of measurement for $NaNO_2$ is a little narrow:

$$\beta_{s,KNO_3} > \beta_{s,NaNO_2} > \beta_{s,HTS} > \beta_{s,NaNO_3}$$

$$C_{v,NaNO_3} > C_{v,HTS} > C_{v,NaNO_2} > C_{v,KNO_3}$$

The sound velocity in $NaNO_3$ is greater than that in KNO_3 and conversely for β_s, while in $NaNO_2$ both u and β_s are greater than those of $NaNO_3$. Since the size of the cation is smaller in $NaNO_3$ than in KNO_3, the coordination in the structure would make the sound velocity in $NaNO_3$ greater than in KNO_3. For $NaNO_2$, the librational contribution between cation and anion becomes more important than for $NaNO_3$ from the structural difference of the anion, and this causes the sound velocity in $NaNO_2$ to be greater than that in $NaNO_3$ although $\beta_{s,NaNO_2}$ is greater than $\beta_{s,NaNO_3}$.

Glossary

u	sound velocity, m s^{-1}
T	temperature, K
ΔL	change in distance between the conductor and the reflector, m
ΔT	change in time interval, s
β_s	adiabatic compressibility, $m^2 N^{-1}$
ρ	density, g cm^{-3}
C_p	isobaric specific heat, J $mol^{-1} K^{-1}$
C_v	isochoric specific heat, J $mol^{-1} K^{-1}$
α	thermal expansivity, K^{-1}
M	molar volume

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Isobaric Binary Vapor-Liquid Equilibria for the Systems Allyl Alcohol-Toluene and Toluene-Benzaldehyde

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Isobaric vapor-liquid equilibria for the binary systems allyl alcohol-toluene and toluene-benzaldehyde were measured at 760 ± 1 mmHg pressure by using a modified Jones vapor recirculatory still. The system allyl alcohol-toluene has shown positive deviations from Raoult's law. Redlich-Kister, Wilson, NRTL, and UNIQUAC models were employed to correlate the experimental data. The system toluene-benzaldehyde was nearly ideal in its behavior, and the data were correlated by the method of Hirata.

Isobaric vapor-liquid equilibrium (VLE) data at 760 ± 1 mmHg pressure were determined for the systems allyl alcohol-toluene and toluene-benzaldehyde. The VLE data of the former system find use in the purification of allyl alcohol. Toluene-benzaldehyde mixtures occur in the manufacture of benzaldehyde from toluene. Hence, knowledge of vapor-liquid equilibrium data on these systems is of use in the design of separation equipment. The VLE data on allyl alcohol-toluene mixtures at 760-mmHg pressure and at 90 °C were reported in the literature (*1*, *2*).

Experimental Section

Purity of Chemicals. Analytical-grade allyl alcohol and toluene were distilled in a Defton column, and the middle fractions were collected and used. Benzaldehyde, also of analytical grade, was distilled under vacuum, and the heart cuts of the distillate were used in the experimental runs. The physical constants of the pure components, compared with the literature values (*3*), are presented in Table I along with the source of the chemicals. Special care was taken to see that benzaldehyde did not come in contact with oxygen in the air during the distillation and use in the equilibrium still by connecting an alkaline pyrogallol tower to the system to prevent atmospheric oxidation of benzaldehyde.

Apparatus, Technique, and Analysis. The VLE data were measured by using the Jones vapor recirculatory still modified by Ward (*4*). The operation of the still was described previously (*5*). Vapor condensate and liquid-phase samples were analyzed by precision refractometry (Abbe's refractometer) at 30 ± 0.1 °C with the aid of calibration curves constructed from n_D vs. x data measured for synthetic binary mixtures. The equilibrium temperatures were taken with a mercury-in-glass thermometer having an accuracy of ±0.1 °C. The estimated precision of the equilibrium mixture composition measurements was ±0.006 mole fraction for allyl alcohol-toluene mixtures and ±0.01 mole fraction for toluene-benzaldehyde mixtures.

Results and Discussion

The vapor-liquid equilibrium data for the two systems studied are given in Tables II and III.

The liquid-phase activity coefficients for each component were calculated from the experimental data by using eq 1. At

$$\gamma_i = \Pi\phi_i^{v} y_i/(P_i^{s}\phi_i^{s} x_i) \tag{1}$$

atmospheric pressure, the ratio ϕ_i^{v}/ϕ_i^{s} was found to be around unity. Hence, it was ignored in the calculations. This is in

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Table I. Physical Constants of the Chemicals

chemical	source	bp, °C exptl	bp, °C lit. (*3*)	refractive index at 30 °C exptl	refractive index at 30 °C lit. (*3*)	vapor-pressure equation
allyl alcohol	BDH India[a]	97.1	97.08	1.4090	1.4090	$\log P = 11.18664 - 4068.457/(392.732 + t)$
toluene	BDH India[a]	110.6	110.6	1.4912	1.4912	$\log P = 6.95105 - 1342.310/(219.187 + t)$
benzaldehyde	BDH India[a]	179.0	179.0	1.5400	1.5401[b]	$\log P = 45.625 - 4536.82/T - 12.3189 \log T$

[a] BDH Chemicals Division, Glaxo Laboratories (India) Limited. [b] Calculated by using dn/dt.

Table II. Vapor-Liquid Equilibrium Data for the System Allyl Alcohol (1)-Toluene (2) at a Pressure of 760 mmHg

temp, °C	x_1	y_1	temp, °C	x_1	y_1
107.1	0.017	0.079	92.0	0.452	0.555
105.5	0.028	0.134	91.7	0.530	0.577
98.0	0.121	0.351	91.5	0.603	0.607
97.0	0.152	0.386	91.9	0.756	0.696
96.1	0.162	0.407	94.0	0.909	0.825
95.3	0.194	0.419	94.1	0.922	0.861
93.8	0.247	0.467			

Table III. Vapor-Liquid Equilibrium Data for the System Toluene (1)-Benzaldehyde (2) at a Pressure of 760 mmHg

temp, °C	x_1	y_1 exptl	y_1 calcd (Raoult's law)
166.4	0.077	0.418	0.400
160.9	0.097	0.522	0.462
153.2	0.158	0.583	0.600
146.9	0.209	0.658	0.679
141.1	0.281	0.745	0.758
138.6	0.327	0.790	0.795
134.8	0.380	0.836	0.831
131.8	0.424	0.863	0.855
126.7	0.490	0.896	0.885
122.7	0.615	0.939	0.933
114.5	0.846	0.993	0.989

accordance with the suggestion of Hudson and Van Winkle (*6*). The vapor-pressure equations used in the calculations are listed in Table I.

Allyl Alcohol-Toluene System. The system exhibited positive deviations from Raoult's law as observed from the activity-coefficient data. It formed an azeotrope at 62 mol % allyl alcohol and at a temperature of 91.4 °C. The experimental azeotropic data are found to be in good agreement with the data of Horsley (*7*). Further, the experimental azeotropic composition was verified and confirmed in a laboratory fractionation set up under total reflux conditions.

The experimental *T-x-y* data were found to be thermodynamically consistent by the Herington method (*8*).

Four models describing the activity coefficient in the liquid phase were tried to fit the experimental data.

(i) Redlich-Kister polynomial expansions as modified by Chao and Hougen (*9*):

$$\ln (\gamma_1/\gamma_2) = A + B(x_2 - x_1) - C(6x_1x_2 - 1) - D(x_2 - x_1)(1 - 8x_1x_2) \tag{2}$$

$$Q = x_1x_2[B' - C'(x_1 - x_2) + D'(x_1 - x_2)^2] \tag{3}$$

(ii) Wilson (*10*):

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right] \tag{4}$$

$$\ln \gamma_2 = -\ln (x_2 - \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right] \tag{5}$$

Table IV. Model Parameters for Allyl Alcohol-Toluene System at 760-mmHg Pressure

	parameters	y_1[a]
	Redlich-Kister	
A	0.0228	0.0121
B	0.5330	
C	0.0470	
D	0.0355	
B'	0.6352	
C'	0.07874	
D'	0.07537	
	Wilson Model	
$(\lambda_{12} - \lambda_{22}), (\lambda_{21} - \lambda_{11})$	900.2861, 294.6341	0.0123
	NRTL Model ($\alpha_{12} = 0$)	
$(g_{12} - g_{22}), (g_{21} - g_{11})$	545.8001, 426.7179	0.0131
	NRTL Model (*T-x* Data, $\alpha_{12} = 0.4$)	
$(g_{12} - g_{22}), (g_{21} - g_{11})$	791.585, 498.789	0.020
	UNIQUAC Model	
$(u_{12} - u_{22}), (u_{21} - u_{11})$	−20.6189, 417.2956	0.013

[a] Absolute average deviation in vapor composition.

where

$$\Lambda_{ij} = (V_j^L/V_i^L) \exp[-(\lambda_{ij} - \lambda_{ii})/RT]$$

(iii) NRTL with a preset value of α_{12} (*11*):

$$\ln \gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + G_{21}x_2}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + G_{12}x_1)^2}\right] \tag{6}$$

$$\ln \gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + G_{12}x_1}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + G_{21}x_2)^2}\right] \tag{7}$$

where

$$\tau_{12} = (g_{12} - g_{22})/RT \qquad \tau_{21} = (g_{21} - g_{11})/RT$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \qquad G_{21} = \exp(-\alpha_{12}\tau_{21}) \qquad g_{12} = g_{21}$$

(iv) UNIQUAC (*12*):

$$\ln \gamma_1 = \ln \frac{\Phi_1}{x_1} + \left(\frac{z}{2}\right)q_1 \ln \frac{\theta_1}{\Phi_1} + \Phi_2\left(l_1 - \frac{r_1}{r_2}l_2\right) - q_1 \ln (\theta_1 + \theta_2\tau_{21}) + \theta_2q_1\left(\frac{\tau_{21}}{\theta_1 + \theta_2\tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1\tau_{12}}\right) \tag{8}$$

$$\ln \gamma_2 = \ln \frac{\Phi_2}{x_2} + \left(\frac{z}{2}\right)q_2 \ln \frac{\theta_2}{\Phi_2} + \Phi_1\left(l_2 - \frac{r_2}{r_1}l_1\right) - q_2 \ln (\theta_2 + \theta_1\tau_{12}) + \theta_1q_2\left(\frac{\tau_{12}}{\theta_2 + \theta_1\tau_{12}} - \frac{\tau_{21}}{\theta_1 + \theta_2\tau_{21}}\right) \tag{9}$$

where

$$l_1 = (z/2)(r_1 - q_1) - (r_1 - 1)$$

$$l_2 = (z/2)(r_2 - q_2) - (r_2 - 1)$$

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

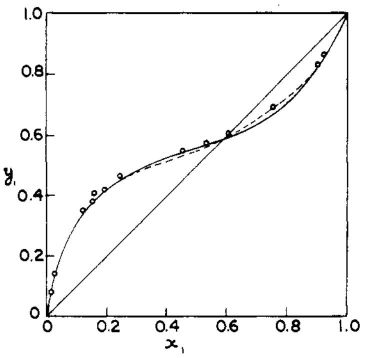

Figure 1. Equilibrium curve for the system allyl alcohol-toluene: (O) experimental; (- - -) Wilson; (—) Redlich-Kister.

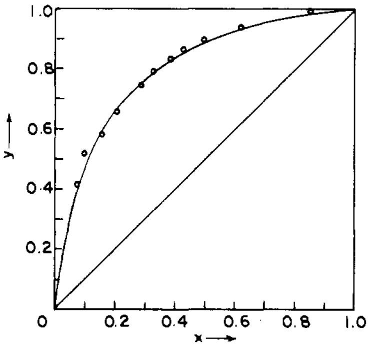

Figure 2. Equilibrium curve for the system toluene-benzaldehyde: (O) experimental data; (—) Raoult's law.

$$\Phi_1 = x_1r_1/(x_1r_1 + x_2r_2) \qquad \Phi_2 = x_2r_2/(x_1r_1 + x_2r_2)$$

$$\tau_{12} = \exp[-(u_{12} - u_{22})/RT]$$

$$\tau_{21} = \exp[-(u_{21} - u_{11})/RT]$$

The parameters of the Redlich-Kister equations were obtained by following the method of Chao (*13*), whereas the parameters of the Wilson, NRTL, and UNIQUAC equations were evaluated by using a nonlinear optimization method (*14*) with an objective function based on the calculated and experimental activity coefficients.

Further, the model parameters for NRTL equations were determined by following the procedure described by Fields (*15*) using the experimental T-x data. All of the model parameters are listed in Table IV along with the absolute average deviations between the experimental and calculated vapor-phase mole fractions. The Redlich-Kister and Wilson models represented the experimental data better than the other models. Figure 1 shows the equilibrium curve for the allyl alcohol-toluene system denoting the calculated vapor composition values using Redlich-Kister and Wilson equations.

Toluene-Benzaldehyde System. The mixture of toluene-benzaldehyde was found to be nearly ideal. The y-x diagram is shown in Figure 2. The vapor composition of the more volatile component was calculated from the vapor-pressure data by using Raoult's law and was compared with the experimental values. The absolute average deviation in y_1 is 1.52%. A linear relation resulted when the data were correlated by the method of Hirata (*16*). As the data conform with Raoult's law within the experimental errors, the data are thermodynamically consistent.

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Glossary

A, B, C, D, B', C', D'	parameters in Redlich-Kister model
G_{12}, G_{21}	parameters in NRTL model
$(g_{12} - g_{22})$, $(g_{21} - g_{11})$	energetic parameters in NRTL model
l_1, l_2	as defined in eq 8 and 9
n_D	Na D line refractive index
P_i^s	saturation pressure of pure component
Q	excess free energy function
q	pure-component area parameter
R	gas constant
r	pure-component volume parameter
t, T	temperature
$(u_{12} - u_{22})$, $(u_{21} - u_{11})$	energetic parameters in UNIQUAC model
V_i^L	liquid molar volume of pure component i
x	liquid-phase mole fraction
y	vapor-phase mole fraction
z	lattice coordination number

Greek Letters

α_{12}	nonrandomness constant in NRTL model
γ	liquid-phase activity coefficient
θ	area fraction in UNIQUAC model
λ_{ij}	energetic parameter in Wilson model
π	total pressure
Φ	volume fraction in UNIQUAC model
ϕ_i^s	standard-state fugacity coefficient of pure component
ϕ_i^v	vapor-phase fugacity coefficient

Subscripts

i, j, 1, 2	components

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