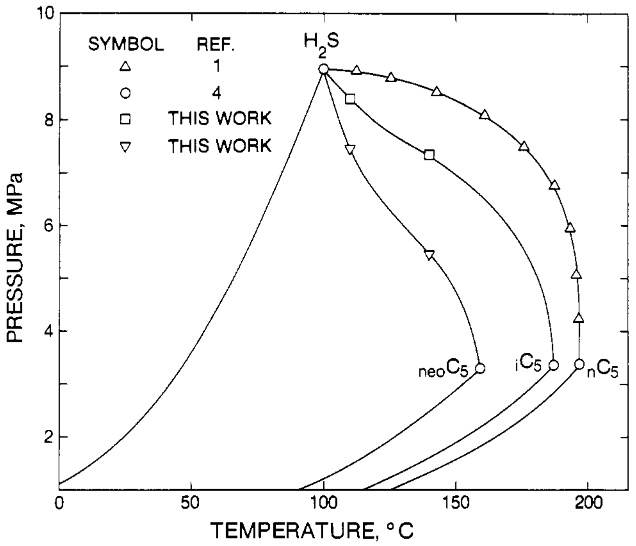

Figure 5. Critical loci in the isopentane (iC_5)–, neopentane ($neoC_5$)–, and *n*-pentane (nC_5)–hydrogen sulfide binary systems.

neopentane–hydrogen sulfide. It also indicates that the shape of the critical locus is different for straight-chain and branched-chain C_5-alkanes.

The experimental data on the behavior of the pentane isomer–hydrogen sulfide binary systems will be useful for evaluating the optimum binary interaction parameters in equation of state modeling of systems containing these components.

Glossary

K	equilibrium ration, *y*/*x*
P	pressure, MPa, psia
t	temperature, °C
x	mole fraction of component in liquid phase
y	mole fraction of component in vapor phase

Subscripts

i	component (*i* = 1, isopentane; *i* = 2, neopentane, *i* = 3, hydrogen sulfide)

Registry No. H_2S, 7783-06-4; isopentane, 78-78-4; neopentane, 463-82-1.

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Isothermal Vapor–Liquid Equilibria for the 1,2-Dichloroethane–Anisole and Trichloroethylene–Anisole Systems

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Vapor–liquid equilibrium (VLE) data have been measured for the binaries 1,2-dichloroethane–anisole and trichloroethylene–anisole at 353 and 373 K and pressures below atmospheric. The data were reduced using Barker's method, and they were found to be thermodynamically consistent. In addition, VLE predictions by the UNIFAC activity coefficient model were compared to experimental data.

Introduction

The system 1,2-dichloroethane–trichloroethylene forms a homogeneous azeotrope, with a boiling temperature of 355 K at atmospheric pressure (*1*). The separation of these substances can be performed by extractive distillation. Among the potential solvents, aromatic ethers show some attractive properties, like low volatility, high thermal stability, and relatively high polarity. The evaluation of their solvent properties for this specific separation is hindered by the lack of VLE data of the aromatic ethers with 1,2-dichloroethane and trichloroethylene.

In the present work, vapor–liquid equilibrium data for the binary mixture of 1,2-dichloroethane and trichloroethylene with anisole (methyl phenyl ether) were measured at 353 and 373 K, and interaction coefficients for the UNIQUAC equation (*2*) were computed. Comparison of the experimental data with vapor–liquid equilibrium predictions by the UNIFAC group contribution method (*3*) indicates the need for using two different ether groups: paraffinic and aromatic.

Experimental Section

The experimental measurements were carried out in a glass, 230-cm^3 capacity, recirculating still (Rock and Siege type, Normag). The equilibrium temperature was measured with a 100-Ω Pt resistance thermometer, via a digital meter (Systemteknik AB, S1220), with an accuracy of 0.01 K. The pressure was measured to within 1 mbar with a pressure controller (Normag) using a piezoresistive sensor.

The equilibrium vapor and liquid compositions were obtained by gas chromatography (Varian 3700 with a Hewlett Packard 3392 integrator), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used, together with a 2-m, $^1/_8$-in.-o.d. stainless steel separation column, packed with Porapak Q 50/80. The injector, oven, and detector temperatures were set at 493, 483, and 493 K, respectively. The carrier gas was nitrogen, with a flow of 25 cm^3/min. The chemicals used were chromatographic grade commercial reagents: anisole from Baker Chemical Co., trichloroethylene from Carlo Erba, and 1,2-dichloroethane from Mallinkrodt. Their purities, as measured by gas chromatography, were better than 99.9%.

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Table I. Vapor Pressure of Pure Components Ps, Antoine Coefficients *A*, *B*, and *C*, and Standard Deviations σ(Ps)

component	no. of data points *N*	temp range/K	Antoine coefficients[a] *A*	*B*	*C*	$\sigma(\text{Ps})^b$
1,2-dichloroethane	10	297-356	7.1557	1274.31	-50.040	0.02
trichloroethylene	10	311-359	7.0268	1225.75	-54.967	0.72
anisole	7	351-375	7.5253	1693.50	-50.661	0.12

[a] $\log(\text{Ps}/\text{mbar}) = A - B/((T/\text{K}) + C)$. [b] $\sigma(\text{Ps}) = (\text{Ps}_{\text{expt}} - \text{Ps}_{\text{calc}})^2/(N - 3)$.

Table II. Vapor Pressure *P*, Liquid Mole Fraction x_1, Vapor Mole Fraction y_1, Second Molar Virial Coefficients B_{ij}, Liquid Molar Volumes V_i, and Mean Deviations $\delta(P)$ and $\delta(y_1)$ for 1,2-Dichloroethane (1)–Anisole (2) at Given Temperature *T*

T = 353.15 K			T = 373.15 K		
P/mbar	x_1	y_1	*P*/mbar	x_1	y_1
84	0.0000	0.0000	187	0.0000	0.0000
109	0.0339	0.2486	191	0.0029	0.0235
135	0.0653	0.4203	245	0.0392	0.2551
208	0.1538	0.6480	303	0.0807	0.4114
276	0.2408	0.7576	337	0.1038	0.4908
322	0.2994	0.8036	410	0.1495	0.6020
360	0.3483	0.8483	416	0.1517	0.7098
411	0.3958	0.8660	489	0.2092	0.7118
465	0.4511	0.8921	559	0.2636	0.7380
525	0.5171	0.9171	628	0.3025	0.7810
590	0.5979	0.9387	715	0.3654	0.8202
636	0.6497	0.9462	884	0.4787	0.8761
683	0.7089	0.9589			
736	0.7767	0.9748			
845	0.9217	0.9914			
894	1.0000	1.0000			
$\delta(P/\text{mbar})^a = 1.21$ $\delta(y_1)^b = 0.0052$ $V_1/(\text{cm}^3\ \text{mol}^{-1}) = 77.59$ $V_2/(\text{cm}^3\ \text{mol}^{-1}) = 112.03$			$\delta(P/\text{mbar})^a = 2.46$ $\delta(y_1)^b = 0.0053$ $V_1/(\text{cm}^3\ \text{mol}^{-1}) = 79.75$ $V_2/(\text{cm}^3\ \text{mol}^{-1}) = 114.36$		
$B_{11}/(\text{cm}^3\ \text{mol}^{-1}) = -922.50$ $B_{22}/(\text{cm}^3\ \text{mol}^{-1}) = -2104.90$ $B_{12}/(\text{cm}^3\ \text{mol}^{-1}) = -1285.10$			$B_{11}/(\text{cm}^3\ \text{mol}^{-1}) = -801.00$ $B_{22}/(\text{cm}^3\ \text{mol}^{-1}) = -1779.80$ $B_{12}/(\text{cm}^3\ \text{mol}^{-1}) = -1109.00$		

[a] $\delta(P/\text{mbar}) = (\sum|\text{P}_{\text{expt}} - \text{P}_{\text{calc}}|)/(N - 2)$. [b] $\delta(y_1) = (\sum|y_{1,\text{expt}} - y_{1,\text{calc}}|)/(N - 2)$.

Table III. Vapor Pressure *P*, Liquid Mole Fraction x_1, Vapor Mole Fraction y_1, Second Molar Virial Coefficients B_{ij}, Liquid Molar Volumes V_i, and Mean Deviations $\delta(P)$ and $\delta(y_1)$ for Trichloroethylene (1)–Anisole (2) at Given Temperature *T*

T = 353.15 K			T = 373.15 K		
P/mbar	x_1	y_1	*P*/mbar	x_1	y_1
84	0.0000	0.0000	187	0.0000	0.0000
109	0.0356	0.2486	251	0.0524	0.2849
144	0.0826	0.4560	305	0.0959	0.4405
206	0.1673	0.6542	411	0.1699	0.6105
245	0.2099	0.7270	480	0.2149	0.6869
292	0.2766	0.7857	594	0.3086	0.7692
348	0.3650	0.8384	686	0.3791	0.8225
427	0.4709	0.8827	813	0.4778	0.8753
492	0.5447	0.9162	926	0.5684	0.9034
557	0.6298	0.9415			
612	0.7178	0.9642			
687	0.8191	0.9726			
751	0.9031	0.9858			
825	1.0000	1.0000			
$\delta(P/\text{mbar})^a = 2.62$ $\delta(y_1)^b = 0.0049$ $V_1/(\text{cm}^3\ \text{mol}^{-1}) = 94.12$ $V_2/(\text{cm}^3\ \text{mol}^{-1}) = 112.03$			$\delta(P/\text{mbar})^a = 1.58$ $\delta(y_1)^b = 0.0039$ $V_1/(\text{cm}^3\ \text{mol}^{-1}) = 96.63$ $V_2/(\text{cm}^3\ \text{mol}^{-1}) = 114.36$		
$B_{11}/(\text{cm}^3\ \text{mol}^{-1}) = -1138.80$ $B_{22}/(\text{cm}^3\ \text{mol}^{-1}) = -2104.90$ $B_{12}/(\text{cm}^3\ \text{mol}^{-1}) = -1539.80$			$B_{11}/(\text{cm}^3\ \text{mol}^{-1}) = -977.60$ $B_{22}/(\text{cm}^3\ \text{mol}^{-1}) = -1779.80$ $B_{12}/(\text{cm}^3\ \text{mol}^{-1}) = -1313.10$		

[a] $\delta(P/\text{mbar}) = (\sum|P_{\text{expt}} - P_{\text{calc}}|)/(N - 2)$. [b] $\delta(y_1) = (\sum|y_{1,\text{expt}} - y_{1,\text{calc}}|)/(N - 2)$.

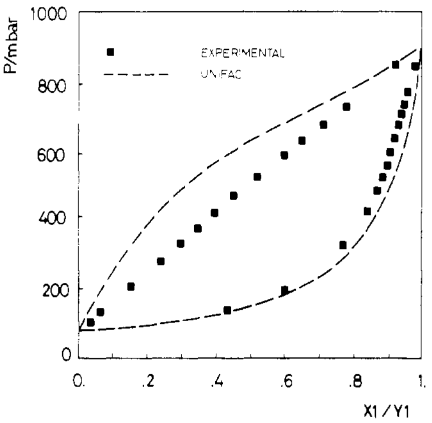

Figure 1. Experimental and calculated bubble-point and dew-point pressures *P* for the 1,2-dichloroethane (1)–anisole (2) system at 353 K.

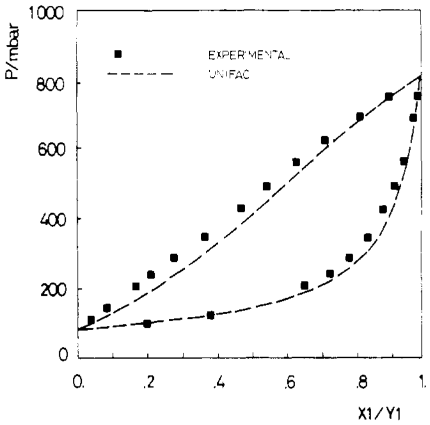

Figure 2. Experimental and calculated bubble-point and dew-point pressures *P* for the trichloroethylene (1)–anisole (2) system at 353 K.

Results and Discussion

The vapor pressures of the pure components were first measured to check the purity of the chemicals and to ascertain the best operating conditions for the VLE measurements. Table I summarizes the fit of the experimental vapor pressures to the Antoine equation. Comparison with data from the literature (*4*) shows differences lower than 1%.

Tables II and III contain the experimental VLE data for the anisole–1,2-dichloroethane and anisole–trichloroethylene systems, respectively. Two isotherms per binary were measured, at 353 and 373 K. The pressure values reported are the result of minor corrections carried out on the experimental data, to take into account small temperature differences between the various data points.

The experimental data were checked for thermodynamic consistency using Barker's method, following the procedure proposed by Christiansen and Fredenslund (*5*). Vapor-phase fugacity coefficients were estimated by means of the virial equation of state, with second virial coefficients predicted from the Hayden–O'Connell (*6*) correlation. Tables II and III include the mean deviations in pressure and vapor-phase compositions, for each measured isotherm. These deviations are within the

Table IV. Infinite Dilution Activity Coefficients γ_i^∞ Experimental (expt) and Predicted by UNIFAC (UNI) at Temperature T

system	T/K	$\gamma_{1,\mathrm{expt}}^\infty$	$\gamma_{2,\mathrm{expt}}^\infty$	$\gamma_{1,\mathrm{UNI}}^\infty$	$\gamma_{2,\mathrm{UNI}}^\infty$
1,2-dichloroethane (1)–	353.15	1.04	1.44	2.18	3.01
anisole (2)	373.15	1.03	1.52	2.12	2.88
trichloroethylene (1)–	353.15	0.82	0.93	0.57	0.78
anisole (2)	373.15	0.95	0.98	0.62	0.84

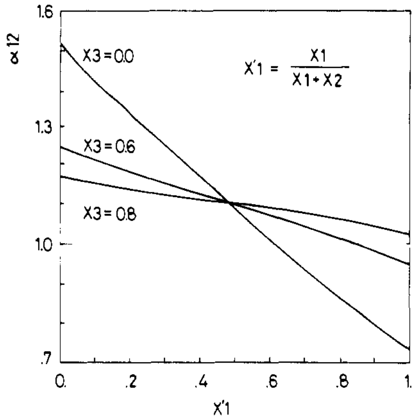

Figure 3. Predicted (UNIQUAC) relative volatilities (α_{12}) of 1,2-dichloroethane (1) with respect to trichloroethylene (2) at 353.15 K for different anisole (3) mole fractions x_3.

experimental uncertainties. The data are, therefore, considered to be thermodynamically consistent.

Both systems showed nearly ideal behavior, as it can be inferred from the dew and bubble pressure diagrams in Figures 1 and 2. Also shown in these figures are the UNIFAC vapor–liquid equilibrium predictions. The UNIFAC group contribution model for liquid-phase activity coefficients was used together with the virial equation of state for vapor-phase fugacity and the Hayden–O'Connell (*6*) correlation for second virial coefficients. The values of the pure component properties used in the predictions were taken from Reid et al. (*7*) and Prausnitz et al. (*2*). The UNIFAC group volume and surface parameters and energy interaction parameters were taken from Gmehling et al. (*8*) and Macedo et al. (*9*). For the UNIFAC predictions, the anisole molecular structure was built adding the aliphatic ether group ("OCH_3") to the phenyl group ("AC" + 5 "ACH"). Table IV contains the infinite dilution activity coefficients predicted by UNIFAC and the experimental ones, as obtained from the thermodynamic consistency test. For both systems the UNIFAC predictions showed significant deviations from the experimental data. The results obtained in this work seem to indicate the necessity of introducing a specific aromatic ether group in the UNIFAC parameter table, in order to improve the model predictions. Experimental work is under way to determine interaction parameters for a new "$ACOCH_2$" group.

Table V. UNIQUAC Volumes r, Surfaces q, and Interaction Parameters A_{ij} for 1,2-Dichloroethane (1), Trichloroethylene (2), and Anisole (3)

			A_{ij}/K		
substance	r	q	1	2	3
1	2.931	2.528	0	34.66	6.519
2	3.262	2.848	15.34	0	−9.166
3	4.167	3.208	−1.784	3.991	0

The present experimental data for 1,2-dichloroethane–anisole and trichloroethylene–anisole and the 1,2-dichloroethane–trichloroethylene data of Sagnes and Sanchez (*10*) were reduced using the UNIQUAC model (*2*), through a maximum likelihood procedure, as described by Kemeny et al. (*11*). Table V contains the UNIQUAC parameters for the three binary mixtures. On the basis of these parameters, the UNIQUAC model was used to predict the relative volatilities of the pair 1,2-dichloroethane–trichloroethylene, in ternary mixtures with anisole. The relative volatilities were calculated as

$$\alpha_{12} = \frac{\gamma_1 Ps_1}{\gamma_2 Ps_2}$$

where γ represents the UNIQUAC activity coefficients and Ps the Antoine vapor pressures of 1,2-dichloroethane (1) and trichloroethylene (2). It can be seen from Figure 3 that a relatively high concentration of anisole in the liquid phase is required for breaking the azeotrope between 1,2-dichloroethane and trichloroethylene.

Registry No. Anisole, 100-66-3; 1,2-dichloroethane, 107-06-2; trichloroethylene, 79-01-6.

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