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Derivation of the Bubble Pressure Surface, *P*(*x*,*T*), of a Binary Mixture by Ebulliometry: The System $C_3H_3F_5 + C_4H_2F_8$

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A high-pressure metal ebulliometer has been used to determine the infinite dilution activity coefficients for the azeotropic binary system 1,1,2,2,3-pentafluoropropane (HFC245ca) + 1,1,1,2,2,3,3,4-octofluorobutane (HFC338mccq) over the temperature range 300 K to 375 K. Pressures ranged from 98 kPa to 970 kPa. These results, combined with previously determined vapor pressures of the pure components, the Wilson activity coefficient model for the liquid, and a virial coefficient model for the vapor, allowed the calculation of the dew and bubble curves over the experimental temperature range.

Introduction

Trichlorofluoromethane (CFC11) has a normal boiling point temperature of $T_b = 297$ K, making it one of the least volatile of the commonly used CFC's. Both 1,1,2,2,3-pentafluoropropane (HFC245ca, T_b = 298 K) and 1,1,1,-2,2,3,3,4-octofluorobutane (HFC338mccq, T_b = 300 K) would be potential replacements in thermal machinery. Their less-flammable minimum-boiling azeotropic mixture could be an even better replacement. We have measured several of the thermophysical properties of HFC245ca (Defibaugh et al., 1996) and the vapor pressure curve of HFC338mccq (called simply HFC338 hereafter) (Defibaugh et al., 1997). In this work we describe phase equilibrium measurements made on the binary mixture in a high-pressure metal ebulliometer. The ebulliometer was used to determine the infinite dilution activity coefficients of each component over a range of temperatures. These quantities, along with an activity coefficient model for the liquid phase and an estimated equation of state for the vapor phase, allowed calculation of the phase equilibrium boundaries, dew and bubble curves, over a fairly wide range of temperatures and pressures. We are aware of only one other published experimental study on this system, and comparisons are made with those results.

At a fixed temperature, the bubble pressure curve of a binary system is given by (Van Ness and Abbott, 1982)

$$P = \gamma_1 x_1 P_1^{\sigma} \Phi_1 + \gamma_2 x_2 P_2^{\sigma} \Phi_2 \tag{1}$$

where

$$\Phi_i = \frac{\phi_i^{\sigma}}{\phi_i} \exp\left[\frac{(P - P_i^{\sigma})v_i}{RT}\right] \tag{2}$$

Here, x_i are the liquid-phase mole fractions, the P_i^{σ} are the vapor pressures of the pure components, ϕ_i are the gas-phase fugacity coefficients, γ_i are the activity coefficients, and the v_i are liquid molar volumes. The corresponding dew curve can be calculated from

$$y_i = (\gamma_i x_i P_i^{\sigma} \Phi_i)/P \tag{3}$$

The dew and bubble curves are found by iteration of eqs 1−3 beginning with assumed values for the x_i and the initial estimate $\Phi_i = 1$. Before this solution can be performed, however, some means of calculation are needed for the γ_i and ϕ_i. In this work, we use the two-parameter Wilson model to obtain the liquid-phase activity coefficients. The gas-phase fugacity coefficients are obtained with the aid of an equation of state. Here, we use a virial coefficient model (Weber, 1994) to estimate *B* and *C* for the two components and for the mixture.

The Wilson model for the excess Gibbs free energy of the system contains two system-dependent, temperature-dependent parameters, Λ_{12} and Λ_{21}. These parameters are most easily obtained from the infinite dilution activity coefficients of the two components at the desired temperature

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

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

where the γ_1^{∞} are the activity coefficients of the solutes at infinite dilution.

The next section gives a brief description of the apparatus and techniques used to determine the activity coefficients at infinite dilution. The last section presents the results in the form of plots of the phase boundaries.

Experimental Section

A complete description of the apparatus has been given by Weber and Silva (1996). The comparative ebulliometer consisted of two stainless steel boilers connected through a stainless steel manifold. Between each boiler and the manifold was a reflux condenser, which confined the samples to the boilers. Each boiler was fitted with a platinum resistance thermometer and a capsule-type electric heater. In each, a Cottrell, or vapor lift pump, sprayed a heated mixture of liquid and vapor sample onto the thermometer well; thus, the measured temperatures were boiling temperatures. The temperatures in the boilers were measured with a precision of about ±2 mK to ± 5 mK. Temperature differences were more important than absolute accuracy in the temperature measurements, as will be seen below.

Cylindrical, thermostated metal shields surrounded the boilers. They were controlled at temperatures about 15 K below the temperatures of the boilers. The outsides of the shields, as well as the tops and bottoms of the boilers, were well insulated. A commercial pressure controller was used

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to maintain a constant pressure of helium gas in the manifold between the condensers, with a tolerance of ±20 Pa. This pressure determined the boiling temperatures in the boilers.

In normal operation, each boiler was loaded with approximately 50 cm^3 of the liquid solvent, component 1. In the test boiler this amount was carefully measured by weighing. The helium pressure was set, the condensers were cooled, and the heaters were activated; after about 1 h the boilers came to a steady-state condition at nearly the same temperature. Any small initial temperature difference, ΔT_0, usually a few milliKelvins, was noted and subtracted from all subsequent measured values of ΔT. Next, a small measured amount of gaseous solute, component 2, was added to one boiler. The solute loading system employed a small calibrated volume at ambient temperature and a pressure gauge; it was previously described by Weber and Silva (1996). When steady-state conditions were reestablished, a small temperature difference, ΔT, could be measured between the two boilers. These temperature measurements allowed the calculation of the quantity $(\partial T/\partial z_2)_p^\infty$, the change in temperature with the overall mole fraction of the solute at infinite dilution. In this measurement, the second boiler served as a reference, and its temperature compensated for any drift in the pressure controller.

The above procedure was followed in the present work, with one exception. The supply of one of the components, HFC338, was very limited. Hence, it was not possible to allocate 50 cm^3 of that liquid to the reference boiler. Therefore, a third fluid, 1,1,1,2-tetrafluoroethane (HFC134a) was used as the reference fluid. As a result ΔT_0 had a value close to 55 K, rather than being a few milliKelvins. The quantity of interest remained $(\Delta T - \Delta T_0)$, where ΔT refers to the temperature difference between the two boilers. The thermometers and pressure controller were sufficiently stable that this arrangement caused no problems. The vapor pressures of HFC134a have been accurately reported by Goodwin et al. (1992), and the temperature of the reference boiler was used as the measure of the system pressure. The pressure gauge was used merely as a sensor for the pressure controller.

The quantity desired is $(\partial T/\partial x_2)_p^\infty$, the change in temperature as a function of the liquid-phase solute mole fraction, x_2. Therefore, the total mole fraction, z_2, must be adjusted to account for the vapor phase. This adjustment is found from a mass balance relationship that depends on the amount of vapor phase present and also on the relative volatilities of the components. It has the form

$$x_2/z_2 = (1 + f)/(1 + K_2^\infty f) \tag{5}$$

where f is the ratio of moles of vapor to moles of liquid, n_v/n_l, and K_2^∞ is the distribution coefficient y/x at infinite dilution. The number of moles of vapor consisted of two parts, the free gaseous vapor and the condensed vapor running down the walls of the boiler in the form of a liquid film. The amount of the first was found from the geometry of the apparatus with the aid of the virial coefficients; the amount of the second, the holdup correction, was found from a calibration experiment, see Weber and Silva (1996). In this work, the difference between x and z varied from 2.7% to 8%. When the above adjustments have been made, the activity coefficient at infinite dilution can then be calculated with the relationship derivable from the general coexistence equation for binary VLE (Thomas et al. (1982); see also Van Ness and Abbott (1982))

Table 1. Measured ΔT as a Function of Overall Concentration for the System HFC245ca (1) + HFC338 (2)

Δz_1	$(\Delta T - \Delta T_0)$/K	T/K	Δz_2	$(\Delta T - \Delta T_0)$/K
		300 K		
0.004 15	−0.040		0.003 21	−0.039
0.008 31	−0.088			
		325 K		
0.008 30	−0.116			
0.011 1	−0.149			
		350 K		
0.004 22	−0.047		0.006 34	−0.046
		375 K		
			0.004 38	-0.012_5
			0.008 70	-0.030_7

$$\gamma_2^\infty = \left(\frac{\phi_2 P_1^\sigma}{\phi_2^\sigma P_2^\sigma}\right)\left(\frac{1 - \left(1 - \dfrac{P_1^\sigma v_1}{RT} + \dfrac{P_1^\sigma}{\phi_1^\sigma}\left(\dfrac{\partial \phi_1}{\partial P}\right)_T^\sigma\right)\left(\dfrac{\mathrm{d}\ln P_1^\sigma}{\mathrm{d}T}\right)\left(\dfrac{\partial T}{\partial x_2}\right)_p^\infty}{\exp(P_1^\sigma - P_2^\sigma)\, v_2/RT}\right) \tag{6}$$

where the symbols have the definitions given earlier. Interchanging the solvent and solute allowed the determination of γ_1^∞. The distribution coefficient can be calculated from

$$K_2^\infty = \gamma_2^\infty \frac{P_2^\sigma \phi_2^\sigma}{P_1^\sigma \phi_2} \exp[(P_1^\sigma - P_2^\sigma)\, v_2/RT] \tag{7}$$

Equations 5−7 are solved by iteration.

Equations 1−7 can be used to calculate the phase boundaries, dew and bubble curves, at the experimental temperatures. If we assume that the excess enthalpy at infinite dilution is relatively constant with temperature, then the activity coefficients can be expressed as a simple function of temperature

$$\ln \gamma_i^\infty = a_i + b_i/T \tag{8}$$

Equation 8 can be used to smooth the data, make calculations at interpolated temperatures, and make short extrapolations beyond the experimental temperature range.

Results and Comparisons

Experimental measurements were made at four temperatures: 300 K, 325 K, 350 K, and 375 K. Experimental pressures varied from 98 kPa to 970 kPa. The experimental results are given in Table 1, and the $(\partial T/\partial z)_p^\infty$ and the derived quantities are given in Table 2. It has been our experience with the systems studied in this apparatus that bubble curves are essentially straight lines, within the accuracy of our measurements, for solute concentrations up to several mole percent. Therefore the derivatives were found by straight-line differences between the experimental datum and the origin, $\Delta T/\Delta z_2$. Since the sample of HFC338 was very limited, when it was used as the solvent only one filling of the boiler was available for all measurements. Therefore the solute concentrations z_1 were cumulative from one experimental isotherm to the next, and the “origin” was shifted by the amount added for the previous isotherm. However, the maximum concentration did not exceed 2.5 mol %, and we estimate that the measurements provide a good approximation of the limiting slope of the bubble curve. As a result, however,

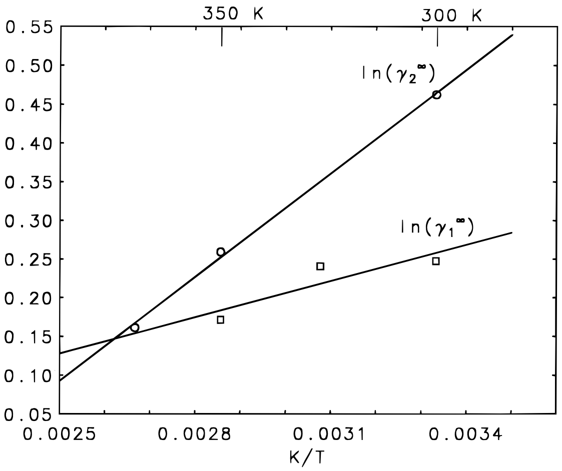

Figure 1. Experimental activity coefficients at infinite dilution for the system HFC245ca (1) + HFC338 (2); lines, eq 8.

Table 2. Derived Experimental Results for the System HFC245Ca (1) + HFC338 (2)

	300 K	325 K	350 K	375 K
$(\partial T/\partial z_1)_p^\infty$ /K	−10.3	−13.7	−11.2	
$(\partial T/\partial z_2)_p^\infty$ /K	−12.0		−7.32	−3.31
$(\partial T/\partial x_1)_p^\infty$ /K	−10.7	−14.7	−12.1	
$(\partial T/\partial x_2)_p^\infty$ /K	−12.6		−7.66	−3.40
f_1	0.12	0.21	0.43	
f_2	0.12		0.39	0.88
γ_1^∞	1.282	1.273	1.187	
γ_2^∞	1.583		1.292	1.181
K_1^∞	1.38	1.37	1.26	
K_2^∞	1.45		1.17	1.06
Λ_{12}	0.44384		0.64316	
Λ_{21}	1.34728		1.18922	

the experimental ΔT's were small, and the temperature derivatives were therefore subject to rather large uncertainties, estimated to be of the order of ±1 K (8% at 300 K to 30% at 375 K). However, reference to eq 6 reveals that, for minimum boiling azeotropes, the right-hand side is the sum of two terms. The first term is primarily the ratio of the two pure-fluid vapor pressures, a quantity that is known quite accurately. This term is considerably larger than the second term, which contains the experimental measurement. Thus any uncertainty in $\Delta T/\Delta z$ is greatly attenuated in the calculation of the activity coefficient. Sample calculations show that the relative uncertainty is reduced by a factor of 0.26 at 300 K, which decreases to a factor of 0.045 at 375 K. Thus we estimate that the activity coefficient has an uncertainty no greater than 3%.

The activity coefficients at infinite dilution are shown in Figure 1. Smoothed results have been calculated by using eq 8, with the values $a_2 = -1.025$, $b_2 = 447.0$ K, $a_1 = -0.2636$, and $b_1 = 156.5$ K, to produce the Wilson parameters necessary to implement eq 1. In addition, the gas-phase equations of state for the two pure components and for the mixture are needed to calculate the fugacitiy coefficients in eqs 2 and 3. As stated earlier, we used the virial coefficient model of Weber (1994) to estimate B and C in each case. The necessary physical parameters are given in Table 3. The resulting calculated dew and bubble curves at 300 K and 375 K are shown in Figure 2. In Figure 2 it is seen that this system forms a positive azeotrope, and the azeotropic composition migrates toward the more volatile component (HFC245ca) with increasing temperature.

The two-parameter Wilson model has been shown (Weber and Silva, 1996) to be capable of giving P, T, x, y results that are in agreement with direct experimental measurements for systems of hydrofluorocarbons. Vapor-phase fugacity calculations require a knowledge of the equation of state for the mixture. Calculation of the interaction second virial coefficient, B_{12}, requires an estimate for the binary interaction parameter, k_{12}, which is best estimated from one or more reliable gas-phase PVT measurements for the mixture. Such data are not available for this system. We assigned the value $k_{12} = 0.03$, which was found by fitting a Peng−Robinson equation of state to the initial slopes of the bubble curve at the pure HFC338 end (the end far removed from the azeotrope). This value gave the best representation over the experimental temperature range. Once B_{12} has been found, the mixture third virial coefficients can also be calculated (Weber, 1994).

Table 3. Parameters of the Components Used for Calculation of the Virial Coefficients

	HFC245ca	HFC338
T_c/K	447.6[a]	431.95[a]
P_c/kPa	3920	2725
ω	0.353	0.40
μ/D	1.76[b]	1.87[b]
v_c/L·mol^{-1}	0.256[c]	0.353[c]

[a] Schmidt, 1996. [b] Goodwin and Mehl, 1996. [c] Defibaugh et al., 1996, 1997.

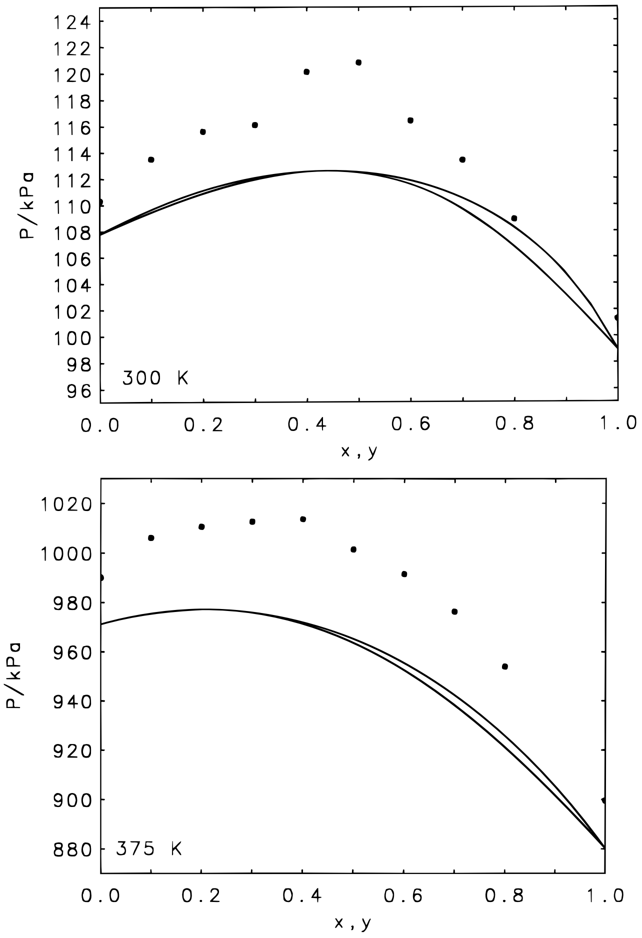

Figure 2. Calculated phase boundaries for the system HFC245ca + HFC338 at 300 K (top) and 375 K (bottom).

Table 4 gives the location of the azeotrope at the experimental temperatures, using the value $k_{12} = 0.03$. Under the assumption that the uncertainty in the activity coefficients at infinite dilution is ±3%, we estimated the uncertainties in some of the derived functions. At 300 K the maximum uncertainty in g^E for the equimolar mixture

Table 4. Calculated Azeotropes for the System HFC245ca (1) + HFC338 (2)

T/K	P^{AZ}/kPa	x_2^{AZ}
300	112.6	0.44
325	263.0	0.39
350	534.2	0.32
375	977.1	0.21

is ±19 J/mol (9%), the uncertainty in the azeotropic pressure is ±0.9 kPa (0.8%), and the uncertainty in the azeotropic composition is less than ±1 mol %. At 375 K these uncertainties are ±15 J/mol (12%), ±6 kPa (0.6%), and ±4 mol %, respectively.

The above uncertainties were calculated with the assumption that the Wilson model provides the correct behavior for this system. This hypothesis can only be tested by comparison with experimental data. Beyerlein et al. (1996) have reported vapor pressure measurements (bubble pressures) for this system at 10 fixed compositions, including the pure fluids, over the same temperature range. We have calculated pressures from their reported vapor pressure functions at 300 K and 375 K for all 10 compositions, and these points are shown in Figure 2. We see that, although the standard deviation of their vapor pressure curves is only about 0.3%, their values fall systematically about 2% higher than our bubble curves. Since these differences are also observed for the pure fluids, where we have measured vapor pressures, the differences appear to be between the experimental measurements and do not imply that the Wilson model is incorrect. Beyerlein et al. say that their pressure measurements may have an uncertainty of as much as 3%; therefore we may say that we agree within their reported uncertainty. Their measurements indicate an azeotropic composition of $x_2 = 0.45$ at 300 K, which compares well with our value, 0.44. At 375 K, however, their pressure measurements indicate a value of 0.35, compared to 0.21 in Table 4. This difference may be due to experimental imprecision at 375 K since only 0.3% separates their pressures at 0.2 and 0.4.

Literature Cited

Beyerlein, A. L.; DesMarteau, D. D.; Naik, K. N.; Xie, Y. Physical Properties of Fluorinated Propane and Butane Derivatives and the Vapor Pressure of R-245ca/338mccq Mixtures as R-11 Alternatives. *ASHRAE Trans.* **1996** *102* (1), 3968.

Defibaugh, D. R.; Gillis, K. A.; Moldover, M. R.; Schmidt, J. W.; Weber, L. A. Thermodynamic Properties of $CHF_2-CF_2-CH_2F$, 1,1,2,2,3-Pentafluoropropane. *Int. J. Refrig.* **1996** *19*, 285−294.

Defibaugh, D. R.; Hurly, J. J.; Moldover, M. R.; Schmidt, J. W.; Weber, L. A.; Carrillo-Nava, E. Thermodynamic Properties of HFC-338mccq $CF_3-CF_2-CF_2-CH_2F$, 1,1,1,2,2,3,3,4-Octofluorobutane. J. Chem. Eng. Data **1997**, *42* 488−496.

Goodwin, A. R. H.; Mehl, J. 1996, to be published.

Goodwin, A. R. H.; Defibaugh, D. R.; Weber, L. A. The Vapor Pressure of 1,1,1,2-Tetrafluoroethane (R134a) and Chlorodifluoromethane (R22). *Int. J. Thermophys.* **1992**, *13*, 837−854.

Schmidt, J. W. 1996, private communication.

Thomas, E. R.; Newman, B. A.; Nicolaides, G. L.; Eckert, C. A. Limiting Activity Coefficients from Differential Ebulliometry. *J. Chem. Eng. Data* **1982**, *27*, 233.

Van Ness, H. C.; Abbott, M. M. *Classical Thermodynamics of Nonelectrolyte Solutions*; McGraw-Hill: New York, 1982.

Weber, L. A. Estimating the Virial Coefficients of Small Polar Molecules. *Int. J. Thermophys.* **1994**, *15*, 461−482.

Weber, L. A.; Silva, A. M. Design of a High-Pressure Ebulliometer, with Vapor-Liquid Equilibrium Results for the Systems $CHF_2Cl + CF_3-CH_3$ and $CF_3-CH_2F + CH_2F_2$. *Int. J. Thermophys.* **1996**, *17*, 873−888.

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