Isobaric Vapor-Liquid Equilibrium of Binary Mixture of Methyl Acetate with Isopropylbenzene at 97.3 kPa

Seema Kapoor, Baljinder K. Gill, and V. K. Rattan

***Abstract*—**Isobaric vapor-liquid equilibrium measurements are reported for the binary mixture of Methyl acetate and Isopropylbenzene at 97.3 kPa. The measurements have been performed using a vapor recirculating type (modified Othmer's) equilibrium still. The mixture shows positive deviation from ideality and does not form an azeotrope. The activity coefficients have been calculated taking into consideration the vapor phase nonideality. The data satisfy the thermodynamic consistency tests of Herington and Black. The activity coefficients have been satisfactorily correlated by means of the Margules, NRTL, and Black equations. A comparison of the values of activity coefficients obtained by experimental data with the UNIFAC model has been made.

***Keywords*—**Binary mixture, Isopropylbenzene, Methyl acetate, Vapor-liquid equilibrium.

I. Introduction

PROCESSES based on distillation operations are extensively used for the separation of a great number of liquid mixtures. For this reason, knowledge of vapor-liquid equilibrium data is of great importance, to accurately design the required equipment. Such information can be obtained experimentally or estimated by using generalized methods for calculation of the properties of the mixtures. For ideal system, it is relatively easy to estimate vapor-liquid equilibrium. However, most systems of industrial interest show deviations from the ideal behavior. Very limited work has been reported on vapor-liquid equilibrium study of binary mixtures containing isopropylbenzene as one of the components. Isobaric vapor-liquid equilibrium data for binary mixtures of vinyl acetate and ethyl formate with cumene has been studied and reported in [1]. In the present work, experimental vapor-liquid equilibrium data for binary mixture of methyl acetate with isopropylbenzene 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 binary system studied has wide boiling range i.e. 95.2 K. The system does not form an azeotrope.

The compounds studied have a wide range of applications and are of great industrial importance. Isopropyl benzene (Cumene) 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 isopropylbenzene include crude petroleum and coal tar. Methyl acetate, also known as methyl ethanoate, is a clear, flammable liquid with a characteristic, not unpleasant smell like certain glues or nail polish removers. Methyl acetate has characteristics very similar to its analog ethyl acetate. Methyl acetate is used as a solvent in glues and nail polish removers, in chemical reactions and for solvent extractions.

II. Experimental

Chemicals: Methyl acetate was obtained from C.D.H (P) Ltd., India and isopropylbenzene was obtained from Merck-Schuchardt, Germany. Both chemicals were AR grade materials and had purities (by chromatographic analysis, as given by the manufacturer in area percent) of 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 I.

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

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III. 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:

$$\gamma_1 = (P y_1 / P_1^0 x_1)\exp[\{(B_{11} - V_1)(P - P_1^0)/RT\} + (P\delta_{12} y_2^2)/RT] \quad (1)$$

$$\gamma_2 = (P y_2 / P_2^0 x_2)\exp[\{(B_{22} - V_2)(P - P_2^0)/RT\} + (P\delta_{12} y_1^2)/RT] \quad (2)$$

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

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 III. Table II gives the physical constants of the pure components. The pure component vapor pressures (P^0) were calculated according to the Antoine equation:

$$Log\,(P^0 / 0.133) = A - [B/(C + T - 273.15)] \quad (4)$$

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

The Yen and Woods [7] method was used for the estimation of liquid molar volumes. The Pitzer and Curl equation modified by Tsonopoulos [8] was used in the evaluation of second virial coefficient as well as cross virial coefficients in this work.

The x_1, y_1 and T, x_1, y_1 plots for methyl acetate and isopropylbenzene system at 97.3 kPa are given in Fig. 1 and Fig. 2 respectively. Fig. 3 gives the comparison of experimental activity coefficient data of this system with those calculated using the UNIFAC model [9].

According to the data reported in Table III, the system shows positive deviations from ideal behaviour. The experimental results are well supported by few related earlier studies of acetates and aromatic compounds [10]-[15]. The data for the systems were assessed for thermodynamic consistency by applying the Herington area test [16] and Black test [17]. 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 5.971 %. It shows that the experimental data are thermodynamically consistent. The activity coefficients were correlated with Margules, NRTL [18], and Black equations. The adjustable parameter α_{12} for the NRTL correlation equation was set equal to 0.45. 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 square method of Nagahama, Suzuki, and Hirata as used by Rattan et al [19]. The correlation parameters A_1, A_2, A_3 and deviation in vapor phase composition for the system are listed in Table IV. The NRTL equation gave the best fit with 0.08660 as the average absolute deviation in the vapor phase composition of methyl acetate.

TABLE I
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.
Methyl acetate	1.358164	1.35890 [4]	330.10	330.40 [21]
Isopropylbenzene	1.488292	1.48890 [4]	425.63	425.60 [21]

TABLE II
Physical Constants of the Pure Compounds

Constant	Methyl acetate	Isopropylbenzene
Molecular wt	74.08 [22]	120.20 [22]
Boiling point at 101.3 kPa (K)	330.40 [21]	425.60 [21]
Refractive index, n_D at 298.15 K	1.35890 [4]	1.48890 [4]
T_c (K)	506.80 [21]	631.13 [20]
P_c (kPa)	4688.8 [21]	3208.1 [20]
$V_c \cdot 10^6$ ($m^3 \cdot mol^{-1}$)	228.00 [21]	428.00 [20]
Accentric factor, ω	0.326 [21]	0.325 [22]
Dipole moment, μ (Debyes)	1.72 [4]	0.39 [4]
Constants of Antoine's equation, eq.4		
A	7.06524[23]	6.93160 [23]
B	57.630 [23]	1457.318 [23]
C	219.726[23]	207.370 [23]

TABLE III
Vapor –Liquid Equilibrium Data of the Methyl Acetate (1) + Isopropylbenzene (2) System

T (K)	x_1	y_1	$\ln\gamma_1$	$\ln\gamma_2$
329.08	0.9875	0.9989	0.00629	0.79658
329.65	0.9409	0.9950	0.03153	0.77168
330.81	0.8826	0.9900	0.05191	0.71908
332.40	0.8238	0.9850	0.06337	0.65023
333.16	0.7998	0.9833	0.06633	0.59633
335.48	0.7400	0.9780	0.06377	0.50505
337.72	0.6856	0.9726	0.06357	0.43565
339.95	0.6357	0.9675	0.06422	0.36316
341.03	0.5998	0.9650	0.08658	0.29537

343.39	0.5430	0.9595	0.10866	0.20879
348.17	0.4538	0.9450	0.13142	0.13669
350.85	0.4061	0.9353	0.15505	0.10730
356.81	0.3241	0.9092	0.18618	0.08363
368.15	0.2158	0.8437	0.22151	0.05794
373.52	0.1797	0.8040	0.22489	0.05080
384.27	0.1176	0.7024	0.26495	0.03812
401.20	0.0525	0.4736	0.32162	0.02279
411.07	0.0258	0.2798	0.31792	0.03318
414.47	0.0186	0.2173	0.33421	0.01811
419.55	0.0085	0.1105	0.34496	0.00367
422.18	0.0032	0.0435	0.34546	0.00422

TABLE IV
CORRELATION PARAMETERS FOR ACTIVITY COEFFICIENT AND DEVIATION IN VAPOR-PHASE COMPOSITION

Correlations	A_1	A_2	A_3	Deviation (Δy)
NRTL	1.04380	-0.23275	-	0.08660
Margules	0.33475	0.69086	-0.45242	0.09510
Black	0.49543	0.86011	-0.16270	0.09834

Fig. 1 shows the experimental vapor–liquid equilibrium data for the binary mixture. In Fig. 2, the Temperature vs. Composition curves are drawn for the binary system at 97.3 kPa. Fig. 3 shows the plot of ln value of activity coefficients as calculated from the experimental data as well as by UNIFAC method vs. composition for the binary mixture. The graph clearly indicates positive deviations from ideal behavior for the binary system studied. The mixture does not form an azeotrope.

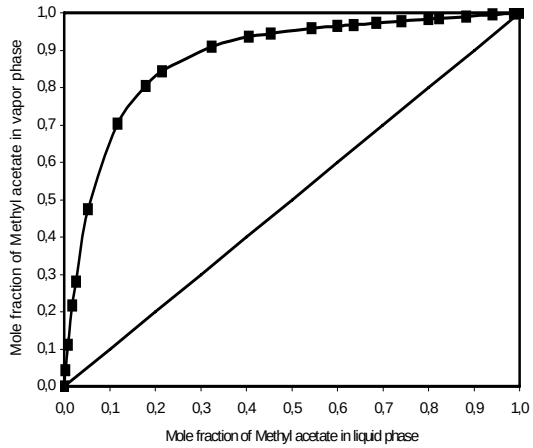

Fig. 1 VLE of the Methyl acetate + Isopropylbenzene system at 97.3 kPa

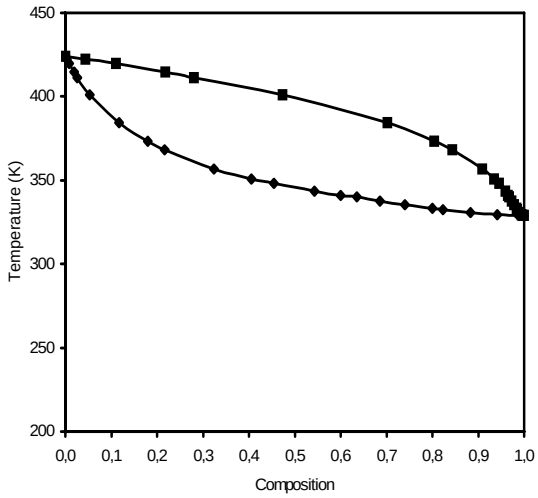

Fig. 2 Temperature vs. Composition curves for the Methyl acetate + Isopropylbenzene system at 97.3 kPa

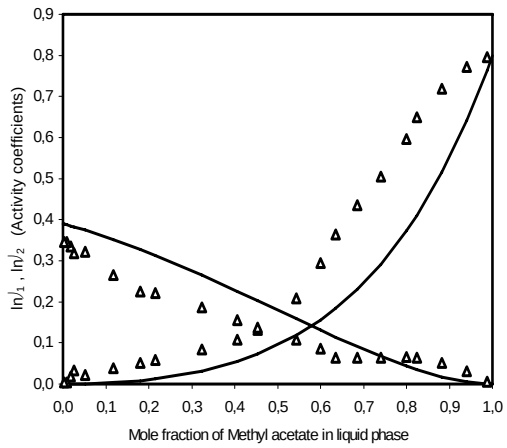

Fig. 3 Plot of $\ln\gamma_1$, $\ln\gamma_2$ vs. composition for the Methyl acetate + Isopropylbenzene system at 97.3 kPa. Δ, experimental; —, UNIFAC

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