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Isobaric Vapor-Liquid Equilibrium data for Binary Mixtures of *n*-Butylamine and Triethylamine with Cumene at 97.3 kPa

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Abstract**—**Isobaric vapor-liquid equilibrium measurements are reported for the binary mixtures of *n*-Butylamine and Triethylamine with Cumene at 97.3 kPa. The measurements have been performed using a vapor recirculating type (modified Othmer's) equilibrium still. The binary mixture of *n*-Butylamine + Cumene shows positive deviation from ideality. Triethylamine + Cumene mixture shows negligible deviation from ideality. None of the systems form an azeotrope. The activity coefficients have been calculated taking into consideration the vapor phase nonideality. The data satisfy the thermodynamic consistency test of Herington. The activity coefficients have been satisfactorily correlated by means of the Margules, NRTL, and Black equations. The activity coefficient values obtained by the UNIFAC model are also reported.

Keywords**—**Binary mixture, Cumene, ***n***-Butylamine, Triethylamine, Vapor-liquid equilibrium.

I. INTRODUCTION

SEPARATION of liquid mixtures by distillation is one of the most important processes in chemical industries. For the design of distillation columns, knowledge of vapor-liquid equilibrium data is of utmost importance. Due to complex vapor-liquid equilibrium problems arising from numerous new industrial processes, there is a need for the accurate vapor-liquid equilibrium determinations experimentally. In addition to this, experimental data are required to update and improve the data bank used to fit the model parameters of various theoretical models. Very limited work has been reported on vapor-liquid equilibrium study of binary mixtures containing cumene as one of the components. Isobaric vapor-liquid equilibrium data for binary mixtures of *N*-Methylacetamide and *N,N*-Dimethylacetamide with Cumene has been studied and reported in [1]. In the present work, experimental vapor-liquid equilibrium data for binary mixtures of *n*-Butylamine and Triethylamine 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 binary system *n*-Butylamine + Cumene has a wide boiling range i.e. 75 K and the other binary system Triethylamine + Cumene has a boiling range of 62.60 K. None of the systems form an azeotrope.

The compounds studied have a wide range of applications and are of great industrial importance. 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. *n*-Butylamine is used as an intermediate in the synthesis of dyes, drugs, rubber additives, emulsifiers, tanning agents and insecticides. It is also used as a vulcanizing accelerator for rubber and as a curing agent for polymers. Triethylamine is commonly employed in organic synthesis as a base, most often in the preparation of esters and amides with acyl chlorides. It is also used in the synthesis of pesticides, pharmaceuticals, paints and coatings. Other applications of Triethylamine include curing, hardening and corrosion inhibition for polymers and its use as a propellant.

II. EXPERIMENTAL

Chemicals: *n*-Butylamine and Triethylamine 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 98.0 %, 99.0 % 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 refractive indices for the pure compounds and comparing them with the values 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, and in temperature were ± 0.02 K.

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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.

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 experimental vapor-liquid equilibrium data (T, x_1, and y_1) at 97.3 kPa along with the calculated activity coefficients for *n*-Butylamine + Cumene are presented in Table III and for Triethylamine + Cumene are presented in Table IV. 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 data for the systems were assessed for thermodynamic consistency by applying the Herington area test [9]. It shows that the experimental data are thermodynamically consistent. The activity coefficients were correlated with Margules, NRTL [10], and Black equations. The adjustable parameter α_{12} for the NRTL correlation equation was set equal to 0.40 for the *n*-Butylamine + Cumene system and was set equal to 0.41 for the Triethylamine + 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 square method of Nagahama, Suzuki, and Hirata as used by Rattan et al [11]. The correlation parameters A_1, A_2, A_3 and deviation in vapor phase composition for the *n*-Butylamine + Cumene system and the Triethylamine + Cumene system are listed in Table V and Table VI respectively. The Black equation gave the best fit with 0.0375 as the average absolute deviation in the vapor phase composition of *n*-butylamine for the *n*-Butylamine + Cumene system. The Margules equation gave the best fit with 0.0359 as the average absolute deviation in the vapor phase composition of triethylamine for the Triethylamine + Cumene system.

TABLE I
REFRACTIVE INDEX, n_D AT 298.15 K

	n_D	
Compound	Exptl.	Lit.
n-Butylamine	1.398392	1.39870 [4]
Triethylaminee	1.398190	1.39800 [4]
Cumene	1.488292	1.48890 [4]

TABLE II
PHYSICAL CONSTANTS OF THE PURE COMPOUNDS

Constant	*n*-Butylamine	Triethylamine	Cumene
Molecular wt	73.14 [12]	101.193 [12]	120.20 [12]
Boiling point at 101.3 kPa (K)	349.50 [13]	362.50 [13]	425.60 [13]
Refractive index, n_D at 298.15 K	1.39870 [4]	1.39800 [4]	1.48890 [4]
T_c (K)	531.9 [13]	535.0 [13]	631.13 [14]
P_c (kPa)	4198.9 [13]	3029.3 [13]	3208.1 [13]
$V_c \cdot 10^6$ ($m^3 \cdot mol^{-1}$)	277.0 [15]	389.0 [13]	428.0 [14]
Accentric factor, ω	0.329 [13]	0.319 [12]	0.325 [12]
Dipole moment, μ (Debyes)	1.37 [4]	0.87 [4]	0.39 [4]
Constants of Antoine's equation, eq.4			
A	6.94519[16]	7.18658 [16]	6.93160 [16]
B	1157.810 [16]	1341.30 [16]	1457.318 [16]
C	207.80[16]	222.00 [16]	207.370 [16]

TABLE III
VAPOR –LIQUID EQUILIBRIUM DATA OF THE BUTYLAMINE (1) + CUMENE (2) SYSTEM

T (K)	x_1	y_1	$\ln\gamma_1$	$\ln\gamma_2$
349.20	0.9880	0.9984	0.00408	0.34245
349.73	0.9698	0.9961	0.00356	0.31802
351.08	0.9188	0.9892	0.00836	0.28297
352.19	0.8805	0.9840	0.01103	0.25198
354.35	0.8150	0.9742	0.01199	0.20576
356.51	0.7478	0.9628	0.02093	0.17938
360.25	0.6493	0.9426	0.03051	0.14099
361.75	0.6137	0.9338	0.03400	0.13186
363.70	0.5661	0.9217	0.04591	0.11156
368.95	0.4662	0.8872	0.05548	0.08129
373.56	0.3900	0.8521	0.06965	0.05818
378.74	0.3144	0.8060	0.09516	0.03879
384.97	0.2426	0.7407	0.11485	0.02707
389.38	0.1997	0.6868	0.12807	0.02291
394.05	0.1583	0.6225	0.15379	0.01703
397.58	0.1317	0.5688	0.16802	0.01415
406.01	0.0793	0.4196	0.18965	0.01192
413.85	0.0406	0.2548	0.19982	0.00792
418.32	0.0216	0.1487	0.20397	0.00461
422.87	0.0040	0.0299	0.20990	0.00170

TABLE IV
VAPOR –LIQUID EQUILIBRIUM DATA OF THE TRIETHYLAMINE (1) + CUMENE (2) SYSTEM

T (K)	x_1	y_1	$\ln\gamma_1$	$\ln\gamma_2$
362.45	0.9686	0.9949	-0.00500	0.04423
363.69	0.9213	0.9866	-0.00066	0.04408
364.56	0.8922	0.9809	-0.00031	0.05186
365.88	0.8505	0.9726	-0.00018	0.03999
367.67	0.7979	0.9606	-0.00121	0.03725
368.75	0.7684	0.9534	-0.00246	0.03075
370.96	0.7092	0.9370	-0.00293	0.02681
373.05	0.6575	0.9205	-0.00408	0.02375
375.77	0.5944	0.8973	-0.00447	0.01987
379.33	0.5197	0.8636	-0.00504	0.01637
382.05	0.4676	0.8355	-0.00499	0.01281
384.86	0.4195	0.8052	-0.00676	0.00585
388.16	0.3647	0.7640	-0.00346	0.00425
391.95	0.3100	0.7152	-0.00143	-0.00637
395.45	0.2628	0.6632	0.00314	-0.00933
401.17	0.1924	0.5631	0.01646	-0.00629
406.66	0.1352	0.4531	0.02758	-0.00406
411.93	0.0888	0.3388	0.04228	-0.00965
416.09	0.0540	0.2292	0.06039	-0.00342
418.84	0.0336	0.1546	0.08411	-0.00350
421.96	0.0130	0.0646	0.10004	-0.00280

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

Correlations	A_1	A_2	A_3	Deviation (Δy)
Margules	0.2296	0.3195	0.0881	0.0394
NRTL	0.5677	-0.2334	-	0.0411
Black	0.2146	0.3065	0.0142	0.0375

TABLE VI
CORRELATION PARAMETERS FOR ACTIVITY COEFFICIENT AND DEVIATION IN VAPOR-PHASE COMPOSITION FOR THE TRIETHYLAMINE (1) + CUMENE (2) SYSTEM

Correlations	A_1	A_2	A_3	Deviation (Δy)
Margules	0.1010	0.0533	0.0874	0.0359
NRTL	-0.4686	0.6619	-	0.0366
Black	0.0948	0.0385	0.0100	0.0511

Fig. 1 shows the experimental vapor–liquid equilibrium data for the *n*-Butylamine + Cumene binary mixture. In Fig. 2, the Temperature vs. Composition curves are drawn for the *n*-Butylamine + Cumene system at 97.3 kPa.

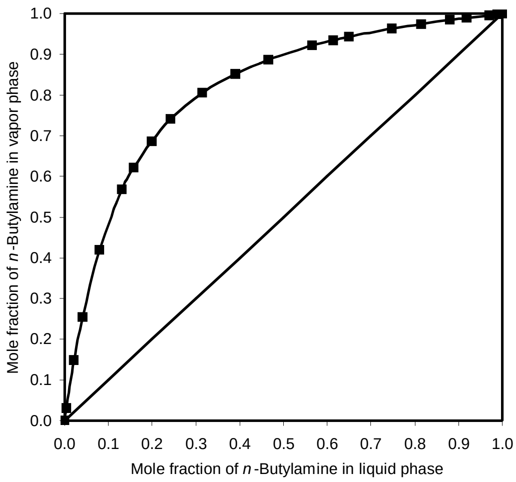

Fig. 1. VLE of the *n*-Butylamine + Cumene system at 97.3 kPa.

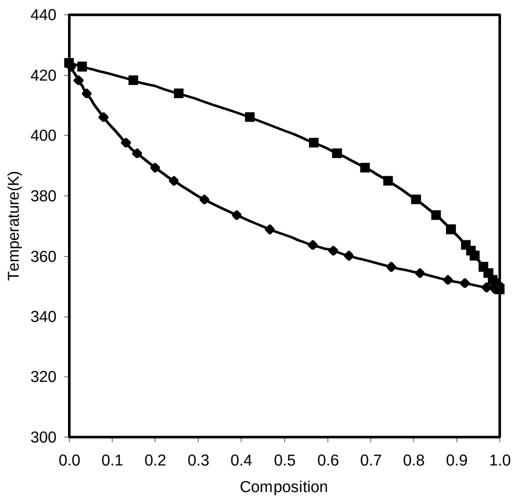

Fig. 2. Temperature vs. Composition curves for the *n*-Butylamine + Cumene system at 97.3 kPa.

Fig. 3 shows the plot of ln value of activity coefficients as obtained by UNIFAC method [17] vs. composition for the *n*-Butylamine + Cumene system. The graph clearly indicates positive deviation from ideal behavior for the binary system studied. The mixture does not form an azeotrope. Fig. 4 shows the plot of y vs. y_c for the *n*-Butylamine + Cumene system using NRTL equation.

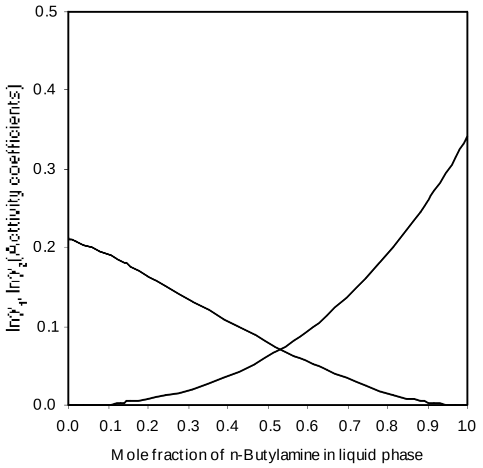

Fig. 3. Plot of $\ln\gamma_1$, $\ln\gamma_2$ vs. composition for the *n*-Butylamine + Cumene system at 97.3 kPa. —, UNIFAC.

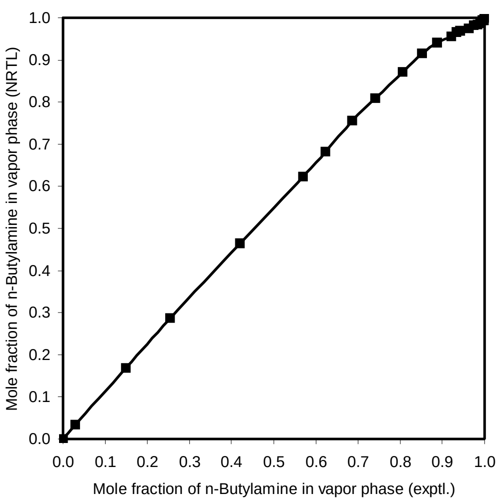

Fig. 4. Plot of y vs. y_c for the *n*-Butylamine + Cumene system using NRTL equation

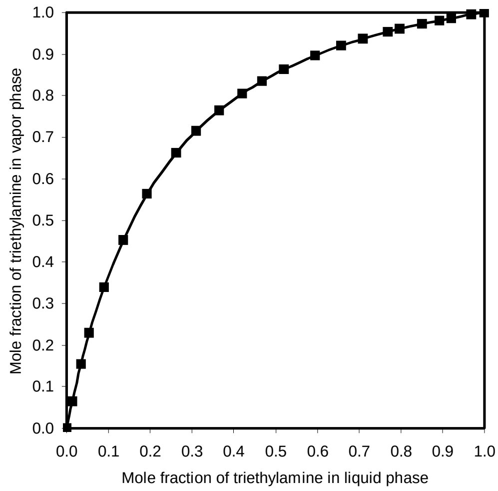

Fig. 5. VLE of the Triethylamine + Cumene system at 97.3 kPa.

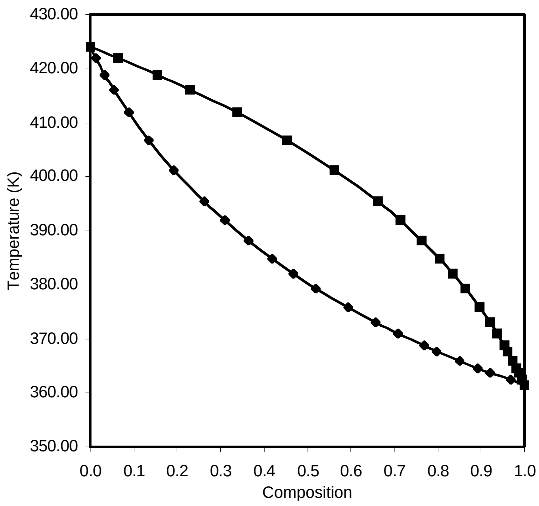

Fig. 6. Temperature vs. Composition curves for the Triethylamine + Cumene system at 97.3 kPa.

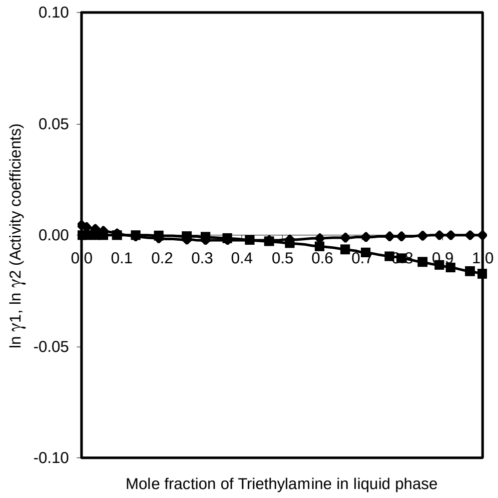

Fig. 7. Plot of lnγ_1, lnγ_2 vs. composition for the Triethylamine + Cumene system at 97.3 kPa. —, UNIFAC.

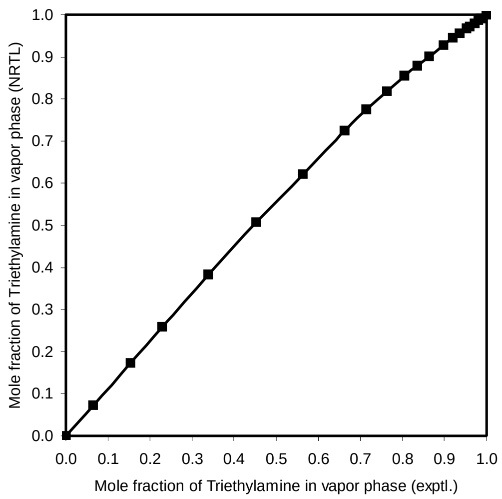

Fig. 8. Plot of y vs. y_c for the Triethylamine + Cumene system using NRTL equation

Fig. 5 shows the experimental vapor–liquid equilibrium data for the Triethylamine + Cumene binary mixture. In Fig. 6, the Temperature vs. Composition curves are drawn for the Triethylamine + Cumene system at 97.3 kPa. Fig. 7 shows the plot of ln value of activity coefficients as obtained by UNIFAC method [17] vs. composition for the Triethylamine + Cumene system. The graph shows nearly ideal behavior for the binary system studied. The mixture does not form an azeotrope. Fig. 8 shows the plot of y vs. y_c for the Triethylamine + Cumene system using NRTL equation.

IV. CONCLUSION

Vapor-Liquid equilibrium data at P=97.3 kPa has been obtained for the two binary systems; *n*-Butylamine + Cumene and Triethylamine + Cumene. Both mixtures are non-azeotropic in nature. Whereas the *n*-Butylamine + Cumene binary mixture shows positive deviation from ideality, the Triethylamine + Cumene binary mixture shows negligible deviation from ideality.

This work will be of great use in improving the databank for estimation of model parameters for mixtures formed by cumene with amines, and thus will enhance the predictability of the group contribution model.

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