troublesome, because it has been determined by an extrapolation technique. One of the outstanding features of this infrared analysis technique is that it has facilitated the actual experimental determination of the end point.

The upper limit of 5 weight % salt could be extended by aliquot dilution with pure acetonitrile. Extension beyond the plait point by this method is not recommended.

The plait points for the two systems were determined by the novel technique of rectilinear diameters proposed by Renard and Heichelheim (*6*). These values differed from values determined by the conventional Coolidge (*2*) technique of extrapolation of the conjugation curve to the binodal curve by 5.1 and 4.7% for the diammonium citrate and diammonium phosphate systems, respectively.

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Isothermal Vapor-Liquid Equilibrium Data by Total Pressure Method

Systems Acetaldehyde-Ethanol, Acetaldehyde-Water, and Ethanol-Water

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Isothermal vapor-liquid equilibrium data were obtained by the total pressure method for the binary systems acetaldehyde-ethanol, acetaldehyde-water, and ethanol-water at 10°, 15°, 20°, 25°, and 30° C, using a modified Menzies and Smith's isoteniscope. Barker's method was employed for the numerical calculations.

AT A STAGE of the catalytic process for the manufacture of acetaldehyde from ethanol, the separation of components of the acetaldehyde-ethanol-water mixture is necessary. Vapor-liquid equilibrium data were nonexistent in the literature for the working range of interest in this process.

This paper presents the vapor-liquid equilibrium data for the binary systems acetaldehyde-ethanol, acetaldehyde-water, and ethanol-water at 10°, 15°, 20°, 25°, and 30° C, obtained through the method of total pressure.

The total pressure method for obtaining vapor-liquid equilibrium data consists of the determination of the total pressure above a liquid solution of known composition in equilibrium at a fixed temperature. Analyses of the liquid and vapor phases are not necessary.

The binary data have been extended to the ternary system acetaldehyde-ethanol-water by means of the Redlich-Kister equation, assuming ideal behavior of the vapor phase within the temperature interval under consideration (*11*).

APPARATUS

The experimental apparatus (Figure 1) is a modification of Menzies and Smith's isoteniscope (*3*). Serrano (*10*) tested it with the system chloroform-ethanol, in the range 30° to 50° C and his equilibrium data agreed with those of the literature (*9*).

The apparatus consists of a cylindrical bulb, *A*, of approximately 25 ml, containing the liquid mixture; a capillary mercury manometer, *B*, to establish the equilibrium; a mercury reservoir, *C*; and the open-tube mercury manometer, *F*, which was designed to measure pressures up to 1480 mm of Hg.

The liquid mixtures were prepared from the pure components using a microburet (precision, ±0.02 ml). The maximum error involved in this operation was estimated as 0.25% (*13*).

After degassing the sample, sections *A* and *B* were placed in a thermostatic bath, controlled by a mercury thermostat (accuracy, ±0.1° C). The equilibrium is established when the heights of mercury in both branches of the manometer

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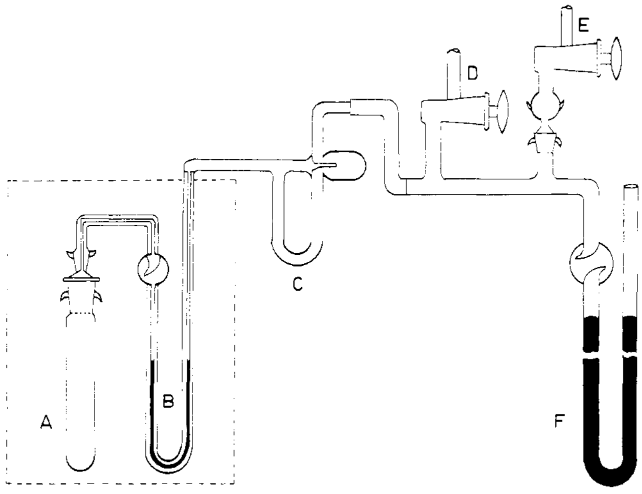

Figure 1. Apparatus

B are equal, and this can be attained by introducing air through stopcock *D* or *E*. The total pressure is given by the difference between the atmospheric pressure, measured by a barometer (accuracy, ±0.1 mm of Hg) and the displacement in manometer *F*, which is read by means of a cathetometer.

RESULTS

Experimental Data. Measurements of total pressure were made for the systems acetaldehyde-ethanol, acetaldehyde-water, and ethanol-water for values of the liquid phase concentration $x_1 = 0.1, 0.3, 0.5, 0.7$, and 0.9, at temperatures of 10°, 15°, 20°, 25°, and 30° C.

The results are presented in Table I.

Calculation of Thermodynamic Properties. Redlich-Kister coefficients for the binary systems were calculated by Barker's method of successive approximations (*1*), taking into account nonideal behavior of the vapor phase.

The activity coefficients were obtained from the Redlich-Kister equation:

$$\ln\gamma_1 = (1 - x_1)^2 [B_{12} - C_{12}(1 - 4\ x_1) + D_{12}\ (1 - 8\ x_1 + 12\ x_1^2)] \quad (1)$$

Vapor compositions were calculated by the equation

$$\ln\gamma_1 = \frac{\ln Py_1}{P_1^\circ\ x_1} + \frac{(\beta_{11} - v_1^{\circ L})(P - P_1^\circ) + \delta_{12}P\ (1 - y_1)^2}{RT} \quad (2)$$

where

$$\delta_{12} = 2\beta_{12} - \beta_{11} - \beta_{12} \quad (2a)$$

Table I. Data for Systems Acetaldehyde-Ethanol, Acetaldehyde-Water, and Ethanol-Water

		Acetaldehyde(1)-Ethanol(2)				Acetaldehyde(1)-Water(3)				Ethanol(2)-Water(3)			
	Temp., °C	P_{exptl}, mm Hg	$P_{\text{exptl}} - P_{\text{calcd}}$, mm Hg	γ_1	γ_2	P_{exptl}, mm Hg	$P_{\text{exptl}} - P_{\text{calcd}}$, mm Hg	γ_1	γ_3	P_{exptl}, mm Hg	$P_{\text{exptl}} - P_{\text{calcd}}$ mm Hg	γ_2	γ_3
0.1	10	34.8	0.2	0.257	1.000	179.9	−0.6	3.386	1.024	14.3	0.0	2.477	1.001
	15	46.8	−0.5	0.298	0.986	197.4	−0.3	2.990	1.018	20.4	0.0	2.698	1.011
	20	55.3	0.7	0.217	0.966	216.3	0.0	2.653	1.016	28.5	0.0	2.828	1.015
	25	73.6	1.7	0.229	0.953	252.6	0.0	2.501	1.018	39.1	0.0	2.937	1.016
	30	116.9	2.0	0.412	0.983	302.8	−0.2	2.515	1.017	53.0	0.0	3.025	1.016
0.3	10	75.0	−0.1	0.395	0.885	307.1	1.6	1.955	1.167	19.5	0.1	1.707	1.110
	15	115.4	0.6	0.510	0.860	365.5	0.8	1.900	1.136	27.3	−0.1	1.785	1.123
	20	141.7	−0.5	0.521	0.783	418.2	0.0	1.786	1.117	37.1	0.0	1.749	1.144
	25	202.1	−1.2	0.621	0.757	472.8	0.0	1.640	1.126	50.6	0.0	1.173	1.152
	30	262.9	−1.5	0.661	0.876	553.3	0.5	1.615	1.132	68.5	−0.1	1.811	1.155
0.5	10	182.3	−0.1	0.689	0.609	378.8	−2.5	1.476	1.404	21.3	0.0	1.253	1.363
	15	250.5	−0.6	0.773	0.653	456.3	−1.4	1.444	1.363	29.9	0.1	1.280	1.400
	20	316.2	0.5	0.802	0.593	539.2	0.1	1.397	1.316	40.2	0.1	1.252	1.427
	25	415.5	1.4	0.857	0.619	622.3	0.0	1.315	1.301	54.5	0.0	1.261	1.442
	30	500.4	0.6	0.864	0.736	709.1	−0.6	1.265	1.329	73.3	0.0	1.266	1.462
0.7	10	343.9	0.2	0.959	0.377	435.3	1.5	1.205	1.917	22.3	−0.2	1.051	1.764
	15	422.6	0.5	0.959	0.477	521.9	1.4	1.179	0.857	31.2	0.0	1.059	1.849
	20	508.7	0.4	0.952	0.463	623.2	−0.1	1.162	1.744	41.9	−0.1	1.051	1.841
	25	612.1	−1.5	0.935	0.547	743.7	0.0	1.133	1.633	51.1	0.0	1.057	1.868
	30	757.3	1.0	0.972	0.620	851.4	−0.1	1.096	1.646	76.8	0.4	1.052	1.916
0.9	10	462.7	−0.6	1.001	0.326	475.7	1.6	1.029	3.730	23.9	0.3	1.000	2.103
	15	562.2	−0.6	1.002	0.413	576.5	−1.1	1.024	3.344	32.0	−0.1	1.001	2.265
	20	679.4	0.4	0.998	0.390	700.0	0.3	1.022	2.982	43.5	0.0	1.001	2.192
	25	823.9	2.0	0.986	0.431	852.7	0.1	1.019	2.552	58.8	0.0	1.001	2.266
	30	980.2	−4.3	1.000	0.564	1001.4	1.9	1.012	2.284	77.9	−0.5	1.000	2.287

The second virial coefficients of acetaldehyde, reported by Rowlinson (*8*), were used, with extrapolation to 10° C. The virial coefficients for ethanol (β_{22}) and water (β_{33}) were obtained, respectively, by the Kretschmer and Wiebe (*6*) and Keyes, Smith, and Gerry (*5*) equations,

$$\beta_{22} = 290 - 0.284 \exp (2730/T) \tag{3}$$

$$\beta_{33} = 18\left[1.89 - \frac{2641.62}{T} \times 10^{80870\,T^{-2}}\right] \tag{4}$$

The method of Stockmayer potential (*4*) was used to predict the mixture virial coefficients β_{13}, β_{12}, and β_{23}.

The excess free energies were also calculated using Equation 5

$$g^E = RT \sum_{i=1}^{2} x_i \ln\gamma_i \tag{5}$$

A Fortran IV program was written to perform all these calculations, taking into account nonideal behavior of the vapor phase. The same results were obtained by setting the virial coefficients equal to zero—i.e., assuming ideal vapor phase. The differences between the calculated and experimental values of the total pressure, shown in Table I, indicate the adequacy of the fit.

The variations of the activity coefficients with liquid concentration for the three binary systems are also shown in Table I.

The Redlich-Kister coefficients are presented in Table II.

Figures 2, 3, and 4 present the calculated *x*-*y* diagrams for the binary systems at 25° C.

The binary results can be extended to the ternary systems using a "quasi-fourth-order" Redlich-Kister equation (Equation 6), taking the ternary constants equal to zero.

$$\begin{aligned}\ln\gamma_1 = {} & x_2\, x_3 \left[(B_{12} + B_{13} - B_{23}) + C_{12}\,(2x_1 - x_2) + C_{13}\,(2x_1 - x_3) + \right. \\ & 2\,C_{23}\,(x_3 - x_2) + D_{12}\,(x_1 - x_2)\,(3x_1 - x_2) + D_{13}\,(x_1 - x_3)\,(3x_1 - x_3) - \\ & \left. 3\,D_{23}\,(x_3 - x_2)^2\right] + x_2^2\left[B_{12} + C_{12}\,(3x_1 - x_2) + D_{12}\,(x_1 - x_2)\,(5x_1 - x_2)\right] + \\ & x_3^2\left[B_{13} + C_{13}\,(3x_1 - x_3) + D_{13}\,(x_1 - x_3)\,(5x_1 - x_3)\right]\end{aligned} \tag{6}$$

Similar equations can be obtained for $\ln\gamma_2$ and $\ln\gamma_3$ by cyclic permutation of the subscripts.

The ternary activity coefficients can be calculated for any liquid concentration using the constants from Table II.

Table II. Redlich-Kister Coefficients

System	*t*, ° C	B_{12}	C_{12}	D_{12}
Acetaldehyde(1)-ethanol(2)	10	−1.737	0.247	0.643
	15	−1.366	0.337	0.229
	20	−1.487	0.604	−0.117
	25	−1.265	0.651	−0.513
	30	−0.904	0.322	0.016
		B_{13}	C_{13}	D_{13}
Acetaldehyde(1)-water(3)	10	1.457	0.099	0.339
	15	1.354	0.115	0.210
	20	1.218	0.120	0.183
	25	1.075	0.020	0.216
	30	1.038	−0.099	0.127
		B_{23}	C_{23}	D_{23}
Ethanol(2)-water(3)	10	1.072	−0.168	−0.165
	15	1.168	−0.180	−0.152
	20	1.159	−0.262	−0.104
	25	1.196	−0.267	−0.081
	30	1.232	−0.287	−0.118

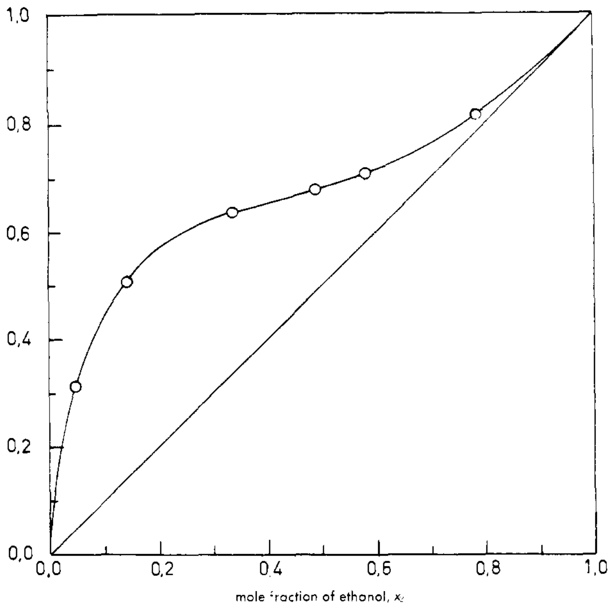

Figure 2. *x*-*y* diagram of ethanol-water mixture
O Experimental
—Calculated

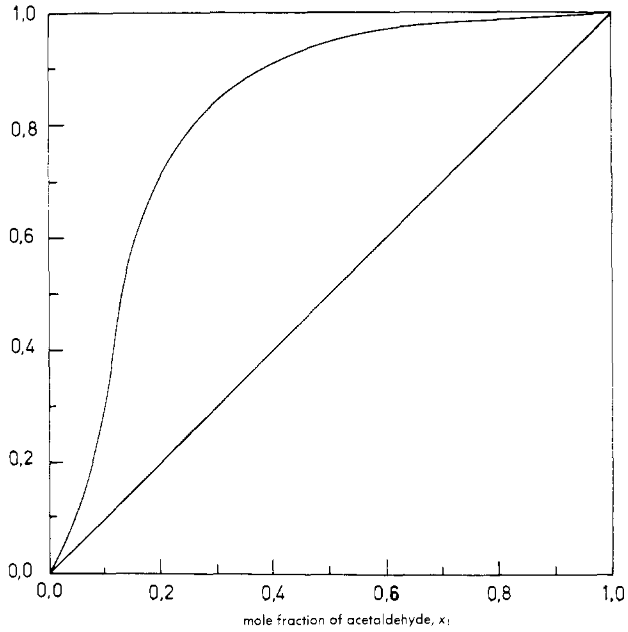

Figure 3. *x*-*y* diagram of acetaldehyde-ethanol mixture
—Calculated

If the vapor phase of the ternary system is taken as ideal, the concentrations are easily calculated, solving the system of equations

$$\frac{y_1}{y_2} = \frac{P_1^\circ\gamma_1 x_1}{P_2^\circ\gamma_2 x_2} \tag{7}$$

$$\frac{y_1}{y_3} = \frac{P_1^\circ\gamma_1 x_1}{P_3^\circ\gamma_3 x_3} \tag{8}$$

$$y_1 + y_2 + y_3 = 1 \tag{9}$$

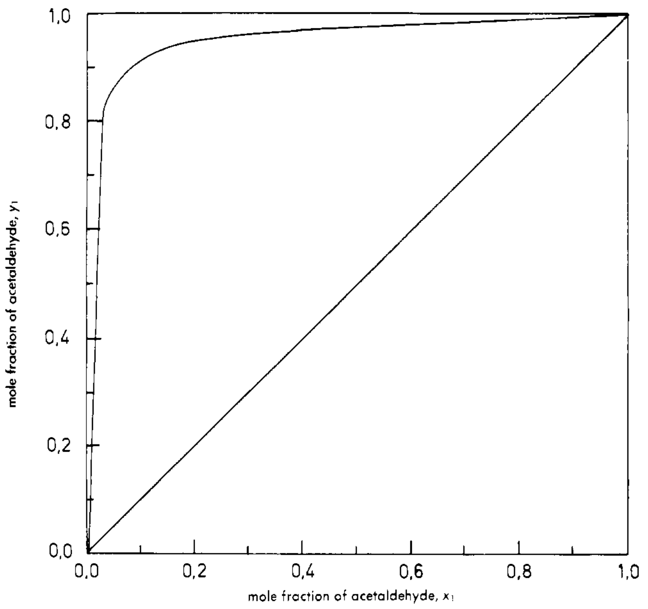

Figure 4. x-y diagram of acetaldehyde-water mixture
—Calculated

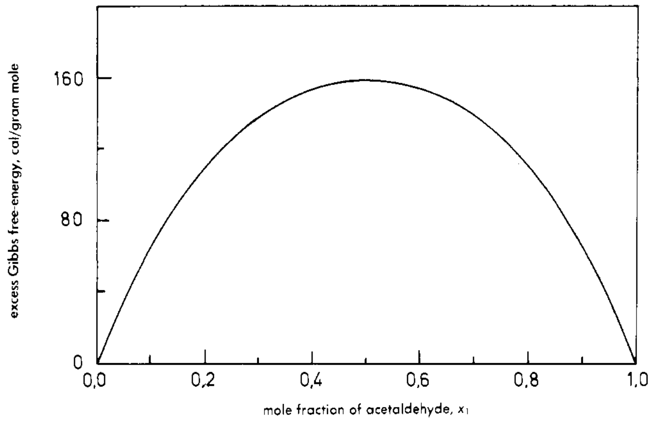

Figure 5. Molar excess Gibbs free energy of acetaldehyde-water mixture
—Calculated

CONCLUSIONS

The data on ethanol-water mixture at 25° C are compared with Dobson's data (*2*) in Figure 2, demonstrating the efficiency of the modified isoteniscope.

The acetaldehyde-water system approaches the regular behavior at 25° C, as can be seen by inspection of Figure 5. According to Rowlinson (*7*), this fact may be due to the presence of —CH_3 groups which reduces the total number of hydrogen bonds in the mixture.

The three binary mixtures exhibit ideal vapor phase in the range 10° to 30° C. The differences between the experimental and calculated pressures shown in Table I can give an indication of the thermodynamic consistency of the experimental points.

NOMENCLATURE

B_{ij}, C_{ij}, D_{ij} = binary Redlich-Kister coefficients, Equation 1
g^E = molar excess Gibbs free-energy, cal/gram mole
P = total pressure, mm of Hg
P° = vapor pressure of pure component, mm of Hg
R = universal gas constant, cal/(gram mole) (° K)
T = absolute temperature, ° K
v = partial molal volume, cm^3/gram mole
x = liquid phase mole fraction
y = vapor phase mole fraction

Greek Letters

β_{ij} = mixture second virial coefficients, cm^3/gram mole
β_{ii}, β_{jj} = pure component second virial coefficients, cm^3/gram mole
γ_i = activity coefficient
δ_{ij} = $2\beta_{ij} - \beta_{ii} - \beta_{jj}$

Subscripts

i, j = component 1, 2, or 3
1, 2, 3 = acetaldehyde, ethanol, and water, respectively

Superscripts

$^\circ$ = pure component
L = liquid

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