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Vapor−Liquid Equilibrium Data for *N*-Methylacetamide and *N*,*N*-Dimethylacetamide with Cumene at 97.3 kPa

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Isobaric vapor−liquid equilibrium (VLE) measurements are reported for binary mixtures of *N*-methylacetamide and *N*,*N*-dimethylacetamide with cumene at 97.3 kPa. The data were obtained using a vapor recirculating type (modified Othmer's) equilibrium still. Both mixtures show positive deviation from ideality. Both the systems form azeotropes. 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 NRTL equation.

Introduction

All compounds studied have a wide range of application and are of considerable industrial importance. *N*,*N*-Dimethylacetamide is a very effective solvent used in separation technology. Furthermore, it is a very good polymer solvent, dissolving polyacrylates and polyesters. Cumene (isopropyl benzene) is used to manufacture 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.

Experimental determinations of vapor−liquid equilibrium (VLE) are indispensable for the design of distillation columns and the selection of solvents. For the design of distillation columns, the knowledge of azeotropic points is most important. A data bank with azeotropic data is useful for supplementing the already available software tools for the synthesis of rectification processes because with simple search algorithms, suitable solvents for azeotropic distillation can be selected. In combination with the data bank for activity coefficients at infinite dilution, simple programs also allow the choice of selective solvents for extractive distillation. Furthermore, from the pressure (temperature) dependence of the azeotropic composition, it can be determined if pressure swing distillation can be applied or if the separation problem (azeotropic point) disappears at lower or higher pressures.

However, group contribution predictive methods such as UNIFAC[1] need a lot of experimental information to determine the interaction parameters of the functional groups. When this work began, the interaction parameters between the functional groups ACH and CONH + CON were not available. We therefore decided to study the VLE of *N*-methylacetamide and *N*,*N*-dimethylacetamide with cumene experimentally to contribute to the generation of the database for the UNIFAC group contribution method. In the present work, experimental VLE data for binary mixtures of *N*-methylacetamide and *N*,*N*-dimethylacetamide 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 previously described.[2,3]

Table 1. Refractive Index, n_D, at 298.15 K for *N*,*N*-Dimethylacetamide and Cumene and at 301.15 K for *N*-Methylacetamide and Boiling Point, T_b, at 101.3 kPa

	n_D		T_b/K	
compound	exptl	lit.	exptl	lit.
N-methylacetamide	1.428542	1.4286[4]	479.15	479.15[15]
N,*N*-dimethylacetamide	1.435070	1.4356[4]	438.77	439.25[15]
cumene	1.488292	1.4889[13]	425.44	425.60[14]

Table 2. Physical Constants of the Pure Compounds

constant	cumene	*N*-methyl-acetamide	*N*,*N*-dimethyl-acetamide
molecular wt	120.20[15]	73.09[15]	87.12[15]
boiling point/K (at 101.3 kPa)	425.60[14]	479.15[15]	439.25[15]
T_c/K	631.13[14]	690.0[14]	637.0[14]
P_c/kPa	3208.17[14]	4978.79[18]	3920.31[14]
$V_c \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	428.00[14]	267.00[18]	321.00[18]
accentric factor, ω	0.325[15]	0.435[18]	0.3635[18]
dipole moment, μ/D	0.39[13]	4.27[4]	3.71[4]
constants of eqs 4 and 5			
A	6.05545[16]	−5.45449[17]	6.88718[17]
B	1457.318[16]	−8672.558[17]	1889.100[17]
C	207.370[16]	56.319[17]	221.000[17]
D		$1.84 \cdot 10^{-7}$ [17]	

Experimental Section

Chemicals. *N*-Methylacetamide and cumene were obtained from Merck-Schuchardt, Germany. *N*,*N*-Dimethylacetamide was obtained from C.D.H (P) Ltd., India. All chemicals were AR grade materials and had purities (by chromatographic analysis) of 99.0 %, 99.0 %, and 98.0 %, respectively. The chemicals were purified using standard procedures[4] and stored over molecular sieves. We checked the purity of the chemicals by measuring the normal boiling points and refractive indices for the pure compounds and comparing them with those reported in the literature. The results are listed in Table 1.

Apparatus and Procedure. We obtained the VLE data by using a modified version of an 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.[5] All of 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.

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Table 3. Vapor−Liquid Equilibrium Data of the Cumene (1) + *N*-Methylacetamide (2) System at 97.3 kPa

T/K	x_1	y_1	γ_1	γ_2
423.62	0.9820	0.9708	0.9979	8.5677
423.15	0.9500	0.9289	0.9986	7.6370
422.48	0.8965	0.8906	1.0320	5.8008
421.50	0.8190	0.8719	1.1336	4.0173
424.15	0.7670	0.8539	1.1094	3.2440
425.15	0.7110	0.8391	1.1473	2.7824
425.53	0.6220	0.8457	1.3094	2.0131
427.09	0.5500	0.8360	1.4089	1.7042
427.83	0.4890	0.8310	1.5470	1.5083
428.27	0.4510	0.8293	1.6562	1.3970
429.04	0.3700	0.8151	1.9476	1.2845
429.22	0.3198	0.8110	2.2325	1.2085
432.15	0.2740	0.7858	2.3540	1.1637
434.44	0.1911	0.7598	3.0932	1.0858
444.15	0.1036	0.6614	3.9837	1.0136
453.15	0.0480	0.5061	5.4292	1.0598
465.00	0.0207	0.2894	5.6672	1.0568
473.36	0.0067	0.1156	5.9936	1.0349

Table 4. Vapor−Liquid Equilibrium Data of Cumene (1) + *N*,*N*-Dimethylacetamide (2) System at 97.3 kPa

T/K	x_1	y_1	γ_1	γ_2
423.46	0.9964	0.9764	0.9931	10.0052
422.62	0.9880	0.9426	0.9874	7.4372
421.45	0.9730	0.8982	0.9839	6.0751
420.02	0.9380	0.8157	0.9612	5.0038
419.35	0.8800	0.7728	0.9875	3.2537
418.33	0.8287	0.7644	1.0647	2.4395
418.25	0.7221	0.7243	1.1602	1.7644
418.43	0.6420	0.7034	1.2612	1.4654
418.76	0.5520	0.6762	1.3984	1.2653
419.10	0.5060	0.6502	1.4541	1.2263
419.27	0.4000	0.5789	1.6308	1.2090
419.85	0.3240	0.5313	1.8203	1.1733
420.94	0.2340	0.4562	2.1052	1.1616
422.28	0.1800	0.4118	2.3881	1.1266
424.71	0.1130	0.3349	2.9113	1.0942
427.55	0.0740	0.2732	3.3824	1.0524
430.55	0.0349	0.1850	4.5208	1.0370
434.42	0.0122	0.0977	6.2445	1.0036

The estimated uncertainties in the measurements of mole fraction were ± 0.0002, in refractive index were ± 0.000002, 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[6] 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 cumene and *N*,*N*-dimethylacetamide were calculated according to the Antoine equation

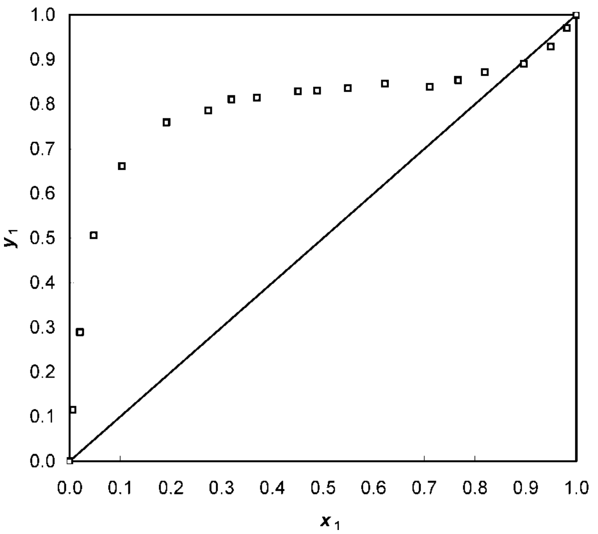

Figure 1. Plot of vapor−liquid equilibrium data for the system cumene (1) + *N*-methylacetamide (2) at 97.3 kPa.

$$\log(P^0/\text{kPa}) = A - [B/(C - 273.15) + (T/\text{K})] \quad (4)$$

and pure component vapor pressures (P^0) for *N*-methylacetamide were calculated according to the equation

$$\ln(P^0/\text{kPa}) = A\ln T + B/T + C + DT^2 \quad (\text{Here } T \text{ is in K}) \quad (5)$$

The Antoine's constants A, B, and C and constants A, B, C, and D for eq 5 are reported along with physical constants of pure components in Table 2. The experimental VLE data (T, x_1, and y_1) at 97.3 kPa along with the calculated activity coefficients are presented in Tables 3 and 4.

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 x_1, y_1 plot for the *N*-methylacetamide + cumene system at 97.3 kPa is given in Figure 1. The experimental activity coefficient data of this system and the curves obtained from the NRTL equation are represented in Figure 2. Figure 3 gives the excess Gibbs free energy calculated from experimental data for the *N*-methylacetamide + cumene system. The x_1, y_1 plot for the *N*,*N*-dimethylacetamide and cumene system at 97.3 kPa is given in Figure 4. Figure 5 represents the experimental activity coefficient data and the curves obtained from the NRTL equation for this system. Figure 6 gives the excess Gibbs free energy calculated from experimental data for the *N*,*N*-dimethylacetamide and cumene system.

According to the data reported in Tables 3 and 4, *N*-methylacetamide + cumene as well as the *N*,*N*-dimethylacetamide and cumene system show positive deviations from ideal behavior. The calculated excess Gibbs free energy, G^E, over the whole composition range, as shown in Figures 3 and 6, also indicates positive deviations from ideal behavior. We assessed the data for the systems for thermodynamic consistency by applying the Herington area test[9] and Black test.[10] According to the method suggested by Herington, from $\ln(\gamma_1/\gamma_2)$, x_1 plots, the value of $(D-J)$ is < 10 %, numerically equal to −8.9 % for

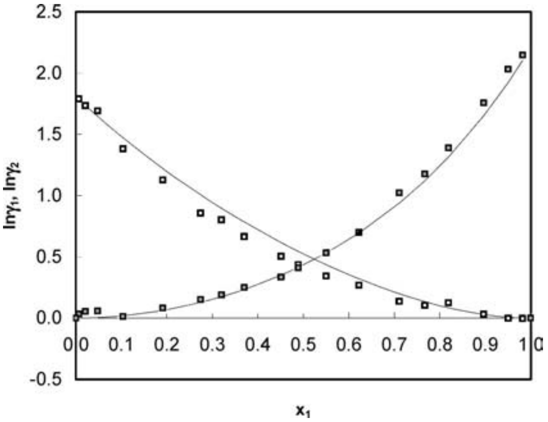

Figure 2. Plot of ln γ_1, ln γ_2 versus x_1 for the system cumene (1) + *N*-methylacetamide (2) at 97.3 kPa: □, experimental; —, NRTL.

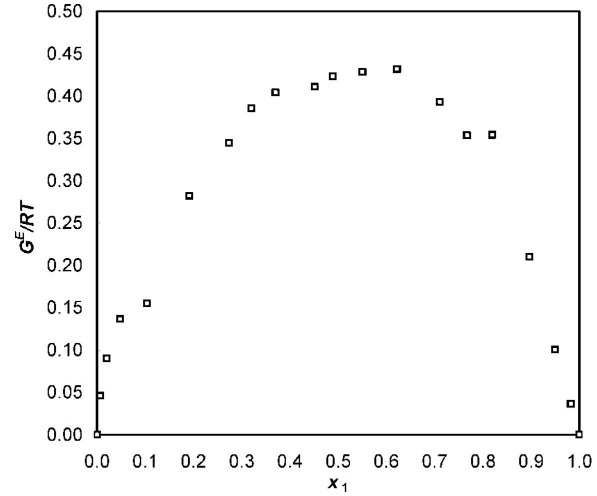

Figure 3. Plot of G^E/RT versus x_1 for the system cumene (1) + *N*-methylacetamide (2) at 97.3 kPa.

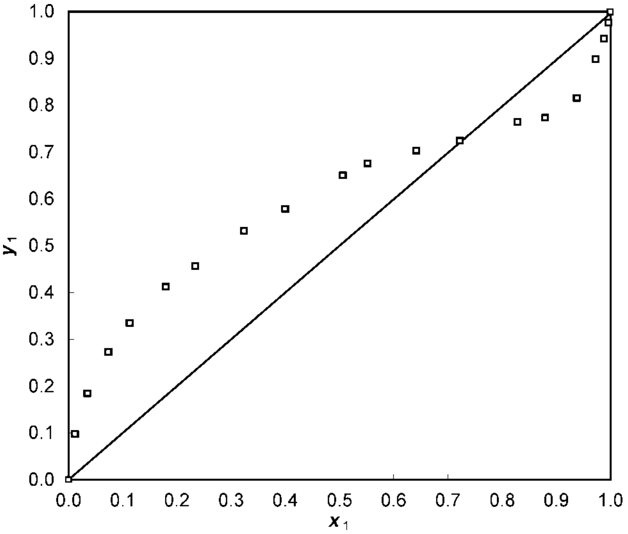

Figure 4. Plot of vapor−liquid equilibrium data for the system cumene (1) + *N*,*N*-dimethylacetamide (2) at 97.3 kPa.

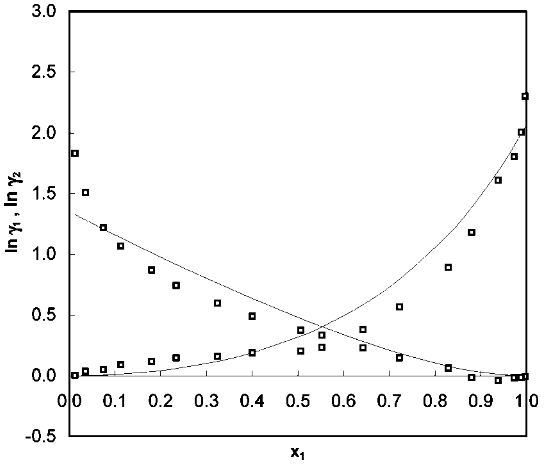

Figure 5. Plot of ln γ_1, ln γ_2 versus x_1 for the system cumene (1) + *N*,*N*-dimethylacetamide (2) at 97.3 kPa: □, experimental; —, NRTL.

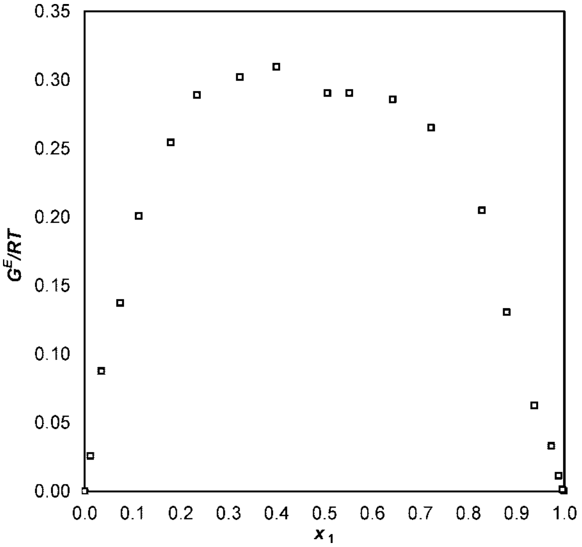

Figure 6. Plot of G^E/RT versus x_1 for the system cumene (1) + *N*,*N*-dimethylacetamide (2) at 97.3 kPa.

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

system	correlations	τ_{12}	τ_{21}	deviation (Δy)
cumene + *N*-methylacetamide	NRTL	1.55200	0.88042	0.071
cumene + *N*,*N*-dimethylacetamide	NRTL	1.72490	0.39120	0.048

the *N*-methylacetamide + cumene system and −3.4 % for the *N*,*N*-dimethylacetamide + cumene system. Therefore, the experimental data are thermodynamically consistent. The activity coefficients were correlated with the NRTL[11] equation. The nonrandomness parameter α_{12} for the NRTL correlation equation was set equal to 0.33 for the *N*-methylacetamide + cumene system and 0.34 for the *N*,*N*-dimethylacetamide + cumene system. 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.[12] The correlation parameters τ_{12}, τ_{21}, and deviation in vapor phase composition for both systems are listed in Table 5. For the *N*-methylacetamide + cumene system, the NRTL correlation gives a root-mean-square deviation in the vapor-phase composition of 0.071. For the *N*,*N*-dimethylacetamide + cumene system, the root-mean-square deviation in the vapor-phase composition as calculated by NRTL correlation is 0.048. The binary mixture of *N*-methylacetamide and cumene has a wide boiling range of 55.15 K, and it forms an azeotrope at $x_1 = 0.88$ and $T = 421.50$ K. The binary mixture of *N*,*N*-dimethylacetamide and cumene has a narrow boiling range of just 13.77 K, and it forms an azeotrope at $x_1 = 0.72$ and $T = 418.25$ K.

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