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Isobaric Vapor–Liquid Equilibrium of Binary Mixtures of Vinyl Acetate and Ethyl Formate with Cumene at 97.3 kPa

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Isobaric vapor–liquid equilibrium (VLE) measurements are reported for binary mixtures of vinyl acetate and ethyl formate with cumene at 97.3 kPa. The data were obtained using a vapor recirculating type (modified Othmer's) equilibrium still. Both mixtures show positive deviation from ideality. None of the systems form an azeotrope. The experimental data obtained in this study are thermodynamically consistent according to the Herington and Black tests. The activity coefficients have been satisfactorily correlated by means of the Margules, Redlich–Kister, and NRTL equations. A comparison of the values of activity coefficients obtained by experimental data with the UNIFAC model is included in this paper.

Introduction

The experimental determination of vapor–liquid equilibrium (VLE) data is an important contribution to chemical engineering as the data are necessary for the correct design of distillation columns. Very limited work has been reported on the vapor–liquid equilibrium study of binary mixtures containing cumene as one of the components. Isobaric vapor–liquid equilibrium data at 97.3 kPa have been reported by Kapoor et al.[1] for the binary mixture of vinyl acetate + *p*-xylene. In the present work, experimental vapor–liquid equilibrium data for binary mixtures of vinyl acetate and ethyl formate with cumene are reported. The measurements were performed under isobaric conditions at a pressure of 97.3 kPa using a modified version of the recirculating type equilibrium still that has been described earlier.[2,3] The two binary systems studied have wide boiling ranges, i.e., (79.6 and 98.1) K, respectively. None of the systems form an azeotrope.

All compounds studied have a wide range of applications and are of great industrial importance. Cumene (isopropyl benzene) is used to manufacture other chemicals such as phenol, acetone, acetophenone, and methyl styrene. It is used as a thinner in paints, lacquers, and enamels. Also, it is a component of high-octane motor fuels. Natural sources of cumene include crude petroleum and coal tar. Ethyl formate is used for the synthesis of vitamin B_1 and as a flavor in the food industry. It is also used as a solvent for acetyl cellulose and nitrocellulose. The vinyl acetate monomer is a chemical building block used to manufacture a wide variety of polymers such as polyvinyl acetate, polyvinyl alcohol, polyvinyl acetals, ethylene vinyl acetate copolymers, and ethylene vinyl alcohol. These polymers are commonly used in the production of plastics, films, lacquers, laminating adhesives, elastomers, inks, glue, acrylic fibers, paper coatings, floor tiling, and safety glasses.

Table 1. Refractive Index n_D at 298.15 K and Boiling Point T_b at 101.3 kPa

	n_D		T_b/K	
compound	exptl	lit.	exptl	lit.
vinyl acetate	1.392364	1.393400[19]	345.95	346.00[20]
ethyl formate	1.359010	1.357500[19]	327.32	327.50[20]
cumene	1.488292	1.488900[19]	425.44	425.60[20]

Table 2. Physical Constants of the Pure Compounds

constant	vinyl acetate	ethyl formate	cumene
molecular wt.	86.091[19]	74.08[21]	120.20[21]
boiling point/K (at 101.3 kPa)	346.00[20]	327.5[20]	425.60[20]
refractive index n_D (at 298.15 K)	1.393400[19]	1.357500[19]	1.488900[19]
T_c/K	525.0[20]	508.5[20]	631.13[20]
P_c/kPa	42.931[20]	46.780[20]	31.67[20]
$V_c \cdot 10^6/m^3 \cdot mol^{-1}$	265.00[20]	229.00[20]	428.00[20]
accentric factor, ω	0.34[20]	0.285[20]	0.325[21]
dipole moment, μ/D	1.79[19]	1.94[19]	0.39[19]
constants of antoine's equation, eq 4			
A	7.21010[22]	7.00902[22]	6.93160[22]
B	1296.130[22]	1123.943[22]	1457.318[22]
C	226.655[22]	218.247[22]	207.370[22]

Experimental

Chemicals. Vinyl acetate and ethyl formate were obtained from C.D.H (P) Ltd., India, and cumene was obtained from Merck-Schuchardt, Germany. All chemicals were AR grade materials and had purities (by chromatographic analysis, as given by the manufacturer in area percent) of 99.0 %, 98.0 %, and 99.0 %, respectively. The chemicals were purified using standard procedures[4] and stored over molecular sieves. The purity of the chemicals was checked by measuring the normal boiling points and refractive indices for the pure compounds and comparing with those reported in the literature. The results are listed in Table 1.

Apparatus and Procedure. The vapor–liquid equilibrium data were obtained by using a modified version of an equilibrium still. The equilibrated mixtures were analyzed using a Bausch and Lomb Abbe-3L refractometer. The apparatus, modifications,

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Table 3. Vapor–Liquid Equilibrium Data of the Vinyl Acetate (1) + Cumene (2) System at 97.3 kPa

T/K	x_1	y_1	ln γ_1	ln γ_2
345.46	0.9683	0.9937	0.0008	0.9228
346.64	0.9230	0.9850	0.0024	0.8546
347.87	0.8812	0.9780	0.0029	0.7493
349.04	0.8388	0.9709	0.0083	0.6785
349.67	0.8132	0.9670	0.0157	0.6298
351.36	0.7559	0.9590	0.0285	0.5127
353.15	0.6892	0.9501	0.0572	0.3962
355.05	0.6341	0.9412	0.0740	0.3240
357.46	0.5581	0.9284	0.1168	0.2388
359.15	0.4937	0.9142	0.1746	0.2205
361.35	0.4476	0.9030	0.1972	0.1731
364.06	0.3933	0.8836	0.2282	0.1617
369.25	0.3115	0.8449	0.2742	0.1365
375.34	0.2335	0.7898	0.3342	0.1223
384.25	0.1594	0.7065	0.3809	0.0708
390.15	0.1218	0.6357	0.4043	0.0582
393.17	0.1054	0.5952	0.4133	0.0531
399.35	0.0758	0.4989	0.4288	0.0507
406.25	0.0493	0.3814	0.4432	0.0371
412.86	0.0282	0.2531	0.4577	0.0237
415.15	0.0209	0.2027	0.4871	0.0210
418.24	0.0135	0.1422	0.5102	0.0061
421.85	0.0050	0.0563	0.5179	0.0007

Table 4. Vapor–Liquid Equilibrium Data of the Ethyl Formate (1) + Cumene (2) System at 97.3 kPa

T/K	x_1	y_1	ln γ_1	ln γ_2
326.15	0.9930	0.9995	0.0020	0.7959
326.43	0.9791	0.9985	0.0056	0.7714
327.31	0.9412	0.9959	0.0131	0.6872
328.48	0.9004	0.9937	0.0164	0.5410
329.94	0.8435	0.9903	0.0303	0.4456
331.20	0.8000	0.9877	0.0396	0.3838
334.35	0.7090	0.9815	0.0535	0.2736
337.15	0.6422	0.9757	0.0592	0.2123
339.79	0.5869	0.9701	0.0627	0.1629
343.15	0.5224	0.9621	0.0704	0.1094
348.35	0.4430	0.9485	0.0707	0.0469
349.27	0.4146	0.9436	0.1059	0.0496
354.75	0.3408	0.9224	0.1279	0.0332
360.86	0.2654	0.8930	0.1843	0.0115
366.58	0.2140	0.8592	0.2163	0.0083
377.05	0.1440	0.7789	0.2654	0.0094
385.15	0.1036	0.6963	0.3024	0.0154
399.78	0.0541	0.4948	0.3114	0.0247
406.72	0.0355	0.3746	0.3243	0.0214
414.65	0.0180	0.2172	0.3195	0.0129
419.05	0.0095	0.1223	0.3088	0.0041
423.17	0.0014	0.0198	0.3116	0.0020

and analytical techniques have already been described earlier.[5] All the measurements were made at a constant temperature with the help of a circulating-type cryostat (type MK70, MLW, Germany) maintained at a temperature within ± 0.02 K.

The estimated uncertainties in the measurements of mole fraction were ± 0.0002, in refractive index were ± 0.0002, in temperature were ± 0.02 K, and in pressure were ± 0.27 kPa.

Results and Discussion

The liquid-phase activity coefficients (γ) were calculated from the experimental data using the equations[6] below, which take into account the vapor phase nonideality

$$\gamma_1 = (Py_1/P_1^0x_1)\exp[\{(B_{11} - V_1)(P - P_1^0)/RT\} + (P\delta_{12}y_2^2)/RT] \quad (1)$$

$$\gamma_2 = (Py_2/P_2^0x_2)\exp[\{(B_{22} - V_2)(P - P_2^0)/RT\} + (P\delta_{12}y_1^2)/RT] \quad (2)$$

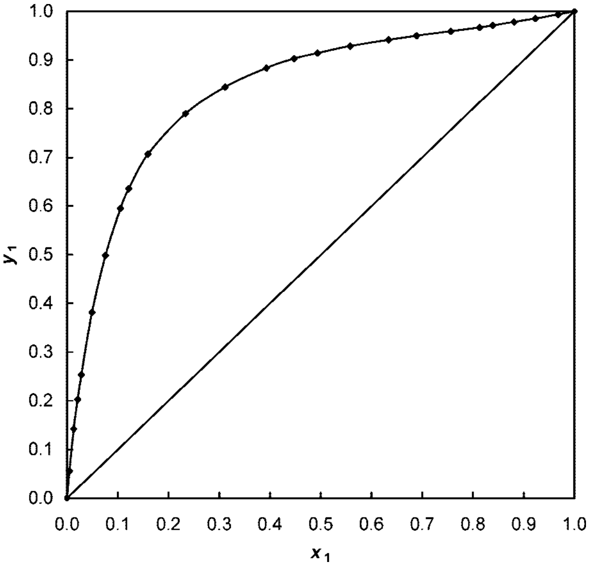

Figure 1. Plot of vapor–liquid equilibrium data for the system vinyl acetate (1) + cumene (2) at 97.3 kPa.

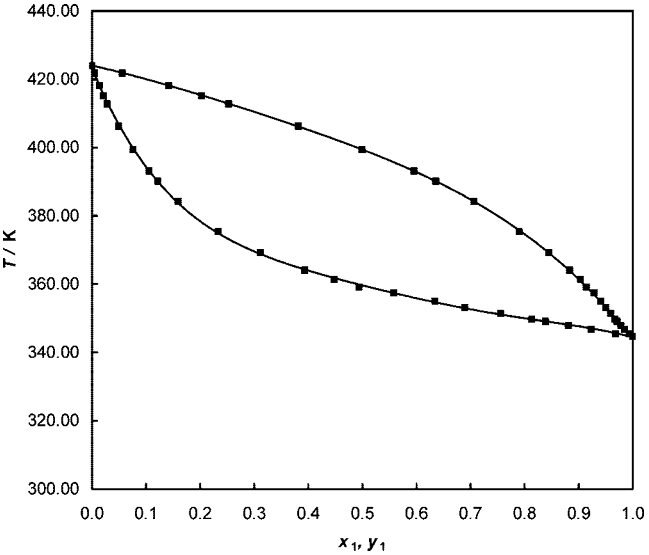

Figure 2. Plot of T vs x_1, y_1 data for the system vinyl acetate (1) + cumene (2).

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \quad (3)$$

where x_1, x_2 and y_1, y_2 are the equilibrium mole fractions of components 1 and 2 in the liquid and vapor phases, respectively; T and P are the boiling point and the total pressure; V_1 and V_2 are the molar liquid volumes; B_{11} and B_{22} are the second virial coefficients of the pure components; and B_{12} is the cross second virial coefficient. The experimental vapor–liquid equilibrium data (T, x_1, and y_1) at 97.3 kPa along with the calculated activity coefficients are presented in Table 3 and Table 4. Table 2 gives the physical constants of the pure components. The pure component vapor pressures (P^0) were calculated according to the Antoine equation

$$\log((P^0/\text{kPa})/0.133) = A - [B/((C - 273.15) + (T/\text{K}))] \quad (4)$$

The Antoine's constants A, B, and C are reported along with physical constants of pure components in Table 2.

The Yen and Woods[7] method was used for the estimation of liquid molar volumes. The Pitzer and Curl equation modified

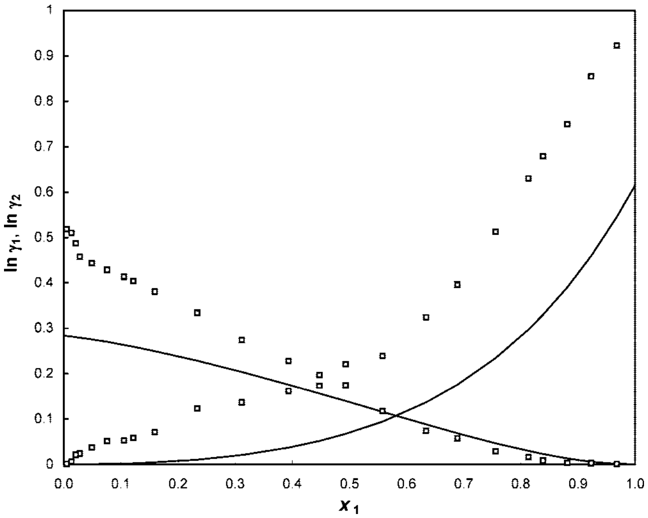

Figure 3. Plot of ln γ_1, ln γ_2 vs x_1 for the system vinyl acetate (1) + cumene (2) at 97.3 kPa: □, experimental; −, UNIFAC.

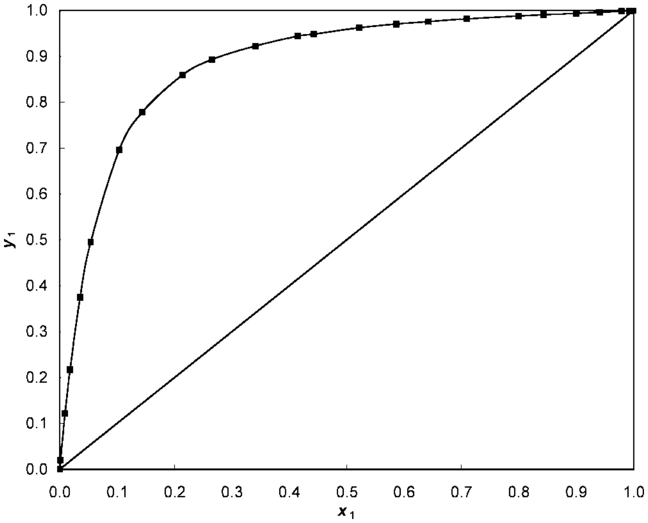

Figure 4. Plot of vapor–liquid equilibrium data for the system ethyl formate (1) + cumene (2) at 97.3 kPa.

by Tsonopoulos[8] was used in the evaluation of second virial coefficients as well as cross virial coefficients in this work.

The x_1, y_1 and T, x_1, y_1 plots for the vinyl acetate + cumene system at 97.3 kPa are given in Figure 1 and Figure 2, respectively. Figure 3 gives the comparison of experimental activity coefficient data of this system with those calculated using the UNIFAC model.[9] The x_1, y_1 and T, x_1, y_1 plots for the ethyl formate + cumene system at 97.3 kPa are given in Figure 4 and Figure 5, respectively. Figure 6 gives the comparison of experimental activity coefficient data of the said system with those calculated using the UNIFAC model.

According to the data reported in Table 3 and Table 4, the vinyl acetate + cumene system as well as the ethyl formate + cumene system show positive deviations from ideal behavior. The experimental results are well supported by few related earlier studies of acetates and aromatic compounds.[10–14] The data for the systems were assessed for thermodynamic consistency by applying the Herington area test[15] and Black test.[16] According to the method suggested by Herington, from $\ln(\gamma_1/\gamma_2)$, x_1 plots, the value of $(D-J)$ is < 10 %, numerically equal to 4.704 % for the vinyl acetate + cumene system and –15.479 % for the ethyl formate + cumene system. It shows that the experimental data are thermodynamically consistent. The activity coefficients were correlated with Margules, Redlich–Kister, and NRTL[17] equations. The adjustable parameter α_{12} for the NRTL correlation equation was set equal to 0.35 for the vinyl acetate + cumene system and 0.49 for the ethyl formate + cumene system. The estimation of parameters for the three correlation equations is based on minimization of $\ln(\gamma_1/\gamma_2)$ as an objective function using the nonlinear least-squares method of Nagahama, Suzuki, and Hirata as used by Rattan et al.[18] The correlation parameters A_1, A_2, and A_3 and deviation in vapor phase

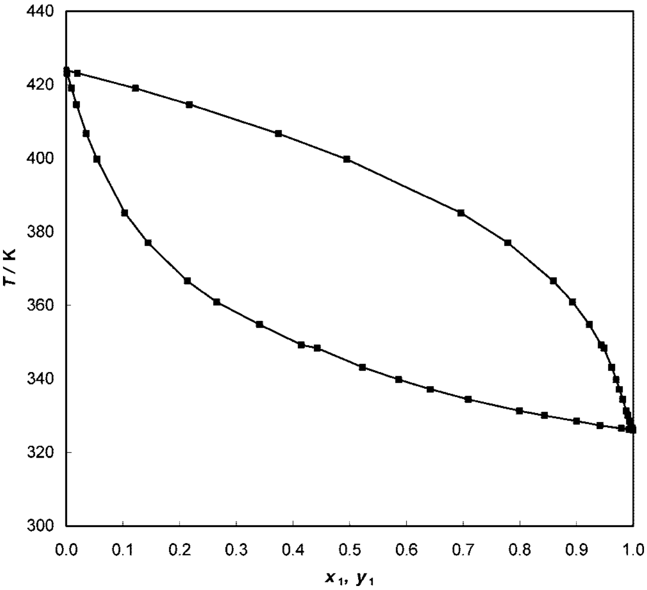

Figure 5. Plot of T vs x_1, y_1 data for the system ethyl formate (1) + cumene (2).

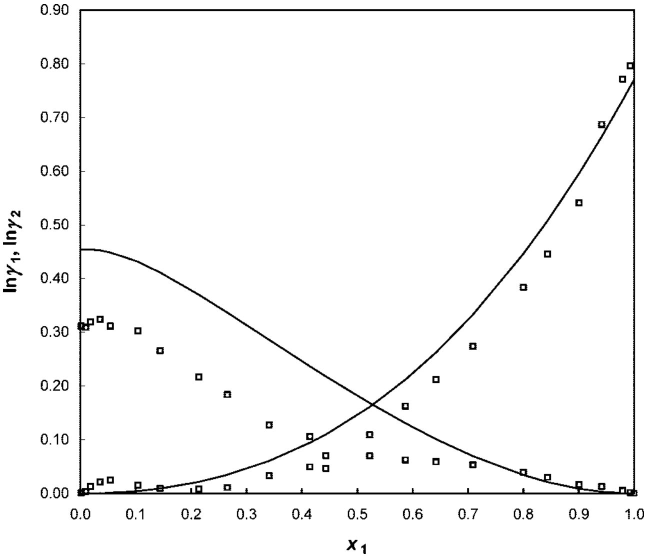

Figure 6. Plot of ln γ_1, ln γ_2 vs x_1 for the system ethyl formate (1) + cumene (2) at 97.3 kPa: □, experimental; −, UNIFAC.

Table 5. Correlation Parameters for Activity Coefficient and Deviation in Vapor Phase Composition

system	correlations	A_1	A_2	A_3	deviation (Δy)
vinyl acetate + cumene	Margules	0.49029	0.91982	−0.01338	0.06858
	Redlich–Kister	0.70840	0.21476	−0.00334	0.06801
	NRTL	1.31067	−0.31094		0.06490
ethyl formate + cumene	Margules	0.34669	0.76376	0.27674	0.08632
	Redlich–Kister	0.48604	0.20854	0.06919	0.08013
	NRTL	1.14502	−0.31764		0.08720

composition for both systems are listed in Table 5. For the vinyl acetate + cumene system, the root-mean-square deviation in the vapor-phase composition lies in the range 0.06490 to 0.06858, whereas for the ethyl formate + cumene system, it lies in the range 0.08013 to 0.08720.

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