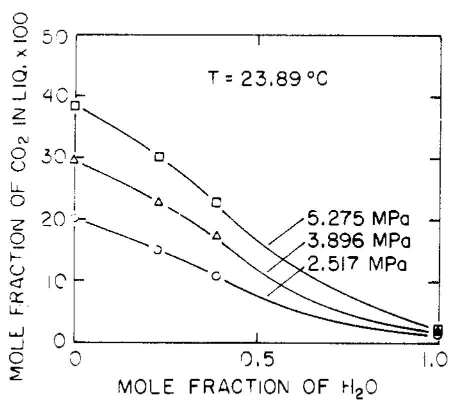

Figure 7. CO_2 solubility in TEG-H_2O solution at 23.89 °C and constant pressures.

(*1*, *6*), to present dehydration and solubility data from 100% glycol to pure water at various temperatures, pressures, and concentrations in Tables I-IV.

The Krichevsky-Kasarnovsky equation has been successfully utilized in the prediction of the carbon dioxide solubility values in aqueous solutions of DEG and TEG and in pure DEG and pure TEG just as in propylene carbonate (*9*).

Acknowledgment

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Registry No. Carbon dioxide, 124-38-9; diethylene glycol, 111-46-6; triethylene glycol, 112-27-6.

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Isobaric Vapor-Liquid Equilibria of the Tetrahydrofuran/Ethanol System at 25, 50, and 100 kPa

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The vapor-liquid equilibrium of the system tetrahydrofuran (THF)/ethanol at 25, 50, and 100 kPa has been determined experimentally by using an equilibrium still of the recirculation type. Data reduction based on the Wilson, NRTL, and UNIQUAC models provides a correlation for γ_i. The tetrahydrofuran/ethanol system forms an azeotrope above 53 kPa. At 100 and 150 kPa, the azeotropic mixtures contain respectively 0.908 and 0.844 mole fraction of tetrahydrofuran.

Introduction

In the present investigation the vapor-liquid equilibrium of the tetrahydrofuran (THF)/ethanol system was measured because there are only conflicting data in the literature for this system. Horsley (*1*) lists an azeotropic point of 0.85 mole fraction THF at atmospheric pressure. From boiling point measurements alone, Yoshikawa, Takagi, and Kato (*2*) have derived an azeotropic point at 0.905 mole fraction THF at 65.7 °C at atmospheric pressure. In contrast, Bernshtein, Generalova, Zelvenskii, and Shalygin (*3*), although employing a refined technique of radiometric analysis (radioactive ethanol with ^{14}C), did not find an azeotrope at atmospheric pressure when the ethanol content is low. In order to clarify these conflicting results, we measured the vapor-liquid equilibrium at 25, 50, and 100 kPa and furthermore the compositions of the azeotrope at 100, 125, and 150 kPa were determined by using a packed column.

Experimental Section

Purity of the Components. The reagents, manufactured by BASF Aktiengesellschaft, Federal Republic of Germany, were used without further purification. Their purity was confirmed by gas chromatography and Karl Fischer titration: tetrahydrofuran, >99.9%; ethanol, >99.9% (water content 0.03).

Apparatus and Procedure. The still used to obtain vapor-liquid equilibrium data was a Hunsmann vapor-liquid recirculation still (*4*), with several modifications suggested by Brunner and Scholz (*5*) and comprising, in the main, an improved protective screen against heat losses, an intensive stirrer for the liquid phase, a nonreturn valve in the condensate return, and simpler sampling of the vapor phase.

With the all-glass equilibrium still, which is shown in Figure 1, equilibrium measurements may be made in the range from 2 to 150 kPa.

Because four Cottrell tubes are employed and a very small volume of condensate (about 2 cm^3) is present, the vapor-liquid equilibrium is established in only 10-15 min. The liquid space in the apparatus is filled so that, when the liquid boils, a continuous stream of vapor-liquid mixture passes through the four Cottrell tubes and bathes the platinum resistance thermometer. In the thermometer space, the liquid and the vapor, which are in equilibrium with each another, are separated. The vapor is

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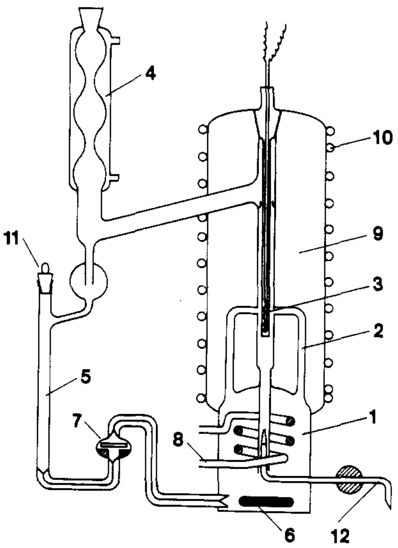

Figure 1. Vapor-liquid equilibrium recirculation still: (1) liquid space; (2) Cottrell tube; (3) platinum resistance thermometer; (4) condenser; (5) condensate line; (6) magnetic stirrer; (7) nonreturn valve; (8) heating coil; (9) vacuum jacket; (10) electric heating tape; (11, 12) sampling of condensate and liquid.

liquefied on the condenser and is recycled to the boiling vessel via condensate line. In particular, a large difference between the boiling point of the liquid and that of the condensate can give rise to concentration gradients in the boiling vessel, and hence to violent and irregular vaporization and delayed boiling, which in turn produce hydraulic shocks in the apparatus. As a result, the liquid level in the condensate line varies, and varying amounts of condensate in the apparatus produce temperature fluctuation in the system.

To avoid such concentration gradients and the associated adverse effects, the liquid is agitated thoroughly with a magnetic stirrer. In addition, a small glass plate is incorporated into the condensate return to act as a sensitive nonreturn valve and prevent the transmission of hydraulic shocks from the liquid space to the condensate line. In this manner, variations in the condensate volume can be kept below 0.01 cm^3, so that even in systems with a high relative volatility the temperature can be kept constant to within 0.05 K. The liquid is heated by means of a heating wire incorporated into a glass coil. The upper part of the apparatus is surrounded by a silver-coated, high-vacuum jacket which, when relatively high temperatures are employed, can be kept approximately at the temperature of the system by means of a regulatable electric heating tape. Because the apparatus is small, it can, if required, be used in a glovebox which is heated or cooled by air. Cooling is necessary when the starting components have very low boiling points, and heating is required when the melting point of one of the starting materials is above room temperature.

Pressures were measured by means of a high-accuracy electronic manometer from MKS Instruments Inc., Burlington, MA, with an accuracy of $\Delta p/p = 5 \times 10^{-4}$. The pressure transducer was calibrated at frequent intervals against a dead-weight gauge. The pressure constancy $\Delta p/p$ was better than 5×10^{-4}. The measured and set values were compared by means of a digital comparator, which controlled a magnetic valve, the leak rate of which could be optimized by means of a precision needle valve to minimize fluctuation of pressure. The temperatures (IPTS-68) were measured by using a temperature meter (from System-technik, Sweden, 1220 series) which was calibrated for use with a Pt 100 transducer and had a digital resolution of 0.01 K and an accuracy of 0.02 K. The temperatures measured were reproducible within 0.05 K.

The compositions of the coexisting phases were determined by gas chromatography.

Table I. Experimental Vapor-Liquid Equilibrium Data for the System Tetrahydrofuran/Ethanol at 25, 50, and 100 kPa and Azeotropic Data at 100, 125, and 150 kPa

p/kPa	x_1	y_1	t/°C
25	0.0	0.0	46.5^b
	0.0146	0.0610	45.7
	0.0438	0.147	44.3
	0.103	0.302	41.6
	0.229	0.506	37.5
	0.569	0.761	31.2
	0.776	0.856	29.7
	0.879	0.9125	28.9
	0.9395	0.9516	28.6
	0.9701	0.9747	28.5
	1.0	1.0	28.4^b
50	0.0	0.0	61.5^b
	0.0256	0.0717	60.4
	0.0579	0.149	59.1
	0.123	0.283	56.8
	0.252	0.464	53.2
	0.449	0.639	49.6
	0.603	0.735	47.9
	0.766	0.827	46.6
	0.862	0.886	46.0
	0.9166	0.9255	45.9
	0.99219	0.99241	45.7
	1.0	1.0	45.7^b
100	0.0	0.0	78.0^b
	0.0172	0.0369	77.4
	0.0536	0.115	76.2
	0.139	0.264	73.8
	0.263	0.428	71.0
	0.497	0.628	67.7
	0.543	0.654	67.2
	0.715	0.762	65.9
	0.857	0.865	65.4
	0.908^a	0.908^a	65.2^a
	0.9180	0.9148	65.4
	0.9499	0.9446	65.4
	0.9815	0.9790	65.5
	1.0	1.0	65.6^b
125	0.871^a	0.871^a	71.8^a
150	0.844^a	0.844^a	77.7^a

[a] Experimental azeotropic point determination using a packed column. [b] The measured boiling temperatures of the pure compounds are in good agreement ($\Delta t \leqslant 0.1$ K) with literature values (Table II) used for data reduction.

Results and Discussion

Provisional measurements of the vapor-liquid equilibrium of the THF/ethanol system at 50 kPa indicate that an azeotrope may be found when the THF content is very high. Horsley (*1*) lists an azeotropic point for this system at atmospheric pressure. Recently the THF/ethanol system at atmospheric pressure was the object of two papers coming to contradictory results. Looking for an azeotrope by radiometric analysis Bernshtein et al. (*3*) did not find any indication of azeotropic behavior. On the other hand, from boiling point measurements Yoshikawa, Takagi, and Kato (*2*) demonstrated the existence of an azeotrope at 65.7 °C with 0.905 mole fraction THF.

In order to clear this conflicting situation we measured the vapor-liquid equilibrium of the THF/ethanol system at 25, 50, and 100 kPa very carefully. Additionally, we examined the existence of azeotropic behavior at 100, 125, and 150 kPa using a packed column. The experimental p-x_1-y_1-t values are presented in Table I. In Figure 2 the differences between vapor- and liquid-phase mole fraction of THF, $y_1 - x_1$, are plotted vs. liquid-phase mole fraction of THF, x_1, at 25, 50, and 100 kPa.

In obtaning the liquid-phase activity coefficients γ_i, we neglected vapor-phase nonideality and the Poynting correction.

$$\gamma_i = y_i p / x_i p_i^{\circ} \tag{1}$$

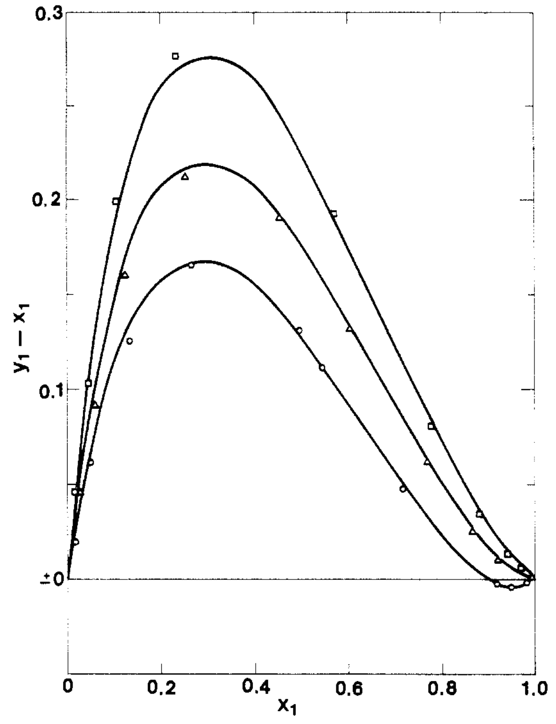

Figure 2. Vapor-liquid equilibria of the THF/ethanol system. Plots of $y_1 - x_1$ vs. x_1: (□) 25, (△) 50, and (○) 100 kPa.

Table II. Physical Data of Pure Species

	tetrahydrofuran	ethanol
parameter of Antoine eq		
A	14.0919 (*11, 12*)	17.1450 (*13*)
B	−2768.38 (*11, 12*)	−3956.07 (*13*)
C	226.25 (*11, 12*)	237.52 (*13*)
v^a/(cm^3/mol) (*9*)	81.55	58.68
r^b (*9*)	2.9415	2.1055
q^c (*9*)	2.720	1.972

[a] Molar volume of liquid. [b] Volume parameter. [c] Area parameter.

γ_i were represented as a function of composition and temperature, on the basis of various local composition models. We have restricted ourselves to the following three models: (1) the Wilson model (*6*), (2) the NRTL model due to Renon and Prausnitz (*7*), and (3) the UNIQUAC model due to Abrams and Prausntiz (*8*).

In this paper, the temperature dependence of the vapor pressure is given by the Antoine equation:

$$\ln (p/\text{kPa}) = A + B/(C + t/°\text{C}) \qquad (2)$$

The Wilson model requires, as a further parameter, the molar volumes of the individual components in the liquid state. In this paper, the molar volume has been employed as a temperature-independent parameter. This is permissible since in the Wilson equation only the ratio of the molar volumes occurs, this being rather temperature independent. The molar volumes of the two substances, and the values of the dimensionless area and volume parameters used in the UNIQUAC model, are taken from Gmehling and Onken (*9*). The physical data relating to the pure species used are given in Table II.

The functions

$$\ln \gamma_i = f(x(1),x(2),...,T) \qquad (3)$$

Table III. Model Parameters of the Binary System THF/Ethanol

Wilson	
$(\lambda_{ij} - \lambda_{ii})/R$	−52.03
$(\lambda_{ji} - \lambda_{jj})/R$	286.90
NRTL (α = 0.3)	
$(g_{ij} - g_{jj})/R$	218.65
$(g_{ji} - g_{ii})/R$	12.01
UNIQUAC	
$(u_{ij} - u_{jj})/R$	216.57
$(u_{ji} - u_{ii})/R$	−80.61

which are derived from the local composition models mentioned, have been described in several publications. In this connection we refer to the data collection of Gmehling and Onken (*9*); the notation employed there will be used in this paper.

The parameters which occur in the model equations and have to be fitted were determined from the measurements made on the binary vapor-liquid-phase equilibrium with the aid of the maximum likelihood principle, using the method of calculation due to Anderson, Abrams, and Grens (*10*). The measured values x_i, y_i, p, and T are considered to be erroneous; the errors are assumed to have a normal distribution with a mean value of 0 and distinct variance. The quantity minimized is thus the sum of the squares of the differences between the measured value and the calculated value, each term of the sum being weighted by the reciprocal value of the corresponding variance.

In order to fix estimates for the standard deviations of the measured variables we make the following assumptions. The experimental x and y values are assumed to be accurate to within unity in the last decimal place given, the error in the temperature measurement is taken as being 0.05 K, and that in the pressure measurement 0.1 kPa.

The nonrandomness parameter α in the NRTL model is fixed at 0.3, a value which has proved suitable for systems such as those being investigated in this case. The NRTL model, like the other models, thus employs only two fitted parameters.

The model parameters of the THF/ethanol system, as calculated from the experimental vapor-liquid equilibrium data, are summarized in Table III. The three local composition models employed prove to be equally suitable for describing this system; no model correlates the experimental data significantly better than the others. In the equilibrium diagrams in Figure 2, the measurements are compared with the curves calculated on the basis of the Wilson model.

The measurements of the equilibrium at 100 kPa show obviously an azeotrope in the range of high THF content. Using the Wilson model, one can calculate the pressure dependence of the azeotrope. Azeotropic behavior is to be expected only above 53 kPa. As the pressure of the system increases, the ethanol content of the azeotropic mixture increases too. At 100 kPa the azeotrope boils at 65.3 °C having 0.894 mole fraction THF. The values of azeotropic composition and temperature determined by the aid of a packed column (about 20 theoretical plates) at 100, 125, and 150 kPa agree well with the calculated values taking into consideration the lower accuracy of the azeotropic measurements.

Acknowledgment

We express our grateful thanks to Dr. F. Caesar, for his kind help in obtaining the gas-chromatographic data.

Glossary

A,B,C	parameters of the Antoine equation
p	total pressure, kPa
$P_i°$	vapor pressure of pure component i, kPa
q	area parameter
R	gas constant
r	volume parameter

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T	temperature, K
t	temperature, °C
v	molar volume, cm^3/mol
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i
g_{ij}, u_{ij}, λ_{ij}	interaction parameter between components i and j
α	nonrandomness parameter
γ_i	activity coefficient of component i

Registry No. Tetrahydrofuran, 109-99-9; ethanol, 64-17-5.

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Measurements of the Vapor–Liquid Coexistence Curve for the Binary R12 + R22 System in the Critical Region

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Measurements of the vapor–liquid coexistence curve in the critical region for the binary dichlorodifluoromethane (CCl_2F_2, R12) + chlorodifluoromethane ($CHClF_2$, R22) system were made by visual observation of the disappearance of the meniscus at the vapor–liquid interface within an optical cell. Fifty-one saturated-vapor densities and thirty-seven saturated-liquid densities for seven different compositions of 0, 10, 20, 30, 50, 75, and 100 wt % R22 between 355 and 385 K ($T_r > 0.96$) were obtained in the range of densities 260–892 kg/m^3 ($0.5 < \rho_r < 1.5$). The experimental error of temperature, density, and mass fraction was estimated within ±10 mK, ±0.5% and ±0.05%, respectively. The composition dependence of the critical parameters is analyzed and discussed on the basis of these measurements.

Although nonazeotropic binary mixtures have recently been considered to be prospective working fluids for refrigeration and heat pump cycles, only limited information about the thermodynamic properties of these substances is available. A binary dichlorodifluoromethane (R12) + chlorodifluoromethane (R22) system is assigned to the refrigerant number of 501 for a mixture of 75 wt % R22. However, Kriebel (*1*) measured the phase equilibria for the R12 + R22 system over the whole range of compositions between 213 and 343 K. He found that the azeotropic composition for this system shifts from 84.5 wt % R22 at 231.65 K to 100 wt % R22 at 258.65 K, above which this system forms no more azeotrope.

We have carried out systematically a thermodynamic investigation on this R12 + R22 system. The *PVTx* measurements were reported (*2*, *3*) and the composition dependence of the thermodynamic state surface (*4*) as well as an analysis on the application to the refrigeration cycle (*5*) was also discussed. This paper reports measurements of the vapor–liquid coexistence curve for seven different compositions, i.e., 0, 10, 20, 30, 50, 75, and 100 wt % R22, by visual observation of the disappearance of the meniscus at the vapor–liquid interface. The composition dependence of the critical parameters including those for both pure components is also reported.

Experimental Section

The vapor–liquid coexistence curve for a certain composition of the binary R12 + R22 system was measured by observing the behavior of the meniscus at the vapor–liquid interface in an optical cell. The experimental apparatus used and the principle of the measurements were described in detail in a previous publication (*6*). With the aim of measuring saturation temperatures for a series of densities along the coexistence curve of a fixed composition successively, we introduced the expansion technique into the meniscus observation. The optical cell was connected with an expansion vessel for repeating expansion procedures from the optical cell to the expansion vessel after the measurement of a saturation temperature. Additionally, another vessel called a supplying vessel was connected with the optical cell and the expansion vessel as shown schematically in Figure 1, which allowed the sample fluid in the supplying vessel to be supplied to the optical cell after completion of a single series of expansion procedures. Careful attention was paid to the expansion procedure in order not to change the sample composition. We performed the expansion procedures at a state where the sample fluid was kept under the homogeneous phase at a constant temperature. In the meantime these three vessels were rocked to homogenize the sample density and composition.

The optical cell was a cylindrical vessel made of 304 stainless steel (50 mm long and 19 mm in inner diameter, 15 cm^3 in inner volume) with two synthetic sapphire windows (15 mm in thickness) using Teflon O rings and Teflon packings for the high-pressure seal. We calibrated the inner volume of the cell by filling the water with known density values under room-temperature conditions with an uncertainty of 0.03%, whenever we disassembled the cell and reassembled it. In this study, the cell was disassembled 4 times due to experimental trouble and reassembled by using new packings. The inner volume of the cell was calibrated each time and the results were 14.973 ± 0.005, 15.176 ± 0.005, 15.153 ± 0.004, and 15.067 ± 0.005

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