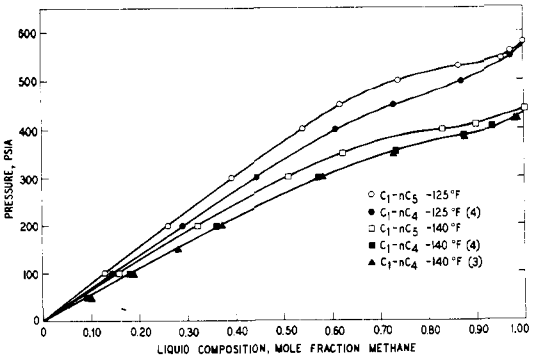


Figure 7. Comparison of methane-pentane and methane-butane at low temperatures

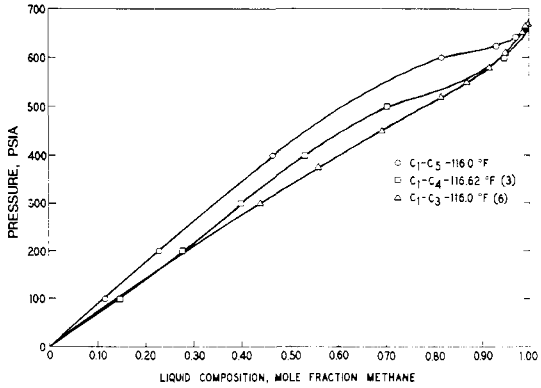


Figure 8. Solubility of methane in propane, butane, and pentane near methane critical temperature

also be in this range. At low pentane concentrations (less than 0.1% in the vapor or less than 10% in the liquid), however, deviations between duplicate samples were sometimes ±10% of the pentane present.

Based on these considerations, a somewhat subjective estimate of error in the *K* value is ±2% for methane, ±5% for pentane to −50°F, and ±10% for pentane at temperatures below −50°F.

Literature Cited

(1) Carruth, G. F., Kobayashi, R., *J. Chem. Eng. Data,* **18** (2), 115 (1973).
(2) Chen, R.J.J., Chappelear, P. S., Kobayashi, R., *ibid.,* **19** (1), 58 (1974).
(3) Elliott, D. G., Chen, R.J.J., Chappelear, P. S., Kobayashi, R., *ibid.,* p 71.
(4) Kahre, L. C., *ibid.,* p 67.
(5) Sage, B. H., Reamer, H. H., Olds, R. H., Lacey, W. N., *Ind. Eng. Chem.,* **34,** 1108 (1942).
(6) Wichterle, I., Kobayashi, R., *J. Chem. Eng. Data,* **17** (1), 4 (1972).

Received for review September 6, 1974. Accepted May 27, 1975.

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

Michael F. Kozempel[1] **and C. Michael Kelly**[2]
U.S. Department of Agriculture, Agricultural Research Service, Eastern Regional Research Center, Philadelphia, Pa. 19118

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 (AC_2O). It was the purpose of this study to determine the vapor-liquid equilibria (VLE) of the ternary system acetone–IPA–AC_2O 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 AC_2O were ACS reagent grade chemicals purchased from J. T. Baker Chemical Co. IPA was purchased from Matheson Coleman & Bell. Acetone, IPA, and AC_2O 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 %.

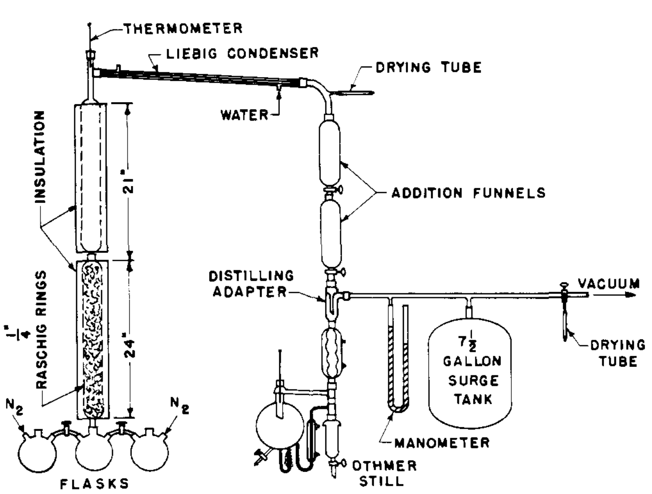


Figure 1. Experimental apparatus

---

[1] To whom correspondence should be addressed.
[2] Present address, Villanova University, Villanova, Pa. 19085.

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 ±0.1°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 ¼-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 $CaSO_4$ 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 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:

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

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–AC_2O, and 0.97 for acetone–AC_2O.

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.

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

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

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

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 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.

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_2O	13.7749	−1143.44	−741155.0

Table VI. Experimental Ternary Data at 55°C

X			Y		
Acetone	IPA	AC_2O	Acetone	IPA	AC_2O
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	...

Acknowledgment

The authors thank M. J. Calhoun for the GLC analysis of the ternary mixtures and also I. A. Wolff and N. C. Aceto of the Eastern Regional Research Center and R. E. White of Villanova University for their mutual cooperation in arranging for this work to be accomplished.

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

Literature Cited

(1) Redlich, O., Kister, A. T., *Ind. Eng. Chem.*, **40**, 345 (1948).
(2) Tobey, S. W., *J. Chem. Educ.*, **35**, 352 (1958).
(3) Wilson, G. M., *J. Am. Chem. Soc.*, **86**, 127 (1964).

Received for review September 16, 1974. Accepted May 13, 1975. Work taken from a master's thesis on file at Villanova University. Use of a company or product name does not imply approval or recommendation to the exclusion of others which may also be suitable.

Dissociation Constants of 1(2-Pyridyl)-2-alkanones

Eldon H. Sund,[1] **Robert J. Cashon,**[2] **and Robert J. Palma, Sr.**[1]
Department of Chemistry, Midwestern University, Wichita Falls, Tex. 76308

The acid dissociation constants of a homologous series of nine 1(2-pyridyl)-2-alkanones were determined by potentiometric titration. These pK_a's correlated with the Taft polar constituent constants (σ^*) for the ketones.

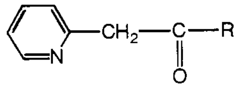
Previous studies have shown a strong correlation between Taft steric substituent constants and the equilibrium values for the enol-keto tautomerism of a series of 1(2-pyridyl)-2-alkanones (*6*). Since the acid dissociation constants for this series of ketones had not been determined, we felt it would be of value to measure these constants as well as to investigate any relationships they might have with Taft steric substituent constants, E_s, and/or Taft polar substituent constants, σ^*.

Experimental

The 1(2-pyridyl)-2-alkanones were prepared by the method of Goldberg et al. (*2*), and the synthesis as well as the physical properties and derivatives of these ketones has been reported previously (*3*). The ketones were purified on a Nester Faust annular teflon spinning band column, and the purity was checked by gas chromatography using a 5-ft × ¼-in., 3% S.E. 30 column in a Varian 90-P aerograph instrument. The pK_a's were determined by potentiometric titrations using conventional calculations (*1*). A Leeds and Northrup Model 7415 research pH meter, Beckman 39099 glass electrodes, and Beckman 39170 calomel reference electrodes were employed to monitor pH. The titrations were performed in a flow-through thermostated titration vessel. The temperature was controlled at 20.0° ± 0.1°C in all titrations with a Haake Model KT-41 constant temperature bath. This titration vessel was fitted with a teflon sealer cap containing the electrodes, nitrogen purge tube, and a 5-ml microburet readable to ±0.001 ml.

All solutions were prepared from distilled and demineralized water having a conductivity of less than 10^{-5} mho. Aqueous solutions (0.01*M*) of the ketones were placed in the titration vessel and purged for 10 min prior to titration with purified nitrogen gas. A slow stream of nitrogen was thereafter maintained for stirring and only discontinued during readings. The

Table I. pK_a's of 1(2-Pyridyl)-2-alkanones



R	pK_a	SD	σ^* (*5*)
CH_3	4.587	0.037	0.000
C_2H_5	4.677	0.013	−0.100
n-C_3H_7	4.634	0.003	−0.115
iso-C_3H_7	4.671	0.006	−0.190
n-C_4H_9	4.647	0.005	−0.130
iso-C_4H_9	4.595	0.004	−0.125
sec-C_4H_9	4.594	0.017	−0.210
tert-C_4H_9	4.743	0.019	−0.300
n-C_5H_{11}	4.670	0.011	−0.162 (*4*)

---

[1] To whom correspondence should be addressed.
[2] Present address, Department of Biochemistry, Johns Hopkins University, Baltimore, Md.