent. This study continues a previous investigation into the use of trifluoromethane (R-23) and hexafluoroethane (R-116) as supercritical solvents [4].

In this study, the critical loci of three systems, R-23 + (n-propane or n-hexane) and R-116 + n-propane were measured using a critical point determination apparatus, and were compared to values either extrapolated using the method described by Ungerer et al. [5], or calculated using the method of Heidemann and Khalil [6]. Ju et al. [7] measured several isotherms of the (R-23 + n-propane) system at temperatures of between $T = (283.15$ and $313.15)$ K. To supplement this data, several additional VLE isotherms were measured for the (R-23 + n-propane) system using a static-analytic apparatus, and are reported in this work. Both the VLE measurements and the critical loci measurements were performed at the Centre for Thermodynamics of Processes (CTP).

VLE results for the (R-116 + n-propane) system were obtained from the work of Ramjugernath et al. [8]. For the (R-23 + n-hexane) system, the data of Williams-Wynn et al. [4] were used, and for the (R-116 + n-hexane), the data that were reported by Ramjugernath et al. [9] were extrapolated to the critical point.

2. Experimental

2.1. Materials

The suppliers, CAS numbers and stated purities of the chemicals that were used in this study are listed in Table 1. The critical properties of the components are provided in Table 2

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Table 1
Chemical suppliers, CAS numbers and stated purities.

	Supplier	CAS Number	Stated purity
Trifluoromethane, R23, CHF$_3$	Climalife	75-46-7	0.995[b]
Hexafluoroethane, R116, C$_2$F$_6$[a]	Air Liquide	76-16-4	0.99999[b]
n-Propane, C$_3$H$_8$[a]	Messer	74-98-6	0.99995[b]
n-Hexane, C$_6$H$_{14}$	Sigma-Aldrich	110-54-3	0.99 [c]

[a] Further purification of components was not undertaken.
[b] Volumetric (molar) basis.
[c] Mass basis.

Table 2
Critical properties from literature data.

	T_c/K	P_c/MPa	Ω
Trifluoromethane, R23, CHF$_3$[a]	299.07[a]	4.836[a]	0.264[c]
Hexafluoroethane, R116, C$_2$F$_6$	293.04[b]	3.042[b]	0.229[b]
n-Propane, C$_3$H$_8$	369.95[b]	4.246[b]	0.152[b]
n-Hexane, C$_6$H$_{14}$	507.40[b]	3.014[b]	0.301[c]

[a] Ref. [25].
[b] Ref. [26].
[c] Ref. [27].

2.2. Experimental apparatus

Two different apparatus were used in this work. A static-analytic apparatus was used to measure the isothermal VLE for the system (R-23 + n-propane), and a critical point determination apparatus was used to measure the critical loci of the three systems.

2.3. Static-analytic apparatus

The static-analytic apparatus used in this study uses a capillary sampler (ROLSI™) [10] to sample the liquid and vapour phases. The equipment is similar to that depicted in Fig. 1, which was used by Juntarachat et al. [11].

The equilibrium cell is submerged into a thermo-regulated liquid bath which is maintained at a constant temperature. The deviations of the temperature within the bath are less than 0.01 K. The temperature of the fluid inside the equilibrium cell is monitored by two platinum resistance thermometer probes (Pt100) connected to a data acquisition unit (HP34970A) [12]. The use of two probes enables any gradients within the cell to be quantified, and the average of the two measurements is used as the measured temperature.

The Pt100 probes were calibrated against a 25 Ω reference platinum resistance thermometer (Hart Scientific). This Pt25 reference probe was calibrated by the "Laboratoire National d'Essais de Paris" based on the 1990 International Temperature Scale (ITS 90). The maximum error given by the calibration of the reference probes is estimated to be within 0.05 K.

The pressure is measured using one of two pressure transducers (DRUCK, 0–3 MPa, 0–30 MPa) installed on the apparatus. The choice of pressure transducer is dependent upon the maximum pressures generated by the system being characterised. The two pressure transducers are also connected to the data acquisition unit (HP34970A). The pressure transducers were calibrated against an automated pressure calibrator (GE Sensing, model PACE 5000). The pressure uncertainties from the transducers are estimated to be within 0.2 kPa for the "0–3 MPa" pressure transducer and 0.6 kPa for the "0–30 MPa" pressure transducer.
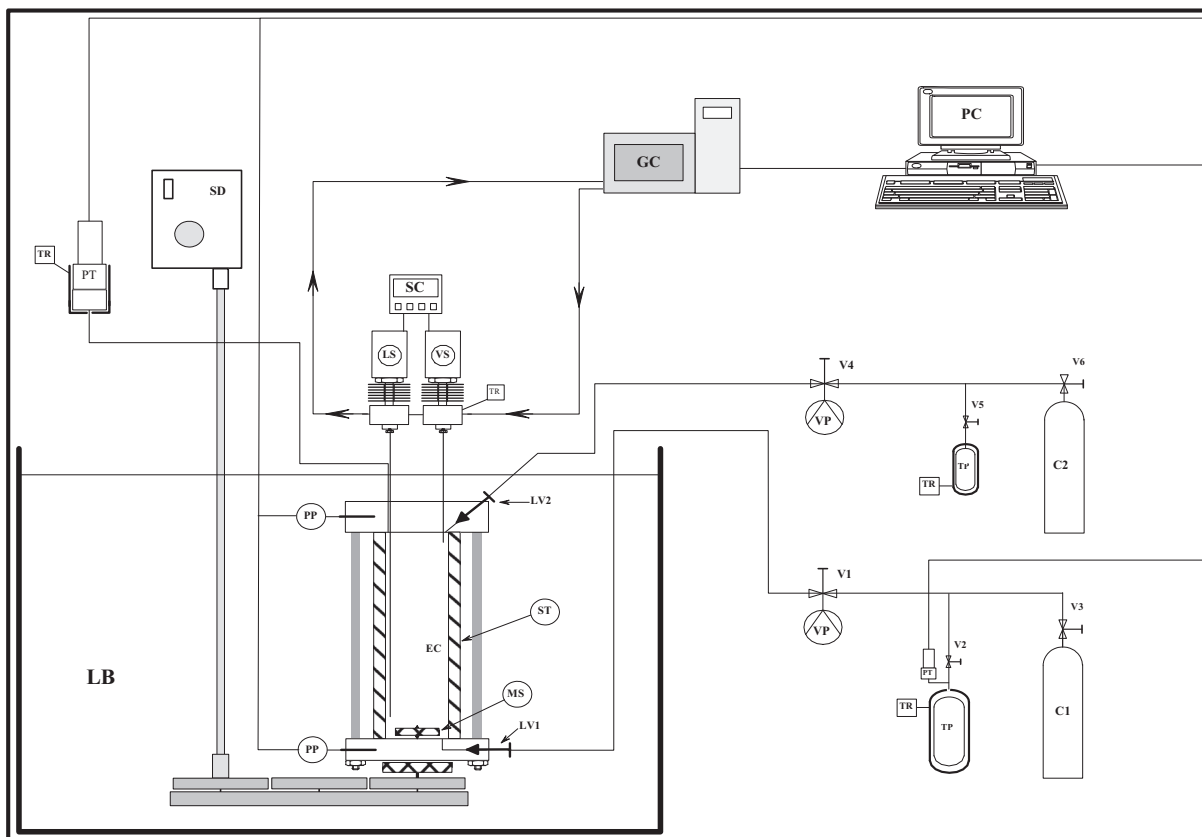

Fig. 1. Flow diagram of the static-analytic apparatus, as was used by Juntarachat et al. [11]. EC: equilibrium cell; LV: loading valve; MS: magnetic stirrer; PP: platinum resistance thermometer probe; PT: pressure transducer; RT: temperature regulator; LB: liquid bath; TP: thermal press; C1: more volatile compound; C2: less volatile compound; V: valve; GC: gas chromatograph; LS: liquid sampler; VS: vapour sampler; SC: sample controlling; PC: personal computer; VP: vacuum pump.