J. Chem. Eng. Data **2008,** *53,* 2041–2043 **2041**

Experimental Isobaric Vapor−Liquid Equilibrium Data for Binary Mixtures of Cyclic Ethers with (1-Methylethyl)benzene

Baljinder K. Gill,*,[†] Virender K. Rattan,[‡] and Seema Kapoor[‡]

Department of Chemical Engineering & Technology, Panjab University, Chandigarh-160014, India, and Department of Chemical Engineering, Beant College of Engineering and Technology, Gurdaspur-143521, India

Isobaric vapor−liquid equilibrium (VLE) measurements are reported for binary mixtures of tetrahydrofuran and tetrahydropyran with (1-methylethyl)benzene at 97.3 kPa. The data were obtained using a vapor recirculating-type (modified Othmer's) equilibrium still. Both mixtures show negative 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 and NRTL equations. Excess Gibbs free energy has been calculated from the experimental data. The vapor−liquid equilibrium predictions have been done by the UNIFAC group contribution method too.

Introduction

Experimental determinations of vapor−liquid equilibrium are indispensable for the design of distillation columns and the selection of solvents. Since the literature available on the vapor−liquid equilibrium study of binary mixtures containing (1-methylethyl)benzene, as one of the components, is very scarce, the necessity to study this class of binary mixtures was realized. In the present work, experimental vapor−liquid equilibrium data for binary mixtures of (1-methylethyl)benzene with tetrahydrofuran and tetrahydropyran 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.[1,2] The two binary systems studied have wide boiling ranges, i.e., (86.48 and 64.60) K, respectively. None of the systems form an azeotrope.

All compounds studied are of great industrial importance. Cyclic ethers are used as important solvents, chemical intermediates, and monomers for ring-opening polymerization. Tetrahydrofuran is an industrial solvent and a chemical intermediate widely recognized for its unique combination of useful properties. It is used as a resin solvent in PVC top coating, printing ink for plastics, cellophane coatings, as a reaction solvent for Grignard's reagent, steroids, and high molecular weight organic polymers, and as a chemical intermediate for polytetramethylene ether glycols and natural gas odorants. Selected alkylated analogues of tetrahydrofuran and tetrahydropyran are used as solvents for electrolytes in batteries having alkali metal negative electrodes. (1-Methylethyl)benzene, also known as 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 (1-methylethyl)benzene include crude petroleum and coal tar.

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.
tetrahydrofuran	1.404430	1.40496[3]	339.20	339.115[15]
tetrahydropyran	1.418994	1.41862[3]	361.31	361.00[16]
(1-methylethyl)benzene	1.488292	1.48890[3]	425.63	425.60[16]

Table 2. Physical Constants of the Pure Compounds

constant	tetrahydrofuran	tetrahydropyran	(1-methylethyl) benzene
molecular wt.	72.11[17]	86.13[17]	120.20[17]
boiling point/K (at 101.3 kPa)	339.115[15]	361.00[16]	425.60[16]
refractive index n_D (at 298.15 K)	1.40496[3]	1.41862[3]	1.48890[3]
T_c/K	540.1[16]	572.2[16]	631.13[18]
(P_c/101.3)/kPa	51.221[16]	47.076[16]	31.67 [18]
$V_c \cdot 10^6/\mathrm{m}^3 \cdot \mathrm{mol}^{-1}$	224.00[16]	263.00[16]	428.00 [18]
accentric factor, ω	0.217[16]	0.218[16]	0.325[17]
dipole moment, μ/D	1.75[3]	1.63[3]	0.39[3]
constants of antoine's equation, eq 4 and eq 5			
A	6.99515[19]	5.85520[10]	6.93160[19]
B	1202.290[19]	1131.930[10]	1457.318[19]
C	226.254[19]	205.830[10]	207.370[19]

Experimental

Chemicals. Tetrahydrofuran was obtained from C.D.H (P) Ltd., India; tetrahydropyran was obtained from Lancaster Synthesis, Germany; and (1-methylethyl)benzene 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 99.5 %, 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 1.

Apparatus and Procedure. The vapor−liquid equilibrium data were obtained by using a modified version of the equilib-

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* Corresponding author. E-mail: bkg-72@hotmail.com. Tel.: 91 9815998804. Fax: +91-1874-221463.

[†] Beant College of Engineering and Technology.

[‡] Panjab University.

10.1021/je800087p CCC: $40.75

Table 3. Vapor−Liquid Equilibrium Data of the Tetrahydrofuran (1) + (1-Methylethyl)benzene (2) System at 97.3 kPa

T/K	x_1	y_1	γ_1	γ_2
338.27	0.9865	0.9993	1.0007	0.8511
340.35	0.9431	0.9969	0.9789	0.8596
343.14	0.8732	0.9922	0.9663	0.8686
344.75	0.8354	0.9890	0.9594	0.8753
347.15	0.7822	0.9839	0.9493	0.8797
349.70	0.7287	0.9775	0.9402	0.8876
353.58	0.6488	0.9657	0.9342	0.8970
356.39	0.5954	0.9555	0.9317	0.9047
360.34	0.5276	0.9391	0.9284	0.9123
365.31	0.4532	0.9148	0.9240	0.9181
368.65	0.4070	0.8942	0.9235	0.9322
373.25	0.3525	0.8632	0.9183	0.9399
382.48	0.2597	0.7849	0.9109	0.9493
387.35	0.2184	0.7328	0.9061	0.9558
392.90	0.1768	0.6644	0.8996	0.9600
398.15	0.1402	0.5872	0.8979	0.9665
403.65	0.1050	0.4923	0.8994	0.9744
409.33	0.0734	0.3821	0.8948	0.9778
413.43	0.0519	0.2910	0.8929	0.9817
419.05	0.0242	0.1500	0.8906	0.9872
421.21	0.0144	0.0926	0.8894	0.9874

Table 4. Vapor−Liquid Equilibrium Data of the Tetrahydropyran (1) + (1-Methylethyl)benzene (2) System at 97.3 kPa

T/K	x_1	y_1	γ_1	γ_2
360.85	0.9802	0.9973	0.9938	0.9422
361.30	0.9690	0.9957	0.9906	0.9428
362.88	0.9231	0.9886	0.9867	0.9434
364.41	0.8810	0.9814	0.9827	0.9436
365.15	0.8599	0.9775	0.9820	0.9453
367.81	0.7891	0.9626	0.9786	0.9473
370.05	0.7336	0.9489	0.9761	0.9475
373.35	0.6582	0.9263	0.9719	0.9499
376.20	0.5979	0.9043	0.9692	0.9520
379.69	0.5299	0.8739	0.9664	0.9549
381.85	0.4899	0.8528	0.9659	0.9578
386.07	0.4185	0.8072	0.9647	0.9614
389.36	0.3680	0.7667	0.9630	0.9657
391.55	0.3364	0.7372	0.9620	0.9689
393.51	0.3101	0.7096	0.9597	0.9704
398.15	0.2512	0.6369	0.9572	0.9742
404.24	0.1823	0.5263	0.9541	0.9773
409.65	0.1267	0.4096	0.9531	0.9821
414.08	0.0853	0.3013	0.9512	0.9853
416.96	0.0602	0.2245	0.9492	0.9869
421.32	0.0227	0.0924	0.9503	0.9932

rium 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.

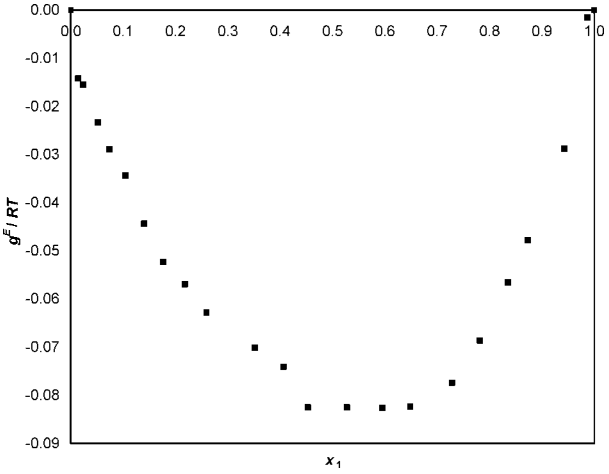

Figure 1. Plot of g^E/RT vs x_1 for the system tetrahydrofuran (1) + (1-methylethyl)benzene (2) at 97.3 kPa.

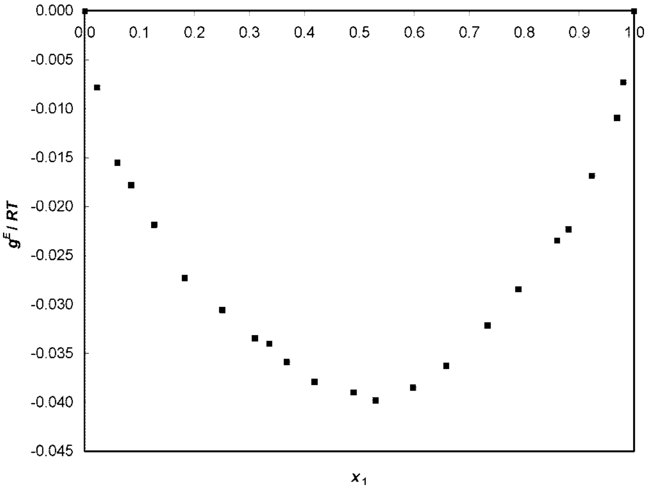

Figure 2. Plot of g^E/RT vs x_1 for the system tetrahydropyran (1) + (1-methylethyl)benzene (2) at 97.3 kPa.

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[5] given below, which take into account the vapor phase nonideality

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

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

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

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 2 gives the physical constants of the pure components. The pure component vapor pressures (P^0) for tetrahydrofuran and (1-methylethyl)benzene were calculated according to the Antoine equation

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

and the pure component vapor pressures (P^0) for tetrahydropyran were calculated according to the Antoine equation

$$\log(P^o/\text{kPa}) = A - [B/((C - 273.15) + (T/\text{K}))] \quad (5)$$

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

The Yen and Woods[6] method 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

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

system	correlations	A_1	A_2	A_3	deviation (Δy)
tetrahydrofuran + (1-methylethyl)benzene	Margules	−0.11608	−0.15092	−0.06606	0.06072
	NRTL	−0.94042	1.14246	–	0.05970
tetrahydropyran + (1-methylethyl)benzene	Margules	−0.05339	−0.04998	−0.01985	0.03475
	NRTL	0.63307	−0.57246	–	0.03440

coefficients as well as cross virial coefficients in this work. The cross second virial coefficient B_{12} has the same temperature dependence that B_{11} and B_{22} have. Mixing rules make it possible to relate the characteristic constants to pure-component parameters. The experimental vapor−liquid equilibrium data (T, x_1, and y_1) at 97.3 kPa along with the activity coefficient values calculated from the experimental data are presented in Table 3 and Table 4. The UNIFAC method[8] has been used to predict vapor−liquid equilibrium for both the systems. Figure 1 gives the excess Gibbs free energy calculated from experimental data for the tetrahydrofuran + (1-methylethyl)benzene system. Figure 2 gives the excess Gibbs free energy calculated from experimental data for the tetrahydropyran + (1-methylethyl)benzene system.

The activity coefficient values calculated from experimental data indicate slight negative deviations from ideal behavior for the tetrahydrofuran + (1-methylethyl)benzene system as well as the tetrahydropyran + (1-methylethyl)benzene system. The calculated excess Gibbs free energy, g^E, over the whole composition range as shown in Figure 1 and Figure 2 also indicates negative deviations from ideal behavior. The experimental results are well supported by the earlier related studies.[9,10] Predictions by the UNIFAC method show slightly positive deviations from ideality for both the systems. The average deviation Δy obtained by the UNIFAC predictive method is 0.09822 for the tetrahydrofuran + (1-methylethyl)benzene system and is 0.07153 for the tetrahydropyran + (1-methylethyl)benzene system.

The data for the systems were assessed for thermodynamic consistency by applying the Herington area test[11] and Black test.[12] According to the method suggested by Herington, from $\ln(\gamma_1/\gamma_2)$ vs x_1 plots, the value of $(D - J)$ is < 10 %, numerically equal to −15.88 % for the tetrahydrofuran + (1-methylethyl)benzene system and 3.43 % for the tetrahydropyran + (1-methylethyl)benzene system. It shows that the experimental data are thermodynamically consistent. The activity coefficients were correlated with Margules and NRTL[13] equations. The mixture nonrandomness parameter, α_{12}, for the NRTL equation was set equal to 0.30 for both the systems. The estimation of parameters for the 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.[14] The correlation parameters A_1, A_2, and A_3 and deviation in vapor phase composition for both the systems are listed in Table 5. For the tetrahydrofuran + (1-methylethyl)benzene system, NRTL and Margules correlations give root-mean-square deviation in the vapor-phase composition as 0.05970 and 0.06072, respectively. For the tetrahydropyran + (1-methylethyl)benzene system, root-mean-square deviations in the vapor-phase composition as calculated by NRTL and Margules correlations are 0.03440 and 0.03475, respectively.

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Received for review February 5, 2008. Accepted July 3, 2008.

JE800087P