International Journal of Thermophysics, Vol. 17, No. 4, 1996

Design of a High-Pressure Ebulliometer, with Vapor–Liquid Equilibrium Results for the Systems $CHF_2Cl + CF_3–CH_3$ and $CF_3–CH_2F + CH_2F_2$

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Received October 12, 1995

We describe the design and operation of a new high-pressure metal ebulliometer which can operate at pressures to at least 3 MPa in the range 220–400 K. Infinite-dilution activity coefficients are presented for the system $CHF_2Cl + CF_3–CH_3$ at 275 K and for the system $CF_3–CH_2F + CH_2F_2$ at 260, 280, and 300 K. The Wilson activity coefficient model and a virial coefficient model are applied to these systems, and the phase equilibrium conditions are calculated. The results are shown to agree well with predicted and with published measured values. The excess enthalpy is calculated and compared with results from a Peng–Robinson equation of state. Vapor densities on the dew curves are given.

KEY WORDS: activity coefficients; chlorodifluoromethane (R22); difluoromethane (R32); ebulliometry; phase equilibrium; refrigerant mixtures; 1,1,1-trifluoroethane (R143a); 1,1,1,2-tetrafluoroethane (R134a).

1. INTRODUCTION

An ebulliometer is an instrument used to measure the boiling temperature of a liquid at a selected superimposed pressure. In principle, it is similar to an ordinary open reflux condenser/boiler that operates at ambient pressure. Modifications such as sophisticated design, pressure control, energy flux control, and accurate temperature measurement transform an ordinary laboratory apparatus into a precision measurement device. Because the liquid sample is actively boiling in the apparatus, this technique is known as

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0195-928X/96/0700-0873$09.50/0

a "dynamic" one to distinguish it from "static" techniques in which the liquid is quiescent.

Ebulliometry is a relatively old technique [1], and as a result, many different boiler designs have evolved. The goal of any design is the promotion of smooth, even boiling and the minimization of superheating. The two main applications are the study of the boiling points of pure fluids and of binary mixtures. The results of these measurements are the vapor pressures of pure fluids and the determination of the thermodynamic properties of binary mixtures through the derivation of the limiting activity coefficients of the two components at infinite dilution, γ_i^∞ and γ_j^∞. These two activity coefficients of a binary system can be directly related to the two adjustable parameters in any of the widely used models for the calculation of the excess Gibbs free energy of mixtures. Those models can then be used to calculate the activity coefficients and Gibbs free energy of the binary system at all compositions; the models can then be extended to multi-component systems once γ_i^∞ and γ_j^∞ have been determined for all binary pairs. In addition, with the aid of a model for the gas-phase fugacity coefficients, the phase boundaries (bubble curve and dew curve) can be calculated.

Most ebulliometers have been constructed of glass, and they have necessarily been used at pressures less than about 300 kPa and usually at temperatures from about 300 to about 473 K. We are aware of only a few metal ebulliometers which have been used to higher pressures: Ambrose and Sprake [2], Olson [3], Defibaugh [4], and Wísniewska et al. [5]. In each case, these devices have been used at ambient temperatures or higher.

We describe here the design, construction, and testing of a new all-metal ebulliometer which we have built for measurements up to moderately high pressures over a wide range of temperatures, including temperatures well below ambient. Some pure fluid vapor pressures for CH_2F_2 (R32) and C_2HF_5 (R125) measured in this apparatus have already been reported, [6]. Here we give results for the binary systems $CHF_2Cl + C_2H_3F_3$ (R22 + R143a) and $C_2H_2F_4 + CH_2F_2$ (R134a + R32). Comparisons are made with other reported data for these systems, where available.

2. EXPERIMENTS

Other metal ebulliometers described in the literature have been of the single-boiler type, which utilizes a gauge to measure pressures. The technique employed here is known as comparative ebulliometry because it compares the temperatures in two boilers operating at the same pressure. The apparatus is symmetric, with one-half being shown schematically in Fig. 1. The central portion of a boiler, known as the equilibrium chamber (labeled c in Fig. 1), is made from a heavy-wall stainless-steel tube, 5 cm in I.D. and 18 cm long. An opening, running most of the length of the tube, is covered by a fluted glass window sealed with a PTFE gasket. The window is held in place by a heavy stainless-steel flange secured to the tube with four large U-bolts. The ends of the tube are closed with thick stainless-steel caps which are drilled and tapped for pipe threads. Two stainless-steel housings are screwed into these openings and sealed with PTFE tape. The lower one, the boiler (a), is fitted with a reentrant well which holds a capsule-type electric heater. The upper housing is fitted with a thermometer well (e) which runs most of the length of the equilibrium chamber. A small-diameter steel wire (h) is tack-welded in the form of a helix on the outside of the well. A Cottrell, or vapor lift pump (b), made of Pyrex glass tubing, fits over the heater well and rises into the equilibrium chamber, where it splits into three branches to form a cage around the thermometer well.

Two boilers, fitted with reflux condensers (f), are connected through a manifold which contains helium gas. The Cottrell pumps are mounted inside the heavy-walled vessels in order to give them a more symmetrical shape, which facilitates thermostating. Electrical energy supplied by a capsule heater causes the liquid to boil inside the pump. Rising vapor bubbles

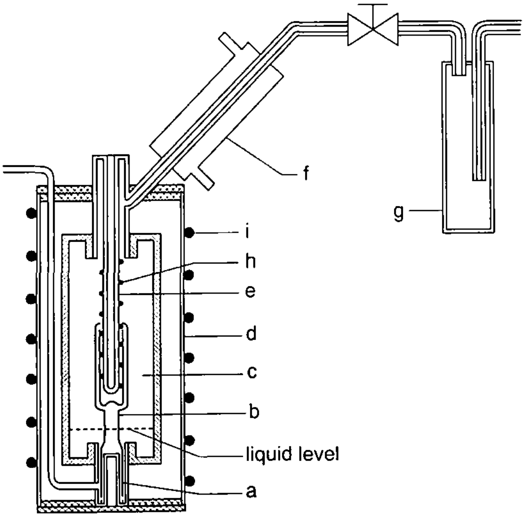

Fig. 1. Schematic diagram of one-half of the apparatus: a, boiler; b, pump; c, equilibrium chamber; d, shield; e, thermometer well; f, condenser; g, cold trap; h, steel wire; i, thermostating tubes.

lift slugs of liquid and vapor inside the pump, and the liquid/vapor mixture is sprayed onto the thermometer well, where the helical wire prolongs contact between the liquid and the well. The intimate mixture of liquid and vapor in the pump facilitates equilibrium of the phases, and any superheat dissipates while the sample is rising. Long-stem platinum resistance thermometers in the wells measure the boiling temperature in each boiler with a precision of about ±5 mK. Surrounding each boiler is a cylindrical metal shield (d), which is thermostated by tubes (i) containing circulated methanol supplied by thermostated baths. The outer surfaces and ends of the cylinders are insulated. The apparatus is filled so that the liquid surface level (shown in Fig. 1) is located in the lower part of the equilibrium chamber. The upper portion of the liquid acts as a mixing chamber for fluid returning to the boiler. Since the apparatus is of all-metal construction, there is no drip counter. Instead, the boiling rate is monitored by measuring the electric power input of the heaters. The apparatus has been designed to operate at pressures to at least 3 MPa in the temperature range 220–400 K.

A pressure controller, connected between a helium cylinder and the manifold, maintains the pressure of the system with a tolerance of ±20 pa. This establishes the boiling temperatures in the two boilers. The boiling action of the sample forces the pressurizing helium and any other noncondensable impurities out of the boiler and into the manifold. A dynamic fluid interface forms in the reflux condenser. Above the interface the gas is essentially pure helium. Below the interface the gas is condensing vapor of the fluid in the boiler. This dynamic interface has the great advantage that it eliminates any loss of sensitivity and hysteresis associated with mechanical separators that are used to isolate samples in static measurements. A small hydrostatic pressure correction accounts for the pressure difference between the condenser and the thermometer well. Two liquid nitrogen-cooled traps (g) in the manifold ensure that there is no cross-contamination between the boilers.

The apparatus can be used in either of two modes. For measuring vapor pressures of pure fluids, a reference fluid is placed in one boiler, and the test fluid is placed in the other one. We have used 2,2-dichloro-1,1,1-trifluoroethane (R123) as a reference fluid because it has a volatility which allows the boiler to operate in a convenient temperature range at the pressures of interest. We have previously measured the vapor pressure of R123 [7], and the temperature of the boiling R123 determines the system pressure. This technique does not rely on a pressure gage. Typical results were shown for R32 and R125 (CF_3CHF_2) in Ref. 6.

The apparatus can also be used to determine the bubble pressure curves of binary mixtures. In this mode of operation, approximately 50 cm^3

of liquid solvent is placed in each boiler. In one boiler the amount is carefully measured by weighing; this operation may involve weighing a small high-pressure cylinder since the solvent may be a gas at ambient conditions. The helium pressure is set with the controller, the reflux condensers are cooled, and the heaters are activated. The thermostated shields are controlled at a temperature about 15° lower than the temperature of the boilers. After a period of time, when both boilers are operating normally, the temperature of each is measured to ensure that they are both operating at the same temperature. Then a small measured amount of solute is added to one boiler. The equilibrium temperature, at constant pressure, of that boiler will change by a small amount, ΔT. In classical low-pressure ebulliometry the solute is introduced through a septum by means of a syringe. For these studies, however, the solutes are gases at pressures in the range 0.4–1.6 MPa (the vapor pressure of the solute) at room temperature. Therefore we have developed a solute loading system which uses a multiport, two-position rotary valve of the type that is used in gas chromatography. Gaseous solute from a supply cylinder, at a measured pressure, is loaded into a calibrated sample loop which is connected across two ports of the valve. When the valve is rotated the solute is flushed into the boiler with helium gas supplied from a high-pressure hand pump. The pressure in the ebulliometer is upset by this process; however, the pressure controller ejects the excess helium, and the system returns to a steady state in about 45 min. The exact amount of solute is determined from the measured pressure, the calibrated volume of the sample loop, and an estimated virial equation of state [8]. In this mode of operation, the purpose of the second boiler is to ensure that the system pressure remains constant. Its temperature is used to calculate the experimental pressure from the vapor pressure curve of the solvent. The measured ΔT is the difference between the temperatures of the two boilers.

Several such additions are made until the total solute mole fraction is in the range 0.01–0.04. Then ΔT may be plotted against z_2, the overall mole fraction of the solute (the feed fraction). The dependence of ΔT on z_2 is a virtually straight line which passes through the origin. From this curve we determine $(\partial T/\partial z_2)_p^\infty$, the slope at infinite dilution. However, this slope must be adjusted in order to obtain the desired quantity, $(\partial T/\partial x_2)_p^\infty$, the slope with respect to the liquid-phase mole fraction.

The measured overall mole fraction, z_2, must be adjusted to find x_2 by accounting for the amount of sample in the vapor phase. This adjustment is expressed in terms of the fraction, $f = n_v/n_l$, the number of moles in the vapor phase divided by the number of moles in the liquid phase. This correction is generally considerably larger than that made in a typical static phase-equilibrium measurement. The "vapor" phase has two parts, the vapor volume itself (~325 cm^3 in this case) and the vapor which has condensed in the reflux condenser and which runs down the walls of the boiler in the form of a liquid film. The first correction is made with the aid of the virial coefficients [8, 9]. The second is called the holdup correction, and it must be measured in a calibration experiment.

The literature on ebulliometry reveals that the holdup correction has been determined by several different techniques. Most of them utilize a system having a great volatility difference between the solute and the solvent and require that the liquid phase composition be determined independently. To do this, we chose the system R124 (solute) + R123 (solvent) at a temperature of 297 K. At this temperature the system pressure is only 90 kPa, the vapor pressure of the solvent, and, therefore, the correction due to the vapor volume, was small. The R124 (CHF_2CF_2Cl) solute was added to one boiler until $z_2 \approx 0.01$. A small sample of the liquid phase was taken and analyzed with a gas chromatograph. Then the entire sample was withdrawn and mixed well, and another sample was analyzed. The ratio of the chromatograph peak areas of these two samples allowed the determination of x_2/z_2 without the necessity of finding the chromatograph response factors. The relationship among z_2, x_2, and f has been given by Rogalski and Malanowski [10] as

$$x_2/z_2 = (1+f)/(1+K_2^\infty f) \tag{1}$$

where $K_2^\infty = y_2/x_2$ at infinite dilution. Since K_2^∞ is usually unknown, the solution for x_2 involves the iterative solution of Eq. (1) with Eqs. (2) and (5) given below. After the small amount of sample in the vapor phase was subtracted, the liquid film in the holdup correction was found to have a volume of about 1.8 cm^3 when the electric power input to the boiler was 18 W. This volume depends on the power input and also on the heat of vaporization of the liquid, and a small correction is made for the heat of vaporization of the system of interest. Knowledge of the liquid density, estimated from a properties package such as REFPROP [11], allows the determination of the number of moles of condensed vapor in the film. This quantity added to the amount of free vapor allows the fraction f in Eq. (1) to be determined for any system. Since the working pressures in these measurements are higher than those normally encountered in ebulliometry, f also has a larger value, in the range 0.05–0.40. The difference between x_2 and z_2 also depends on the relative volatility of the components, and it varies from 0 (same volatility) to about 25%. This correction makes possible the calculation of $(\partial T/\partial x_2)_p^\infty$, the initial slope of the bubble curve, from the experimental measurements.

3. ANALYSIS

The relationship between the initial slope of the bubble curve and the activity coefficient was given by Gautreaux and Coates [12] and, in more modern form, by Thomas et al. [13]. It has the form

$$\gamma_2^{\infty} = \frac{\varphi_2 P_1^{\sigma}}{\varphi_2^{\sigma} P_2^{\sigma}} \times \left[\frac{1-(1-(P_1^{\sigma} v_1/RT)+(P_1^{\sigma}/\varphi_1^{\sigma})(\partial\varphi_1/\partial P)_T^{\sigma})(d\ln P_1^{\sigma}/dT)(\partial T/\partial x_2)_p^{\infty}}{\exp[(P_1^{\sigma}-P_2^{\sigma})\, v_2/RT]} \right] \tag{2}$$

where P_1^{σ} and P_2^{σ} are the vapor pressures of the pure components, the ϕ's are vapor-phase fugacity coefficients obtained from the virial coefficient model, and the v's are liquid molar volumes. By interchanging the solvent and the solute, γ_1^{∞} can also be obtained.

The activity coefficients at infinite dilution may be used to determine the two adjustable parameters in any of the widely used empirical models for the excess Gibbs free energy of the binary system. We use the model given by Wilson [14],

$$g^{\mathrm{E}} = -x_1 \ln(x_1 + A_{12} x_2) - x_2 \ln(x_2 + A_{21} x_1) \tag{3}$$

The parameters, A, are most easily determined from the limiting values of the activity coefficients, where

$$\ln \gamma_1^{\infty} = 1 - \ln A_{12} - A_{21} \tag{4a}$$

and

$$\ln \gamma_2^{\infty} = 1 - \ln A_{21} - A_{12} \tag{4b}$$

With the values of the A's, the activity coefficients, γ_1 and γ_2, and g^{E} can be calculated at all compositions. The distribution coefficient, K_2^{∞}, may be found from

$$K_2^{\infty} = \gamma_2^{\infty} \frac{P_2^{\sigma}}{P_1^{\sigma}} \frac{\varphi_2^{\sigma}}{\varphi_2} \exp[(P_1^{\sigma} - P_2^{\sigma})\, v_2/RT] \tag{5}$$

As stated above, Eqs. (1), (2) and (5) are solved by iteration. Letting $x_2 \approx z_2$ provides a good starting value for the activity coefficient. For the system, R124 (2) dissolved in R123 (1) at 297 K, used for the holdup correction, three determinations yielded $\gamma_2^\infty = 1.30 \pm 0.04$, $K_2^\infty = 5.4 \pm 0.2$, $f = 0.067$, and $x_2/z_2 = 0.78$.

At any point on the phase boundary, the bubble pressure, P is given by

$$P = \gamma_1 x_1 P_1^\sigma \phi_1 + \gamma_2 x_2 P_2^\sigma \phi_2 \tag{6}$$

where

$$\phi_i = \frac{\varphi_i^\sigma}{\varphi_i} \exp[(P - P_i^\sigma) v_i/RT] \tag{7}$$

and the vapor composition is obtained from

$$y_i = \gamma_i x_i P_i^\sigma \phi_i/P \tag{8}$$

The dew and bubble curves are found by iteration of Eqs. (6)–(8) beginning with an assumed value for x_i and the initial estimate, $\phi_i = 1$. The convergence is rapid.

4. RESULTS

The results shown in Refs. 6 and 15 indicate that this apparatus can measure pure fluid vapor pressures with a precision of about ±0.02% (1σ) without any appreciable systematic deviations.

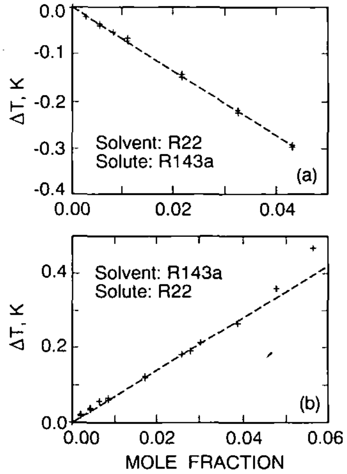

Fig. 2. Experimental results for the system R22 + R143a; change in temperature at constant pressure as a function of the overall mole fraction of the solute.

Table I. Thermodynamic Properties of the System R22 (1) + R143a (2) at 275 K

P (kPa)	x_2	y_2	ρ_v (mol · L^{-1})	γ_1	γ_2	g^E (J · mol^{-1})
529.1	0.00	0.000	0.2602	1.000	0.995	0.0
540.6	0.10	0.117	0.2677	1.000	0.996	−1.0
552.4	0.20	0.230	0.2754	1.000	0.997	−1.8
564.4	0.30	0.339	0.2834	1.000	0.998	−2.4
576.7	0.40	0.445	0.2918	0.999	0.998	−2.8
589.3	0.50	0.546	0.3006	0.999	0.999	−2.9
602.1	0.60	0.644	0.3096	0.998	0.999	−2.8
615.2	0.70	0.738	0.3190	0.998	1.000	−2.4
628.6	0.80	0.829	0.3287	0.997	1.000	−1.8
642.2	0.90	0.916	0.3387	0.996	1.000	−1.0
656.1	1.00	1.000	0.3491	0.995	1.000	0.0

Figure 2 shows experimental results for the binary system R22 (1) + R143a (2) at a temperature of 275 K. This system was chosen for the first test of the apparatus with mixtures because Morrison and McLinden [16] predicted that it would be nearly ideal. Therefore, the measured slopes of the bubble curve should have nearly the values given by Raoult's Law [$(\partial T/\partial x)_p = \pm 6.86$ K for this system at 600 kPa], γ_1 and γ_2 should be nearly unity, and g^E should be small. The measured values were $(\partial T/\partial x_2)_p^\infty = -6.61 \pm 0.34$ K (average of 3) and $(\partial T/\partial x_1)_p^\infty = 6.99 \pm 0.19$ K (average of 4). This indicates that there is a very small negative deviation from Raoult's law. The results are summarized in Table I, where it can be seen that the maximum value of g^E is only about -3 J · mol^{-1}, and the

Table II. Experimental Parameters for the System R134a (1) + R32 (2)

	260 K	280 K	300 K
$(\partial T/\partial z_1)_p^\infty$	15.7		25.2
$(\partial T/\partial x_1)_p^\infty$	15.0		22.3
$(\partial T/\partial z_2)_p^\infty$	−49.4	−43.7	−37.8
$(\partial T/\partial x_2)_p^\infty$	−57.3	−51.8	−44.9
γ_1^∞	1.416	(1.272)^a	1.160
γ_2^∞	1.181	1.097	1.011
K_1^∞	0.53	(0.56)^a	0.57
K_2^∞	3.16	2.57	2.09
A_{12}	0.42861	0.41822	0.35725
A_{21}	1.49973	1.63117	1.88117

^{a} Values in parentheses are interpolated.

Table III. Thermodynamic Properties of the System R134a (1) + R32 (2)

P (kPa)	x_2	y_2	ρ_v ($\mathrm{mol \cdot L^{-1}}$)	γ_1	γ_2	g^E ($\mathrm{J \cdot mol^{-1}}$)
$T = 260$ K						
176.8	0.00	0.000	0.0874	1.000	1.181	0.0
217.7	0.10	0.258	0.1081	1.001	1.162	34.2
257.6	0.20	0.434	0.1286	1.004	1.143	64.5
296.2	0.30	0.562	0.1488	1.010	1.123	90.0
333.3	0.40	0.659	0.1686	1.020	1.102	109.8
368.7	0.50	0.737	0.1878	1.037	1.080	122.6
402.4	0.60	0.800	0.2064	1.063	1.058	126.7
434.3	0.70	0.855	0.2242	1.103	1.038	119.9
464.5	0.80	0.904	0.2413	1.164	1.020	99.4
493.4	0.90	0.951	0.2578	1.259	1.006	61.2
521.6	1.00	1.000	0.2740	1.415	1.000	0.0
$T = 280$ K						
372.6	0.00	0.000	0.1790	1.000	1.097	0.0
439.9	0.10	0.224	0.2123	1.000	1.091	20.9
507.3	0.20	0.391	0.2463	1.002	1.083	40.1
574.5	0.30	0.521	0.2812	1.004	1.074	57.0
641.1	0.40	0.625	0.3165	1.010	1.064	71.0
706.5	0.50	0.710	0.3521	1.019	1.052	80.9
770.4	0.60	0.781	0.3878	1.034	1.040	85.4
832.4	0.70	0.842	0.4231	1.058	1.027	82.7
892.3	0.80	0.897	0.4581	1.098	1.014	70.2
950.3	0.90	0.948	0.4926	1.163	1.004	44.4
1007.0	1.00	1.000	0.5268	1.272	1.000	0.0
$T = 300$ K						
702.6	0.00	0.000	0.3361	1.000	1.011	0.0
800.5	0.10	0.193	0.3841	1.000	1.017	3.5
902.2	0.20	0.351	0.4354	0.999	1.021	8.4
1007.3	0.30	0.482	0.4901	0.998	1.024	14.5
1115.4	0.40	0.592	0.5484	0.997	1.026	21.3
1225.8	0.50	0.684	0.6101	0.998	1.025	28.2
1337.5	0.60	0.763	0.6750	1.002	1.022	34.2
1449.3	0.70	0.832	0.7426	1.011	1.017	37.7
1559.8	0.80	0.892	0.8121	1.031	1.011	36.3
1668.3	0.90	0.946	0.8829	1.073	1.004	25.9
1774.9	1.00	1.000	0.9545	1.160	1.000	0.0

activity coefficients are very near unity. The experimental values found were $K_2^\infty = 1.18$, $K_1^\infty = 0.82$, $\gamma_2^\infty = 0.995$, and $\gamma_1^\infty = 0.995$, with an experimental precision of about 1%. The Wilson parameters were found to be $\Lambda_{12} = 1.1837$ and $\Lambda_{21} = 0.8363$. However, for calculating the gas-phase fugacities, the binary interaction parameter, k_{12}, was set equal to 0 due to the absence of any experimental data for this system. This results in an additional 1–3% uncertainty in the γ^∞'s. The system may be considered ideal (where $\Lambda_{12} = \Lambda_{21} = 1$) within experimental uncertainty. The uncertainty in k_{12} also causes an additional uncertainty of an estimated 2–4 kPa in the dew/bubble pressure at the equimolar composition; this amount

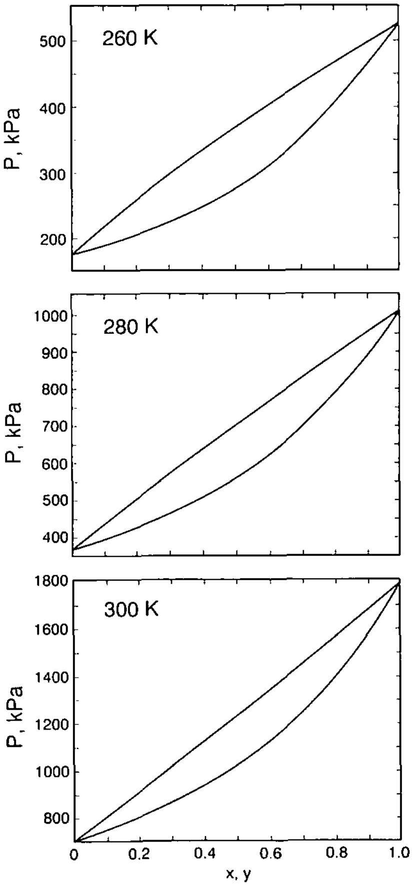

Fig. 3. Phase boundaries for the system R134a + R32 calculated with Eqs. (5)–(8).

decreases to 0 for the pure fluids. Also given in Table I are the vapor densities on the dew curve, calculated with the estimated virial coefficients [8].

The second system studied was the binary, R134a (1) + R32 (2). Measurements were made at three temperatures, 260, 280, and 300 K, and pressures ranged from 177 to 1775 kPa. The nonideality of this system is larger than that of the first one studied. The experimental parameters are given in Table II. The thermodynamic properties, including the phase boundaries calculated with Eqs. (5)–(8), are given in Table III and illustrated in Fig. 3. The deviations from Raoult's law vary from slightly positive at 260 K to slightly negative at 300 K. The excess Gibbs free energy is positive, but decreases with temperature.

Over moderate ranges of temperature, at temperatures well removed from the critical region, the activity coefficients can be represented with a temperature dependence of the form

$$\ln \gamma_i^{\infty} = a_i + b_i/T \tag{9}$$

Equation (9) can be used for interpolation between experimental isotherms and for short extrapolations to produce a (T, x, y) phase boundary surface. With the aid of Eqs. (6)–(8) values of (P, T, x, y) can be calculated. From these results, we find $a_1 = -1.1481$, $b_1 = 388.86$ K, $a_2 = -0.9919$, and

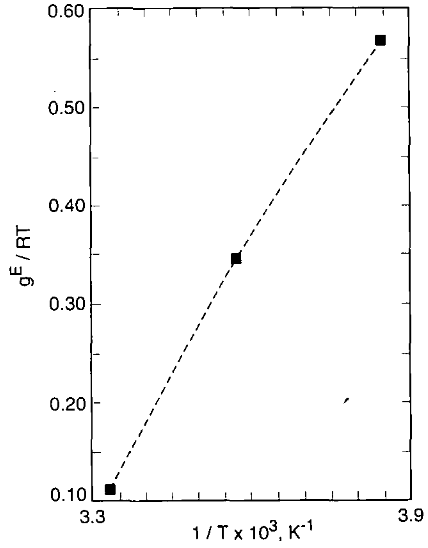

Fig. 4. Excess Gibbs free energy of the equimolar composition of the system R134a + R32 as a function of the inverse of the temperature.

$b_2 = 301.84$ K. Fit of Eq. (9) to the γ_2^∞ data indicates a precision of 0.7% (1σ). Overall uncertainty of the activity coefficients is estimated to be about ±1.5%. The resulting uncertainty in the bubble pressure for an equimolar mixture would be ±2 kPa at 260 K (where $P = 368$ kPa), increasing to ±5 kPa at 300 K ($P = 1226$ kPa). At the end points, these uncertainties decrease to those of the pure fluid vapor pressures, estimated to be 0.03–0.05%. The corresponding uncertainty in g^E is $\pm 10\ \mathrm{J \cdot mol^{-1}}$ at 260 K and $\pm 7\ \mathrm{J \cdot mol^{-1}}$ at 300 K.

Knowledge of the temperature dependence of g^E makes possible the calculation of the excess enthalpy, h^E, via the Gibbs–Helmholtz relationship,

$$(\partial[g^\mathrm{E}/RT]/\partial[1/T])_{p,x} = h^\mathrm{E}/R \tag{10}$$

Figure 4 shows how g^E varies with temperature. If we neglect the small effect of the pressure dependence, the present data yields, for example, the value $h^\mathrm{E} = 743\ \mathrm{J \cdot mol^{-1}}$ for the equimolar mixture at 280 K.

5. COMPARISONS WITH THE LITERATURE

In the previous section, we have given estimates of the uncertainties resulting from the experimental measurements. There are other uncertainties due to the fact that we have used models to calculate the vapor-phase fugacity coefficients and liquid-phase activity coefficients. The virial equation of state used for the vapor is based on some data [8] and a proven model for extrapolation of that data. We estimate that it causes less than 1-kPa uncertainty in the bubble pressure for the equimolar mixture. For the liquid phase, we have used an empirical model, the Wilson model [14]. Although it is widely used, we do not know whether it has been tested on the type of systems studied here. Therefore, it is important to compare our results with the rather limited data published for the system R134a + R32.

Olson [17] has provided a basis for estimating the uncertainty of the excess enthalpy, h^E, given above. From his examples, we estimate the uncertainty to be about 20%, or $\pm 150\ \mathrm{J \cdot mol^{-1}}$ at 280 K, for the equimolar composition. We have fitted a Peng–Robinson equation of state to our VLE results by optimizing the value of the binary interaction parameter, k_{12}, used with that equation. The best value of the parameter is a function of temperature; the value $k_{12} = 0.014$ provided a good representation of our P, x, y data at 280 K. However, that value of k_{12} leads to a calculated excess enthalpy for the equimolar mixture, $h^\mathrm{E} = 290\ \mathrm{J \cdot mol^{-1}}$ at 280 K, which appears to be outside our range of uncertainty. A value of k_{12} in the range 0.04–0.05 is required to produce a value of h^E which is consistent with the present results. It is interesting to note that such a value for k_{12} is close to the one which we used to represent the interaction second virial coefficient for this system. We consider this comparison to be an illustration of the inadequacy of a cubic equation such as the Peng–Robinson equation to provide a good overall representation of the properties of such a polar system.

Widiatmo et al. [18] have published bubble pressures of the system R134a + R32 for five compositions in the temperature range 280–340 K, at 10-K intervals. Our smoothed results were interpolated or extrapolated to their experimental temperatures with the aid of Eq. (9) and compared in the interval 280–310 K. After the deletion of one obviously erroneus datum,

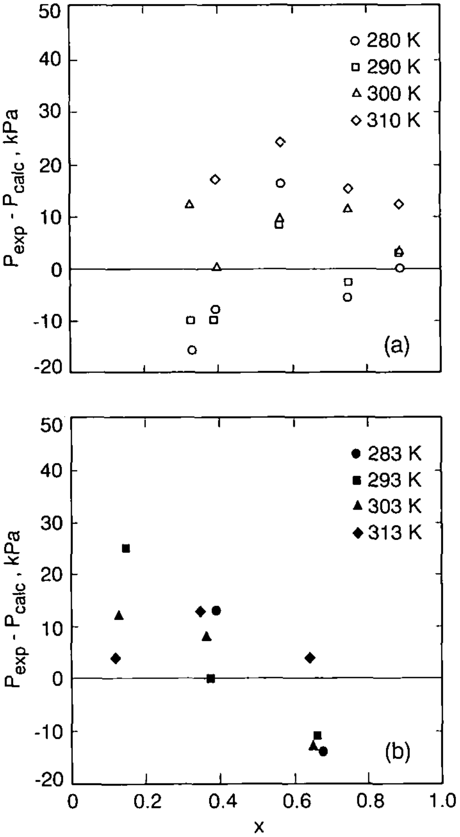

Fig. 5. Deviations of published bubble pressures from our calculated values, interpolated with the aid of Eq. (9); (a) Widiamo et al. [18]; (b) Higashi [19].

their 19 other experimental bubble pressures exhibited an average absolute deviation of 10 kPa from our smooth surface; the bias was +4 kPa. Their claimed experimental uncertainty was ±15 kPa in pressure, and therefore we consider these differences to constitute satisfactory agreement. The deviations are shown in Fig. 5a.

Higashi [19] measured the dew and bubble curves of the system R134a + R32 in the range 283–313 K. A comparison of his bubble pressures with our results showed, after deletion of one datum, an average absolute deviation of 11 kPa and a bias of +4 kPa. A comparison of the vapor compositions gave $\langle \Delta y_2 \rangle = -0.012$. His claimed experimental uncertainties were ±0.4% in pressure and ±0.004 in composition. Comparison with his vapor pressures of the pure fluids showed better agreement: $\langle |\Delta P| \rangle = 2$ kPa, or 0.2%. The bubble pressure deviations are shown in Fig. 5b.

Fujiwara et al. [20] reported P, x, y data for six compositions at 273.15 K. The agreement with his bubble pressures is less satisfactory; $\langle \Delta P \rangle = -34$ kPa (5.5%), and $\langle \Delta y_2 \rangle = -0.02$.

Kleemiss [21] measured P, x, y data for this system in the range 303–343 K for $x_2 \simeq 0.45$. Comparisons at his two lowest temperatures, both requiring short extrapolations of our data, showed $\langle \Delta P \rangle = +(6 \pm 8)$ kPa and $\langle \Delta y_2 \rangle = -0.02$.

Although the above comparisons are not definitive, they do set upper bounds on uncertainties due to the activity coefficient model used for this system. In general, we may say that we agree with all of the reported bubble pressures within the recognized experimental uncertainties. However, there appear to be some small systematic differences in the values of y_2. Therefore, we attempted to make some independent numerical tests of the effect of the activity coefficient model used. We found that any changes in γ_i, which resulted in changes in the bubble pressures of the magnitudes noted above, had a negligible effect on the calculated values of y_2. The reason for this is seen in Eqs. (6) and (8), where the ratio γ_i/P tends to be relatively insensitive to the activity coefficient model.

6. CONCLUSIONS

We have described the design and operation of a new high-pressure ebulliometer which can be used to measure vapor pressures and phase equilibrium conditions for binary mixtures over a wide range of temperatures. We have presented results for two candidate binary refrigerant systems, and we have made a careful analysis of the estimated uncertainties of both the measured and the calculated properties of these systems. We have compared our results with values published in the literature for the system R134a + R32 and have found good agreement with the data of Widiatmo et al. [18], Higashi [19], and with Kleemiss [21] but not with the data of Fujiwara et al. [20]. It appears that the latter data are inconsistent with the others mentioned and with our own. We conclude that the Wilson model provides a good description of the liquid-phase activity coefficients for such systems of fluorinated hydrocarbons and that this apparatus should be useful in the study of the phase boundaries and thermodynamics of other candidate binary refrigerant systems.

ACKNOWLEDGMENT

The development and construction of the ebulliometer were supported by the Division of Engineering and Geosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-A105-88ER13823.

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