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Isobaric Vapor–Liquid Equilibrium of Binary Systems of Hexane or Octane with 1,2-Dimethylbenzene or 1,3-Dimethylbenzene at 101.3 kPa

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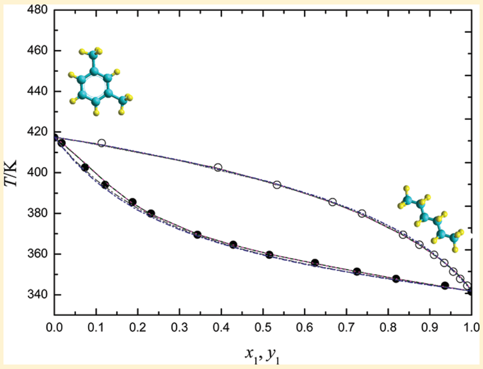
ABSTRACT: Isobaric vapor–liquid equilibrium (VLE) data for the binary mixtures of hexane or octane with 1,2-dimethylbenzene or 1,3-dimethylbenzene were obtained at 101.3 kPa by using a recirculation type of apparatus. All of the experimental VLE data passed the thermodynamic consistency tests of the Herington and the van Ness methods. No azeotrope was found in these binary systems, and each system exhibited large deviations from ideal behavior. The experimental VLE data were correlated well with the Wilson, the nonrandom two-liquid (NRTL), and the universal quasichemical (UNIQUAC) activity coefficient models, respectively. The predictive capability of the universal functional (UNIFAC) and the conductor-like screening model for realistic solvents (COSMO-RS) was also evaluated with the experimental values. These two models fail to quantitatively predict the VLE properties for the octane-containing systems.



INTRODUCTION

The knowledge of vapor–liquid equilibrium (VLE) properties of mixtures is not only fundamentally but also practically important for process development. In the refinery industry, the separation of aliphatic and aromatic hydrocarbons is commonly encountered. VLE data of the related mixtures are essential. Recently, Calvarb et al.[1] found that dimethylbenzenes can be extracted from a liquid mixture of dimethylbenzenes and hexane by using the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate, [EMim][ESO$_4$]. Also, several studies on other thermodynamic properties at different conditions have been published.[2−4] For the system of hexane + 1,4-dimethylbenzene, isothermal VLE data at 313.15 K have been reported by Goral,[5] isobaric VLE data ($T-x$) for the same system at 95 kPa by Prasad et al.,[6] and also isobaric VLE data (T-x,y) at 101.3 kPa by Michishita et al.[7] The isobaric VLE data for the binary systems of 1,2-, 1,3-, or 1,4-dimethylbenzene with cyclohexane and heptane at 101.3 kPa were reported by Tojo et al.,[8,9] with methyl-2-propanol at 101.3 kPa by Monton et al.,[10] with ethenylbenzene at (5 and 15) kPa by Loras et al.,[11] with ethylbenzene at 100.65 kPa by Mattedi et al.,[12] and with ethylbenzene at (6.66 and 26.66) kPa by Monton et al.[13]

In our previous work,[14] we reported the isobaric VLE data of nonane with cyclohexane, methylbenzene, 1,3-dimethylbenzene, or 1,4-dimethylbenzene at 101.3 kPa. In this paper, the isobaric VLE data were measured for the binary systems of hexane or octane with 1,2-dimethylbenzene or 1,3-dimethylbenzene at 101.3 kPa by using a circulating type of apparatus. The Herington[15] area test and the point-to-point test of the van Ness[16] method as modified by Fredunsland et al.[17] were used to check the thermodynamic consistency of the experimental data. In the reduction of VLE data, the fugacity coefficient of each constituent compound in the vapor phase was calculated by using the two-term virial equation of state incorporated with the Hayden and O'Connell (HOC) model[18] for estimating the second virial coefficients. The nonideality of liquid phase was represented by the Wilson,[19] the nonrandom two-liquid (NRTL),[20] or the universal quasichemical (UNIQUAC)[21] activity coefficient models. In this study, we also checked the predictive capability of the universal functional (UNIFAC)[17] and the conductor-like screening model for realistic solvents (COSMO-RS)[22] for the systems investigated.

EXPERIMENTAL SECTION

Materials. All of the chemicals used were of analytical grade and purchased from commercial sources. The suppliers and the purities of the chemicals are given in Table 1. The purity of each chemical was checked by gas chromatography (GC) and the impurity levels found were less than 0.003 in mass fraction. The purities of the chemicals were reconfirmed by measuring their density (ρ) and boiling point, and compared with literature values. Both showed good agreement with the literature values,[23−26] as can be also seen in Table 1. The density of pure components was measured by using a digital vibrating-tube densimeter (DMA 4500, Anton Paar), with an accuracy of ± 0.00005 g·cm^{-3}. Boiling points were measured by a recirculation-type equilibrium apparatus, which was equipped

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Table 1. Material Description, Densities (ρ) at T = 298.2 K, and Boiling Points T of Pure Components[a]

				ρ/g·cm^{-3}		T/K	
compound	source	mass fraction purity	purification method	this work	lit.	this work	lit.
hexane	Acros	0.9972	none	0.65529	0.65493[b]	341.5	341.88[b]
octane	Aldrich	0.9994	none	0.69868	0.69868[c]	398.8	398.86[c]
1,2-dimethylbenzene	Alfa Aesar	0.9995	none	0.87550	0.8755[d]	417.3	417.55[d]
1,3-dimethylbenzene	Acros	0.9999	none	0.86007	0.86009[e]	412.3	412.27[e]

[a] $u(\rho)$ = 0.00005 g·cm^{-3}; $u(T)$ = 0.1 K, where u is the standard uncertainty. [b] Taken from ref 23. [c] Taken from ref 24. [d] Taken from ref 25. [e] Taken from ref 26.

Table 2. Experimental Vapor−Liquid Equilibrium Data for the Binary System of Hexane (1) + 1,2-Dimethylbenzene (2) at 101.3 kPa[a]

T/K	x_1	y_1	γ_1	γ_2	B_{11}	B_{22}	B_{12}
341.5	1.000	1.000	1.000		−1371.7	−2799.8	−703.1
344.4	0.936	0.990	0.982	1.656	−1339.2	−2718.7	−687.4
347.8	0.819	0.973	1.001	1.378	−1302.6	−2628.3	−669.5
351.4	0.725	0.956	1.005	1.283	−1265.5	−2537.7	−651.4
355.7	0.625	0.935	1.014	1.178	−1223.3	−2435.9	−630.5
359.6	0.515	0.910	1.081	1.091	−1186.9	−2349.1	−612.3
364.6	0.429	0.875	1.099	1.074	−1142.5	−2244.8	−589.9
369.5	0.343	0.836	1.164	1.031	−1101.5	−2149.6	−569.0
379.9	0.231	0.737	1.196	1.000	−1021.5	−1967.8	−527.6
385.5	0.187	0.667	1.182	1.003	−981.9	−1879.8	−506.8
394.0	0.122	0.534	1.214	1.006	−926.1	−1757.8	−477.2
402.6	0.074	0.393	1.243	0.972	−874.1	−1646.6	−449.3
414.6	0.018	0.113	1.177	0.971	−808.4	−1509.1	−413.4
417.3	0.000	0.000		1.000	−794.6	−1480.6	−405.7

[a] $u(T)$ = 0.1 K; $u(x_1)$ = 0.005; $u(y_1)$ = 0.005.

Table 3. Experimental Vapor−Liquid Equilibrium Data for the Binary System of Hexane (1) + 1,3-Dimethylbenzene (2) at 101.3 kPa[a]

T/K	x_1	y_1	γ_1	γ_2	B_{11}	B_{22}	B_{12}
341.5	1.000	1.000	1.000		−1371.7	−2727.9	−696.1
344.5	0.900	0.983	1.011	1.499	−1338.1	−2646.8	−679.9
346.9	0.812	0.974	1.037	1.109	−1312.1	−2584.7	−667.3
348.9	0.740	0.963	1.063	1.055	−1291.1	−2534.7	−657.0
351.1	0.673	0.952	1.087	1.000	−1268.5	−2481.4	−645.9
355.3	0.557	0.932	1.147	0.893	−1227.1	−2384.6	−625.4
366.3	0.352	0.846	1.241	0.933	−1128.0	−2157.7	−575.6
371.2	0.296	0.798	1.236	0.955	−1087.8	−2067.6	−555.1
375.8	0.249	0.744	1.230	0.975	−1051.9	−1988.3	−536.6
388.3	0.148	0.566	1.194	0.988	−963.0	−1795.6	−490.0
396.4	0.095	0.413	1.149	0.994	−911.1	−1686.1	−462.4
401.7	0.063	0.295	1.115	0.995	−879.4	−1620.0	−445.3
412.2	0.000	0.000		1.000	−821.0	−1500.5	−413.5

[a] $u(T)$ = 0.1 K; $u(x_1)$ = 0.005; $u(y_1)$ = 0.005.

with a thermocouple calibrated to an uncertainty of ± 0.1 K. All of the materials were used without further purification.

Apparatus and Procedure. The isobaric VLE data were obtained by using a recirculation-type phase equilibrium still (NGW Co.). The schematic diagram and the working procedure of this apparatus were described by Shiah et al.[27] In each experimental run, about 100 cm^3 of liquid mixture was injected in the still. During the course of measurement, the isobaric condition (i.e., 101.3 ± 0.2 KPa) was maintained by using a pressure adjustment system directly attached to the equilibrium still.[14] A mercury barometer (model 453, stability = ± 0.1 kPa, Princo Instruments) was used for atmospheric pressure measurement.

When the temperature remained constant for at least two hours, equilibrium conditions were assumed to be attained, and the equilibrium temperature was recorded. The equilibrium temperature was measured by a digital thermometer (TES 1310 type-K), which was calibrated with a precise platinum thermometer (model-1560, Hart Scientific Co.) to an uncertainty of ± 0.1 K. Vapor and liquid samples were collected for analysis under equilibrium conditions.

Analysis. The compositions of vapor and liquid samples were analyzed by a gas chromatograph (model 8700, China Chromatography) with a thermal conductivity detector and a stainless-steel column (model SE-30, Supelcoport, 80/100 mess, 14′ × 1/8″, 20 %). Helium (purity > 0.9995 in mass

Table 4. Experimental Vapor–Liquid Equilibrium Data for the Binary System of Octane (1) + 1,2-Dimethylbenzene (2) at 101.3 kPa[a]

T/K	x_1	y_1	γ_1	γ_2	B_{11}	B_{22}	B_{12}
398.8	1.000	1.000	1.000		−1831.7	−1694.3	−632.3
399.4	0.924	0.942	1.004	1.237	−1823.3	−1686.6	−629.6
401.0	0.786	0.836	1.005	1.187	−1801.0	−1666.4	−622.4
402.6	0.667	0.740	1.006	1.157	−1779.1	−1646.6	−615.4
404.5	0.537	0.641	1.032	1.090	−1753.7	−1623.6	−607.1
406.0	0.436	0.557	1.064	1.060	−1734.0	−1605.7	−600.7
408.8	0.309	0.438	1.101	1.018	−1698.0	−1573.2	−588.9
409.3	0.297	0.423	1.093	1.014	−1691.7	−1567.5	−586.8
410.5	0.234	0.360	1.147	0.999	−1676.8	−1554.0	−581.8
412.3	0.182	0.291	1.141	0.989	−1654.7	−1534.0	−574.5
415.0	0.091	0.163	1.199	0.980	−1622.3	−1504.8	−563.7
415.7	0.065	0.123	1.246	0.980	−1614.1	−1497.4	−561.0
417.3	0.000	0.000		1.000	−1595.5	−1480.6	−554.7

[a] $u(T) = 0.1$ K; $u(x_1) = 0.005$; $u(y_1) = 0.005$.

Table 5. Experimental Vapor–Liquid Equilibrium Data for the Binary System of Octane (1) + 1,3-Dimethylbenzene (2) at 101.3 kPa[a]

T/K	x_1	y_1	γ_1	γ_2	B_{11}	B_{22}	B_{12}
398.8	1.000	1.000	1.000		−1831.7	−1655.6	−624.0
399.2	0.934	0.948	1.005	1.116	−1826.1	−1650.6	−622.2
400.0	0.843	0.869	1.000	1.156	−1814.9	−1640.7	−618.6
400.9	0.741	0.783	1.001	1.132	−1802.4	−1629.7	−614.6
401.6	0.659	0.718	1.014	1.096	−1792.8	−1621.2	−611.5
402.5	0.556	0.632	1.034	1.072	−1780.5	−1610.4	−607.6
403.9	0.450	0.540	1.053	1.041	−1761.7	−1593.7	−601.5
405.5	0.351	0.438	1.052	1.033	−1740.5	−1575.1	−594.6
406.2	0.320	0.413	1.069	1.011	−1731.4	−1567.0	−591.6
407.3	0.249	0.338	1.094	1.002	−1717.1	−1554.5	−587.0
409.8	0.131	0.191	1.105	0.991	−1685.5	−1526.6	−576.5
411.4	0.038	0.064	1.228	0.994	−1665.7	−1509.1	−570.0
412.3	0.000	0.000		1.000	−1654.7	−1499.4	−566.4

[a] $u(T) = 0.1$ K; $u(x_1) = 0.005$; $u(y_1) = 0.005$.

fraction) was used as a carrier gas. The response of gas chromatography was analyzed by a peak-ABC chromatograph data handling system.

Before making the analysis, the gas chromatography was calibrated by using several standard samples with known compositions over the entire composition range. These standard samples were prepared gravimetrically with an electronic balance (R&D model GR-200) to the uncertainty of ± 0.01 mg. By using the calibration curve, compositions of vapor and liquid phases are measured from the average of at least three replications. The uncertainty of the composition measurement was estimated to within ± 0.005 in mole fraction.

■ RESULTS AND DISCUSSION

Experimental Data and Reliability Test. The isobaric VLE data (T, x_i, y_i) and the corresponding activity coefficient (γ_i) at 101.3 kPa for the binary systems of hexane (1) + 1,2-dimethylbenzene (2), hexane (1) + 1,3-dimethylbenzene (2), octane (1) + 1,2-dimethylbenzene (2), and octane (1) + 1,3-dimethylbenzene (2) are listed in Tables 2 to 5, respectively. The VLE phase diagrams of these binary systems are presented in Figures 1 to 4. All binary systems investigated were found to be nonazeotropic in nature.

The thermodynamic consistency of all of the experimental data were checked by using the Herington area test method.[15]

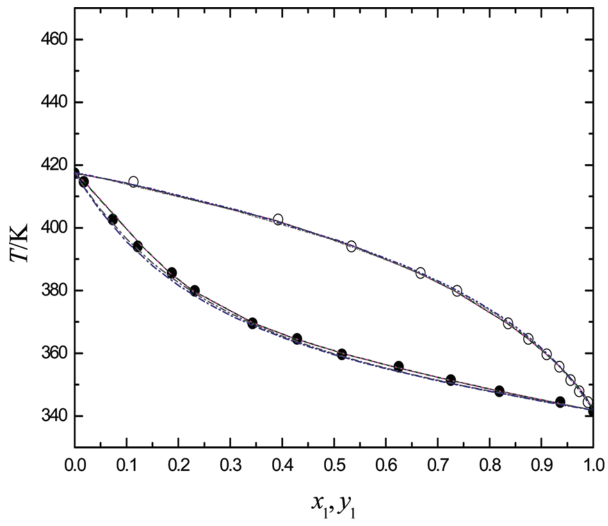

Figure 1. Plot of experimental equilibrium temperature at 101.3 kPa against the mole fraction of hexane (1) + 1,2-dimethylbenzene (2); ●, experimental liquid phase and ○, experimental vapor phase; —, calculated liquid and vapor compositions from the NRTL model; ----, calculated liquid and vapor compositions from the Wilson model; ···, calculated liquid and vapor compositions from the UNIQUAC model; -·-, predicted liquid and vapor compositions from the UNIFAC model; -··-, predicted liquid and vapor compositions from the COSMO-RS model.

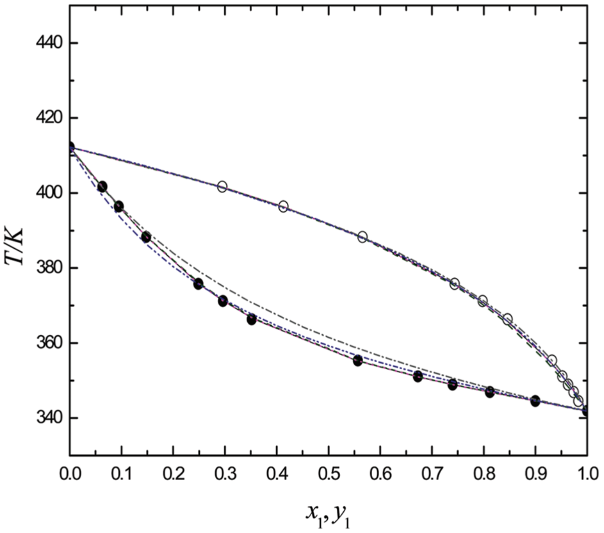

Figure 2. Plot of experimental equilibrium temperature at 101.3 kPa against the mole fraction of hexane (1) + 1,3-dimethylbenzene (2); ●, experimental liquid phase and ○, experimental vapor phase; —, calculated liquid and vapor compositions from the NRTL model; ----, calculated liquid and vapor compositions from the Wilson model; ···, calculated liquid and vapor compositions from the UNIQUAC model; -··-, predicted liquid and vapor compositions from the UNIFAC model; -···-, predicted liquid and vapor compositions from the COSMO-RS model.

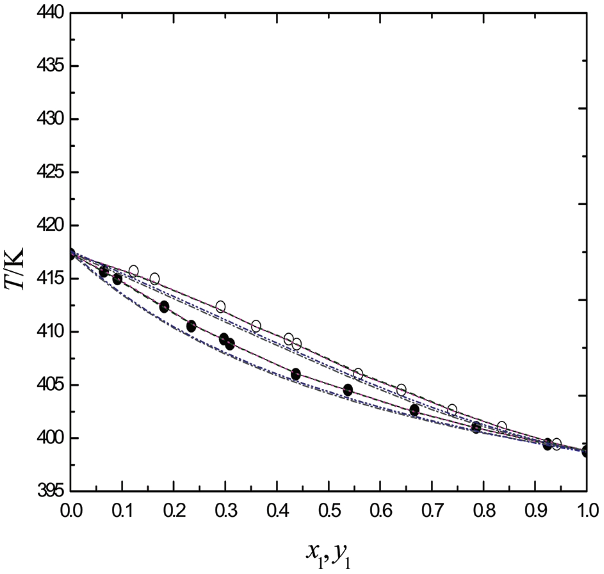

Figure 3. Plot of experimental equilibrium temperature at 101.3 kPa against the mole fraction of octane (1) + 1,2-dimethylbenzene (2); ●, experimental liquid phase and ○, experimental vapor phase; —, calculated liquid and vapor compositions from the NRTL model; ----, calculated liquid and vapor compositions from the Wilson model; ···, calculated liquid and vapor compositions from the UNIQUAC model; -··-, predicted liquid and vapor compositions from the UNIFAC model; -···-, predicted liquid and vapor compositions from the COSMO-RS model.

The data can be considered to be thermodynamically consistent, if $D - J < 10$. Table 6 lists the results of the consistency test which shows that all of the systems pass this criterion.

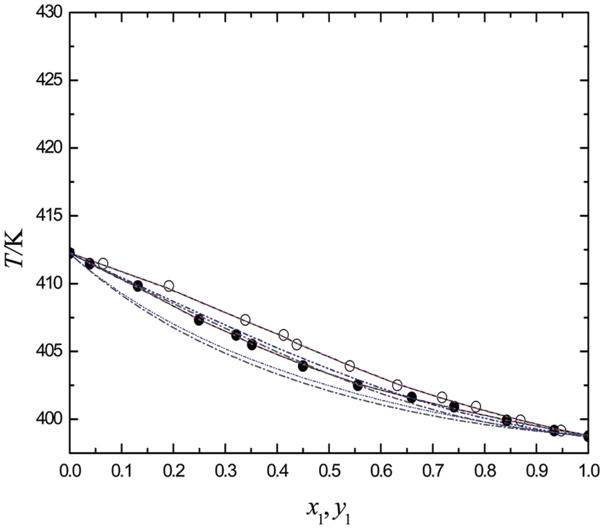

Figure 4. Plot of experimental equilibrium temperature at 101.3 kPa against the mole fraction of octane (1) + 1,3-dimethylbenzene (2); ●, experimental liquid phase and ○, experimental vapor phase; —, calculated liquid and vapor compositions from the NRTL model; ----, calculated liquid and vapor compositions from the Wilson model; ···, calculated liquid and vapor compositions from the UNIQUAC model; -··-, predicted liquid and vapor compositions from the UNIFAC model; -···-, predicted liquid and vapor compositions from the COSMO-RS model.

Table 6. Results of the Herington Thermodynamic Consistency Test

system	$D - J$
hexane + 1,2-dimethylbenzene	0.5
hexane + 1,3-dimethylbenzene	3.2
octane + 1,2-dimethylbenzene	5.3
octane + 1,3-dimethylbenzene	0.5

Vapor–Liquid Equilibrium Calculation. At VLE, the fugacity of each component i in the vapor phase should equal to that in the liquid phase,

$$f_i^{\mathrm{V}} = f_i^{\mathrm{L}} \tag{1}$$

or

$$y_i \phi_i^{\mathrm{V}} P = x_i \gamma_i f_i^{\mathrm{oL}} \tag{2}$$

where f, ϕ, y, P, x, and γ refer to the fugacity, fugacity coefficient, vapor composition, pressure, liquid composition, and activity coefficient, respectively. The superscripts V, L, and o represent the vapor phase, liquid phase, and standard state, respectively, and the subscript i stands for component i. From the above equation, the activity coefficient of component i can be expressed as

$$\gamma_i = (y_i \phi_i^{\mathrm{V}} P)/\{x_i P_i^{\mathrm{s}} \phi_i^{\mathrm{s}} \exp[V_i^{\mathrm{L}}(P - P_i^{\mathrm{s}})/RT]\} \tag{3}$$

where V, R, and T are the molar volume, gas constant, and temperature, respectively. The superscript s represents a saturation condition. The fugacity coefficients ϕ_i^{V} and ϕ_i^{s} were calculated from the two-term virial equation by using the Hayden and O'Connell (HOC) model[18] for the estimation of the self and the cross second virial coefficients (B_{11}, B_{22}, and B_{12}). Since no complex formation in the systems was investigated, the association and salvation parameters (η)

Table 7. Physical Properties of Pure Components[a]

	T_C	P_C	V_C	μ	R_d				
compound	K	kPa	$cm^3 \cdot mol^{-1}$	Debye	Å	Z_C	ω	r^b	q^c
hexane	507.6	3025	371	0	3.769	0.266	0.3013	4.4997	3.856
octane	568.7	2490	486	0	4.546	0.256	0.3995	5.8484	4.936
1,2-dimethylbenzene	630.3	3732	370	0.6296	3.836	0.264	0.3101	4.6579	3.536
1,3-dimethylbenzene	617.0	3541	375	0.2997	3.937	0.259	0.3265	4.6579	3.536

[a] Taken from the Aspen properties databank. [b] Volume parameter of the UNIQUAC model. [c] Surface area parameter of the UNIQUAC model.

Table 8. Parameters of the Extended Antoine Equation[a,b]

compound	$A_1{}^b$	$B_2{}^b$	$C_3{}^b$	$D_4{}^b$	$E_5{}^b$	$10^6 \cdot F_6{}^b$	$G_7{}^b$	T_1/K	T_2/K
hexane	97.74	−6995.5	0	0	−2.70	12.30	2	177.83	507.60
octane	89.17	−7900.2	0	0	−11.00	7.18	2	216.38	568.70
1,2-dimethylbenzene	83.49	−7955.2	0	0	−10.08	5.95	2	247.98	630.30
1,3-dimethylbenzene	78.19	−7615.9	0	0	−9.30	5.56	2	255.30	617.00

[a] Taken from the Aspen property databank. [b] Extended Antoine equation: $\ln(P_i^s = A_1 + (B_2/T + C_3) + D_4T + E_5 \ln T + F_6T^{G_7}$ for $T_1 < T < T_2$, where P^s is in kPa and T in K.

Table 9. Interaction Binary Parameters and Root-Mean-Square Deviations

model	parameters		rmsd ΔT^a/K	rmsd ΔP^a/kPa	rmsd $100\Delta x^a$	rmsd $100\Delta y^a$
Hexane (1) + 1,2-Dimethylbenzene (2)						
Wilson[b]	$M_{12} = 8.53$	$N_{12}(K) = -3264.65$	0.194	0.021	0.606	0.626
	$M_{21} = -7.58$	$N_{21}(K) = 2778.76$				
NRTL[c,d]	$A_{12} = 9.44$	$B_{12}(K) = -3511.54$	0.193	0.021	0.608	0.620
	$A_{21} = -11.08$	$B_{21}(K) = 4254.55$				
UNIQUAC[e]	$P_{12} = -3.68$	$Q_{12}(K) = 1439.18$	0.191	0.021	0.640	0.615
	$P_{21} = 4.86$	$Q_{21}(K) = -1907.02$				
Hexane (1) + 1,3-Dimethylbenzene (2)						
Wilson[b]	$M_{12} = 2.84$	$N_{12}(K) = -799.46$	0.040	0.004	0.298	0.634
	$M_{21} = -14.81$	$N_{21}(K) = 4691.03$				
NRTL[c,d]	$A_{12} = 18.10$	$B_{12}(K) = -5470.73$	0.044	0.004	0.208	0.278
	$A_{21} = -0.17$	$B_{21}(K) = -380.25$				
UNIQUAC[e]	$P_{12} = -10.69$	$Q_{12}(K) = 3249.18$	0.038	0.003	0.203	0.346
	$P_{21} = 1.89$	$Q_{21}(K) = -379.08$				
Octane (1) + 1,2-Dimethylbenzene (2)						
Wilson[b]	$M_{12} = 4.81$	$N_{12}(K) = -2073.23$	0.166	0.021	0.379	0.504
	$M_{21} = 0.17$	$N_{21}(K) = -44.45$				
NRTL[c,d]	$A_{12} = -1.46$	$B_{12}(K) = 411.72$	0.150	0.019	0.430	0.468
	$A_{21} = -5.52$	$B_{21}(K) = 2560.44$				
UNIQUAC[e]	$P_{12} = -1.92$	$Q_{12}(K) = 875.41$	0.132	0.017	0.460	0.447
	$P_{21} = 4.23$	$Q_{21}(K) = -1867.41$				
Octane (1) + 1,3-Dimethylbenzene (2)						
Wilson[b]	$M_{12} = 8.79$	$N_{12}(K) = -3761.66$	0.112	0.014	0.222	0.227
	$M_{21} = -0.98$	$N_{21}(K) = 506.30$				
NRTL[c,d]	$A_{12} = 2.78$	$B_{12}(K) = -1313.65$	0.107	0.013	0.227	0.226
	$A_{21} = -11.47$	$B_{21}(K) = 4938.34$				
UNIQUAC[e]	$P_{12} = -0.57$	$Q_{12}(K) = 317.79$	0.112	0.014	0.232	0.229
	$P_{21} = 2.39$	$Q_{21}(K) = -1073.17$				

[a] rmsd $\Delta M = (1/n_p \sum_{k=1}^{n_p} (M_k^{calc} - M_k^{expt})^2)^{0.5}$, where n_p is the number of data points and M represents T, P, x_1, or y_1. [b] Wilson model: $\ln A_{ij} = [M_{ij} + N_{ij}/T]$. [c] NRTL model: $\tau_{ij} = [A_{ij} + B_{ij}/T]$. [d] The value of α was fixed at 0.3 for each binary system. [e] UNIQUAC model: $\tau_{ij} = [\exp(P_{ij} + Q_{ij}/T)]$.

were assigned as zero for all components. The input parameters, including the critical properties (T_C and P_C), dipole moment (μ), and the radius of gyration (R_d), are given in Table 7. The calculated values of virial coefficients for each system investigated are listed in Tables 2 to 5. The tabulated activity coefficients (γ_i) in Tables 2 to 5 were calculated from eq 3 with the experimental values of x_i, y_i, T, and P, and the vapor pressure (P_i^s) of component i was calculated from the extended Antoine equation:

$$\ln(P_i^S) = A_1 + \frac{B_2}{T + C_3} + D_4T + E_5 \ln T + F_6T^{G_7} \quad (4)$$

The values of the coefficients A_1 to G_7 for each component i were taken from the Aspen property databank and are listed in

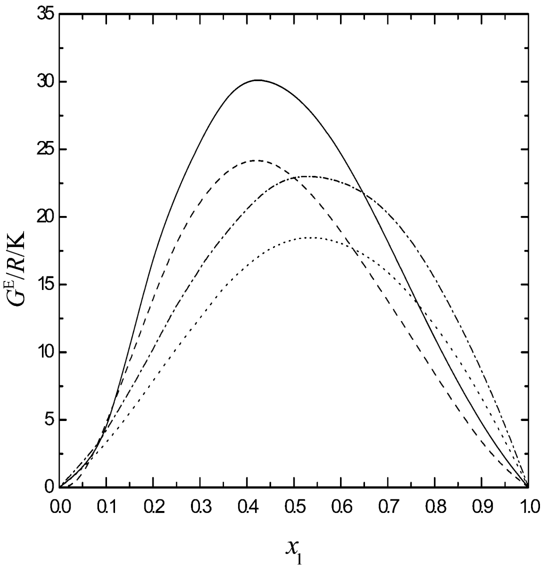

Figure 5. Plot of estimated values of excess Gibbs free energy at 101.3 kPa from the NRTL model against mole fraction; —, hexane (1) + 1,2-dimethylbenzene (2); ----, hexane (1) + 1,3-dimethylbenzene (2); -·-, octane (1) + 1,2-dimethylbenzene (2); ···, octane (1) + 1,3-dimethylbenzene (2).

Table 8. The liquid molar volume V_i^L of pure component i was estimated from the Rackett model[28] modified by Yamada and Gunn.[29] The critical properties (T_C, P_C, V_C, Z_C), acentric factor (ω), dipole moment (μ), the radius of gyration (R_d), and the parameters of the UNIQUAC model (r and q) of each component, which are needed in the phase equilibrium calculation, were also taken from Aspen property databank and are listed in Table 7.

Correlation and Prediction. The Wilson,[19] NRTL,[20] and UNIQUAC[21] combined with the HOC models were used to correlate the experimental VLE data for each binary system. The value of α_{ij} in the NRTL model was fixed at 0.3. The data correlation was performed by using Aspen plus V7.1. In the data reduction process, the Britt and Luecke[30] algorithm based on the maximum likelihood principle was adopted to minimization of the following objective function:

$$F = \sum_{k=1}^{n_p} \left\{ \left[\frac{(P_k^{\text{calc}} - P_k^{\text{expt}})}{\sigma_P} \right]^2 + \left[\frac{(T_k^{\text{calc}} - T_k^{\text{expt}})}{\sigma_T} \right]^2 + \left[\frac{(x_{1,k}^{\text{calc}} - x_{1,k}^{\text{expt}})}{\sigma_{x_1}} \right]^2 + \left[\frac{(y_{1,k}^{\text{calc}} - y_{1,k}^{\text{expt}})}{\sigma_{y_1}} \right]^2 \right\} \quad (5)$$

where n_p is the number of data points. The superscripts of calc and expt represent the calculated and the experimental values, respectively. The standard deviations (σ) of temperature and pressure are 0.1 K and 0.2 kPa, respectively, and those of liquid and vapor compositions are 0.005. The results of data correlation are given in Table 9, and graphical representation can be seen in Figures 1 to 4.

Figures 1 to 4 reveal that the calculated results from these three models almost overlap with the experimental points. Table 9 also shows that the deviations between the experimental and the calculated values are very small. All of these three models represent satisfactorily the VLE behavior for the binary systems of hexane or octane with 1,2-dimethylbenzene or 1,3-dimethylbenzene at 101.3 kPa. In general, the NRTL model yields slightly better results. According to the thermodynamic consistency test method of van Ness[16] modified by Fredunsland et al.,[17] the experimental VLE data are consistently provided, and the mean absolute deviation between calculated and measured vapor composition, Δy, is less than 0.01. As can be seen from Table 9, all of the binary systems satisfied this criterion.

In this study we also attempt to test the predictive capability of a group contribution model, the UNIFAC,[17] and a quantum approach based method, the COSMO-RS,[22] for the systems investigated. The comparison between experimental and predicted values can be seen in Figures 1 to 4. Both the UNIFAC and the COSMO-RS models fail to quantitatively predict the VLE properties of the octane-containing systems (as shown in Figures 3 and 4), while good agreement between the predicted and the experimental values was found from the hexane-containing systems (as shown in Figures 1 and 2).

To understand the nonideality of these binary systems investigated, the excess Gibbs free energies G^E were calculated by using the following equation:

$$G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad (6)$$

where the activity coefficients, γ_i, were estimated from the NRTL model using the binary parameters as given in Table 9. Figure 5 shows the variation of excess Gibbs free energy with composition for these four systems. Each system investigated exhibits positive values of G^E over the entire composition range. The values of G^E for these systems follow the order of hexane (1) + 1,2-xylene (2) > hexane (1) + 1,3-xylene (2) > octane (1) + 1,2-dimethylbenzene (2) > octane (1) + 1,3-dimethylbenzene (2).

■ CONCLUSION

Isobaric VLE data have been determined experimentally for the binary systems of hexane + 1,2-dimethylbenzene, hexane + 1,3-dimethylbenzene, octane + 1,2-dimethylbenzene, and octane + 1,3-dimethylbenzene at 101.3 kPa over the entire composition range. No azeotrope formation was observed these four binary systems. In general, the nonideality of these four systems follows the order of hexane (1) + 1,2-xylene (2) > hexane (1) + 1,3-xylene (2) > octane (1) + 1,2-dimethylbenzene (2) > octane (1) + 1,3-dimethylbenzene (2). The Herington area test and the point-to-point test of the van Ness as modified by Fredunsland et al. were used to check the reliability of experimental results, and all four binary systems passed both thermodynamic consistency test criteria. The Wilson-HOC, the NRTL-HOC, and the UNIQUAC-HOC models were used, respectively, to correlate the experimental isobaric VLE data for each binary system. Good correlations were found from all three models, with the NRTL model yielding slightly better results. These new VLE data were also used to examine the predictive capability of two solution models, UNIFAC and COSMO-RS. It was found that both models failed to quantitatively predict the VLE properties for octane-containing systems.

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