parameters, Z_{RA}, and the resulting average deviations of the calculated densities are given in Table V. Critical parameters were taken from Reid, Sherwood, and Prausnitz (*13*). Those not given in ref *13* were calculated by using Lydersen's method. Note that a reduction of p_c for methyl bromide from 83.4 to 75 atm results in a marked improvement in the fit. The 83.4 atm value is calculated from Lydersen's method. There appears to be no experimental vapor pressure data upon which to base a better estimate of the critical pressure. Published values of the vapor pressure of methyl bromide above the normal boiling temperature appear to have been obtained by extrapolation of the low-temperature data of Egan and Kemp (*14*).

The density of 1-chlorobutane at 25 °C was found to be slightly high (+0.21%) relative to the results of other workers (*11*). This can be accounted for by the presence of 0.6–0.7% of dichlorobutanes in the sample.

Materials

Ethyl chloride and methyl bromide purchased from the Matheson Co. were stated to have purities of 99.7 and 99.5%, respectively. 1-Chloropropane, 1-chlorobutane, and 1-bromopropane were purchased from MCB Manufacturing Chemists. Ethyl bromide from Fisher Scientific Co. was purified by liquid-phase thermal diffusion. A gas chromatographic analysis of 1-choropropane showed that it contained 0.4% 2-chloropropane and no other detectable impurities. A similar analysis of 1-bromopropane indicated that the sample was 99.6% 1-bromopropane. There were no detectable impurities in the purified ethyl bromide sample (sensitivity: 0.01 area %).

Registry No. 1-Chloropropane, 540-54-5; 1-chlorobutane, 109-69-3; methyl bromide, 74-83-9; ethyl bromide, 74-96-4; 1-bromopropane, 106-94-5.

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Isobaric Vapor–Liquid Equilibrium of 2,2,2-Trifluoroethanol with Water and 1-Propanol Binary Systems

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Liquid–vapor equilibrium data of two binary systems containing 2,2,2-trifluoroethanol with water and 1-propanol are reported. The results are correlated by Van Laar, Wilson, and NRTL equations. The excess Gibbs energies of the two binary systems are compared to those of ethanol with the same components.

Introduction

Organic fluorocarbons and their water mixtures have been identified and proposed for use in Rankine engines for various terrestrial and space applications (*1*).

Among those, pure trifluoroethanol, commercially called fluorinol, and its water mixtures, have been selected and subjected to extensive dynamic testing for thermal stability (*2*). Unfortunately, thermodynamical properties and liquid–vapor equilibrium data for trifluoroethanol and its water mixtures are scarce.

Table I. Physical Properties of Compounds[a]

	water	fluorinol	1-propanol
T_{nb}, °C	100	73.94^c	97.30^c
A	7.9668	6.84069^d	7.9973^b
B	1668.21	952.466^d	1569.70^b
C	228.00	166.587^d	209.50^b
N_D	1.3333	$<1.3000^c$	1.3850^c
v_{25}	18.00	72.25^c	74.75^c

[a] A, B, and C are the Antoine constants of $\log P = A - B/(C + t)$, P in Torr, t in °C. v_{25} is the molar volume in cm^3/mol at 25 °C. [b] Reference *4*. [c] This work. [d] Reference *3*.

The development of prediction methods such ASOG or UNIFAC requires data on some representative binary systems. In this paper isobaric liquid–vapor equilibrium data of two binary systems, trifluoroethanol and water and 1-propanol, are reported. The data are correlated by the Van Laar, Wilson, and NRTL equations.

Experimental Section

Purity of Materials. All chemicals are commercially available. The trifluoroethanol was employed without further purification after gas chromatographic analysis failed to show any significant impurities. The other components were distilled twice. The propanol was dried on molecular sieve 3 Å. The main physical properties of the three components are shown in Table I.

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Table II. Liquid-Vapor Equilibrium Experimental Results for the Water (1)-2,2,2-Trifluoroethanol (2) System at 760 Torr

t, °C	x_1	y_1	t, °C	x_1	y_1
74.68	0.1076	0.0776	79.22	0.6209	0.3813
75.56	0.2242	0.1664	79.63	0.6859	0.3905
75.66	0.2524	0.1859	79.96	0.7074	0.4101
76.37	0.3168	0.2285	80.01	0.7170	0.4114
77.02	0.3978	0.2761	80.33	0.7517	0.4213
77.16	0.4377	0.2917	80.67	0.7834	0.4300
77.72	0.4705	0.3145	80.81	0.8306	0.4323
78.31	0.5315	0.3424	81.23	0.8366	0.4371
78.72	0.5983	0.3656	81.48	0.8509	0.4438

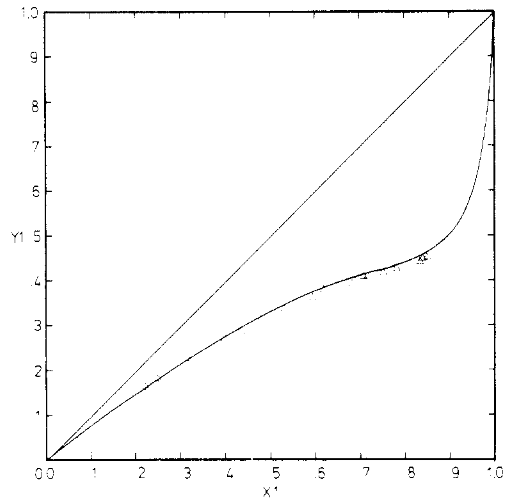

Figure 1. X–Y diagram at 760 Torr for the water–fluorinol system: Δ, experimental; —, NRTL.

Liquid–Vapor Equilibrium Measurements. The liquid–vapor equilibrium properties were determined by using an isobaric stage still from Fisher Co. In this recirculating still, a mixture is boiled to produce a stream of liquid and vapor, in intimate contact. This liquid–vapor mixture, pumped by a Cotrell pump, flows over the thermometer well. The liquid and the vapor totally condensed (the condensate) are returned via two hold-up traps directly to the boiler.

The still is operated until a steady state is reached at which the boiling temperature is constant. In this state, samples of the liquid and the condensate are taken for analysis. The temperature is measured with a Pt thermometer (accuracy of 0.05 °C) and the pressure with a mercury manometer (accuracy of 0.05 Torr).

Analysis. For the two binary systems, the compositions of the liquid and vapor phases are obtained by chromatographic analysis on a Perkin-Elmer 990 gas chromatograph; the stationary phase, in each case, is Hyprose SP80. For the propanol–fluorinol mixtures, the analysis is also performed by refractive index measurements. The difference between the two methods does not exceed 0.001 in molar composition.

Measurements of refractive index of well-known composition propanol–fluorinol solutions give a calibration curve the equation of which is

$$x_1 = -97.7068 + 173.447n_D - 102.374n_D^2 + 20.649n_D^3 \quad (1)$$

(component 1 is always the first cited).

Results

The experimental liquid–vapor equilibrium results at 760 Torr are given in Table II and III and in Figures 1 and 2.

Table III. Liquid-Vapor Equilibrium Results for the 1-Propanol (1)-2,2,2-Trifluoroethanol (2) System at 760 Torr

t, °C	x_1	y_1	t, °C	x_1	y_1
75.12	0.0562	0.0127	94.16	0.7507	0.6386
75.91	0.0936	0.0228	94.90	0.7924	0.7064
76.85	0.1333	0.0361	95.24	0.8132	0.7356
79.03	0.2130	0.0711	95.58	0.8357	0.7976
80.50	0.2703	0.0982	95.95	0.8612	0.8171
82.03	0.3192	0.1341	96.20	0.8862	0.8503
83.39	0.3586	0.1630	96.40	0.9015	0.8719
85.49	0.4315	0.2229	96.55	0.9175	0.8949
88.29	0.5242	0.3208	96.68	0.9375	0.9208
90.20	0.5869	0.4011	96.76	0.9522	0.9397
91.61	0.6428	0.4774	96.85	0.9664	0.9587
93.08	0.7059	0.5679	96.87	0.9771	0.9671

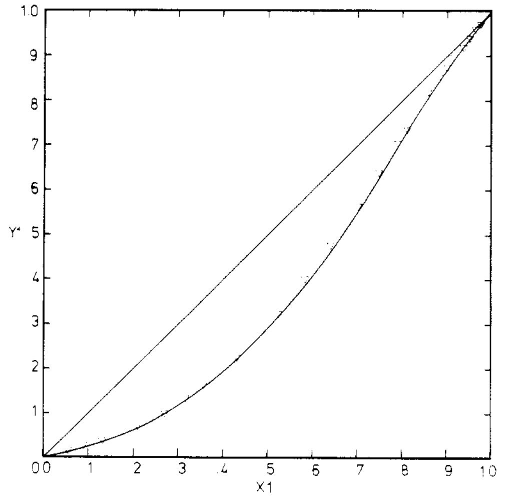

Figure 2. X–Y diagram at 760 Torr for the propanol–fluorinol system: Δ, experimental; — NRTL.

The results are fitted by three solution models, Van Laar, Wilson, and NRTL relations.

The activity coefficients relation are

for Van Laar:

$$\ln \gamma_1 = \frac{A}{\left(1 + \frac{Ax_1}{Bx_2}\right)^2} \quad (2)$$

$$\ln \gamma_2 = \frac{B}{\left(1 + \frac{Bx_2}{Ax_1}\right)^2} \quad (3)$$

for Wilson:

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2}\right) \quad (4)$$

$$\ln \gamma_2 = -\ln (x_2 + x_1\Lambda_{21}) - x_1\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2}\right) \quad (5)$$

where

$$\Lambda_{12} = \frac{v_2}{v_1} \exp\left[-\left(\frac{\lambda_{12} - \lambda_{11}}{RT}\right)\right] \quad (6)$$

$$\Lambda_{21} = \frac{v_1}{v_2}\exp\left[-\left(\frac{\lambda_{12} - \lambda_{22}}{RT}\right)\right] \qquad (7)$$

for NRTL relations:

$$\ln \gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right] \qquad (8)$$

$$\ln \gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right] \qquad (9)$$

where

$$G_{12} = \exp\left(-\alpha_{12}\frac{C_{12}}{RT}\right) \qquad (10)$$

$$G_{21} = \exp\left(-\alpha_{12}\frac{C_{21}}{RT}\right) \qquad (11)$$

$$\tau_{12} = C_{12}/RT \qquad (12)$$

$$\tau_{21} = C_{21}/RT \qquad (13)$$

The model parameters are for Van Laar relations A, B; for Wilson equations, $\lambda_{12} - \lambda_{11}$, $\lambda_{12} - \lambda_{22}$; and for the NRTL relations, the parameters are temperature dependent:

$$C_{12} = C_{12}^0 + C_{12}^t t \qquad (14)$$

$$C_{21} = C_{21}^0 + C_{21}^t t \qquad (15)$$

$$\alpha_{12} = \alpha_{12}^0 + \alpha_{12}^t t \qquad (16)$$

There are two parameters for Van Laar and Wilson models and six for the NRTL one. They are obtained by a grid research of the minimum of the objective function (OF), defined by

$$\mathrm{OF} = \frac{1}{n}\sum\left[\left|\frac{p_e - p_c}{p_e}\right| + W_y\left|\frac{y_e - y_c}{y_e}\right|\right] \qquad (17)$$

where n is the number of experimental results (Table IV).

In the liquid-vapor equilibrium experiments, the vapor composition is generally known with less accuracy. Thus, the weight of the vapor composition in the objective function must be reduced by introducing a factor W_y less than unity. The chosen value of W_y is 0.5 as a result of our own analysis of the pressure and vapor composition measurement accuracies.

Discussion

The excess Gibbs energies, calculated from Wilson relations, of trifluoroethanol and ethanol (*6*, *7*) aqueous solutions are shown in Figure 3. The quasi-similarity of the two curves a and b supposes a similar behavior of these two systems. The slightly higher values of the excess Gibbs energies for the fluoroalcohol suggest that the liquid fluoroalcohol contains a higher proportion of non-hydrogen-bonded hydroxyl groups than the hydrocarbon alcohol. That conclusion is confirmed by the values of the standard enthalpies of transfer from the pure liquid state to the aqueous solution at infinite solution, −1.81 kcal/mol for the trifluoroethanol and −2.41 kcal/mol (*8*, *9*) for the ethanol.

No strong interactions and no association between trifluoroethanol and water molecules are observed in the temperature and pressures ranges of liquid–vapor equilibrium experiments. The good stability of trifluoroethanol and its water mixtures recommends their use as thermal fluid in Rankine engines.

Table IV. Model Parameters[a]

	water–TFE	propanol–TFE
	Van Laar	
A	0.793	-0.569
B	2.226	-0.607
(OF), %	0.9	0.3
	Wilson	
$\lambda_{12} - \lambda_{11}$	871.5	-293.4
$\lambda_{12} - \lambda_{22}$	2155.8	-101.1
(OF), %	1.9	0.4
	NRTL	
C_{12}^0	1463.4	269.5
C_{21}^0	-400.8	-661.3
α_{12}^0	0.342	0.254
C_{12}^t	4.081	0.338
C_{21}^t	1.691	0.068
α_{12}^t	0.000	-0.001
(OF), %	0.6	0.7

[a] All energy parameters are given in cal/mol. In all calculations, the gaseous phase is perfect.

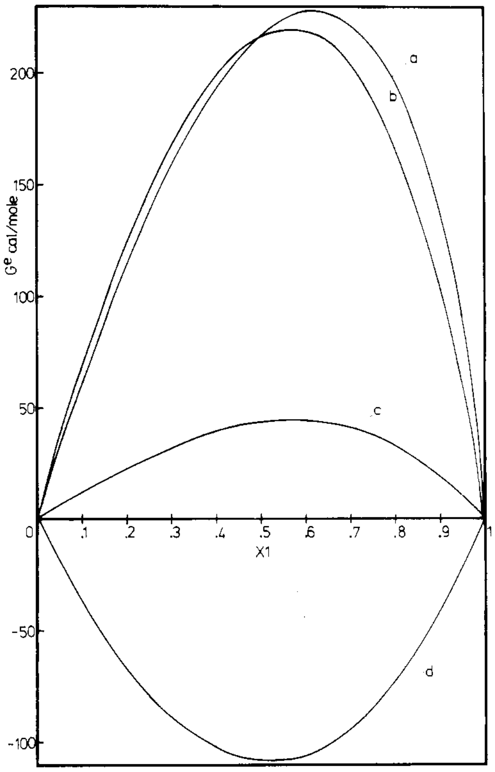

Figure 3. Excess Gibbs energies at 300 K from Wilson relations: (a) water–fluorinol; (b) water–ethanol; (c) propanol–ethanol; (d) propanol–fluorinol.

On Figure 3 are also represented the excess Gibbs energies (also from Wilson relations) of trifluoroethanol (curse d) and ethanol (curse c) mixtures with propanol. The propanol–ethanol system is a quasi-ideal solution; the average deviation from nonideality is only about 15%. The propanol–fluorinol mixtures show negative deviations from Raoult's law, pointing to strong interactions between the two molecules. This is confirmed by negative values of two Wilson parameters, activity coefficients less than unity, and an exothermic heat of mixing (*10*). The substitution of hydrogen atoms by fluorine is the main reason. The interaction between the fluoromethyl group, $-CF_3$, and the hydroxyl group is thus greater than that between the methyl group, CH_3, and the hydroxyl.

Glossary

n_D	refractive index at 20 °C
P	pressure, Torr
t	temperature, °C
T	temperature, K
v	molar volume of liquid

x	liquid mole fraction
y	vapor mole fraction

Subscripts

1, 2	component 1 or 2
e, c	experimental or calculated

Registry No. 2,2,2-Trifluoroethanol, 75-89-8; 1-propanol, 71-23-8.

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Solubilities of Solid *n*-Nonacosane and *n*-Tritriacontane in Supercritical Ethane

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The solubilities of solid *n*-nonacosane (n-$C_{29}H_{60}$) and *n*-tritriacontane (n-$C_{33}H_{68}$) in supercritical ethane at temperatures between 308.1 and 318.1 K and pressures up to 20 MPa have been measured and are reported in this paper. The results complement our previous results for the solubilities of *n*-octacosane (n-$C_{28}H_{58}$), *n*-triacontane (n-$C_{30}H_{62}$), and *n*-dotriacontane (n-$C_{32}H_{66}$) in ethane.

Introduction

As outlined elsewhere (*1*) odd-numbered *n*-alkanes exhibit different trends in their solid-state properties than even-numbered members of the *n*-alkane series. It may therefore be attractive to exploit these differences to separate close-boiling members of the series using supercritical fluids.

We have studied the solubilities of five solid *n*-alkanes having 28–33 carbon atoms in supercritical ethane, near the critical point of ethane. The solubilities of *n*-nonacosane (n-$C_{29}H_{60}$) and *n*-tritriacontane (n-$C_{33}H_{68}$) in supercritical ethane are reported here. The solubilities of even-numbered *n*-alkanes (n-$C_{28}H_{58}$, n-$C_{30}H_{62}$, n-$C_{32}H_{64}$) in ethane were reported in an earlier publication (*1*).

Experimental Section

The apparatus and experimental procedure have been described in detail elsewhere (*1*). The apparatus is a single-pass flow system of the type used by Kurnik et al (*2*), McHugh and Paulaitis (*3*), and Adachi et al. (*4*), with the solubilities of the solid determined gravimetrically.

Ethane was first liquefied and then compressed to the desired pressure by means of a Milton Roy minipump. Its temperature was increased to the desired value in a heat exchange coil immersed in a constant temperature bath. The temperature in the bath was maintained constant within ±0.1 K. The supercritical fluid was then brought into contact with the solid solute in a high-pressure view cell which was also immersed in the constant temperature bath. Layers of glass beads were packed with the solute in the equilibrium cell to increase contact between the supercritical ethane and the solid solute. The loaded supercritical fluid was then depressurized by using a micrometering valve and the deposited solute was collected in a separation vessel. The temperature in the equilibrium cell was measured with a copper-constantan thermocouple calibrated against an NBS-certified platinum resistance thermometer, and the pressure was measured with a Heise gauge calibrated against a dead weight gauge. We estimate the precision of our temperature and pressure measurements to be ±0.1 K and ±0.05 MPa, respectively. The depressurized solvent volume was measured with an estimated precision of 0.5% by using a wet test meter. The accuracies were typically twice the values given above.

Table I. Experimental Solubilities ($y_2 \times 10^3$) of Solid *n*-Alkanes in Supercritical Ethane

	T = 308.1 K		T = 313.1 K	T = 318.1 K
P, MPa	q = 29	q = 33	q = 33	q = 33
6.47	2.32 ± 0.04	0.371 ± 0.01	0.228 ± 0.01	0.183 ± 0.01
10.20	4.32 ± 0.05	0.963 ± 0.01	1.15 ± 0.02	1.54 ± 0.01
12.12	8.29 ± 0.14	1.14 ± 0.01	1.47 ± 0.02	1.96 ± 0.02
13.64	9.91 ± 0.14	1.36 ± 0.02	1.72 ± 0.02	2.97 ± 0.04
16.67	14.2 ± 0.32	1.64 ± 0.02	2.24 ± 0.03	
20.20		2.37 ± 0.03	2.93 ± 0.05	

Source and Purity of the Materials

The solid *n*-nonacosane and *n*-tritriacontane were obtained from Wiley Organics and Fluka Chemical Corp. and had a stated purity of 99% and 97%, respectively. They were used without further purification. Ethane was furnished by the Matheson Gas Co. with a purity of 99+% and was also used without further purification.

The crystallinity of the solid samples was confirmed in two ways. First, a melting–freezing point check was carried out on a Thomas Hoover capillary apparatus. Both the melting and freezing of each hydrocarbon occurred at a single temperature which was within ±0.5 °C of the value reported by the supplier. In addition, one sample of each hydrocarbon was analyzed on a Philips θ-2θ X-ray diffractometer. Sharp peaks in the X-ray diffraction scans were noted in each case, confirming that the hydrocarbons were crystalline.

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