X_3^{sat}	mole fraction solubility of the solute
ϕ_1°, ϕ_2°	ideal volume fraction compositions of the solvent mixture, calculated as if the solute were not present
ϕ_3^{sat}	ideal volume fraction fraction solubility of the solute
rms deviation	$= [\sum(\%\ \text{deviations})^2/N]^{1/2}$, %

Subscripts

$X_i^\circ = 1$	value in pure solvent *i*
mon	denotes the value is calculated by assuming the solute exists entirely in monomeric form
dim	denotes the value is calculated by assuming the solute completely dimerizes in solution
1, 2	solvent components
3	solute

Registry No. CCl_4, 56-23-5; C_6H_{12}, 110-82-7; *n*-C_7H_{16}, 142-82-5; *n*-C_8H_{18}, 111-65-9; *i*-C_8H_{18}, 540-84-1; phenylacetic acid, 103-82-2.

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Isobaric Vapor-Liquid Equilibria of the Binary Systems Consisting of Anisaldehyde, Methyl Anisate, and Anisyl Alcohol at 2 kPa

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The vapor pressures of the three pure components anisaldehyde, methyl anisate, and anisyl alcohol have been determined experimentally, together with the three binary vapor-liquid equilibria. The vapor pressures have been measured ebulliometrically, and the vapor-liquid equilibria by using a recirculation-type equilibrium still. The methyl anisate/anisyl alcohol system forms an azeotrope. Data reduction based on the Wilson, NRTL, and UNIQUAC models provides a correlation for the activity coefficients γ_i.

Introduction

In connection with the problem of separating anisaldehyde (4-methoxybenzaldehyde), methyl anisate (methyl 4-methoxybenzoate), and anisyl alcohol (4-methoxybenzyl alcohol) by distillation, the vapor pressures of the pure components, and the three corresponding binary vapor-liquid phase equilibria, have been measured. Because anisyl alcohol is thermally unstable, the separation by distillation has to be carried out under reduced pressure. Hence, the binary vapor-liquid phase equilibria have been measured at 2 kPa.

Experimental Section

Purity of Components. The reagents were manufactured by BASF Aktiengesellschaft, Federal Republic of Germany. Their purity was confirmed by gas chromatography. The aldehyde and alcohol had a mole fraction purity better than 99.5%, while the mole fraction purity of the ester was 99.9%.

Apparatus and Procedure. The vapor pressures of the pure components have been determined ebulliometrically with an apparatus similar to apparatus I, described by Ambrose and Sprake (*1*). The apparatus used to obtain vapor-liquid equilibrium data was a modified Hunsmann vapor-liquid recirculation still (*2*) with several modifications suggested by Brunner and Scholz (*3*, *4*).

Table I. Experimental Vapor Pressure of Anisaldehyde

t/°C	p°/kPa	t/°C	p°/kPa	t/°C	p°/kPa
74.7	0.15	110.9	1.00	189.0	20.0
83.6	0.25	126.3	2.00	212.6	40.0
92.5	0.40	146.0	4.50	233.8	70.0
100.4	0.60	167.9	10.0	248.7	100.0

Table II. Experimental Vapor Pressure of Methyl Anisate

t/°C	p°/kPa	t/°C	p°/kPa	t/°C	p°/kPa
108.6	0.54	151.4	3.70	181.5	11.20
121.3	1.00	160.2	5.20	191.8	15.70
132.7	1.71	168.2	7.00	198.7	19.50
137.9	2.15				

Table III. Experimental Vapor Pressure of Anisyl Alcohol

t/°C	p°/kPa	t/°C	p°/kPa	t/°C	p°/kPa
80.6	0.060	114.3	0.50	162.2	5.00
87.9	0.10	127.3	1.00	179.8	9.99
98.6	0.20	141.4	2.00		

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 against a dead-weight gage. The pressure constancy $\Delta p/p$ was better than 5×10^{-4}. The temperatures (IPTS-68) were measured by using a calibrated temperature meter (from Systemteknik, Sweden, 1220 series) which had a digital resolution of 0.01 K and whose accuracy was estimated to be 0.02 K. The temperatures measured were reproducible within 0.05 K.

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Table IV. Physical Data of Pure Species

	anisaldehyde	methyl anisate	anisyl alcohol
parameters of Antoine eq			
A	15.8392	15.4022	15.9174
B	-5322.90	-5005.47	-4949.53
C	225.28	203.88	183.71
$v^a/(\mathrm{cm}^3/\mathrm{mol})$	121.6	142.4	124.5
r^b	4.9986	5.9037	5.2050
q^c	3.876	4.656	4.052

[a] Molar volume of liquid (25 °C). [b] Volume parameter. [c] Area parameter.

Table V. Experimental Vapor-Liquid Equilibrium Data at 2 kPa for the Anisaldehyde (1)/Methyl Anisate (2) System

t/°C	x_1	y_1	t/°C	x_1	y_1
136.4[a]	0.0	0.0	130.1	0.569	0.668
136.2	0.0289	0.0447	128.9	0.686	0.768
135.8	0.0558	0.0869	127.9	0.802	0.859
134.8	0.167	0.238	126.6	0.9583	0.9738
132.4	0.373	0.483	126.5	0.9874	0.9912
130.5	0.545	0.650	126.2[a]	1.0	1.0

[a] Calculated by using the Antoine equation.

The compositions of the coexisting phases were determined by gas chromatography, with an accuracy $\Delta x/x$ of about 0.02. The reproducibility of measurements on the same sample was better than $\Delta x/x = 0.01$.

Results and Discussion

***Vapor Pressure*.** The experimental results of the vapor pressure measurements are summarized in Table I-III. The data were correlated with the aid of the Antoine equation:

$$\ln\,(p^\circ/\mathrm{kPa}) = A + B/(C + t/^\circ\mathrm{C}) \qquad (1)$$

The parameters A, B, and C are given in Table IV. The correlation gives mean standard deviations of 0.5%, 0.5%, 0.25%, respectively, for the experimental data.

Particular care was required in carrying out measurements on anisyl alcohol since this substance is relatively sensitive to heat and eliminates water on prolonged heating, the aromatic nucleus probably being alkylated.

In the pressure range and temperature range of interest, the literature contains virtually no data on the vapor pressures of the substances investigated. The vapor pressures for anisaldehyde in data compilations (*5*, *6*) are in very good agreement with our measurements, the maximum deviations $\Delta p^\circ/p^\circ$ being less than 0.04. The values given by Nowak (*7*) differ very greatly from the literature values and from our own results and are as much as 20% too low, especially at low pressures. For methyl anisate and anisyl alcohol, no reliable data were found in the literature.

Vapor-Liquid Equilibria The experimental vapor-liquid equilibrium results for the three binary systems at 2 kPa are summarized in Tables V-VII. The anisaldehyde/methyl anisate system shows virtually ideal behavior, whereas the methyl anisate/anisyl alcohol system forms an azeotrope with a minimum boiling point at high ester mole fractions. The thermal instability of the anisyl alcohol is expected to cause problems primarily in the measurement of the boiling point, whereas the mole fractions of the coexisting phases are affected only to a small extent when slight decomposition takes place. For this reason, the boiling points of the two systems containing anisyl alcohol were not measured; instead, Tables VI and VII contain calculated boiling points.

Table VI. Experimental Vapor-Liquid Equilibrium Data at 2 kPa for the Anisaldehyde (1)/Anisyl Alcohol (2) System

t^b/°C	x_1	y_1	t^b/°C	x_1	y_1
141.4[a]	0.0	0.0	132.6	0.451	0.639
140.8	0.0238	0.0396	129.2	0.698	0.826
140.6	0.0346	0.0692	127.3	0.878	0.9357
139.9	0.0654	0.141	126.5	0.9660	0.9885
137.6	0.174	0.315	126.2[a]	1.0	1.0
134.5	0.338	0.518			

[a] Calculated by using the Antoine equation. [b] Boiling points are calculated by using the UNIQUAC model.

Table VII. Experimental Vapor-Liquid Equilibrium Data at 2 kPa for the Methyl Anisate (1)/Anisyl Alcohol (2) System

t^b/°C	x_1	y_1	t^b/°C	x_1	y_1
141.4[a]	0.0	0.0	136.7	0.626	0.660
141.2	0.0165	0.0238	136.4	0.759	0.771
140.7	0.0502	0.0731	136.3	0.886	0.886
139.6	0.146	0.204	136.4	0.955	0.942
138.6	0.263	0.339	136.4	0.987	0.978
137.9	0.370	0.448	136.4[a]	1.0	1.0
137.2	0.495	0.544			

[a] Calculated by using the Antoine equation. [b] Boiling points are calculated by using the UNIQUAC model.

The thermodynamic relationship

$$y_i p = x_i \gamma_i p_i^\circ \qquad (2)$$

was applied to the experimental equilibrium data; because of the low system pressure, a gas-phase correction can be omitted.

The activity coefficient γ_i is a function of temperature and mole fraction. We have employed equations based on various local-composition models to describe the functional relationship. The three models used here are the following: (1) the Wilson model (*8*), (2) the NRTL model due to Renon and Prausnitz (*9*), and (3) the UNIQUAC model due to Abrams and Prausnitz (*10*). The compilation by Gmehling and Onken (*11*) contains a summary of the corresponding model equations in tabular form in the Introduction.

With the three local-composition models, further data for the pure components are required; these data are given in Table IV, together with the Antoine parameters. The volume parameter r and area parameters q for the UNIQUAC model (*10*) are relative values for the van der Waals volume and the van der Waals area of the particular molecule and have been calculated from group contributions, in accordance with Bondi (*12*, *13*). The molar volume at 25 °C can be calculated from density measurements. For anisaldehyde and anisyl alcohol, these data can be found in the literature (*14*, *15*). Since the melting point of methyl anisate is 47 °C, we have calculated a hypothetical molar volume for the liquid state at 25 °C from the values for anisaldehyde and anisyl alcohol, using the van der Waals volumes.

The parameters for the three local-composition models were determined from the measured data for the binary phase equilibria by regression analysis. The calculation procedure used was based on the maximum likelihood principle and has been proposed by Anderson, Abrams, and Grens (*16*). All three models are very suitable for correlating the measured data; there is no significant difference in the quality of the correlation. For the three binary systems together, the standard deviations of x_i and y_i are 0.001 and 0.004, respectively; the standard deviation of p is 0.025 kPa. For the temperature t, this deviation can be calculated only for the anisaldehyde/methyl anisate system, where temperature measurements are available; its value is 0.01 K.

The parameters of the three models for the three systems investigated are summarized in Table VIII. In Figure 1, the experimental data are compared with the equilibrium curves calculated on the basis of the UNIQUAC model. In each case,

Table VIII. Model Parameters for the Three Binary Systems

	anisaldehyde (1)/ methyl anisate (2)	anisaldehyde (1)/ anisyl alcohol (2)	methyl anisate (1)/ anisyl alcohol (2)
	Wilson Model		
$(\lambda_{12} - \lambda_{11})/R$	231.36	-176.12	20.917
$(\lambda_{21} - \lambda_{22})/R$	-185.82	338.09	109.43
	NRTL Model ($\alpha = 0.3$)		
$(g_{12} - g_{22})/R$	-184.56	418.94	46.737
$(g_{21} - g_{11})/R$	236.78	-261.18	81.498
	UNIQUAC Model		
$(u_{12} - u_{22})/R$	-110.87	221.97	60.092
$(u_{21} - u_{11})/R$	134.92	-159.12	-28.104

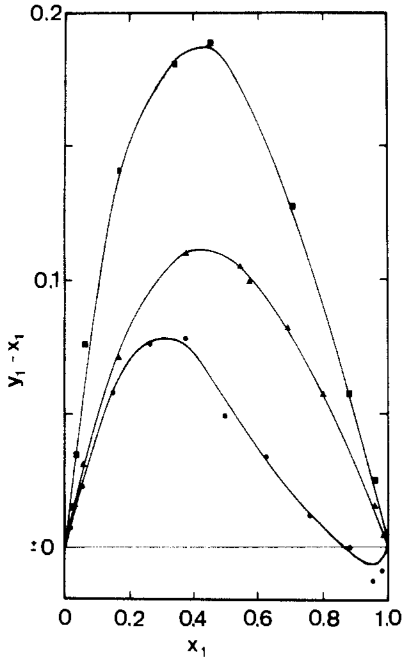

Figure 1. Vapor-liquid equilibria of the three binary systems. Plots of $y_1 - x_1$ vs. x_1: (▲) anisaldehyde (1)/methyl anisate (2), (■) anisaldehyde (1)/anisyl alcohol (2), (●) methyl anisate (1)/anisyl alcohol (2). Equilibrium curves are calculated by using the UNIQUAC model.

the difference $y_1 - x_1$ is plotted against x_1.

The azeotropic data at 2 kPa for the methyl anisate/anisyl alcohol system are 136.3 °C at a mole fraction of 0.892 of methyl anisate.

Acknowledgment

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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
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. Anisaldehyde, 123-11-5; methyl anisate, 121-98-2; anisyl alcohol, 105-13-5.

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Solubilities of Methoxy-1-tetralone and Methyl Nitrobenzoate Isomers and Their Mixtures in Supercritical Carbon Dioxide

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Solubilities in supercritical carbon dioxide at 308 K over a pressure range of 80–280 bar were measured for two sets of isomers: methoxy-1-tetralone and methyl nitrobenzoate. Solubilities of binary mixtures of two isomers within each isomer group in supercritical carbon dioxide were also measured at 308 K and 110 bar. The data show solubility trends within an isomer group, and the influence of solute composition and condensed-phase behavior on the mixture solubilities.

Introduction

Extractions with supercritical fluids as a solvent have received wide attention recently. The major advantages of using supercritical fluids are that the solvent capacities can be controlled by the system pressure and temperature and that the viscosities are lower than conventional liquid solvents. Carbon dioxide is a preferred supercritical solvent, since it is nontoxic, nonflammable, environmentally acceptable, and relatively inexpensive. Its low critical temperature (304 K) is especially suitable for

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