Isobaric Vapor-Liquid Equilibrium Data for Binary Mixture of 2-Methyltetrahydrofuran and Cumene

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

Abstract**—**Isobaric vapor-liquid equilibrium measurements are reported for binary mixture of 2-Methyltetrahydrofuran and Cumene at 97.3 kPa. The data were obtained using a vapor recirculating type (modified Othmer's) equilibrium still. The mixture shows slight negative deviation from ideality. The system does not form an azeotrope. The experimental data obtained in this study are thermodynamically consistent according to the Herington test. The activity coefficients have been satisfactorily correlated by means of the Margules, and NRTL equations. Excess Gibbs free energy has been calculated from the experimental data. The values of activity coefficients have also been obtained by the UNIFAC group contribution method.

Keywords—Binary mixture, 2-Methyltetrahydrofuran, Cumene, Vapor-liquid equilibrium, UNIFAC, Excess Gibbs free energy.

I. INTRODUCTION

EXPERIMENTAL determinations of vapor-liquid equilibrium (VLE) are indispensable for the design of distillation columns and the selection of solvents. Due to meagre availability of experimental data, the constants predicted by the group contribution models do not give very accurate predictions for systems containing cumene as one of the components. The present work aims to contribute to the enlargement of available databank and hence enhance the predictive ability of the group contribution model.

This work forms a part of continuing research [1] on experimental vapor-liquid equilibrium determination for binary mixtures of cyclic ethers with (1-Methylethyl)benzene. IUPAC name of cumene is (1-Methylethyl)benzene. In this work, experimental vapor-liquid equilibrium data for binary mixture of 2-Methyltetrahydrofuran and 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]. The binary system studied has a wide boiling range of 71.94 K and it does not form an azeotrope.

The compounds studied are of great industrial importance. 2-Methyltetrahydrofuran (2-MeTHF) is a versatile and environment friendly solvent derived from a variety of agricultural byproducts. 2-MeTHF is a gasoline extender that has been successfully road-tested in fuel blends. It is a component of P-series fuels that were recently classified as alternative fuels by the US Department of Energy. Success for the P-series fuels would mean a significant increase in its use. In addition, 2-MeTHF is also used as a specialty solvent and as a reactant for the production of chemicals including N-substituted 2-methylpyrrolidines and 2-methylpyrrolidine. MeTHF is a more convenient solvent than tetrahydrofuran for Grignard reagents; it is higher boiling and wet. It is also used as a solvent for other organometallic reagents as well as for electrolytic solutions in lithium batteries. 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 cumene include crude petroleum and coal tar.

II. EXPERIMENTAL

Chemicals: 2-Methyltetrahydrofuran, and Cumene were obtained from Merck-Schuchardt, Germany. The 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 [3] 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 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

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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.

III. RESULTS AND DISCUSSION

The liquid-phase activity coefficients (γ) were calculated from the experimental data using the equations [5] given 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) for Cumene were calculated according to the Antoine equation

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

And the pure component vapor pressures (P^0) for 2-Methyltetrahydrofuran were calculated according to the Antoine equation

$$Log\,(P^0) = A - [B/(C + T - 273.15)] \quad (5)$$

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

TABLE I
REFRACTIVE INDEX, η_D AT 298.15 K AND BOILING POINT, T_b AT 101.3 KPA

	n_D		T_b (K)	
Compound	Exptl.	Lit.	Exptl.	Lit.
2-MeTHF	1.404922	1.404960 [3]	353.36	353.10[3]
Cumene	1.488292	1.488900 [3]	425.63	425.60[13]

TABLE II
PHYSICAL CONSTANTS OF THE PURE COMPOUNDS

Constant	2-MeTHF	Cumene
Molecular wt.	86.13[14]	120.20[14]
Boiling Point at 101.3 kPa (K)	353.10[3]	425.60[13]
Refractive Index at 298.15 K	1.404960[3]	1.488900[3]
T_c (K)	537.00 [13]	631.13[15]
P_c (kPa)	3759.0[13]	3208.1[15]
$V_c \cdot 10^6$ (m^3·mol^{-1})	267[13]	428[15]
Accentric factor, ω	0.264[13]	0.325[14]
Dipole moment, μ (Debyes)	-	0.39[3]
Constants of antoine's equation, Refer to "(4) and (5)"		
A	5.95009[17]	6.93160[16]
B	1175.51[17]	1457.318[16]
C	217.80[17]	207.370[16]

The Redlich-Kwong equation of state [6] was used for the evaluation of second virial coefficients and Amdur-Mason equation [7] was used to calculate the cross virial coefficients in this work. The Yen and Woods [8] method was used for the estimation of liquid molar volumes.

The experimental vapor-liquid equilibrium data (T, x_1, and y_1) at 97.3 kPa are presented in Table III. The activity coefficient values calculated from the experimental data and those predicted by the UNIFAC model [9] are presented in Table IV.

The activity coefficient values calculated from experimental data indicate slight negative deviations from ideal behavior. In accordance to the experimental results, γ_1 varies between 0.9760-1.0773 and γ_2 varies between 0.9633-1.0745. Predictions by the UNIFAC method give positive values for activity coefficients as presented in Table IV. The discrepancy in the experimental results and UNIFAC predictions for binary mixtures of cumene and cyclic ethers has been discussed earlier [1].

TABLE III
VAPOR-LIQUID EQUILIBRIUM DATA OF THE 2-METHF (1) + CUMENE (2) SYSTEM AT 97.3 KPA

T (K)	x_1	y_1
352.06	1.0000	1.0000
352.38	0.9952	0.9995
353.75	0.9593	0.9959
355.35	0.9139	0.9909
358.55	0.8287	0.9797
361.15	0.7611	0.9694
363.25	0.7105	0.9600
366.05	0.6502	0.9468
369.65	0.5756	0.9266
372.85	0.5160	0.9066
375.95	0.4619	0.8837
377.55	0.4369	0.8715
379.55	0.4059	0.8542
382.35	0.3662	0.8282
387.85	0.2955	0.7686
393.51	0.2324	0.6944
396.25	0.2047	0.6537
401.75	0.1541	0.5587
406.95	0.1121	0.4548
410.95	0.0821	0.3626
414.05	0.0590	0.2782
419.25	0.0271	0.1399
424.00	0.0000	0.0000

TABLE IV
ACTIVITY COEFFICIENT DATA FOR THE 2-METHF (1) + CUMENE (2) SYSTEM AT 97.3 KPA

	Experimental		UNIFAC	
x_1	γ_1	γ_2	γ_1	γ_2
0.9952	0.9947	1.0745	1.0000	1.2580
0.9593	0.9870	1.0617	1.0005	1.2288
0.9139	0.9833	1.0440	1.0023	1.1963
0.8287	0.9770	1.0290	1.0086	1.1460
0.7611	0.9776	1.0037	1.0158	1.1143
0.7105	0.9780	0.9959	1.0222	1.0944
0.6502	0.9760	0.9837	1.0310	1.0743
0.5756	0.9796	0.9756	1.0431	1.0542
0.5160	0.9832	0.9665	1.0537	1.0412
0.4619	0.9890	0.9660	1.0638	1.0314
0.4369	0.9903	0.9633	1.0687	1.0275
0.4059	0.9943	0.9642	1.0748	1.0231
0.3662	0.9983	0.9650	1.0829	1.0182
0.2955	1.0084	0.9679	1.0976	1.0111
0.2324	1.0200	0.9722	1.1111	1.0065
0.2047	1.0275	0.9728	1.1170	1.0050
0.1541	1.0406	0.9799	1.1281	1.0027
0.1121	1.0516	0.9847	1.1373	1.0014
0.0821	1.0620	0.9902	1.1439	1.0007
0.0590	1.0739	1.0010	1.1491	1.0004
0.0271	1.0773	1.0005	1.1561	1.0001

The data for the systems were assessed for thermodynamic consistency by applying the Herington area test [10]. According to the method suggested by Herington, from ln (γ_1/γ_2) vs. x_1 plots, the value of ($D - J$) is < 10 %, numerically equal to –11.04 %. It shows that the experimental data are thermodynamically consistent. The activity coefficients were correlated with Margules, Wilson, and NRTL [11] equations. The mixture nonrandomness parameter, α_{12} for the NRTL equation was set equal to 0.30. The estimation of parameters for the three correlation equations is based on minimization of ln (γ_1/γ_2) as an objective function using the nonlinear least-squares method of Nagahama, Suzuki, and Hirata [12]. The correlation parameters A_1, A_2, and A_3 and the deviation in vapor-phase composition are listed in Table V. The NRTL and Margules correlations give root-mean-square deviation in the vapor-phase composition of 2-Methyltetrahydrofuran as 0.04104 and 0.04124 respectively. However, the Wilson equation is found to be unsuitable.

TABLE V
CORRELATION PARAMETERS FOR ACTIVITY COEFFICIENT AND DEVIATION IN VAPOR-PHASE COMPOSITION OF 2-METHF

Correlations	A_1	A_2	A_3	Deviation (Δy)
Margules	0.06766	0.08821	-0.00974	0.04124
NRTL	0.39862	-0.28340	-	0.04104
Wilson	1.18625	0.75852	-	0.12476

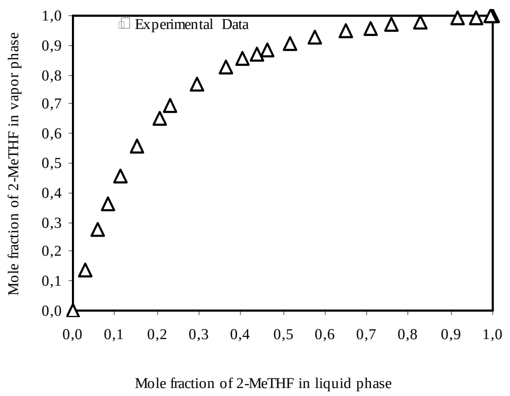

Fig. 1 VLE of the 2-MeTHF + Cumene system at 97.3 kPa

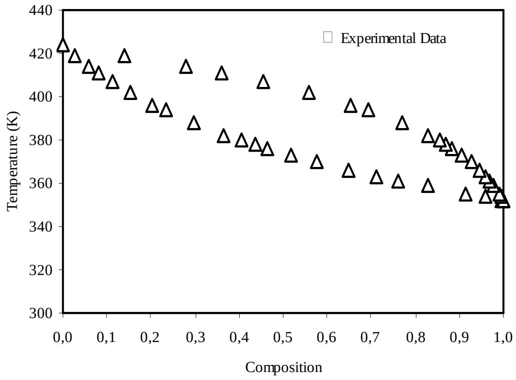

Fig. 2 Temperature vs. Composition curves for the binary system 2-MeTHF + Cumene at 97.3 kPa

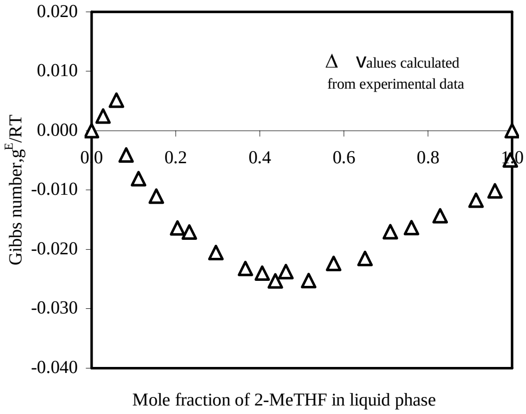

Fig. 3 Gibbs number vs. Composition for 2-MeTHF + Cumene system at 97.3 kPa

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 2-MeTHF + Cumene system at 97.3 kPa. Fig. 3 shows the excess Gibbs function as calculated from the experimental data for the binary mixture. The graph clearly indicates negative deviations from ideal behavior for the binary system studied.

REFERENCES

[1] B. K. Gill, V. K. Rattan, and S. Kapoor, “Experimental isobaric vapor-liquid equilibrium data for binary mixtures of cyclic ethers with (1-Methylethyl)benzene (manuscript– submitted for publication),” Journal of Chemical and Engineering Data, submitted for publication.

[2] B. Kumar and K. S. N. Raju, “Vapor-liquid equilibrium data for the systems 2-Methoxyethanol-Ethylbenzene, 2-Methoxyethanol–p-xylene, and 2-Ethoxyethanol– p-xylene,” Journal of Chemical and Engineering Data, 1977, vol. 22, no.2 , pp. 134-137.

[3] J. A. Riddick, W. B. Bunger, and T. K. Sakano, Organic Solvents: Physical Properties and Methods of Purification, 4th ed., Wiley-Interscience, New York, 1986.

[4] B. K. Sood, O. P. Bagga, and K. S. N. Raju, “Vapor-liquid equilibrium data for systems ethylbenzene–anisole and p-xylene–anisole,” Journal of Chemical and Engineering Data, 1972, no. 4, vol. 17, pp. 435-438.

[5] H. C. Van Ness and M. M. Abbott, Classical Thermodynamics of Non-electrolyte Solutions, McGraw-Hill, New York, 1982.

[6] O. Redlich and J. N. S. Kwong, “On the Thermodynamics of Solutions.V. An Equation of State. Fugacities of Gaseous Solutions,” Chemical Reviews, 1949, vol. 44, no. 1, pp. 233-244.

[7] I. Amdur and E. A. Mason, “Properties of gases at very high temperatures,” Physics of Fluids, 1958, vol.1, no. 5, pp. 370-383.

[8] C. L. Yen and S. S. Woods, “A Generalized equation for computer calculation of liquid densities,” AIChE Journal, 1966, vol. 12, no. 1, pp. 95-99.

[9] J. Gmehling, J. Lohmann, J, and R. Wittig, “ Vapor-liquid equilibria by UNIFAC Group Contribution. 6. Revision and extension,” Industrial Engineering Chemistry Research, 2003, vol. 42, no. 1, pp. 183-188.

[10] E. F. G. Herington, “Tests for the consistency of experimental isobaric vapor-liquid equilibrium data,” Journal of Institute of Petroleum, 1951, vol.37, pp. 457-470.

[11] H. Renon, and J. M. Prausnitz, “ Local compositions in thermodynamic excess functions for liquid mixtures,” AIChE Journal, 1968, vol. 14,no. 1, pp. 135-144.

[12] B. K. Gill, V. K Rattan, and S. Kapoor, “Isobaric vapor-liquid equilibrium of binary mixtures of vinyl acetate and ethyl formate with cumene at 97.3 kPa,” Journal of Chemical and Engineering Data, 2008, vol. 53, no. 1, pp. 145-148.

[13] R. C. Reid, J. M. Prausnitz, and B. E. Poling, The Properties of Gases and Liquids, 4th ed., McGraw-Hill, New York, 1987.

[14] R. M. Stephenson and S. Malanowski, Handbook of the thermodynamics of organic compounds, Elsevier Publications, New York, 1987.

[15] J. A. Riddick, W. B. Bunger, and T. K. Sakano, Organic Solvents: Physical Properties and Methods of Purification, 3rd ed., Wiley-Interscience, New York, 1970.

[16] T. Boublik, V. Fried, and E. Hala, The Vapor Pressures of Pure Substances, Elsevier, New York, 1975.

[17] TRC Tables: Selected values of properties of chemical compounds;, Texas 1972, k–6170.