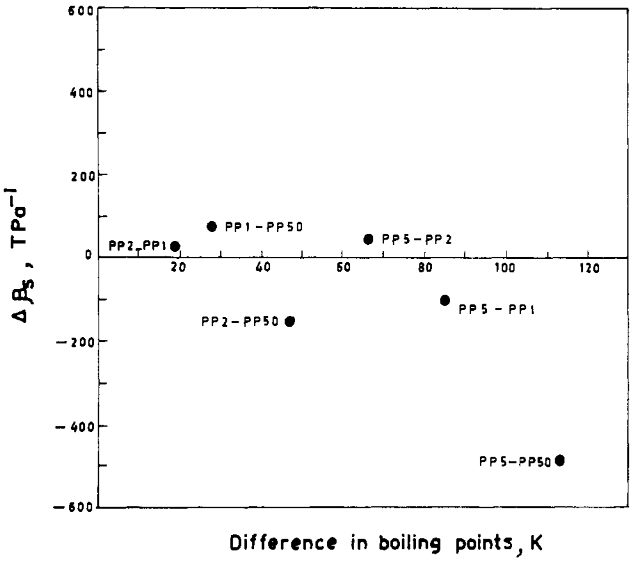

Figure 1. Plot of $\Delta\beta_s$ at equimolar mixture as a function of difference in bp's in six fluorocarbon binary mixtures.

a decreasing trend with increase in difference of boiling points.

This study leads to the possibility of obtaining any desired ultrasonic velocity in the range 477–714 ms^{-1} at 298.16 K, by mixing two distinct fluorocarbon liquids in a definite proportion. The same desired velocity can be obtained by various permutations of fluorocarbon binary liquid mixtures. One can have the choice of selecting an appropriate binary mixture depending on its characteristic impedance suited to the required application.

Acknowledgment

We are indebted to the Director, Regional Research Laboratory, Bhubaneswar, for his kind permission to publish this paper.

Registry No. Flutec PP50, 678-26-2; Flutec PP1, 355-42-0; Flutec PP5, 306-94-5; Flutec PP2, 355-02-2.

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Vapor–Liquid Equilibria for the Chlorobenzene–Nitrobenzene System at 80.0 and 95.0 °C

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Isothermal vapor–liquid equilibrium (VLE) data for the binary system chlorobenzene–nitrobenzene were measured at temperatures of 95.0 and 80.0 °C and total system pressures between 10 and 260 mmHg using a dynamic still. The data obtained in this study are thermodynamically consistent according to the point-to-point consistency test. From these data, the UNIFAC parameters were estimated for the aromatic chloro (ACCl)/aromatic nitro (ACNO2) functional group interactions. These data were also correlated with four liquid-phase activity coefficient models (UNIQUAC, NRTL, Wilson, Van Laar), with the parameters estimated from the maximum-likelihood method.

Introduction

The UNIFAC method is widely used in process engineering applications, especially in phase-equilibrium calculations. This method is very useful in predicting the vapor–liquid equilibrium (VLE) of a system in the absence of experimental information. The UNIFAC method is used to predict activity coefficients in a liquid phase consisting of nonelectrolytic, nonpolymeric mixtures and within a temperature range of 300–425 K and pressures up to a few atmospheres. Fredenslund et al. (*1*) originally developed the UNIFAC method; it was later revised and its applicability range extended by Skjold-Jorgensen et al. (*2*) and Gmehling et al. (*3*).

The main aim of this study was to extend the UNIFAC group interaction parameter table (*3*) by determining the binary interaction parameters between the aromatic chloro/aromatic nitro (ACCl/ACNO2) groups. The parameter estimation technique used is described in Fredenslund et al. (*1*). Isothermal VLE data were measured for the chlorobenzene–nitrobenzene system at 80.0 and 95.0 °C. Only a few data sets for mixtures with aromatic nitro groups have been reported. Nitrobenzene is an industrially important chemical, mainly used in the manufacture of aniline and nitro–chloro derivatives, such as from the nitration of chlorobenzene (*4*).

Equipment and Experiments

The compounds used in this study were chlorobenzene and nitrobenzene. All chemicals were available in relatively high stated purity of at least 99+%. Each chemical was then analyzed on a gas chromatograph to assure the purity of the samples. Extra precautions were taken in handling chlorobenzene and nitrobenzene. A fume hood was used to store these chemicals. Protective equipment such as respirators, clothing, gloves, and eye protection was used according to the standards described in the Material Safety Data Sheets (MSDS) for chlorobenzene and nitrobenzene.

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The equilibrium vessel used in this work was an all-glass, Stage-Muller dynamic still equipped with a Cottrell pump. The still, manufactured by Fischer Labor- und Verfahrenstechnik of West Germany, is capable of handling pressures up to 1500 mbar and temperatures up to 250 °C. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact with the temperature-sensing element. The essential features of the still and the basic procedures for the binary measurements were as described by Eng and Sandler (*5*) and by Willman (6).

The important components of this still include the Cottrell pump, a silver-plated vacuum jacket, and magnetic sampling valves. The vacuum jacket surrounds the equilibrium chamber and eliminates partial condensation of the vapor separating from the liquid at the exit of the Cottrell pump. The magnetic sampling valves allow liquid and vapor samples to be simultaneously collected without disruption of operation of the still.

All experiments were carried out under an inert nitrogen atmosphere. A low nitrogen flow rate through a vernier valve and pressure gauge ensured that the pressure within the equilibrium cell was not affected. The cold traps before the vacuum pump and the manometer prevented condensed vapors from entering the pump internals. A Fisher magnetic stirrer/heater was used to heat the boiling flask of the still with the help of a glycerine oil bath. The magnetic stirrer minimized surging and promoted mixing. The equilibrium temperature was measured with an accuracy of 0.2 °C with a total immersion type thermometer and the pressure was measured with a mercury manometer whose flexible scale allowed compensation for local gravity and temperature effects.

Compositions of the sampled liquid and condensed vapor phases were analyzed with a Perkin-Elmer 900 Series gas chromatograph with a flame ionization detector (FID) connected to a Hewlett-Packard 3390A integrator. A preconditioned DB-5, 5% phenylmethylpolysiloxane megabore column of 15-m length and 1.5-μm film thickness was used. This fused silica megabore column was supplied by J & W Scientific, Inc. The gas chromatograph was used at 30, 70, or 110 °C, depending on the compounds being analyzed.

In order to get an excellent peak symmetry, separation, and column efficiency, all of the samples were diluted with *n*-dodecane. This diluent was added in a known amount to both the calibration mixtures and the samples. Mole fractions were obtained from a calibration curve prepared gravimetrically using a Mettler analytical balance with an accuracy of ±0.0001 gm.

Further details on the experimental apparatus and procedure are given by Varughese (*7*).

Prior to commencing the experiments with chlorobenzene and nitrobenzene, VLE data for the benzene–toluene system were measured at an isotherm of 79.6 °C, to check the performance of the Stage-Muller still. These data, summarized elsewhere (*7*), were in good agreement with the literature data of Beatty and Calingaert (*8*).

Data Analysis

The vapor–liquid equilibrium (VLE) data at low to moderate pressures were correlated in this work by fitting two-parameter Wilson, Van Laar, NRTL, and UNIQUAC equations. The truncated virial equation of state was used to correct for vapor-phase nonidealities, and the Hayden–O'Connell correlation (*9*) was used to obtain the second virial coefficients. The parameters were estimated by a nonlinear regression method, based on the maximum-likelihood principle. When there is significant random error in all the variables, as in these experiments, the maximum-likelihood principle can lead to better parameter estimates than those obtained by other methods (*9*). This method requires data on the critical temperature and pressure, dipole moment, mean radius of gyration, or parachor. These data and the *R* and *Q* values for the UNIQUAC equation are readily available in the literature (*1*, *9*). A fit of the *P*–*T*–*x*–*y* data was used to minimize the errors in all of the experimental measurements by minimizing the following objective function:

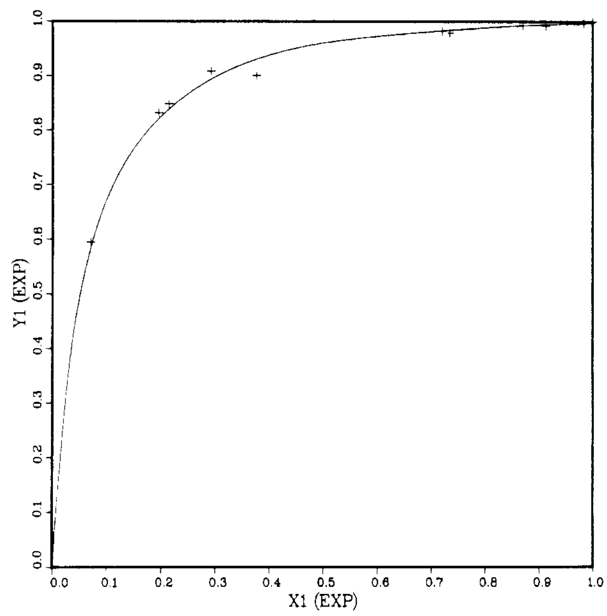

Figure 1. Vapor–liquid equilibria for the system chlorobenzene (1)–nitrobenzene (2) at 95.0 °C.

$$s = \sum_{j=1}^{m} \left[\frac{(P_j^{o} - P_j^{e})^2}{\sigma_P^2} + \frac{(T_j^{o} - T_j^{e})^2}{\sigma_T^2} + \frac{(x_{1j}^{o} - x_{1j}^{e})^2}{\sigma_{x_1}^2} + \frac{(y_{1j}^{o} - y_{1j}^{e})^2}{\sigma_{y_1}^2} \right] \qquad (1)$$

The above summation is over all *m* data points. The superscript e indicates the measured value, while the superscript o indicates the estimated value for each data point, respectively. In this equation, all of the measured data points were used. In eq 1, σ is the estimated standard deviation for each of the measured variables, such as pressure, temperature and liquid-phase and vapor-phase compositions. The standard deviations assumed for the experimental data were σ_P = 1.20 mmHg σ_T = 0.2 °C, σ_{x_1} = 0.003, and σ_{y_1} = 0.005. The estimation of these values has been described by Prausnitz et al. (*9*), and they are consistent with the values used by Willman (*6*) and with the accuracy of the equipment used in this study.

The experimental data obtained from this study were also subjected to a thermodynamic consistency test. From given isothermal *P*–*x* data, *y*'s were calculated and then compared with the experimental *y*'s. A minimum deviation in the *y* values is preferred for consistent data. If a set of data was accepted as consistent, the activity coefficients obtained from the consistency test were then used as the experimental values. These activity coefficients γ_i(exptl) are functions only of the liquid-phase mole fractions and the temperature. The objective function to be minimized for estimating the UNIFAC group interaction parameters was the expression:

$$F = \sum [\ln \gamma_i(\text{exptl}) - \ln \gamma_i(\text{UNIFAC})]_j^2 \qquad (2)$$

where the summations are over all the components (*i*) and data points (*j* = 1, 2, ..., *m*) (*1*).

Results and Discussion

Isothermal VLE measurements were made for the chlorobenzene–nitrobenzene system at 95.0 and 80.0 °C. The raw

Table I. Vapor-Liquid Equilibrium Data for Chlorobenzene (1)-Nitrobenzene (2) at 95.0 °C

point no.	press., mmHg	x_1	y_1
1	17.02	0.0000	0.0000
2	39.99	0.0708	0.5948
3	73.55	0.1963	0.8315
4	77.94	0.2152	0.8484
5	104.30	0.2934	0.9083
6	102.59	0.3771	0.9005
7	165.53	0.6177	0.9702
8	184.22	0.7211	0.9821
9	191.05	0.7349	0.9785
10	205.36	0.8708	0.9928
11	223.87	0.9133	0.9921
12	249.32	0.9830	0.9974
13	259.30	1.0000	1.0000

Table II. Vapor-Liquid Equilibrium Data for Chlorobenzene (1)-Nitrobenzene (2) at 80.0 °C

point no.	press., mmHg	x_1	y_1
1	8.26	0.0000	0.0000
2	19.55	0.0627	0.5724
3	36.79	0.1098	0.7179
4	43.67	0.1682	0.8540
5	65.52	0.3536	0.9298
6	56.39	0.5582	0.9111
7	93.82	0.5657	0.9668
8	109.53	0.7290	0.9867
9	118.12	0.8140	0.9893
10	120.50	0.8109	0.9896
11	128.66	0.8451	0.9942
12	143.38	0.9692	0.9968
13	150.29	1.0000	1.0000

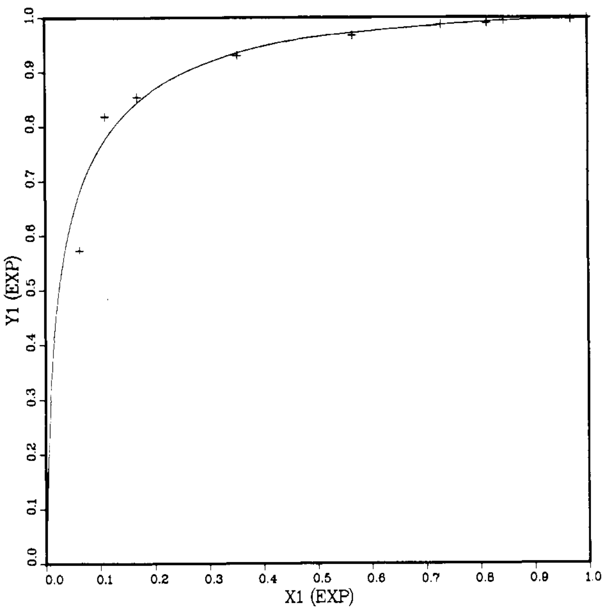

Figure 2. Vapor-liquid equilibria for the system chlorobenzene (1)-nitrobenzene (2) at 80.0 °C.

data are presented in Tables I and II and plotted in Figures 1 and 2. Vapor pressure data were also taken on each of the two pure components and were in close agreement with literature data. These pure component vapor pressure data are reported by Varughese (*7*).

The thermodynamic consistency of the data was checked by the consistency test of Van Ness and Fredenslund (*1*). According to Fredenslund et al., the *P*-*T*-*x*-*y* data are consistent if the average absolute deviation (AAD) between y_1(calculated) and y_1(experimental) is less than 0.01. This corresponds to a reasonable value for the sum of the errors in the measured liquid- and vapor-phase mole fractions.

Table III. UNIFAC Group Interaction Parameters between the ACCl/ACNO2 Groups

	80.0 °C	95.0 °C	combined
$a_{\mathrm{ACCl,ACNO2}}$	−17.522	−88.398	−47.757
$a_{\mathrm{ACNO2,ACCl}}$	566.191	570.055	549.543

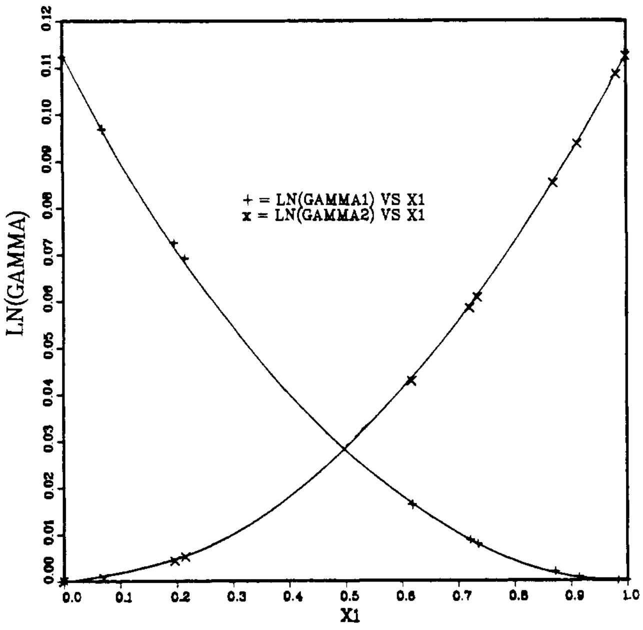

Figure 3. Experimental liquid-phase activity coefficients for the system chlorobenzene (1)-nitrobenzene (2) at 95.0 °C.

Depending on the number of Legendre coefficients used in the data-fitting procedure and the number of data points, the AAD (Δy's) of the chlorobenzene-nitrobenzene isotherms showed deviations ranging from 0.007 85 to 0.030 04 at 80.0 °C and from 0.009 74 to 0.020 34 at 95.0 °C. Upon examining the percentage errors in calculating the activity coefficients [γ_i(calcd)] using the UNIFAC model, it was decided to use the data corresponding to an AAD(Δy) = 0.015 32 for the 95.0 °C isotherm and 0.008 65 for the 80.0 °C isotherm. Only a few data points (points 5 and 6 at 95.0 °C and points 3, 4, and 6 at 80.0 °C) were omitted due to large deviations between the experimental and calculated values in the vapor-phase mole fractions.

The higher AAD(Δx) at 95.0 °C is probably related to the difficulties associated with operating the Stage-Muller still at high temperatures and pressures. Under these conditions, the partial pressure of the nitrogen used to pressurize the still tends to affect the equilibrium pressure of the system. Thus, some VLE data were also taken on this binary system at 110 °C but were discarded as inconsistent.

The UNIFAC model was applied to generate the binary interaction parameters between the chlorobenzene (ACCl) and nitrobenzene (ACNO2) groups, using the data from the consistency tests. The activity coefficients (γ_i) obtained from the consistency tests were used as the experimental values. These γ_i's were assumed to be functions of only the liquid-phase mole fractions and temperature. The parameters that predicted the activity coefficients as close as possible to the experimental values were considered to be the best values. The objective function for this fitting procedure was given in eq 2.

The interaction parameters, evaluated at the separate temperatures of 95.0 and 80.0 °C, are shown in Table III. The experimental activity coefficients (γ_1 and γ_2) versus the liquid-phase mole fractions (x_1 and x_2) are plotted in Figures 3 and

Table IV. Best Fit Parameters of Various VLE Equations for the Chlorobenzene (1)-Nitrobenzene (2) System

T, °C	model[a]	param, units	param 12	param 12	AAD(Δy)	AAD(ΔP), mmHg	AAD(Δx)
95.0	UNIQUAC	a, K	-226.76	397.06	0.0159	0.79	0.0185
	NRTL	Δg, cal/mol	-159.99	674.66	0.0158	0.80	0.0186
	Wilson	$\Delta\lambda$, cal/mol	1070.96	-394.92	0.0158	0.81	0.0188
	Van Laar	A	0.66	0.18	0.0157	0.83	0.0190
	Margules	A	0.11				
80.0	UNIQUAC	a, K	-120.28	203.59	0.0202	0.73	0.0094
	NRTL	Δg, cal/mol	7.38	330.78	0.0201	0.73	0.0094
	Wilson	$\Delta\lambda$, cal/mol	417.03	-72.90	0.0201	0.73	0.0094
	Van Laar	A	0.47	0.31	0.0201	0.73	0.0094
	Margules	A	0.21				

[a] These models correspond to the ones given by Prausnitz et al. (9).

Table V. Activity Coefficients (γ_1 and γ_2) for the Chlorobenzene (1)-Nitrobenzene (2) System

		UNIQUAC		NRTL		Wilson		Van Laar		experimental	
temp, °C	x_1	γ_1	γ_2	γ_1	γ_2	γ_1	γ_2	γ_1	γ_2	γ_1	γ_2
95	0.0000	1.8940	1.0000	1.9069	1.0000	1.9756	1.0000	1.9206	1.0000	1.1188	1.0000
	0.0708	1.5556	1.0064	1.5516	1.0066	1.5544	1.0075	1.5240	1.0074	1.1017	1.0006
	0.1963	1.2150	1.0424	1.2101	1.0429	1.2027	1.0446	1.2018	1.0419	1.0752	1.0043
	0.2152	1.1862	1.0490	1.1823	1.0493	1.1766	1.0507	1.1778	1.0475	1.0716	1.0052
	0.6177	1.0025	1.1530	1.0051	1.1503	1.0094	1.1478	1.0138	1.1448	1.0165	1.0438
	0.7211	0.9994	1.1602	1.0012	1.1593	1.0041	1.1600	1.0069	1.1606	1.0088	1.0601
	0.7349	0.9990	1.1613	1.0006	1.1612	1.0031	1.1633	1.0053	1.1652	1.0079	1.0625
	0.8708	0.9989	1.1614	0.9998	1.1643	1.0012	1.1709	1.0024	1.1773	1.0019	1.0888
	0.9133	0.9994	1.1578	0.9998	1.1644	1.0003	1.1766	1.0008	1.1881	1.0008	1.0981
	0.9830	1.0000	1.1469	1.0000	1.1601	1.0000	1.1821	1.0000	1.2016	1.0000	1.1145
	1.0000	1.0000	1.1457	1.0000	1.1595	1.0000	1.1824	1.0000	1.2027	1.0000	1.1188
80	0.0000	1.6177	1.0000	1.6163	1.0000	1.6012	1.0000	1.5969	1.0000	1.2380	1.0000
	0.0627	1.4980	1.0023	1.4943	1.0023	1.4835	1.0023	1.4821	1.0022	1.2064	1.0008
	0.3536	1.1484	1.0690	1.1464	1.0686	1.1467	1.0669	1.1475	1.0667	1.0933	1.0271
	0.5657	1.0493	1.1549	1.0493	1.1528	1.0503	1.1504	1.0504	1.1507	1.0411	1.0707
	0.7290	1.0188	1.2186	1.0192	1.2159	1.0197	1.2142	1.0197	1.2147	1.0158	1.1202
	0.8140	1.0095	1.2539	1.0097	1.2513	1.0100	1.2504	1.0100	1.2509	1.0074	1.1520
	0.8109	1.0085	1.2587	1.0087	1.2562	1.0090	1.2554	1.0090	1.2560	1.0077	1.1508
	0.8451	1.0044	1.2838	1.0045	1.2818	1.0047	1.2817	1.0047	1.2822	1.0051	1.1648
	0.9692	1.0002	1.3407	1.0002	1.3407	1.0002	1.3427	1.0002	1.3428	1.0002	1.2221
	1.0000	1.0000	1.3556	1.0000	1.3564	1.0000	1.3591	1.0000	1.3591	1.0000	1.2380

Table VI. Estimated Pure and Mixed Virial Coefficients (cm^3/mol) at 95 and 80 °C

	chlorobenzene B_{11}	nitrobenzene B_{22}	chlorbenzene-nitrobenzene B_{12}
80 °C	-1781.5	-3988.8	-2208.3
95 °C	-1575.3	-3338.9	-1950.7

Table VII. Molar Volumes of the Pure Liquids (cm^3/mol)

	80 °C	95 °C
chlorobenzene	109.003	112.721
nitrobenzene	109.487	112.412

4. Table III also shows the best possible parameters by combining both of the data sets at 95.0 and 80.0 °C.

In addition, the experimental data were correlated with four two-parameter equations. The models used were the UNIQUAC, NRTL, Wilson, and Van Laar models. The results of the parameter estimation for these models are given in Table IV. In Table V the activity coefficients using these models are compared with the experimental values. It is evident from these tables that the activity coefficients calculated are almost identical. The models used in this work and the computer programs used to determine the activity coefficients are readily available in the literature (9). The estimated pure and mixed virial coefficients and the molar volumes of the pure liquids at 95 and 80 °C are given in Tables VI and VII. A lower value for the AAD(Δy) and AAD(ΔP) indicates a better representation of the data. An inspection of Figures 3 and 4 shows that the activity coefficients are typically near unity, which is an indication of closely ideal behavior. These figures also indicate that the two Margules constants (A_{12} and A_{21}) should be the same for this binary system (because of the identical infinite dilution values). Thus, also shown in Table IV is the single Margules constant at each of the two temperatures.

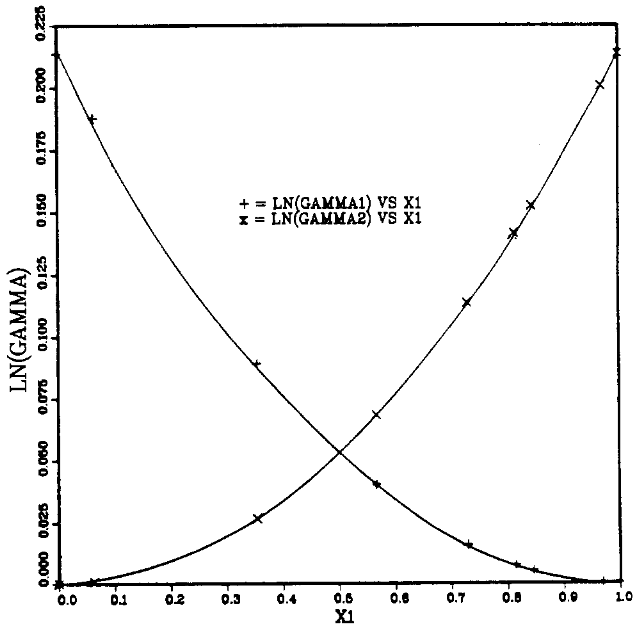

Figure 4. Experimental liquid-phase activity coefficients for the system chlorobenzene (1)-nitrobenzene (2) at 80.0 °C.

Acknowledgment

We thank Professor A. S. Teja for his interest in this work and for the use of his Stage-Muller still.

Glossary

A_{ij}	parameters used in the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations
AAD	average absolute deviation
a_{mn}	interaction parameters in the UNIFAC equations
F	objective function to be minimized in determining UNIFAC parameters
m	number of data points
P	pressure
s	objective function to be minimized in fitting $P-T-x-y$ data
T	temperature
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapor phase
γ_i	activity coefficient of component i in the liquid phase
σ	standard deviation
σ^2	variance

Registry No. PhCl, 108-90-7; $PhNO_2$, 98-95-3; Cl_2, 7782-50-5.

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Vapor Pressure of Pivalaldehyde

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The vapor pressure of pivalaldehyde was measured over the temperature range of 34.6–62.6 °C by use of a Stage–Muller equilibrium still. The experimental data obtained were correlated by the Antoine equation: log $P = A - B/(T + C)$, with $A = 7.088\,01$, $B = 1206.631$, and $C = 214.887$ and where the vapor pressure (P) is in mmHg and the temperature (T) is in °C.

Introduction

There is a relative scarcity of experimental data on the physical properties of pure aldehydes and mixtures containing aldehydes. Undoubtedly, this scarcity derives from the considerable difficulties associated with working with aldehydes in the laboratory, resulting from their instability due to oxidation and polymerization. Thus, for example, in the most recent compilation by Gmehling et al. (*1*) of binary group interaction parameters in the UNIFAC group contribution method for estimating vapor-liquid equilibria (VLE), many of these parameters for the interaction of the aliphatic aldehyde group (CHO) with the other 39 groups currently in this method are not available, including, for example, olefins, aromatic hydrocarbons, aliphatic acids, and multiply chlorinated hydrocarbons.

Pivalaldehyde (or trimethylacetaldehyde) is the simplest aliphatic aldehyde not containing any α-hydrogen atoms. It is also available in relatively pure form at moderate cost. Thus, the objective of this work was the measurement of the vapor pressure of pivalaldehyde at various temperatures. The resulting data should be useful in themselves as pure component information, as well as in support of VLE studies involving this particular aldehyde and aldehydes in general.

Equipment and Experiments

Pivalaldehyde was purchased from Fluka Chemicals in a stated purity of at least 99%. This purity was checked by gas chromatographic analysis prior to the actual vapor pressure measurements.

Table I. Physical Properties of Pivalaldehyde (Trimethylacetaldehyde), $C_5H_{10}O$

property	this study[a]	ref *6*	% Δ[b]
NBP, °C	71.9	74	-2.838
η_D, 20 °C	1.3769	1.3791	-0.159

[a] With trace of hydroquinone (<0.2 wt %) added. [b] % Δ = ((measd prop. − lit. prop.)/lit. prop.) × 100.

The equilibrium vessel used in this work was an all-glass, Stage–Muller dynamic still equipped with a Cottrell pump and was manufactured by Fischer Labor- und Verfahrenstechnik of West Germany. The essential features of the still and the basic procedures for these measurements were as described by Eng and Sandler (*2*) and by Willman (*3*).

All experiments were carried out under an inert nitrogen atmosphere. The temperature was measured with an accuracy of 0.2 °C by use of a total immersion thermometer, and the pressure was measured by use of a mercury manometer whose flexible seals allowed compensation for local gravity and temperature effects. A Fisher VKH100 vacuum/pressure controller maintained the pressure constant to within 0.05 mmHg by usng a solenoid valve. Further details on the experimental apparatus, calibration of the thermometer, and calibration of the equilibrium still are given by Varughese (*4*).

To avoid any oxidation of the pivalaldehyde, a trace of hydroquinone (<0.2 wt. % of the pivalaldehyde used) was introduced into the equilibrium still as described by Wojtasinski (*5*). Analysis for impurities was carried out by chromatographic and refractometric methods. In Table I the characteristics of the pivalaldehyde utilized have been compared with those of the pure material as given in the literature. It is evident from this table that the addition of hydroquinone did not affect the physical properties of pivalaldehyde significantly. No deterioration of the pivalaldehyde was observed in this work; thus, with the precautions noted above, the usage of pivalaldehyde in VLE

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