

Vapor-Liquid Equilibria of Acetone, Isopropenyl Acetate, and Acetic Anhydride

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Isothermal vapor-liquid equilibria of acetone-isopropenyl acetate-acetic anhydride at 55°C were studied. The data were obtained with a commercially available Othmer still and can be satisfactorily correlated with Raoult's law for distillation calculations.

Work is in progress in this laboratory to develop a commercially feasible process for the production of isopropenyl stearate. One potential process is based on the ester interchange reaction of stearic acid with isopropenyl acetate (IPA) to form isopropenyl stearate. The reactor product contains the volatiles, acetone, IPA, and acetic anhydride (AC₂O). It was the purpose of this study to determine the vapor-liquid equilibria (VLE) of the ternary system acetone-IPA-AC₂O for use in the design of distillation columns for separating these compounds from the nonvolatile products and purifying the volatiles for recycle.

Experimental

Materials. Acetone and AC₂O were ACS reagent grade chemicals purchased from J. T. Baker Chemical Co. IPA was purchased from Matheson Coleman & Bell. Acetone, IPA, and

AC₂O were purified by distillation as described under the Apparatus and procedure section. Gas-liquid chromatography analysis of ternary samples indicated maximum impurities of 0.5 wt %.

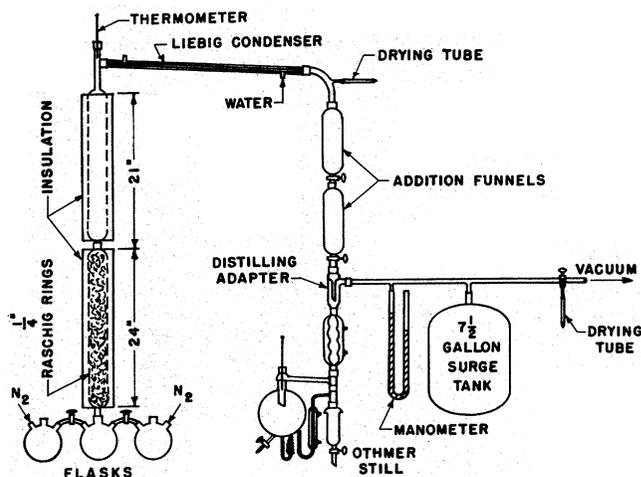


Figure 1. Experimental apparatus

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Apparatus and procedure. An Othmer still, Model 6520-D, purchased from Ace Glass, Inc., Vineland, N.J., was used. The still was insulated with Fiberglas and equipped with a calibrated precision, NBS specification, total immersion thermometer graduated from -10° to 101°C with an accuracy of $\pm 0.1^{\circ}\text{C}$.

Since all three components are hygroscopic, it was necessary to purify and feed the chemicals to the still in situ. Figure 1 shows the physical arrangement to accomplish this. The chemicals were placed in flasks at the bottom of a packed column. The column was packed to a depth of 2 ft with $\frac{1}{4}$ -in.

Raschig rings. A 400-mm Allihn condenser was attached to the flask's top. Both columns were insulated with 1-in. Fiberglas. A thermometer was placed at the top of the Allihn condenser to check the vapor temperature.

The distillate was condensed in a 500-mm Liebig condenser and collected in two 100-ml addition funnels. This section of the apparatus was vented through a distilling adapter equipped with a drying tube.

The addition funnels were used as reservoirs for feeding the still and were connected to the still condenser through a distilling adapter. The side tube of the distilling adapter was

Table I. Raw Data for Thermodynamic Consistency Test

Acetone-isopropenyl acetate $\ln VP_1/VP_2 = 1.459$		Acetone-acetic anhydride $\ln VP_1/VP_3 = 3.192$		Isopropenyl acetate-acetic anhydride $\ln VP_2/VP_3 = 1.733$	
X_1	$\ln \frac{Y_1(1-X_1)}{X_1(1-Y_1)}$	X_1	$\ln \frac{Y_1(1-X_1)}{X_1(1-Y_1)}$	X_2	$\ln \frac{Y_2(1-X_2)}{X_2(1-Y_2)}$
0.041	1.150	0.140	2.914	0.025	1.433
0.052	1.310	0.209	2.801	0.035	1.703
0.059	1.396	0.259	2.997	0.048	1.601
0.069	1.394	0.355	3.026	0.068	1.628
0.081	1.336	0.465	3.064	0.165	1.669
0.085	1.361	0.551	3.000	0.184	1.638
0.098	1.225	0.640	3.048	0.313	1.610
0.112	1.416	0.691	3.194	0.361	1.540
0.207	1.379	0.693	2.980	0.442	1.522
0.292	1.379	0.789	3.092	0.552	1.464
0.342	1.363	0.879	3.823	0.579	1.565
0.390	1.348	0.918	3.391	0.697	1.409
0.448	1.395			0.836	1.498
0.525	1.396			0.909	1.756
0.630	1.396			0.940	1.950
0.665	1.385				
0.694	1.401				
0.750	1.428				
0.761	1.413				
0.791	1.369				
0.834	1.373				
0.842	1.382				
0.859	1.424				
0.878	1.469				
0.881	1.408				
0.908	1.374				
0.910	1.528				
0.936	1.572				

Table II. Vapor-Liquid Equilibria Data for Acetone-IPA at 55°C

X_1	Y_1	π^a	γ_1	γ_2	X_1	Y_1	π^a	γ_1	γ_2
0.041	0.119	186.0	0.7	1.0	0.630	0.873	542.0	1.0	1.1
0.052	0.169	197.5	0.9	1.0	0.665	0.888	565.7	1.0	1.1
0.059	0.202	202.1	0.9	1.0	0.694	0.902	575.6	1.0	1.1
0.069	0.230	207.1	0.9	1.0	0.750	0.926	603.8	1.0	1.0
0.081	0.251	213.3	0.9	1.0	0.761	0.929	614.7	1.0	1.1
0.085	0.266	218.4	0.9	1.0	0.791	0.937	627.3	1.0	1.1
0.098	0.270	216.5	0.8	1.0	0.834	0.952	648.5	1.0	1.1
0.112	0.342	235.0	1.0	1.0	0.842	0.955	654.1	1.0	1.1
0.207	0.509	286.0	1.0	1.0	0.859	0.962	662.5	1.0	1.0
0.292	0.621	338.0	1.0	1.1	0.878	0.969	675.2	1.0	1.0
0.342	0.670	368.0	1.0	1.1	0.881	0.968	674.9	1.0	1.1
0.390	0.711	392.6	1.0	1.1	0.908	0.975	693.4	1.0	1.1
0.448	0.766	430.0	1.0	1.1	0.910	0.979	691.8	1.0	0.9
0.525	0.817	477.0	1.0	1.1	0.936	0.986	705.6	1.0	0.9

^a Total pressure, mm Hg.

connected to a manometer, a 7½-gal surge tank, and to a vacuum pump in sequence.

In practice, the chemicals were charged to the flasks with CaSO₄ dessicant, and the entire apparatus was flushed with oil free nitrogen. The highest boiling compound was charged to the center flask, and the lower boiler(s) to the side flask(s). They were distilled in the order of high boiler to low boiler. Low boiling impurities were discarded through the condenser and distillate tube of the Othmer still. The pressure was adjusted to hold the temperature to 55° ± 0.1°C.

The densities of the pure components were sufficiently different to permit analysis of binary samples by density. Density determinations were made with a nominal 10-ml pycnometer calibrated with distilled, degassed water. The estimated error in the density measurements is ±0.01 mole fraction.

Ternary samples were analyzed by GLC. Good separation of the three components was obtained with a combination ¼-in. column consisting of a 9-ft 20% SE-30 column which was connected to a 5-ft 15% Carbowax-20-M on Gas-Chrom P column. The following conditions were used: helium flow of 46.2 ml/min, injection port temperature of 225°C, oven temperature of 150°C, detector temperature of 210°C, bridge

Table III. Vapor-Liquid Equilibria Data for Acetone-Acetic Anhydride at 55°C

X ₁	Y ₁	π ^a	γ ₁	γ ₃
0.140	0.750	116.3	0.8	1.1
0.209	0.813	151.1	0.8	1.2
0.259	0.875	202.7	0.9	1.1
0.355	0.919	275.0	1.0	1.1
0.465	0.949	360.0	1.0	1.1
0.551	0.961	429.1	1.0	1.2
0.640	0.974	495.3	1.0	1.2
0.691	0.982	537.7	1.0	1.0
0.693	0.978	539.8	1.0	1.3
0.789	0.988	610.7	1.0	1.1
0.879	0.997	668.7	1.0	0.5
0.918	0.997	697.1	1.0	0.8
0.956	1.001	717.0	1.0	...
0.958	1.003	731.0	1.0	...

^a Total pressure, mm Hg.

Table IV. Vapor-Liquid Equilibria Data for IPA-Acetic Anhydride at 55°C

X ₂	Y ₂	π ^a	γ ₂	γ ₃
0.025	0.097	36.1	0.8	1.1
0.035	0.166	38.3	1.1	1.1
0.048	0.200	38.0	0.9	1.1
0.068	0.271	41.6	1.0	1.1
0.165	0.512	58.8	1.1	1.1
0.184	0.537	60.1	1.0	1.1
0.313	0.695	80.2	1.0	1.2
0.361	0.725	88.2	1.0	1.3
0.442	0.784	96.2	1.0	1.2
0.552	0.842	111.9	1.0	1.3
0.579	0.868	115.6	1.0	1.2
0.697	0.904	131.2	1.0	1.4
0.836	0.958	148.5	1.0	1.3
0.909	0.983	156.3	1.0	1.0
0.940	0.991	159.8	1.0	0.8
0.960	1.000	161.6	1.0	...
0.983	1.002	164.6	1.0	...

^a Total pressure, mm Hg.

current of 150 mA, and a 0.3-μl sample size. At the 95% confidence level the error in the acetone analysis was ±0.015 mole fraction, in IPA the error was ±0.016, and in acetic anhydride it was ±0.018. Wet chemical methods of analysis of acetone and acetic anhydride were tried, but IPA interfered with the analyses.

The vapor-pressure measurements of acetone and IPA were made in an apparatus similar to the Tobey modified Ramsay-Young apparatus (2). The vapor pressure of acetic anhydride was measured directly in the Othmer still.

Results

The thermodynamic consistency of the data was checked by the procedure of Redlich and Kister (1). The particular relation used is given in the following equation:

$$\int_{X_i=0}^{X_i=1} \ln \frac{VP_i}{VP_j} dX_i = \int_{X_i=0}^{X_i=1} \ln \frac{Y_i(1-X_i)}{X_i(1-Y_i)} dX_i \quad (1)$$

The integral on the left is equal to $\ln VP_i/VP_j$ at 55°C. The values calculated from the raw data corresponding to values within the integral on the right are listed in Table I. To check the thermodynamic consistency of the data, the integral on the right side of Equation 1 was calculated from a quadratic equation fitted to the raw data. The ratio of the value of the right side to the value of the left side of Equation 1 for the three systems is 0.95 for acetone-IPA, 0.92 for IPA-AC₂O, and 0.97 for acetone-AC₂O.

Tables II-IV list the raw VLE at 55°C for the three binary systems. The tables present the liquid and vapor mole fractions, total pressure, and activity coefficients. The activity coefficients were determined from Equation 2.

$$\gamma_i = Y_i \pi / X_i VP_i \quad (2)$$

The experimental vapor-pressure data were fitted to an equation of the form:

$$\ln VP_i = \alpha + \beta/T + \delta/T^2 \quad (3)$$

Table V lists the constants in this equation for the three compounds. Table VI lists raw ternary VLE data for the system at 55°C.

The data were correlated both by Raoult's law and the Wilson equation (3). However, the system is essentially ideal; therefore, Raoult's law is adequate for distillation design calculations.

Table V. Constants in Vapor-Pressure Equation

Component	α	β	δ
Acetone	18.6143	-3942.3	0.0
IPA	18.3638	-4339.0	0.0
AC ₂ O	13.7749	-1143.44	-741155.0

Table VI. Experimental Ternary Data at 55°C

X			Y		
Acetone	IPA	AC ₂ O	Acetone	IPA	AC ₂ O
0.228	0.288	0.484	0.649	0.287	0.064
0.343	0.232	0.424	0.802	0.163	0.035
0.577	0.147	0.276	0.946	0.054	...
0.578	0.314	0.109	0.911	0.089	...
0.464	0.451	0.085	0.847	0.153	...
0.336	0.583	0.080	0.732	0.268	...
0.224	0.716	0.060	0.573	0.427	...
0.191	0.647	0.162	0.493	0.507	...

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Nomenclature

T = temperature, K

VP = vapor pressure, mm Hg

X = liquid mole fraction

Y = vapor mole fraction

α, β, δ = constants in vapor-pressure equations

γ = activity coefficient

π = total pressure, mm Hg

Subscripts

i = indefinite component number

j = indefinite component number

1 = acetone

2 = isopropenyl acetate

3 = acetic anhydride

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