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Isobaric Vapor–Liquid Equilibrium of (Trifluoromethyl)benzene with Benzene, Toluene, or Chlorobenzene

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Vapor–liquid equilibrium data at 101.325 kPa of three binary systems containing (trifluoromethyl)benzene with benzene, toluene, or chlorobenzene are reported. The results are correlated using the Van Laar and Wilson equations.

Introduction

Organic fluorocarbons take more and more importance in many industrial applications. Some fluoroethanes are already proposed and tested for chlorofluorocarbon substitution (CFC ozone depleting) in refrigerating machines, in heat pumps, and in air conditioning systems. Some high molecular weight fluorinated or chlorinated derivatives are also investigated for use in Rankine engines for terrestrial and space applications (*1*).

The right fluid for a particular application must have many specified qualities, thermodynamic properties, toxicity, inflammability, oil compatibility, ..., so a pure component, of which all properties are fixed, has little or no chance to have these required qualities. Nevertheless, mixtures of two or more components give supplementary degrees of freedom in the choice, in order to improve the properties of the cycling fluid. The calculation of the mixture thermodynamic properties requires liquid–vapor equilibrium data.

For a rapid investigation of a great number of fluid mixtures, it is necessary to use prediction methods such as ASOG or UNIFAC. The exploitation of such models needs also a large range of vapor–liquid equilibrium (VLE) data.

The most often pointed out components as a thermal fluid are formed by a limited number of molecular groups, in the UNIFAC sense, such as alkyl, aryl, hydroxyl, fluoro, or chloro. In a previous paper, we have investigated mixtures of fluoroalcohols and alcohols (*2*). In the present work, isobaric VLE data of three binary systems, (trifluoromethyl)benzene + benzene, + toluene, or + chlorobenzene, are reported. The data are correlated using the Van Laar and Wilson equations.

Experimental Section

Materials. All the chemicals were commercially available (from Merck) and were dried on molecular sieves before use. Their gas chromatographic analysis failed to show any impurities. The measured physical properties of (trifluoromethyl)benzene are listed in Table I together with literature data. The vapor pressure of (trifluoromethyl)benzene was measured by the isotenoscopic method as a function of T and correlated using the Antoine equation:

$$\log (P/\text{kPa}) = A - B/[C + (T/\text{K})] \tag{1}$$

The direct experimental values and the coefficients A, B, and C are given in Table II. The properties of the remaining chemicals are taken from the literature (*3–6*).

Apparatus and Procedure. The VLE properties were determined by means of an isobaric stage still from Fisher Co. In this recirculating still, a mixture is boiled to produce a liquid and vapor steam, in intimate contact. This liquid–vapor mixture, pumped by a Cotrell pump, flows over the thermometer well. The liquid and the totally condensed vapor (the condensate) are returned via two holdup traps directly to the boiler.

Table I. Physical Properties of (Trifluoromethyl)benzene: Normal Boiling Temperature, T_b, Refractive Index, $n(D,$ 293.15 K), and Molar Volume, v/(cm^3 mol^{-1})

T_b/K	$n(D$, 293.15 K)	v(298.15 K)/(cm^3 mol^{-1})
375.19^a	1.4115^a	123.00^a
375.20 (*7*)	1.41225 (*7*)	123.69 (*7*)

^{a} This work.

The still was operated until a steady state was reached at which the boiling temperature is constant. In this state, the liquid and condensate samples were taken for analysis.

The temperature T was measured with a Pt thermometer (accuracy of 0.05 K) and the pressure P with a mercury manometer (accuracy of about 10 Pa).

The atmospheric pressure was corrected to P = 101.325 kPa by supposing the activity coefficients independent of the pressure.

Analysis. For the three binary systems, the liquid and vapor (the condensate) mole fraction compositions were determined, by refractive index measurements and by chromatographic analysis on a Perkin-Elmer 990 gas chromatograph with Hyprose 80 as the stationary phase. If the difference between the compositions given by the two methods of analysis was larger than 0.001, the measurement was repeated.

Results

The experimental VLE data at 101.325 kPa are given in Table III and Figures 1–3.

The results were fitted by two activity coefficient models, Van Laar and Wilson. The Redlich–Kwong equation of state was used to calculate the vapor-phase fugacity coefficients.

The model parameters, A and B for Van Laar and $\lambda_{12} - \lambda_{11}$ and $\lambda_{12} - \lambda_{22}$ for Wilson, defined as in ref 2 were considered independent of the temperature.

The model parameters are obtained by a grid research (*7*) of the minimum of the objective function OF, defined by

$$\mathrm{OF} = \frac{100}{n} \sum \left[\left| \frac{P_{\mathrm{exp}} - P_{\mathrm{calc}}}{P_{\mathrm{exp}}} \right| + W_y \left| \frac{y_{\mathrm{exp}} - y_{\mathrm{calc}}}{y_{\mathrm{exp}}} \right| \right] \tag{2}$$

where n is the number of experimental results.

Effectively, for experimental values of temperatures and liquid-phase mole fractions, the pressures and vapor-phase mole fraction were calculated by using equilibrium relations in which the activity coefficients are given by Van Laar and/or Wilson equations, and then compared with experimental data in eq 2.

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Table II. Vapor Pressure of (Trifluoromethyl)benzene from the Isoteniscopic Method and Antoine Coefficients of Equation 1 (A = 6.09539, B = 1306.3521, and C = −55.769)

T/K	323.36	336.39	344.73	355.18	362.71	368.18	374.35	375.81	384.00
P/kPa	16.34	27.58	37.56	54.01	69.20	81.68	98.94	103.25	130.02

Table III. VLE Results, Temperature T, Liquid Mole Fraction x_1, and Vapor Mole Fraction y_1, for the Solvent + (Trifluoromethyl)benzene Systems at 101.325 kPa and Values of Model Parameters, OF Values (%), Equation 2, and ΔT and Δy, Equations 3 and 4

benzene (1) + (trifluoromethyl)benzene (2)			(trifluoromethyl)benzene (1) + toluene (2)			(trifluoromethyl)benzene (1) + chlorobenzene (2)		
T/K	x_1	y_1	T/K	x_1	y_1	T/K	x_1	y_1
375.19	0.0	0.0	383.77	0.0	0.0	404.87	0.0	0.0
373.91	0.0350	0.0745	383.40	0.0288	0.0445	400.48	0.0757	0.1888
372.80	0.0648	0.1236	382.81	0.0544	0.0807	400.03	0.0867	0.2120
371.90	0.0920	0.1778	383.14	0.0902	0.1285	398.97	0.1039	0.2464
370.61	0.1310	0.2578	381.42	0.1550	0.2118	396.82	0.1401	0.3122
369.23	0.1779	0.3050	380.54	0.2296	0.2917	395.35	0.1670	0.3520
365.82	0.2875	0.4520	379.62	0.3158	0.3810	394.68	0.1940	0.3949
363.44	0.3950	0.5685	379.18	0.3562	0.4233	393.68	0.2205	0.4288
362.56	0.4290	0.6092	378.77	0.3986	0.4666	392.94	0.2403	0.4567
361.43	0.4869	0.6539	378.40	0.4405	0.5030	391.39	0.2812	0.5049
360.68	0.5292	0.6900	377.27	0.6011	0.6554	389.74	0.3393	0.5533
359.57	0.5901	0.7353	376.64	0.6964	0.7350	387.91	0.3969	0.6040
358.57	0.6455	0.7745	376.18	0.7779	0.8061	384.23	0.5327	0.7266
357.27	0.7099	0.8155	375.81	0.8491	0.8673	378.50	0.8356	0.9190
356.40	0.7640	0.8501	375.23	0.9612	0.9649	375.19	1.0	1.0
355.46	0.8323	0.8943	375.19	1.0	1.0			
354.73	0.8820	0.9226						
353.25	1.0	1.0						
Van Laar A = 0.125, B = 0.211			Van Laar A = 0.161, B = 0.134			Van Laar A = 0.536, B = 0.222		
Wilson $\lambda_{12} - \lambda_{11}$ = 36.6 J mol^{-1} $\lambda_{12} - \lambda_{22}$ = 134 J mol^{-1}			Wilson $\lambda_{12} - \lambda_{11}$ = 133 J mol^{-1} $\lambda_{12} - \lambda_{22}$ = 0.3 J mol^{-1}			Wilson $\lambda_{12} - \lambda_{11}$ = −346 J mol^{-1} $\lambda_{12} - \lambda_{22}$ = 622.2 J mol^{-1}		
OF = 0.94 ΔT = 0.4 K Δy = 0.004			OF = 0.20 ΔT = 0.2 K Δy = 0.002			OF = 0.87 ΔT = 0.3 K Δy = 0.003		

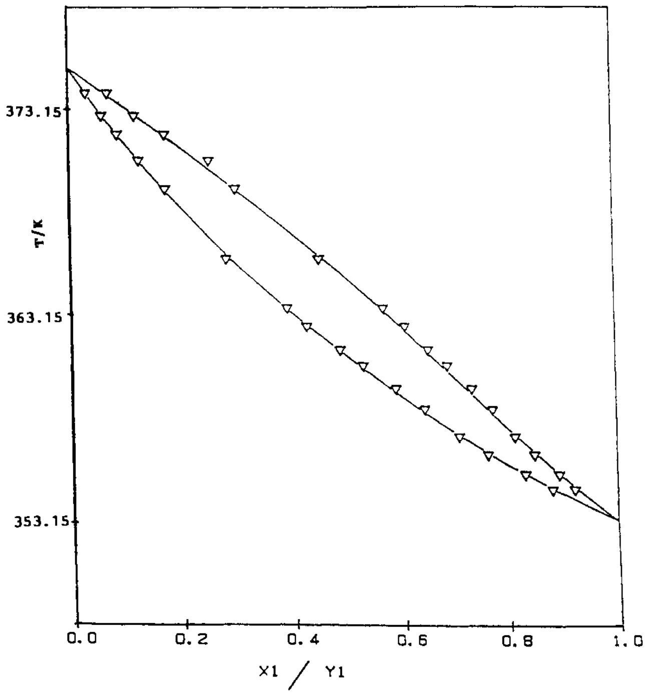

Figure 1. Boiling temperature T/K as a function of mole fraction, x_1 or y_1, of component 1 at 101.325 kPa for benzene (1) + (trifluoromethyl)benzene (2): △, experimental points; —, calculated using Wilson's equations.

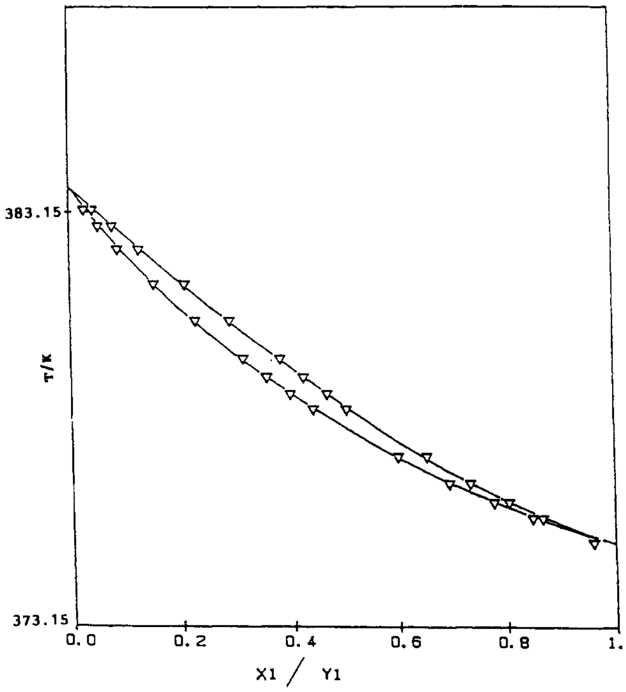

Figure 2. Boiling temperature T/K as a function of mole fraction, x_1 or y_1, of component 1 at 101.325 kPa for (trifluoromethyl)benzene (1) + toluene (2): △, experimental; —, calculated points using Wilson's equations.

In the VLE experiments, the vapor composition is generally determined with less accuracy. Thus, the statistical weight W_y of the vapor composition in the objective function was taken less than unity, W_y = 0.5, as a result of our analysis of the accuracies in pressure and vapor-phase composition. Nevertheless, this value of W_y is somewhat arbitrary.

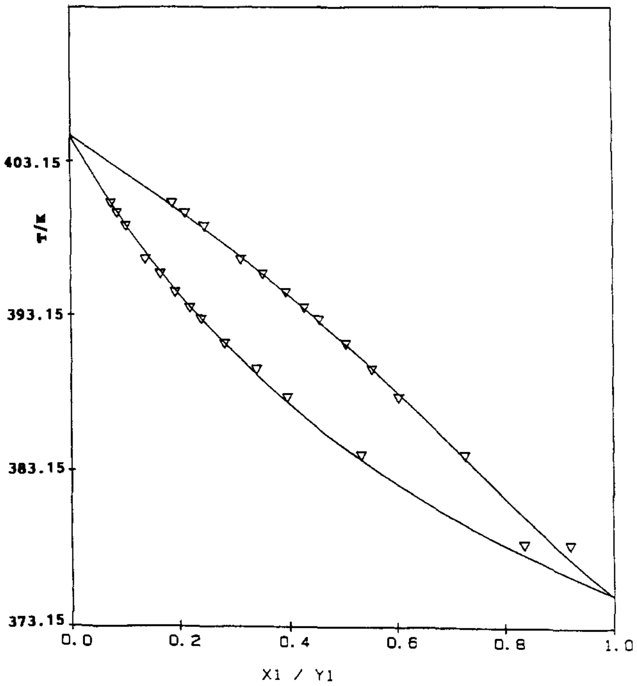

Figure 3. Boiling temperature T/K as a function of mole fraction, x_1 or y_1, of component 1 at 101.325 kPa for (trifluoromethyl)benzene (1) + chlorobenzene (2): △, experimental; —, calculated points using Wilson's equations.

In the same way, but at given experimental pressures and liquid-phase mole fractions, the mean absolute deviation in temperature T

$$\Delta T = \frac{1}{n}\sum |T_{\mathrm{exp}} - T_{\mathrm{calc}}| \qquad (3)$$

and in y_1

$$\Delta y_1 = \frac{1}{n}\sum |y_{1,\mathrm{exp}} - y_{1,\mathrm{calc}}| \qquad (4)$$

are determined.

The model parameters and the mean standard deviations are given in Table III.

Discussion

The molar excess Gibbs energies, G^E, estimated from the Wilson equation (Figure 4) show moderate positive deviations from ideality for the three binary systems, which justifies the use of simple models such as Van Laar or Wilson (H^E was assumed negligible).

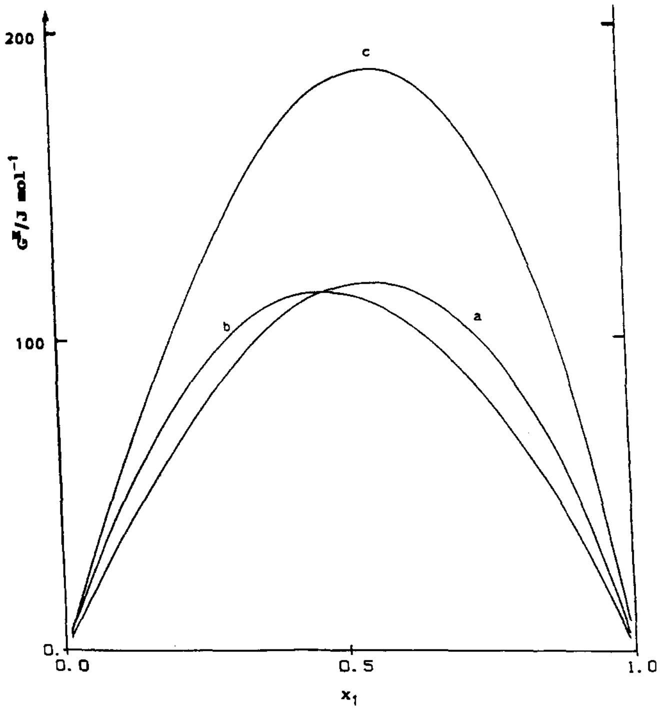

Figure 4. Excess molar Gibbs energies, G^E, at 373.15 K, calculated using Wilson's equation as a function of the mole fraction, x_1, of component 1: (a) (trifluoromethyl)benzene (1) + toluene (2); (b) benzene (1) + (trifluoromethyl)benzene (2); (c) (trifluoromethyl)benzene (1) + chlorobenzene (2).

Indeed, the activity coefficient of (trifluoromethyl)benzene at infinite dilution is 1.24 in benzene, 1.17 in toluene, and 1.71 in chlorobenzene.

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