b = volume van der Waals' constant, cc./gram mole
B = vapor pressure constant, ° K.
C = vapor pressure constant, dimensionless
D = vapor pressure constant, $(° K.)^2$/mm.
n_c = number of carbon atoms in naphthenic ring
P = vapor pressure, mm.
P_b = reference vapor pressure, mm.
P_c = critical pressure, mm.
R = gas constant
T = absolute temperature, ° K.
T_b = reference temperature, ° K.
T_c = critical temperature, ° K.
T_n = normal boiling point, ° K.
X = temperature modulus, $\dfrac{1/T - 1/T_b}{\log T/T_b}$
Y = vapor pressure modulus, $\dfrac{\log P/P_b - D(R/T^2 - P_b/T_b^2)}{\log T/T_b}$

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Vapor Liquid Equilibria at Atmospheric Pressure

Binary Systems of Ethyl Acetate–Benzene, Ethyl Acetate–Toluene, and Ethyl Acetate–*p*-Xylene

A. D. CARR and H. W. KROPHOLLER
Department of Chemistry, University of Cape Town, South Africa

VAPOR-LIQUID equilibrium data at a pressure of 760 mm. of Hg were determined for the three binary systems, ethyl acetate-benzene, ethyl acetate-toluene, and ethyl acetate-*p*-xylene. The experimental results are given in Table I and the temperature *vs.* composition curves are shown in Figures 1, 2, and 3. The activity coefficients plotted in Figures 4, 5, and 6 show that the three systems are relatively symmetrical, and do not exhibit maxima or minima. Also, the molar volumes of the pure components have approximately the same values, so that any of the integrated forms of the Gibbs-Duhem equation is suitable to correlate the data. The van Laar equations have been chosen as most convenient to use. The activity coefficients were calculated from the equation

$$\gamma = y\pi/xp^0$$

and extrapolated to $x = 0$. The values of the van Laar constants so found were then adjusted for each binary mixture to give the curves most representative of all the experimental data. The constants used to calculate the curves in Figures 4, 5, and 6 are given in Table II, with values previously reported (*1*). These earlier values, calculated from total pressure data, are not satisfactory and give errors in the boiling points of binary mixtures of up to 5° and 0.8° C. for the systems ethyl acetate-benzene and ethyl acetate-toluene, respectively.

EXPERIMENTAL

Purity of Compounds. The chemicals used (C.P. grade) were redistilled. The distillates used in the equilibrium still had boiling ranges of not more then 0.025° C. The boiling points and refractive indices of the materials used are given in Table III.

Analysis of Samples. Binary compositions were found from refractive indices at 25° C. using a Zeiss-Abbé refractometer reading to four decimal places and giving an accuracy of analysis of ±0.08 mole %. In the calculation of activity coefficients according to the above equation, this variation in analysis can give a percentage change in γ_2 of ±2, ±0.75,

±0.4, ±0.2 at x_1 = 0.95, 0.85, 0.75, and 0.5, respectively. Alternative chemical methods of analysis were less accurate than the refractive index procedure.

Equilibrium Still. A slightly modified version of the still described by Otsuki and Williams (*3*) was used in the equilibrium determinations. The modification consists of a vertical extension of the boiling flask so that the whole length of the Cottrell tube is surrounded by vapor of essentially the same temperature as the mixture in the tube. This obviates any temperature gradient and hence any fractionation in the Cottrell pump. The secondary heater inside the boiling flask was placed just below the flared opening of the Cottrell tube. To minimize losses of the volatile material in the still, Teflon stopcocks and sleeves on joints were used throughout, and the outlet of the final condenser was connected to a mercury manometer. Temperature readings were corrected to 760 mm. of Hg by allowing for variation in this manometer as well as in barometric pressure. These pressure corrections were based on vapor pressure change with temperature, weighted for the molar composition of the mixture concerned. The change in vapor pressure with temperature is of the same order for all components, and the maximum variation in

Table I. Experimental Data at 760 mm. Hg

Temp., ° C.	x_1	y_1	γ_1	γ_2
	Ethyl Acetate (1)–Benzene (2)			
77.19	0.950	0.951	1.000	1.08
77.23	0.912	0.914	1.000	1.07
77.29	0.857	0.860	0.999	1.075
77.31	0.841	0.845	1.000	1.070
77.32	0.834	0.838	1.001	1.065
77.38	0.774	0.780	1.001	1.060
77.49	0.697	0.707	1.003	1.055
77.67	0.587	0.605	1.015	1.035
77.84	0.528	0.547	1.014	1.032
78.12	0.441	0.465	1.021	1.020
78.19	0.422	0.448	1.027	1.015
78.43	0.359	0.387	1.035	1.008
78.66	0.300	0.329	1.045	1.006
78.96	0.230	0.256	1.050	1.001
79.28	0.160	0.184	1.075	0.998
79.40	0.136	0.157	1.075	0.999
79.77	0.060	0.071	1.09	0.999
79.95	0.027	0.033	1.12	0.999
80.01	0.016	0.020	1.14	1.000
	Ethyl Acetate (1)–Toluene (2)			
77.60	0.970	0.987	1.000	1.23
77.81	0.954	0.980	1.005	1.21
78.39	0.922	0.967	1.006	1.19
78.80	0.891	0.953	1.011	1.18
79.91	0.835	0.928	1.018	1.15
81.14	0.773	0.899	1.020	1.125
82.25	0.715	0.867	1.023	1.110
83.55	0.656	0.837	1.033	1.095
85.16	0.598	0.800	1.035	1.080
89.22	0.452	0.703	1.065	1.043
92.09	0.365	0.629	1.090	1.033
95.02	0.283	0.545	1.110	1.016
95.51	0.270	0.528	1.110	1.017
99.80	0.175	0.391	1.130	1.017
103.46	0.107	0.265	1.17	1.012
106.94	0.048	0.137	1.19	1.011
107.87	0.032	0.097	1.20	1.010
108.82	0.021	0.064	1.21	1.005
	Ethyl Acetate (1)–*p*-Xylene (2)			
77.92	0.965	0.992	1.001	1.64
78.17	0.949	0.989	1.005	1.53
79.20	0.912	0.981	1.009	1.44
80.91	0.846	0.967	1.021	1.35
83.10	0.765	0.948	1.040	1.29
85.65	0.667	0.925	1.057	1.19
86.54	0.635	0.916	1.063	1.20
90.12	0.524	0.878	1.1132	1.150
93.17	0.440	0.847	1.1172	1.090
95.00	0.399	0.825	1.215	1.075
99.62	0.310	0.771	1.270	1.057
105.05	0.235	0.695	1.310	1.035
111.13	0.165	0.612	1.385	1.021
115.97	0.124	0.530	1.415	1.023
119.08	0.100	0.475	1.460	1.009
123.44	0.070	0.384	1.485	1.000
127.88	0.044	0.280	1.55	1.007
130.03	0.033	0.220	1.55	1.014
133.12	0.019	0.138	1.57	1.007
136.54	0.006	0.048	1.60	1.002

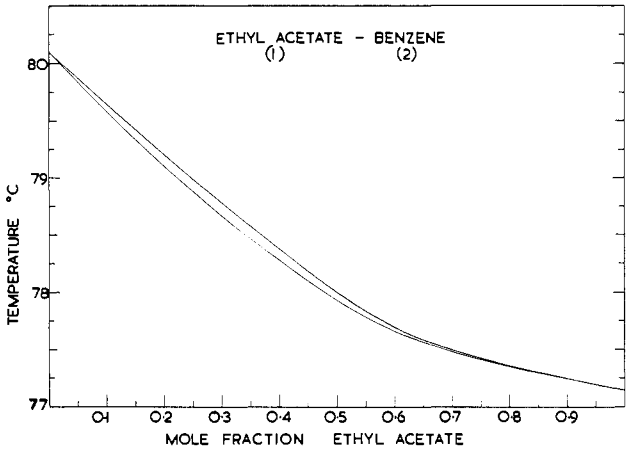

Figure 1. Temperature-composition curves for ethyl acetate–benzene

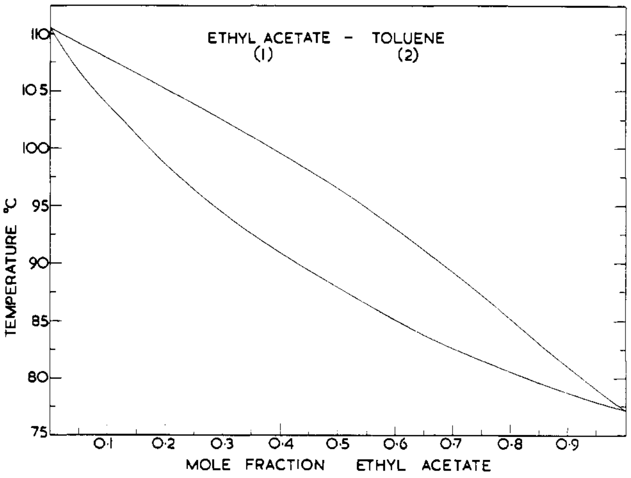

Figure 2. Temperature-composition curves for ethyl acetate–toluene

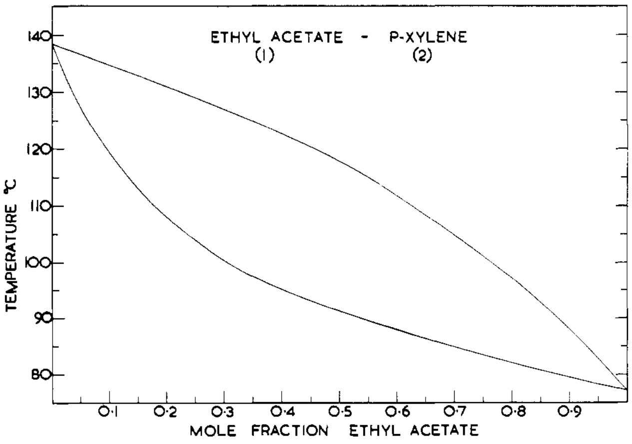

Figure 3. Temperature-composition curves for ethyl acetate–*p*-xylene

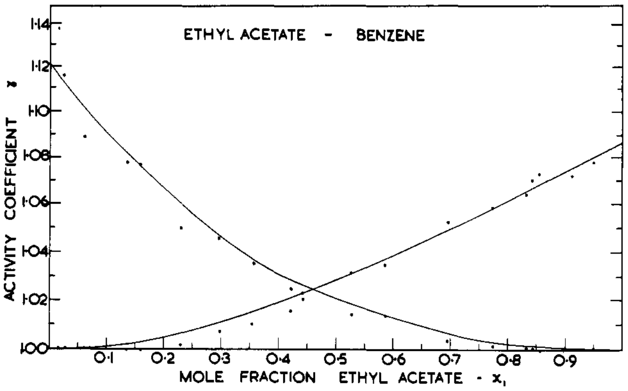

Figure 4. Activity coefficient-composition curves for ethyl acetate–benzene

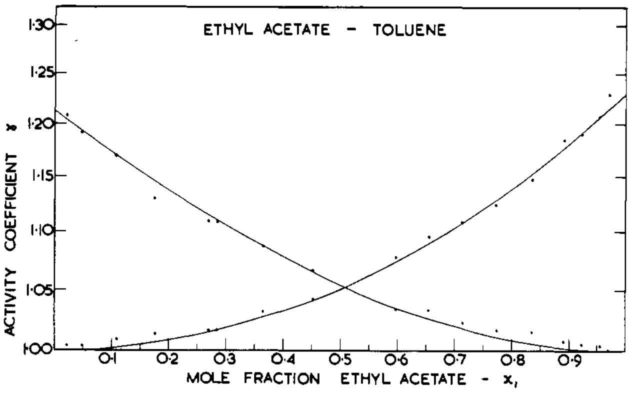

Figure 5. Activity coefficient-composition curves for ethyl acetate–toluene

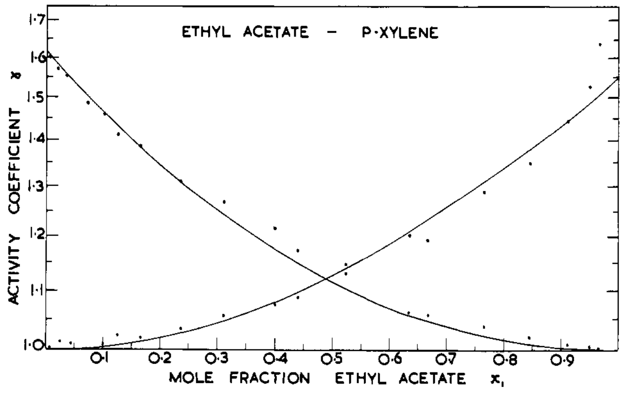

Figure 6. Activity coefficient-composition curves for ethyl acetate–p-xylene

total pressure was 5 mm. of Hg. All runs were of a minimum duration of 4 hours, which was the time required to attain equilibrium.

Table II. Binary Constants for van Laar Equations

(Mixtures are given with the lower boiling component stated first and the constants apply in the same order)

System	A_{12}[a]	A_{21}[a]	A_{12}[b]	A_{21}[b]
Ethyl acetate-benzene	0.050	0.036	0.50	0.40
Ethyl acetate–toluene	0.084	0.090	0.04	0.25
Ethyl acetate-*p*-xylene	0.210	0.190	. . .	. . .

[a] From Figures 4, 5, and 6.

[b] Previously reported.

Table III. Properties of Pure Compounds

Property	Ethyl Acetate	Benzene	Toluene	*p*-Xylene
Refractive index, 25° C., exptl.	1.3700	1.4978	1.4933	1.4926
Boiling point, ° C. at 760 mm. Hg, exptl.	77.14	80.10	110.63	138.38
Boiling point, ° C. at 760 mm. Hg, (*2*)	77.15	80.099	110.626	138.351

Temperature Measurement. A platinum resistance thermometer in conjunction with a five-decade Wheatstone bridge, having a resistance accuracy of ±0.02%, was used for all reported temperatures. These temperatures are, therefore, accurate to ±0.025° C. Measurements with mercury-in-glass thermometers were discarded, as it was necessary to use different thermometers for the three systems, and the required calibrations and stem corrections were tedious and liable to error. Readings with thermistors were insufficiently reproducible for accurate work.

THERMODYNAMIC CONSISTENCY OF RESULTS

The experimentally determined values of γ are, in general, in agreement with the thermodynamically correct values as shown by the van Laar equation curves, within the limits of accuracy of the analytical procedure. Plots of $\log(\gamma_1/\gamma_2)$ *vs.* x showed variations in net area under the curves of 1,5, and 5% for the systems with benzene, toluene, and xylene, respectively. The larger deviations are probably due to the fact that temperature corrections, although desirable in the integrated plots for the two latter systems, were not made because of the absence of the necessary heat of solution data.

NOMENCLATURE

A = constant in van Laar equation
p^0 = vapor pressure
y = mole fraction in vapor phase
x = mole fraction in liquid phase
γ = activity coefficient
π = total pressure

Subscripts 1 and 2 refer to components in binary mixture.

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