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homologous series of ethane + 1-alkanol mixtures from carbon numbers 1 to 10.

In contrast, the volatilities of methanol and 1-decanol and its mixtures are less than that of 1-propanol or 1-butanol. Thus we do not see the pronounced maximum in the UCEP (*K* point) temperatures for the ternary mixtures that we saw with the homologous series of binary mixtures (*10*), also illustrated in Figure 5.

A "fold" in the LLV surface can be observed in Figures 1-4. This fold is associated with a pressure minimum. There is more than one three-phase state at a given temperature and pressure where the surface overlaps itself. Merrill et al. (*16*) mentioned that there was probably a (small) fold in the LLV surface of the system nitrogen + methane + *n*-butane. Recent studies by our group on carbon dioxide + ethane + *n*-tetradecylbenzene (*17*) and carbon dioxide + *n*-butylbenzene + *n*-eicosane (*5*) report more prominent LLV surface folds. Miller and Luks (*18*) mathematically analyzed these folds and drew general conclusions about species separability between the fluid phases present.

Figure 4 illustrates the shape of the envelope of consolute points at 295.15 K for the L_1 and L_2 phases, where a consolute point is the three-phase analogue of a two-phase saturation point. In L_2-dominant runs for initial methanol mole fraction loadings of the order of 0.977 or greater in our experiments, the ethane-rich phase (L_2) selectively extracted enough methanol from the L_1–solute mixture to make it difficult to obtain L_2 compositions or molar volumes in the region of the fold. These portions of the L_2 data are represented by dashed curves, which are meant to imply (only) their existence.

Glossary

AAD	average absolute deviation
K	denotes a *K* point (herein, the UCEP) where L-L=V
LCEP	lower critical end point, or L=L-V
L, L_1, L_2	liquid phases
L-L=V	a three-phase critical end point where the less dense L phase and the V phase are critically identical; also the UCEP (*K* point)
L=L-V	a three-phase critical end point where the two liquid phases are critically identical; also the LCEP
P	pressure
T	temperature
UCEP	upper critical end point, or L-L=V (herein, the *K* point)
v	molar volume of a phase
V	gas phase

Registry No. C_2H_6, 74-84-0; CH_3OH, 67-56-1; 1-decanol, 112-30-1.

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Vapor–Liquid Equilibria of the 1,1,1-Trichloroethane–1-Propanol System at 101.3-kPa Pressure

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The *T–x* data for 1,1,1-trichloroethane–1-propanol mixtures have been measured ebulliometrically at 101.3-kPa pressure. The system shows positive deviations from Raoult's law, forming a minimum boiling azeotrope. The vapor compositions have been predicted by using UNIQUAC and CLC models.

As part of a continuing study of the vapor liquid equilibria of alcohol–chlorohydrocarbon mixtures, the equilibrium temperature–composition data of 1,1,1-trichloroethane–1-propanol mixtures at 101.3-kPa pressure were measured in an all-glass ebulliometer.

Experimental Section

Purity of Chemicals. Reagent grade 1,1,1-trichloroethane, supplied by BDH Chemicals Ltd., Poole, England, and AnalaR grade 1-propanol, supplied by Renaal, Budapest, Hungary, were further purified by distilling in a laboratory packed column. The glass distillation column was of 4-cm diameter and 30-cm length and was packed with 0.4-cm-diameter and 0.7-cm-length hollow cylindrical glass packing. The fraction collected at the boiling point for each chemical was used in the study. The physical properties of the chemicals are listed in Table I, along with the literature (*1–4*) values for comparison.

Equilibrium Still. The equilibrium temperature–liquid composition data were measured in an all-glass Swietoslawski type ebulliometer of 120-cm^3 capacity that was standardized earlier by measuring the *T–x* data of the benzene–cyclohexane system at 101.3-kPa pressure and comparing the data with that reported in the literature (*5*).

The details of the experimental setup of the ebulliometer and its operation are described elsewhere (*6*, *7*). A solution of known composition was prepared by weighing on a precision

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Table I. Physical Properties of Chemicals

chemical	boiling point exptl	boiling point lit.	ref	constants in vapor pressure eq[a] A	B	C	ref
1,1,1-trichloroethane	74.0	73.90	1	6.94983	1217.00	225.00	3
1-propanol	97.1	97.15	2	7.74416	1437.686	198.463	4

[a] $\log P\ (\text{mmHg}) = A - B/(t + C)$.

Table II. Vapor–Liquid Equilibria of 1,1,1-Trichloroethane–1-Propanol at 101.3-kPa Pressure

temp, °C	x	y_{UNIQUAC}	y_{CLC}
97.1	0.000	0.0000	0.0000
91.2	0.051	0.2426	0.2440
88.5	0.082	0.3412	0.3420
87.0	0.101	0.3896	0.3900
81.2	0.206	0.5596	0.5590
80.0	0.237	0.5906	0.5900
79.4	0.258	0.6085	0.6080
78.2	0.307	0.6433	0.6420
76.3	0.412	0.6957	0.6950
75.1	0.521	0.7339	0.7330
74.6	0.554	0.7440	0.7440
74.4	0.582	0.7523	0.7520
74.0	0.637	0.7689	0.7690
73.6	0.705	0.7909	0.7910
73.3	0.782	0.8208	0.8210
73.2	0.801	0.8295	0.8300
73.1	0.918	0.9047	0.9040
73.5	0.956	0.9422	0.9420
74.0	1.000	1.0000	1.0000

electrical balance, which had an accuracy of ±0.0001 g. A 120-mL aliquot of this solution was charged into the boiling chamber. The liquid charge in the ebulliometer was at first slowly heated by switching on the external heater, and when the temperature of the liquid was reaching the boiling temperature, the internal heater was also switched on to maintain uniform boiling of the liquid. The stream of the partially vaporized mixture of liquid and vapor spurted through the Cottrel pump and impinged on the thermowell placed in the equilibrium chamber. Vapor leaving the equilibrium chamber condensed in the water-cooled condenser and returned to the boiling chamber, while the liquid from the equilibrium chamber also trickled down into the boiling chamber. The pressure in the system was maintained at 101.3 kPa by applying a slight positive pressure using nitrogen. When steady state was attained in about 1 h, the equilibrium temperature remained constant and the condition was maintained for 2 h before it was recorded. The pressure was measured with a mercury manometer. The equilibrium temperature was measured with a standard mercury-in-glass thermometer, having an accuracy of ±0.1 °C. The vapor holdup in the ebulliometer was neglected, and the equilibrium liquid composition was taken to be equal to the liquid composition of the charge as the ratio of vapor holdup to the total liquid in the ebulliometer was very small. The experimental T–x data are presented in Table II.

Data Correlation, Results, and Discussion

Estimation of Vapor Composition Using UNIQUAC and CLC Models. The equilibrium vapor composition from T–x data at 101.3-kPa pressure was predicted by using UNIQUAC and CLC models. An iterative nonlinear least-squares minimization procedure was employed with the objective function

$$F = \sum_{1}^{n} [1 - (y_{1,\text{cal}} + y_{2,\text{cal}})]^2 \qquad (1)$$

This procedure optimized parameters of the models while calculating the activity coefficients. The activity coefficients in each model are calculated using the equations given below.

UNIQUAC (*8*)

$$\ln \gamma_1 = \ln (\phi_1/x_1) + (Z/2)q_1 \ln (\theta_1/\phi_1) + \phi_2(l_1 - l_2 r_1/r_2) - q_1 \ln (\theta_1 + \theta_2\tau_{21}) + \theta_2 q_1[\tau_{21}/(\theta_1 + \theta_2\tau_{21}) - \tau_{12}/(\theta_2 + \theta_1\tau_{12})] \qquad (2)$$

$$\ln \gamma_2 = \ln (\phi_2/x_2) + (Z/2)q_2 \ln (\theta_2/\phi_2) + \phi_1(l_2 - l_1 r_2/r_1) - q_2 \ln (\theta_2 + \theta_1\tau_{12}) + \theta_1 q_2[\tau_{12}/(\theta_2 + \theta_1\tau_{12}) - \tau_{21}/(\theta_1 + \theta_2\tau_{21})] \qquad (3)$$

$$l_1 = (Z/2)(r_1 - q_1) - (r_1 - 1); \quad l_2 = (Z/2)(r_2 - q_2) - (r_2 - 1) \qquad (4)$$

$$\theta_1 = x_1q_1/(x_1q_1 + x_2q_2); \quad \theta_2 = x_2q_2/(x_1q_1 + x_2q_2) \qquad (5)$$

$$\phi_1 = x_1r_1/(x_1r_1 + x_2r_2); \quad \phi_2 = x_2r_2/(x_1r_1 + x_2r_2) \qquad (6)$$

$$\tau_{12} = \exp[-(u_{12} - u_{22})/RT]; \quad \tau_{21} = \exp[-(u_{21} - u_{11})/RT] \qquad (7)$$

CLC (*9*)

$$\ln \gamma_1 = (1/RT)(Z/2)[x_{21}^2(g_{21} - g_{11}) + x_2x_{22}x_{12}(g_{12} - g_{22})/x_1] - \ln (x_1 + A_{12}x_2) + x_2[A_{12}/(x_1 + A_{12}x_2) - A_{21}/(x_2 + A_{21}x_1)] \qquad (8)$$

$$\ln \gamma_2 = (1/RT)(Z/2)[x_{12}^2(g_{12} - g_{22}) + x_1x_{11}x_{21}(g_{21} - g_{11})/x_2] - \ln (x_2 + A_{21}x_1) - x_1[A_{12}/(x_1 + A_{12}x_2) - A_{21}/(x_2 + A_{21}x_1)] \qquad (9)$$

$$A_{12} = (V_2/V_1) \exp[-(g_{21} - g_{11})/RT]; \quad A_{21} = (V_1/V_2) \exp[-(g_{12} - g_{22})/RT] \qquad (10)$$

$$x_{12} = x_1 \exp(-g_{12}/RT)/[x_1 \exp(-g_{12}/RT) + x_2\exp(-g_{21}/RT)] \qquad (11)$$

$$x_{21} = x_2 \exp(-g_{21}/RT)/[x_1 \exp(-g_{12}/RT) + x_2\exp(-g_{21}/RT)] \qquad (12)$$

The vapor compositions were calculated by using the expression

$$y_i = \gamma_i x_i P^\circ_i \phi^s_i/P\phi^v_i \qquad (13)$$

The molar volumes are estimated by using a modified Rackett equation (*10*) in the calculations with the CLC model. The pure-component vapor pressures were calculated by using the Antoine constants presented in Table I. The ratio of fugacity coefficients (ϕ^s_i/ϕ^v_i) was set equal to unity. The above procedure to estimate the vapor composition was tested previously with the experimental T–x data of 50 binary systems (*11*). The deviations in experimental and calculated vapor compositions were within the range of experimental uncertainties of the data taken for the study.

The comparison between the vapor compositions predicted by the UNIQUAC and CLC models is given in Table II. The model parameters obtained from the present experimental data are $u_{12} - u_{22} = 433.01$, $u_{21} - u_{11} = -47.88$ for UNIQUAC and $g_{12} - g_{22} = 226.43$, $g_{21} - g_{11} = 30.98$ for CLC. The exper-

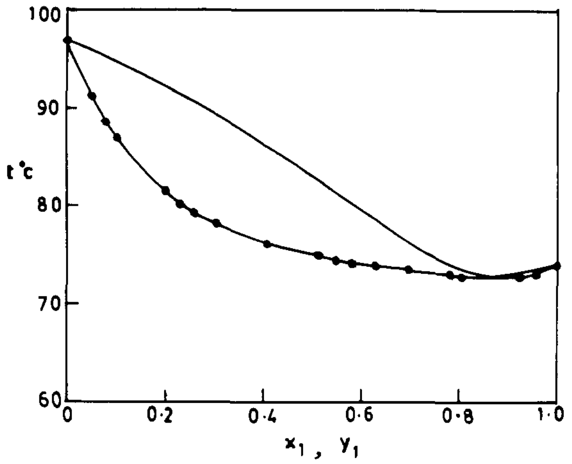

Figure 1. $T-x-y$ diagram for the system 1,1,1-trichloroethane (1)–1-propanol (2) at 101.3 kPa: (●) experimental data; (—) result calculated from UNIQUAC.

imental $T-x$ data are shown along with the predicted vapor composition in Figure 1.

It is observed from the activity coefficient data that the mixtures of the 1,1,1-trichloroethane–1-propanol system show considerable order of nonideality and positive deviation from Raoult's law. The system formed an azeotrope at 73.1 °C, the composition of the chlorohydrocarbon being 86.5 mol %. The experimental data are well correlated by the UNIQUAC and CLC models. The vapor compositions predicted by both models are almost identical.

Glossary

A_{12}, A_{21}	parameters in the CLC model
F	function
g_{11}, g_{12}, g_{21}, g_{22}	energy parameters in the CLC model
l	bulk factor of component
n	number of data points
P°	vapor pressure of the pure component
P	total pressure
q	pure-component area parameter
r	pure-component volume parameter
R	universal gas constant
T	temperature, K
t	temperature, °C
u_{11}, u_{12}, u_{21}, u_{22}	energy parameter in the UNIQUAC equation
V	molar volume
x	liquid composition
y	vapor composition
Z	coordination number

Greek Letters

γ	activity coefficient
ϕ	fugacity coefficient, volume fraction in eq 6
τ_{12}, τ_{21}	parameters in the UNIQUAC equation
θ	area fraction in eq 5

Subscripts

i	any component
1	more volatile component
2	less volatile component
cal	calculated

Superscripts

s	standard state, liquid
v	vapor

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