Isobaric Vapor-Liquid Equilibria of Mesitylene + 1-Heptanol and Mesitylene +1-Octanol at 97.3 kPa

Seema Kapoor, Sushil K. Kansal, Baljinder K. Gill, Aarti Sharma and Swati Arora

Abstract—Isobaric vapor-liquid equilibrium measurements are reported for the binary mixtures of Mesitylene + 1-Heptanol and Mesitylene + 1-Octanol at 97.3 kPa. The measurements have been performed using a vapor recirculating type (modified Othmer's) equilibrium still. Both the mixtures show positive deviation from ideality. The Mesitylene + 1-Heptanol mixture forms an azeotrope whereas Mesitylene + 1- Octanol form a non – azeotropic mixture. The activity coefficients have been calculated taking into consideration the vapor phase nonideality. The data satisfy the thermodynamic consistency tests of Herington, and Hirata. The activity coefficients have been satisfactorily correlated by means of the Margules, Redlich-Kister, Wilson, Black, and NRTL equations. The activity coefficient values have also been obtained by UNIFAC method.

Keywords—Binary mixture, Mesitylene, Vapor-liquid equilibrium, 1-Heptanol, 1-Octanol.

I. INTRODUCTION

THE measurement, modeling and computation of phase equilibria have been one of the most compelling problems of chemical engineering. The variety of experimental and computational methods developed by chemical engineers and physical chemists for measurement and thermodynamic interpretation of vapor-liquid equilibria probably surpasses all other areas of chemical engineering research. The vapor-liquid equilibria information is useful in designing separation processes such as distillation, adsorption, stripping and liquid-liquid extraction, which are major components of industrial processes involving hydrocarbons, and their cost frequently represents a major fraction of total plant cost. Also the vapor-liquid equilibrium studies have assumed greater importance with the expansion of petrochemical industry and the fast increase in number of pure components that are required to be distilled.

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Very limited work has been reported on vapor-liquid equilibrium study of binary mixtures containing mesitylene as one of the components. Such components form industrially important combinations in petroleum and petrochemical industries. In view of their close boiling point and varied binary interactions, separation becomes difficult. For the rigorous simulation and optimization of the separation of C_9 aromatic compounds, an accurate description of vapor-liquid equilibria is required.

As part of a wide experimental and theoretical study on thermodynamic and physicochemical properties of binary liquid mixtures containing C_9 aromatic compounds and linear alcohols, and with the aim of studying in depth, the behavior of these kinds of mixtures, we are reporting experimental vapor-liquid equilibrium data for binary mixtures of mesitylene with 1-heptanol and 1-octanol. 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 [1], [2]. The binary mixture of mesitylene and 1-heptanol has a boiling range of 12.03 K and the binary mixture of mesitylene and 1-octanol has a boiling range of 30.55 K.

II. EXPERIMENTAL

Chemicals: Mesitylene and 1-Octanol were obtained from Merck-Schuchardt, Germany and 1-Heptanol was obtained from Spectrum (P) Ltd., Mumbai, India. All the chemicals were AR grade materials and had purities (by chromatographic analysis) of 99.0 %, 98.5 % and 99.0 % respectively. The chemicals were purified using standard procedures [3] and stored over molecular sieves.

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 [4]. 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.

III. RESULTS AND DISCUSSION

The liquid-phase activity coefficients (γ) were calculated from the experimental data using the equations [5] 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.

Table I 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 I.

The experimental vapor-liquid equilibrium data (T, x_1, and y_1) at 97.3 kPa along with the calculated activity coefficients for Mesitylene + 1-Heptanol are presented in Table II and for Mesitylene + 1-Octanol are presented in Table III. The Lyckman, Eckerts and Prausnitz [6] correlation was used for the estimation of liquid molar volumes. The Pitzer and Curl equation modified by Tsonopoulos [7] was used in the evaluation of second virial coefficient as well as cross virial coefficients in this work.

TABLE I
PHYSICAL CONSTANTS OF THE PURE COMPOUNDS

Constant	Mesitylene	1-Heptanol	1-Octanol
Molecular wt	120.19 [8]	116.20 [8]	130.23 [8]
Boiling point at 101.3 kPa (K)	437.35 [8]	449.38 [8]	468.20 [8]
Refractive index, n_D at 298.15 K	1.4998 [9]	1.4230 [9]	1.4428 [9]
T_c (K)	637.30 [8]	633.00 [8]	652.50 [8]
P_c (kPa)	3170.69 [8]	3041.026 [8]	2859.70 [8]
$V_c \cdot 10^6 \, (m^3 \cdot mol^{-1})$	433 [8]	435 [8]	490 [8]
Accentric factor, ω	0.399 [8]	0.560 [8]	0.587 [8]
Dipole moment, μ (Debyes)	0.1[8]	1.7 [8]	2.0 [8]
Constants of Antoine's equation, eq.4			
A	7.07436 [10]	6.97899 [10]	6.74900 [10]
B	1569.622 [10]	1321.126[10]	1257.560 [10]
C	209.598 [10]	145.985 [10]	129.877 [10]

TABLE II
VAPOR –LIQUID EQUILIBRIUM DATA OF THE MESITYLENE (1) + 1-HEPTANOL (2) SYSTEM

T (K)	x_1	y_1	$\ln \gamma_1$	$\ln \gamma_2$
436.25	0.9880	0.9800	-0.0071	0.8599
435.85	0.9378	0.9150	-0.0136	0.6741
435.65	0.9018	0.8830	-0.0051	0.5424
435.55	0.8225	0.8225	0.0185	0.3706
435.95	0.7217	0.7437	0.0386	0.2760
436.54	0.6146	0.6640	0.0713	0.2030
438.21	0.4463	0.5340	0.1324	0.1170
438.95	0.4007	0.4950	0.1463	0.0960
441.78	0.2806	0.3870	0.1880	0.0233
442.99	0.2316	0.3363	0.2111	0.0013
445.15	0.1394	0.2290	0.2830	-0.0244
446.65	0.0746	0.1370	0.3601	-0.0271
447.65	0.0321	0.0650	0.4347	-0.0201

TABLE III
VAPOR –LIQUID EQUILIBRIUM DATA OF THE MESITYLENE (1) + 1-OCTANOL (2) SYSTEM

T (K)	x_1	y_1	$\ln \gamma_1$	$\ln \gamma_2$
437.34	0.9921	0.9960	-0.0219	0.1798
438.56	0.9609	0.9800	-0.0361	0.1532
439.69	0.9167	0.9571	-0.0402	0.1238
440.15	0.8772	0.9370	-0.0285	0.1052
443.26	0.7116	0.8462	0.0042	0.0458
445.42	0.6088	0.7870	0.0367	0.0000
447.30	0.5512	0.7501	0.0442	-0.0345
449.56	0.4807	0.6990	0.0586	-0.0623
450.88	0.4450	0.6710	0.0648	-0.0788
453.95	0.3646	0.5990	0.0815	-0.1054
456.25	0.3154	0.5499	0.0900	-0.1301
457.55	0.2763	0.5070	0.1127	-0.1313
460.46	0.2060	0.4190	0.1526	-0.1405
461.75	0.1769	0.3780	0.1744	-0.1437
463.05	0.1495	0.3350	0.1941	-0.1448
464.50	0.1134	0.2720	0.2320	-0.1348
465.63	0.0874	0.2210	0.2616	-0.1261
466.10	0.0737	0.1910	0.2760	-0.1156

The data for the systems were assessed for thermodynamic consistency by applying the Herington area test [11] and Hirata test. The tests show that the experimental data are thermodynamically consistent.

The activity coefficients were correlated with Redlich-Kister, Margules, Wilson, Black, and NRTL [12] equations. The adjustable parameter α_{12} for the NRTL correlation equation was set equal to 0.3 for the Mesitylene + 1-Heptanol system and was set equal to 0.4 for Mesitylene + 1-Octanol 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 square method of Nagahama, Suzuki, and Hirata as used by Rattan et al. [13]. The correlation parameters A_1, A_2, A_3 and deviation in vapor phase composition are listed in Table IV for Mesitylene + 1-Heptanol system and in Table V for Mesitylene + 1-Octanol system. The Redlich-Kister equation gave the best fit with 0.0239 as the average absolute deviation in the vapor phase composition of mesitylene for Mesitylene + 1-Heptanol system and The Black equation gave the best fit with 0.0240 as the average absolute deviation in the vapor phase composition of mesitylene for Mesitylene + 1-Octanol system.

TABLE IV
CORRELATION PARAMETERS FOR ACTIVITY COEFFICIENT AND
DEVIATION IN VAPOR-PHASE COMPOSITION FOR THE
MESITYLENE (1) +1- HEPTANOL (2) SYSTEM

Correlations	A_1	A_2	A_3	Deviation (Δy)
Redlich-Kister	0.5198	0.1473	0.2010	0.0239
Margules	0.5753	0.8681	0.8040	0.0241
Black	0.4068	0.7184	0.1577	0.0785
Wilson	1.2800	0.3260	-	0.1965
NRTL	0.7297	0.1428	-	0.0298

TABLE V
CORRELATION PARAMETERS FOR ACTIVITY COEFFICIENT AND
DEVIATION IN VAPOR-PHASE COMPOSITION FOR THE
MESITYLENE (1) +1- OCTANOL (2) SYSTEM

Correlations	A_1	A_2	A_3	Deviation (Δy)
Redlich-Kister	0.3887	-0.0275	-0.1410	0.0459
Margules	0.2751	0.2201	-0.5642	0.0461
Black	0.4182	0.3631	-0.1430	0.0240
Wilson	0.6300	1.0600	-	0.1789
NRTL	0.0921	0.3256	-	0.0362

Fig. 1 shows the experimental vapor–liquid equilibrium data for the binary mixture of Mesitylene + 1-Heptanol. In Fig. 2, the Temperature vs. Composition curves are drawn for the Mesitylene + 1-Heptanol system at 97.3 kPa. The mixture forms an azeotrope corresponding to T= 435.55 K and x= 0.8225. Fig. 3 shows the plot of ln value of activity coefficients as obtained by UNIFAC [14] method vs. composition for the Mesitylene + 1-Heptanol system. The graph clearly indicates positive deviation from ideality. Fig. 4 shows the plot of y vs y_c for the Mesitylene + 1-Heptanol system using NRTL equation.
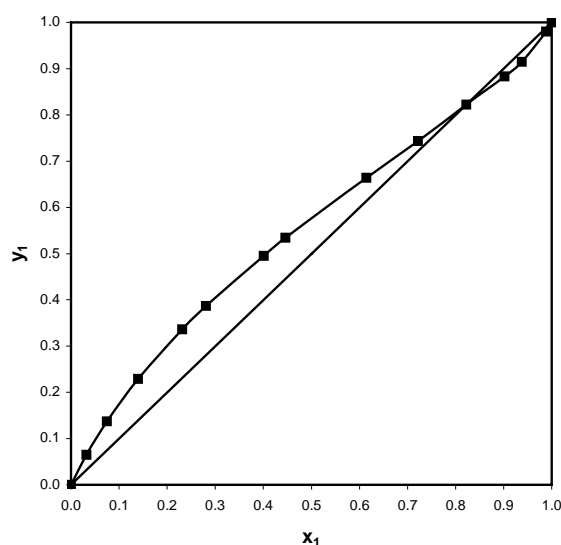

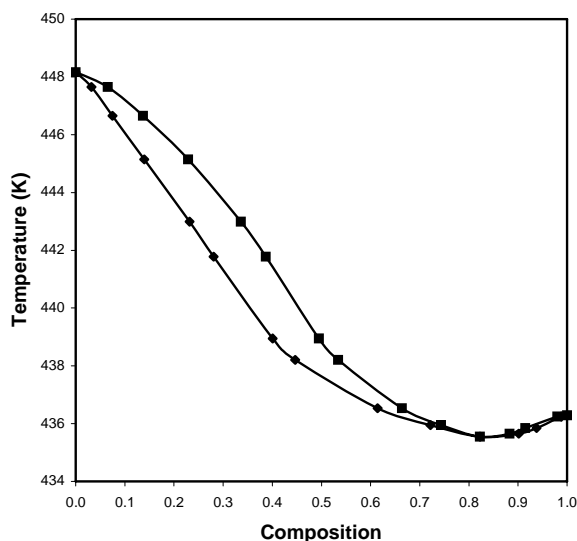Fig. 1. VLE of the Mesitylene + 1-Heptanol system at 97.3 kPa.

Fig. 2. Temperature vs. Composition curves for the Mesitylene + 1-Heptanol system at 97.3 kPa.
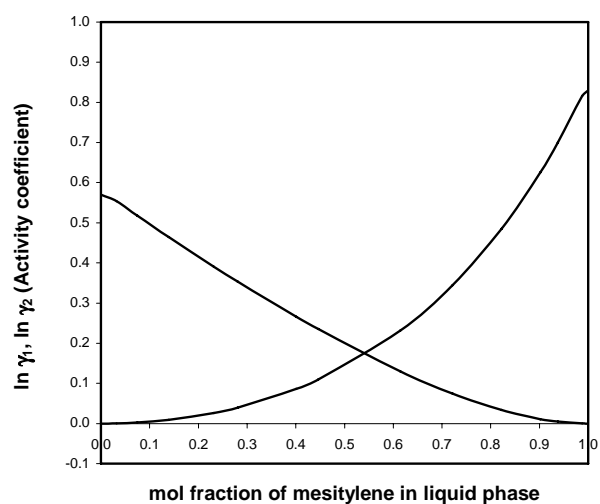
Fig. 3. Plot of $\ln\gamma_1$, $\ln\gamma_2$ vs. composition for the Mesitylene + 1-Heptanol system at 97.3 kPa.
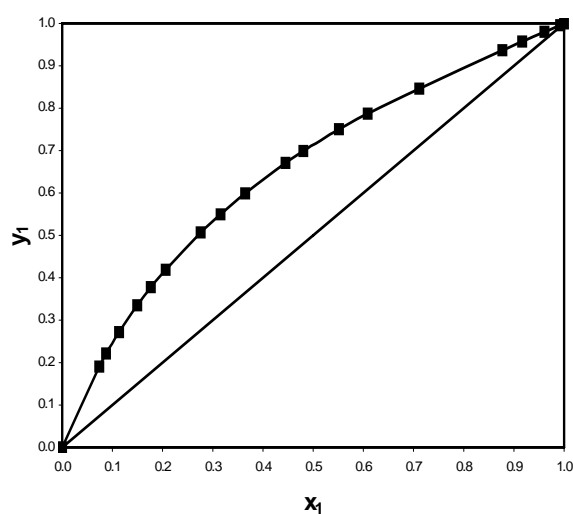—, UNIFAC.

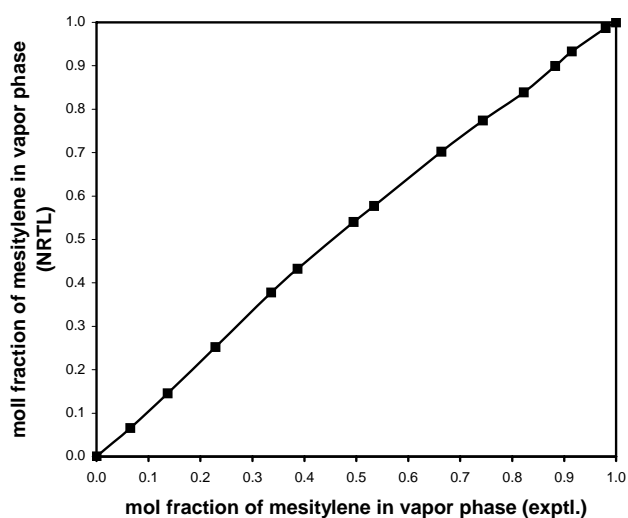Fig. 5. VLE of the Mesitylene + 1-Octanol system at 97.3 kPa.

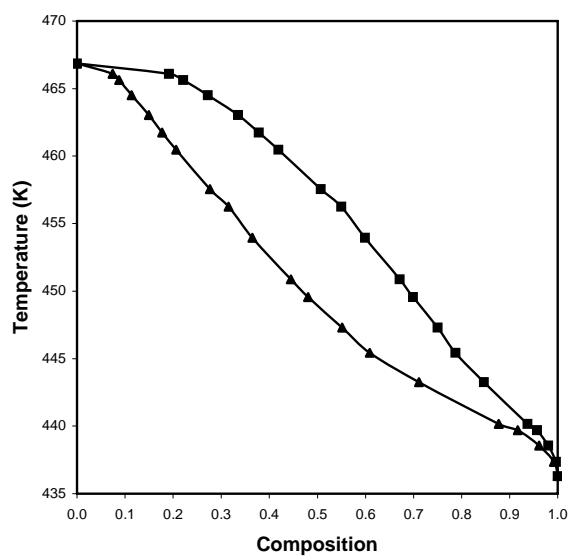Fig.4. y vs y_c plot for the Mesitylene + 1-Heptanol system using NRTL equation.

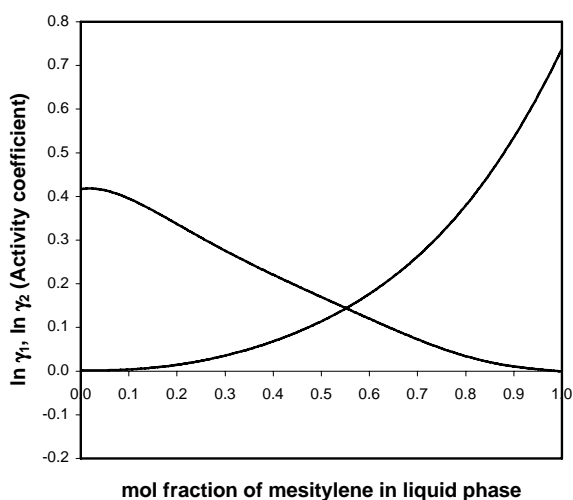Fig. 6. Temperature vs. Composition curves for the Mesitylene + 1-Octanol system at 97.3 kPa.

Fig. 7. Plot of $\ln\gamma_1$, $\ln\gamma_2$ vs. composition for the
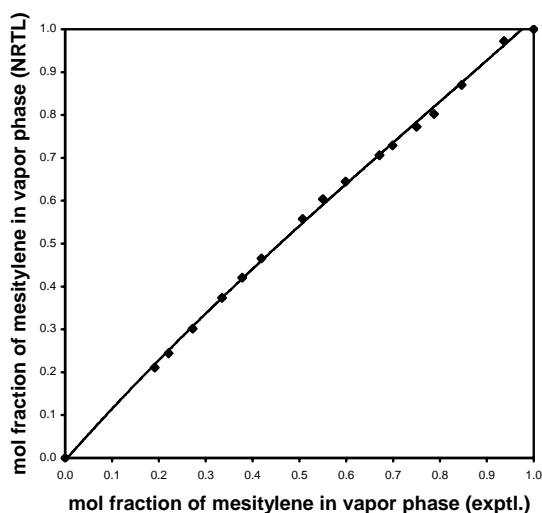Mesitylene + 1-Octanol system at 97.3 kPa.
—, UNIFAC.

Fig. 5 shows the experimental vapor–liquid equilibrium data for the binary mixture of Mesitylene + 1-Octanol. In Fig. 6, the Temperature vs. Composition curves are drawn for the binary system of Mesitylene + 1-Octanol at 97.3 kPa. Fig. 7 shows the plot of ln value of activity coefficients as obtained by UNIFAC method vs. composition for the Mesitylene + 1-Octanol system. The graph clearly indicates positive deviation from ideality. Fig. 8 shows the plot of y vs y_c for the Mesitylene + 1-Octanol system using NRTL equation.

IV. CONCLUSION

Vapor-Liquid equilibrium data at P=97.3 kPa for the binary systems Mesitylene + 1-Heptanol, and Mesitylene + 1-Octanol were determined. Mesitylene forms an azeotrope with 1-Heptanol at this pressure, but not with the immediate next member of the same homologous series i.e. 1-Octanol. The present work will be of great use in updating and improving the databank for estimation of model parameters for mixtures formed by C9 compounds with aliphatic alcohols, and thus will enhance the predictability of the group contribution model.

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Fig. 8. y vs y_c plot for the Mesitylene + 1-Octanol system using NRTL equation.

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