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Vapor–Liquid Equilibrium in Binary Systems of Chlorotrifluoromethane with *n*-Butane and Isobutane

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Vapor and liquid equilibrium phase compositions were determined at 310.93, 350.00, and 400.00 K for the binary systems of chlorotrifluoromethane (R 13) with *n*-butane and with isobutane. The data were fit with the Peng–Robinson equation of state. Henry's constants were derived, and their temperature behavior is compared with a new model calculation.

Introduction

Chlorotrifluoromethane (R 13) is used as a refrigerant in low-temperature specialty situations such as cooling brine solutions, in the lower stage of cascade refrigeration systems, and also in an azeotropic mixture with CHF_3 (R 23) in very low temperature cascade systems. At present it is the only fully halogenated alkane whose future use has not been limited by international agreement (*1*).

Densities and vapor pressures of pure R 13 have been measured by several workers (*2-6*), and several reports exist for the measurement of the densities and vapor–liquid equilibrium properties for R 13 in mixed refrigerant systems, generally with R 12, R 14, and R 23 (*7-12*). As far as we are aware, however, the present measurements are the first that have been reported on mixtures of R 13 with hydrocarbons at elevated temperatures and pressures.

This work is a continuation of our vapor–liquid equilibrium measurements on systems involving one supercritical component. These systems are binary mixtures of a small quasi-spherical molecule, R 13, which has a moderate dipole moment (0.5 D) with the two isomers of a larger nonspherical molecule, butane, which have very small dipole moments ($\leq$0.05 and 0.13 D).

In the next section we give a brief description of the apparatus and then a summary of the experimental results. In the final section we compare our experimental results with a new model for correlating Henry's constant and the partition constant *K* at infinite dilution near the solvent's critical point.

Experimental Section

The apparatus has been described previously (*13*), and only a brief description will be given here. The VLE cell is a heavy-wall vessel (volume approximately 65 cm^3) which is made of 300 series stainless steel and which has a window in one side. Vapor is circulated from the top of the vessel and bubbled through the liquid phase in the bottom by means of a magnetically driven pump. The liquid phase is also circulated via a high-pressure dual piston pump. The system pressure is measured in the liquid circulation line with two digital bourdon gauges having pressure ranges 0–34 and 0–138 bar. Temperature is measured with a probe-type platinum resistance thermometer inserted into the top of the VLE cell. With the exception of the pressure gauges, liquid circulation pump, and the vapor circulation pump motor, the apparatus is mounted inside a convection oven. The oven has a window for visual observations. Rotating sampling valves in the circulation lines allowed small samples of each phase to be analyzed with a gas chromatograph and electronic integrator.

The thermometer and ac bridge had an overall accuracy of ±0.025 K and a sensitivity of better than 0.005 K. The calibration was checked at the triple point of water. The air temperature in the oven had a short-term oscillation of ±0.03 K, and the average temperature could be set and repeated to within about 0.01 K. The temperature homogeneity in the workspace was measured to be about ±0.025 K at 340 K. The pressure gauges were calibrated periodically against laboratory standards, and their accuracy was estimated to be ±0.03 bar.

The relative response factors of the chromatograph for each of the three components were found by using pure samples covering the size range encountered experimentally. For isobutane and *n*-butane they were constant and had relative values of 1.550 and 1.554, respectively. For R 13, however, the factor varied linearly with the area of the peak and had a value of $1.618 + 0.01202A$, where A is proportional to the peak area. In this work A varied from 0 to 20 with the largest values occurring in the vapor phase at the highest pressures and highest R 13 concentrations. The response factors could be determined with a standard deviation of 0.25%, and with the normalizing action of the integrator we estimate the compositions to have an uncertainty given by $|\delta x| = 0.005x_1x_2 + 0.0003$ and $|\delta y| = K_1K_2|\delta x|$ in mole fraction (where $K_i = y_i/x_i$).

The butane samples came from several cylinders having purity levels varying from 99.94 to 99.99 mol%. The R 13 cylinder was certified as having a minimum purity of 99%. In fact, we found that it had a volatile impurity of 0.1%, which appeared to be air. After several samples were taken this impurity dropped to about 0.04%. No other impurities were found with the chromatograph.

Data were measured on isotherms, and each run began with a determination of the vapor pressure of the pure butane. After that successive increments of R 13 were added and the vapor and liquid circulation pumps were run until equilibrium was es-

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Table I. Experimental Vapor Pressures of Butanes

T/K	$P_1{}^a$/bar	$P_2{}^b$/bar	P/bar	P/bar
		n-Butane		
310.93	3.58	3.54	3.54^c	3.562^d
350.00	9.45	9.42	9.46^c	9.446^d
400.00	24.93	24.91	24.89^c	
		Isobutane		
310.93	5.01	4.97	5.01^e	
350.00	12.59	12.56	12.57^e	
400.00		31.83	31.89^e	

$^a P_1$: 0–34 bar gauge. $^b P_2$: 0–138 bar gauge. ^{c}Reference *15*. ^{d}Reference *17*. ^{e}Reference *16*.

Table II. Experimental Results for the R 13 (1) + *n*-Butane (2) System

P/bar	$100x_1$	$100y_1$	P/bar	$100x_1$	$100y_1$
		T = 310.93 K			
4.34	1.36	16.32	25.73	53.97	84.85
5.01	2.61	26.56	27.60	59.57	86.08
6.03	4.59	38.04	29.36	64.62	87.15
8.69	9.89	55.69	31.38	70.08	88.27
11.24	15.42	65.22	33.54	75.85	89.49
13.52	20.59	70.72	35.63	80.99	90.72
16.06	26.84	75.13	37.53	85.16	91.79
18.64	33.72	78.43	39.07	88.43	92.35
21.24	40.91	81.19	40.02	90.40	93.05
23.41	47.27	83.07	40.61	91.71	93.11
		T = 350.00 K			
10.47	1.24	8.97	39.46	43.99	68.34
11.69	2.84	17.29	45.77	55.54	69.42
13.25	4.75	25.25	46.81	58.04	68.62
16.41	8.90	37.97	47.52	60.14	67.13
19.02	12.43	45.31	40.15	45.29	68.42
21.87	16.53	51.31	38.74	42.77	67.68
25.02	21.05	55.66	41.83	48.14	68.96
27.19	24.37	58.72	36.24	38.56	66.05
29.82	28.30	61.55	41.93	48.33	68.06
33.03	33.31	64.32	45.13	54.21	68.93
		T = 400.00 K			
27.34	2.15	6.61	41.49	16.63	27.55
30.27	4.89	12.41	44.58	21.20	28.01
32.72	7.40	17.63	45.35	22.81	30.38
35.14	9.70	21.75	45.50	24.36	29.31
38.26	12.91	24.60			

tablished, which generally occurred in less than 1 h.

Results

In a previous publication (*13*), we reported values for the critical temperature, T_c, and pressure, P_c, of R 13 which were measured in this apparatus. They were, T_c = (301.92 ± 0.04) K and P_c = (38.85 ± 0.04) bar, and they were found by careful visual observations of the disappearance of the meniscus. We also made two determinations of the R 13 vapor pressure at 298.15 and 300.25 K, and our values of 35.67 and 37.38 bar agree very well with the values of 35.65 and 37.38 bar calculated with the curve published by Fernandez-Fassnacht and del Rio (*14*).

Measurements of P, T, x, and y were made for both binary systems R 13 + isobutane and R 13 + *n*-butane at three temperatures, 310.93, 350.00, and 400.00 K. The vapor pressures of the pure butanes were measured at these temperatures, and the results are given in Table I. There we show the measurements with each pressure gauge and, for comparison, the correlations of Goodwin and Haynes (*15*, *16*). Also shown for *n*-butane is a recently published vapor pressure curve by Holldorff and Knapp (*17*) based on their own measurements. We see that the agreement is very good and substantiates our claim of ±0.03 bar accuracy in pressure measurements.

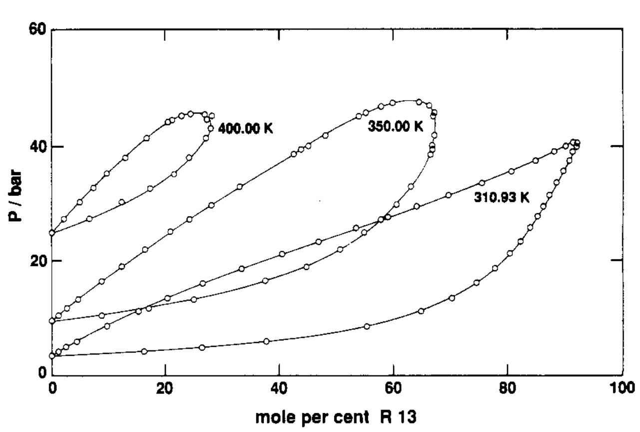

Figure 1. Phase compositions for the system R 13 + *n*-butane.

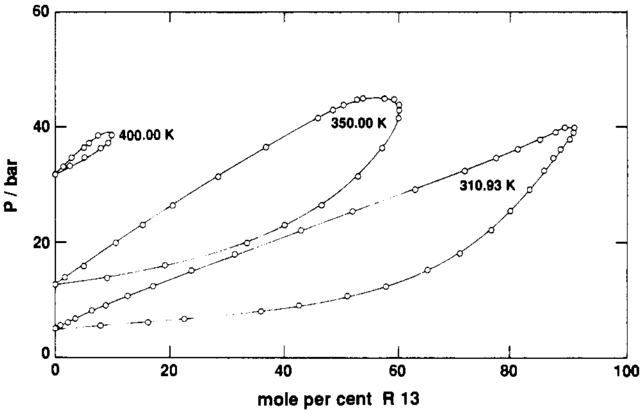

Figure 2. Phase compositions for the system R 13 + isobutane.

Table III. Experimental Results for the R 13 (1) + Isobutane (2) System

P/bar	$100x_1$	$100y_1$	P/bar	$100x_1$	$100y_1$
		T = 310.93 K			
5.47	0.96	7.91	22.14	43.24	77.10
6.04	2.20	16.33	25.28	52.24	80.51
6.61	3.47	22.56	29.15	63.30	83.98
7.99	6.48	36.16	32.38	71.98	86.55
9.03	8.82	42.83	34.47	77.47	88.24
10.63	12.62	51.39	36.08	81.24	89.45
12.44	17.04	58.29	37.73	85.01	90.99
15.13	23.96	65.73	39.03	87.81	91.63
18.03	31.59	71.39	39.76	89.36	91.89
		T = 350.00 K			
14.00	1.95	9.41	36.52	37.43	58.99
16.04	5.16	19.62	41.62	46.58	62.19
19.91	10.88	34.18	45.01	54.60	60.38
23.07	15.65	41.01	44.84	53.54	61.91
26.47	20.84	47.69	43.92	51.14	62.54
31.52	29.02	54.43	42.94	49.08	62.58
		T = 400.00 K			
33.05	1.34	2.55	36.23	5.01	8.04
37.05	5.93	9.44	38.30	7.52	10.03
34.45	2.89	5.23			

The pressure versus phase composition results for R 13 + *n*-butane are given in Table II and illustrated in Figure 1. The results for R 13 + isobutane are given in Table III and Figure 2. The isotherm at 310.93 K was included to allow direct comparison with the behavior of carbon dioxide with the butanes, given in ref *13*. Although CO_2 and R 13 have nearly the same critical temperature, the critical pressure of CO_2 is almost twice that of R 13. Thus there is a greatly increased volatility difference with the butanes. Comparison of the P–x behavior of the two systems with CO_2 and with R 13 as solute show that the dew-point curves are almost identical up to a pressure of around 30 bar and a solute mole fraction of about 0.9. The bubble-point curves, however, are quite different with the solubility of R 13 being about twice that of CO_2 in butane for a given pressure.

The data were correlated successfully with the standard Peng–Robinson equation of state (*20*), using a computer program provided by Ely (*21*). A value of 0.075 was used for the binary interaction parameter k_{ij} for the system R 13 + *n*-butane, and a value of 0.065 was used for R 13 + isobutane. No attempt was made to include a temperature dependence for the *k*'s, nor did one appear to be needed. The dew-point curves were fit with a deviation less than 0.02 in mole fraction, and often within 0.01. The bubble-point curves were generally fit to within 0.01. The fits did not deteriorate appreciably in the critical regions.

Henry's Constant

Solubilities of gases in liquids are often described in terms of Henry's constant. Recently Japas and Levelt Sengers (*18*) have derived exact relations for the value of Henry's constant and its temperature dependence near the solvent's critical point. Since part of our data fall within this range, we have calculated Henry's constant for each of our isotherms and compared the behavior with that predicted by their model.

Japas and Levelt Sengers showed that Henry's constant may be expressed in the asymptotic form:

$$T \ln (H_{1,2}/f_2) = a + b(\rho_2 - \rho_{2,c}) \qquad (1)$$

where $H_{1,2}$ is the Henry's constant of the solute, component 1 (R 13), in the solvent, component 2 (butane), f_2 is the fugacity of pure solvent 2, ρ_2 is the value of the density of pure saturated liquid 2, and $\rho_{2,c}$ is its critical density. Thus *H* is finite at the solvent's critical point, but its temperature derivative diverges as the slope of the density of the saturated liquid solvent, i.e., as $(T_c - T)^{\beta-1}$, with $\beta \approx 0.33$. They derive the value of *b* to be

$$b = \frac{1}{R\rho_{2,c}^{\,2}}\{(\mathrm{d}P/\mathrm{d}x)_{\mathrm{CRL}}^{\mathrm{c}} - (\mathrm{d}P/\mathrm{d}T)_{\sigma}^{\mathrm{c}}(\mathrm{d}T/\mathrm{d}x)_{\mathrm{CRL}}^{\mathrm{c}}\} \qquad (2)$$

The derivatives labeled CRL are the initial slopes of the critical line (at infinite dilution), and the derivative labeled σ is the slope of the solvent's vapor pressure at its critical point. They also derived an expression for the *K* factor ($K_1 = y_1/x_1$) at infinite dilution:

$$T \ln K_1^{\infty} = 2b(\rho_2 - \rho_{2,c}) \qquad (3)$$

Thus we see that K^{∞} approaches a value of 1 at the critical point with a slope twice that of the Henry's constant.

We chose to evaluate the last expression first since *K* can be derived more directly from the experimental measurements. In practice, for dilute solutions, we found it preferable to use the relationship (*19*)

$$K_1^{\infty} = (\mathrm{d}y_1/\mathrm{d}x_1)^{\infty} = 1 + (\Delta Z_2/P_2^{\sigma})(\mathrm{d}P/\mathrm{d}x_1)_T^{\infty} \qquad (4)$$

since the pressure measurements are more precise than vapor composition in this region; ΔZ_2 is the compressibility factor difference between pure vapor and liquid solvent. The results are illustrated in Figure 3, where the densities were taken from ref *15* and *16*. We see that the linear relationship predicted by eq 3 is obeyed very well and that the systems with *n*-butane and with isobutane have somewhat different slopes, 2.59 and 2.21 K m^3/kg, respectively.

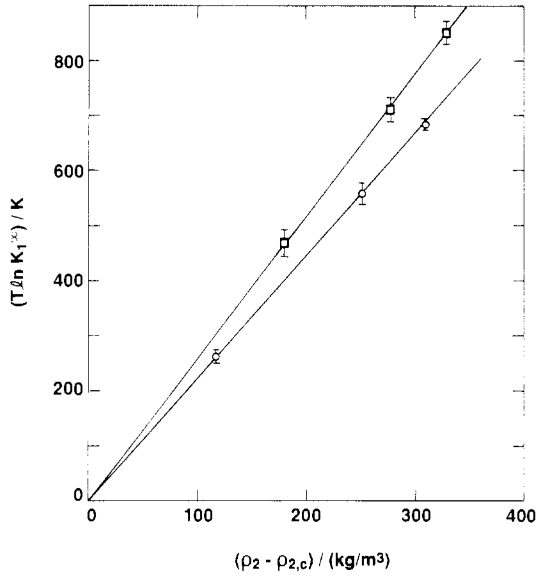

Figure 3. *K* factor at infinite dilution plotted against the density of the pure saturated liquid solvent ρ_2 (□, *n*-butane; ○, isobutane).

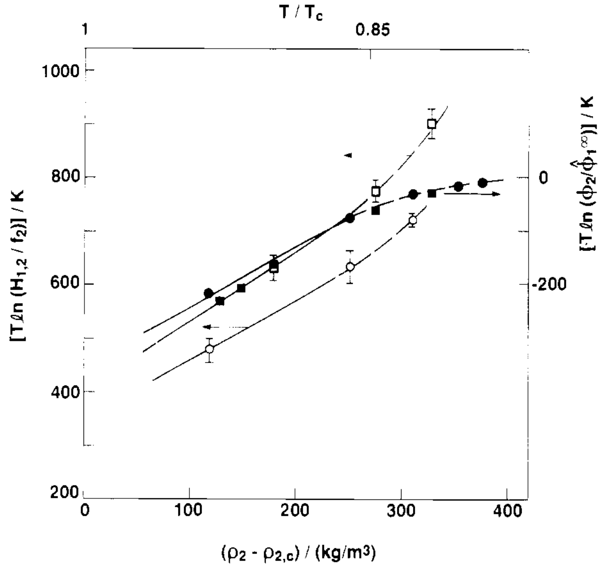

Figure 4. Henry's constant $H_{1,2}$ and fugacity coefficients plotted against ρ_2, the density of the pure saturated liquid solvent (□ and ■, *n*-butane; ○ and ●, isobutane). Filled symbols refer to the fugacity coefficients.

Henry's constant may be found from *K* via

$$H_{1,2}/f_2 = K_1^{\infty}(\hat{\phi}_1^{\infty}/\phi_2) \qquad (5)$$

where the fugacity coefficients are for the infinitely dilute solute in the vapor phase ($\hat{\phi}_1^{\infty}$) and for the pure solvent (ϕ_2). These coefficients were calculated by means of the Peng–Robinson equation of state with the binary interaction coefficients mentioned earlier. From eq 1 and 5 we see that if the slope of $T \ln K_1^{\infty}$ versus $(\rho_2 - \rho_{2,c})$ is $2b$, then the slopes of $T \ln (H_{1,2}/f_2)$ and of $(T \ln \phi_2/\hat{\phi}_1^{\infty})$ versus $(\rho_2 - \rho_{2,c})$ should each be equal to *b*. The results are shown in Figure 4. In this figure we see that the limiting linear relationship, indicated by the solid lines in the figure, breaks down below a reduced temperature of about 0.85 for these systems. Within the applicable region, however, the fugacity coefficient functions, calculated via the Peng–Robinson equation, exhibit slopes equal to approximately one-half the corresponding slopes in Figure 3 for K_1^{∞}. It fol-

Table IV. Experimental Values of Henry's Constant, $H_{1,2}$ (Solute 1 in Solvent 2) and Calculated Fugacity Coefficients

T/K	$H_{1,2}$/bar	$\hat{\phi}_1^\infty$	ϕ_2
	R 13 (1) + n-Butane (2)		
310.93	54.8	0.994	0.908
350.00	72.0	1.002	0.837
400.00	87.7	1.092	0.725
	R 13 (1) + Isobutane (2)		
310.93	44.7	0.987	0.881
350.00	61.9	0.996	0.802
400.00	71.1	1.164	0.677

lows then that the Henry's constant functions also have slopes equal to their respective values of b (1.30 and 1.10 K m^3/kg) in agreement with the model. It is interesting to note that the linear relationship for K_1^∞ in Figure 3 continues to hold at least down to a reduced temperature of 0.72.

The remaining task involves the evaluation of b from the initial slopes of the critical lines in eq 2. This was done by estimating the pressures and compositions at the critical points in Figures 1 and 2. These data along with the critical points of the pure components were treated with several fitting and interpolation techniques to estimate the limiting slopes. The values of b obtained were 1.24 K m^3/kg for R 13 + n-butane and 1.17 K m^3/kg for R 13 + isobutane, with estimated uncertainties of about 6–8%. We feel that the agreement is remarkably good and that these results help substantiate the work of Japas and Levelt Sengers. The values of Henry's constant are given in Table IV along with the calculated values of the fugacity coefficients.

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Registry No. R 13, 75-72-9; butane, 106-97-8; isobutane, 75-28-5.

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Densities and Viscosities of Binary Mixtures of 1-Propanol and 2-Propanol with Acetonitrile

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Densities and viscosities of binary liquid mixtures of acetonitrile with 1-propanol and 2-propanol have been measured at 20, 30, 40, and 50 °C. The calculated excess volumes are positive over the whole range of composition in both systems. The behavior of V^E is discussed considering physical, chemical, and structural effects. Viscosities have also been determined for both systems and analyzed by means of the Batschinski–Hildebrand and McAllister equations. The trends of viscosities are discussed in terms of the free energy, the enthalpy, and the entropy of activation of the viscous flow.

Introduction

Mixtures containing acetonitrile and alcohols have not been sufficiently studied. We report here density and viscosity data for acetonitrile (AN) + 1-propanol (1-PrOH) and AN + 2-propanol (2-PrOH) over the entire mole fraction range at four temperatures: 20, 30, 40, and 50 °C. Recent information about viscosities of these mixtures is scarce in the literature. Viscosities of AN + 2-PrOH were studied by Katz et al. at 50 °C (*1*). Previously Mato and Coca published viscosity measurements in both systems at 25, 35, and 45 °C (*2*). On the other hand, there is enough information about the excess volumes or densities of these mixtures between 25 and 35 °C (*3–5*).

Experimental Section

All organic chemicals used in the study were reagent grade. 1-PrOH and 2-PrOH (BDH, AnalaR grade, 99.5% purity) were dried by refluxing over CaO, distilling, and finally passing through 3-Å molecular sieves. AN (Aldrich, HPLC, 99.9% purity) was only dried with 3-Å molecular sieves. Water contents were checked by Karl Fischer titration. In all cases the water contents in the liquids used were not greater than 0.05% (v/v).

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