



A novel dynamic recirculating apparatus for vapour–liquid equilibrium measurements at moderate pressures and temperatures



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ABSTRACT

A novel dynamic recirculating apparatus has been constructed for the measurement of isobaric and isothermal vapour–liquid equilibrium (VLE) measurements for pressures up to 750 kPa and temperatures up to 600 K. The apparatus has been constructed from 316 stainless steel (SS) and features Pyrex sight glasses in strategic positions to allow for the observation of flow patterns and circulation rates. The capabilities of the apparatus have been demonstrated through the measurement of pure component vapour pressures and binary vapour–liquid equilibrium data. Vapour pressure measurements were undertaken for cyclohexane, *n*-heptane, *n*-octane, ethanol and 1-propanol. Isobaric VLE data have been measured for the (cyclohexane + ethanol) system at pressures of 40.00, 69.81, 97.72 and 150.0 kPa and isothermal VLE data have been obtained for the (2-propanone + 2-butanol) system at a temperature of 373.15 K. The experimental azeotropic temperatures and compositions for the cyclohexane + ethanol isobaric data sets have been determined and correlated to linear functions. The experimental VLE data were correlated to the Wilson, NRTL and UNIQUAC models using the $\gamma - \phi$ approach with the truncated two-term virial equation of state (with the Hayden and O'Connell method for second virial coefficients). Thermodynamic consistency testing for the VLE data sets was performed with the Herington area test for the isobaric data and the point test of Van Ness and Fredenslund for the isothermal data.

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1. Introduction

Contemporary trends in the field of phase equilibrium thermodynamics indicate a significant concentration of efforts in the development of predictive thermodynamic models and theoretical approaches [1–3]. However, the acquisition of accurate experimental thermodynamic data across a wide range of pressures (P) and temperatures (T) remains an integral part of the development and verification of predictive methods and the successful design of industrial separation processes [4,5].

Traditional low-pressure dynamic recirculating stills for vapour–liquid equilibrium (VLE) measurements possess useful advantages over other VLE measurement techniques (e.g. static methods) due to their relatively simple construction and operation coupled with expediency in furnishing a complete VLE data set with both liquid (x) and vapour phase (y) compositions [6]. This has been exemplified in the past design of a successful low-pressure glass VLE still in our laboratories [6]. The usefulness of the all-glass dynamic recirculating VLE still design for the acquisition of reliable

low pressure ($P < 100$ kPa) VLE data has been demonstrated previously [6–11]. A survey of available P – T – x – y VLE data from literature sources [12–14] indicates a substantial gap in the availability of VLE data in the pressure range of 0.1–1 MPa, particularly for aromatic-aliphatic and alcohol-aliphatic mixtures.

Attempts by researchers to extend the recirculating low pressure VLE still design to obtain measurements in the moderate pressure region have been limited. A few older designs include those of Olson [15] and Wiśniewska et al. [16], which were based upon modified ebulliometer designs for VLE measurements at high pressure. Fairly recent designs of VLE equipment, also based on the ebulliometer design, have been developed by Susial et al. for the measurement of VLE data at elevated pressures [17–26]. Both pieces of equipment, one which is constructed from stainless steel (SS) [17] and the other from copper [18], apparently have a large capacity of 400 cm³. Chen et al. [27] have also recently presented work conducted on a SS VLE recirculation still based on a modified Rose still [28]. The measurements presented by Susial et al. [17–26] and Chen et al. [27] thus far have been limited to isobaric data; consequently the ability of their respective equipment designs to acquire isothermal data has not been demonstrated to date. The criticisms of the ebulliometer design and older types of stills for VLE measurements have been discussed elsewhere [6].

In this work, we have retained important features of our low pressure VLE still design [6–11] for the construction of a SS

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Nomenclature

A_{ij}	parameter defined in Eq. (4)
AAD	average absolute deviation
A, B, C	parameters of the Antoine equation
b_{ij}, b_{ji}	binary interaction parameters for the Wilson, NRTL and UNIQUAC activity coefficient models
D, J	parameters of the Herington area test for consistency
EOS	equation of state
G^E	excess molar Gibbs energy (J mol^{-1})
N	number of data points
OD	outer diameter
OF	objective function
P	pressure (kPa)
r	radius of gyration (m)
R	universal gas constant ($\text{J K}^{-1} \text{mol}^{-1}$)
SS	stainless steel
T	temperature (K)
V	liquid molar volume ($\text{cm}^3 \text{mol}^{-1}$)
VLE	vapour–liquid equilibrium
u	standard uncertainty
x	mole fraction in the liquid phase
y	mole fraction in the vapour phase
Z	compressibility factor

Greek letters

Δ	difference between two values
ΔQ	residual quantity
Φ	simplifying term defined in Eq. (3)
α_{ij}	non-randomness parameter of the NRTL model
ϕ	fugacity coefficient
γ	activity coefficient
μ	dipole moment (Debye)
σ	standard deviation
τ	parameter defined in Eqs. (5) and (6)
ω	acentric factor

Superscripts

AZ	azeotropic point
calc	calculated value
exp	experimental value
E	excess property
L	liquid phase property
sat	saturated pure component property
V	vapour phase property

Subscripts

c	critical property
i, j	components i and j
ij	i – j pair interaction
ji	j – i pair interaction

apparatus that would allow for the acquisition of isobaric and isothermal VLE at elevated pressures. The design of the novel VLE apparatus presented in this work has been facilitated through invaluable experience gained from previous attempts in our research group at similar designs together with scrutiny of past dynamic recirculating VLE still designs presented in open literature [6,29,30].

As an initial test of the performance of the apparatus, boiling point temperatures were measured for selected pure substances (cyclohexane, *n*-heptane, *n*-octane, ethanol and 1-propanol). The study of the VLE of hydrocarbon-alcohol mixtures provides an

appropriate test of a newly developed VLE apparatus, since such mixtures exhibit large departures from ideal behaviour and azeotropic points as well [31,32]. The study of the (cyclohexane + ethanol) system at low pressures has been favoured in our laboratories [6–8] as an effective test system and it was decided to follow suit. In addition, the cyclohexane/ethanol separation has a great deal of interest amongst researchers as a challenging separation problem [33]. Novel isobaric (T – x – y) measurements have also been obtained at P =(69.81, 97.72 and 150.0) kPa. To our knowledge, the data set at 150.0 kPa constitutes the first complete P – T – x – y data set for this system above atmospheric pressure, as other studies on this system in this pressure range have either been isothermal (P – x – y) or P – T – x data only [12]. To display the versatility of the apparatus in acquiring isothermal data without any major modifications, novel P – x – y data were obtained for the (2-propanone + 2-butanol) system at T =373.15 K. The measurement and correlation of VLE data for alcohol + ketone systems is of considerable interest due to the complexity of the hydrogen-bonding interactions that characterize such systems [34]. The isothermal VLE data set presented here for (2-propanone + 2-butanol) at pressures above atmospheric (P > 100 kPa) represents a valuable contribution to such studies.

The experimental VLE data measured here have been subjected to data correlation and thermodynamic consistency testing. Correlation of the VLE data was achieved with the Wilson [35], NRTL [36] and UNIQUAC [37] liquid phase local composition models in the γ – ϕ approach [6]. The Hayden and O'Connell method [38] was used to obtain the second virial coefficients for the treatment of the vapour phase non-ideal behaviour with the truncated two-term virial equation of state (EOS). Thermodynamic consistency testing of the isobaric VLE data was performed with the Herington area test [39,40] and the point test of Van Ness et al. [41], as modified by Fredenslund et al. [42], was used for the isothermal data treatment.

2. Experimental

2.1. Materials

The details of the chemicals used in this study are shown in Table 1. Cyclohexane, *n*-heptane, *n*-octane and 1-propanol were fractionally distilled in a glass distillation column packed with glass rings. The initial fraction was discarded in favour of the medium-boiling cut [43]. The ethanol used in this study was purified [43] through the use of a reaction of the alcohol with magnesium turnings activated with iodine, which was then refluxed and finally distilled to collect the purified ethanol. The distilled chemicals were collected and stored over 0.3 nm molecular sieves to remove any traces of water. No further purification of 2-propanone and 2-butanol was performed.

2.2. Apparatus

The liquid and vapour condensate dynamic recirculating VLE apparatus used in this study is shown in Fig. 1. The design of the apparatus was based on the glass VLE still design, that has been previously described elsewhere [6–8], and was constructed from machined 316 SS to extend the pressure range. Pyrex® borosilicate glass inserts were incorporated in strategic sections of the apparatus. The maximum capacity of the VLE still is approximately 180 cm³. The principal sections (reboiler, Cottrell tube, equilibrium chamber, sample traps and the return line) and the auxiliary components of the VLE apparatus are shown in Figs. 1 and 2, respectively.

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