

Vapor-Liquid Equilibria for Benzene-Acetonitrile and Toluene-Acetonitrile Mixtures at 343.15 K

Jean-Pierre Monfort[†]

Instituto Mexicano del Petroleo, Eje Central L. Cardenas 152, Mexico 14, D.F.

Isothermal vapor-liquid equilibria (VLE) have been measured at 343.15 K for the binary systems toluene-acetonitrile and benzene-acetonitrile in a Stage-Muller ebullometer. Thermodynamic consistency of the data has been checked by using the collocation method of Christiansen and Fredenslund. The data have also been correlated with the Wilson, NRTL, and UNIQUAC equations and infinite-dilution activity coefficients have been calculated with the thermodynamic scheme of Eills and Jonah.

Introduction

The calculation of thermodynamic properties of polar or aqueous solutions corresponds to a stage of utmost importance in the design of separation equipment, for instance, in extractive distillation.

This makes it necessary for the chemical engineer to rely upon the most reliable experimental information and, of course, to have it accessible in a quick and relatively economical way. Measurement of P - T - x data of vapor-liquid equilibria (VLE) by ebulliometry has been extensively used as an alternative route for this purpose. In the present study, isothermal VLE have been determined at 343.15 K for the binary systems of benzene-acetonitrile and toluene-acetonitrile. We present data reductions with simple molecular equations and infinite-dilution activity coefficients which have been calculated.

The system toluene-acetonitrile has been reported at 343.15 K by Muthu et al. (1) and at 760 torr by Krishna et al. (2) while the benzene-acetonitrile system has been reported at 760 torr by Raghunath et al. (3) and Krishna et al. and at 348.15 K by Palmer and Smith (4).

Experimental Section

Materials. Table I lists the chemicals used, the physical properties, and our data compared with values from the literature. All products were dried over 4-Å molecular sieves and were used without further purification.

Apparatus. The VLE data for these systems were obtained with a commercial version of the improved Stage-Muller ebullometer (5). A schematic diagram of it appears in Figure 1. The ebullometer was connected through a dry-ice trap to the regulating and measurement pressure devices which included (i) a 260-L vessel which gives a good stability of the mercury column in the mercury manometer, (ii) an aneroid manostat which maintained the pressure inside the ebullometer at any required level, and (iii) a mercury manometer. The mercury heights were determined with a cathetometer whose accuracy is ± 0.01 mmHg.

All observed pressures were corrected to give the equivalent height of a mercury column at 273.15 K and standard gravity. Pressures were measured with an accuracy of ± 0.2 torr.

Temperatures were measured with a platinum thermometer (manufacturer: SYSTEMTEKNIK A. P., Model 51220) with a stated accuracy of 0.01 K.

Compositions of the equilibrium liquid and condensed vapor were obtained from measurement of their refractive indexes at 298.15 K, with an Abbe-type refractometer with an accuracy of ± 0.0002 . Refractive indexes of calibration mixtures were expressed by the equation

$$f(n_D, x) = \frac{n_D^2 - 1}{n_D - 2} \left[\frac{1 - x_1}{\rho_2} + \frac{x_1}{\rho_1} \right] \quad (1)$$

where x_1 is the molar fraction of either toluene or benzene, ρ_2 and ρ_1 being the densities of acetonitrile and of the hydrocarbons, respectively.

Next, the coefficients of the power series in x_1 were determined by using the least-squares technique to fit the $f(n_D, x_1)$ function with orthogonal polynomials as

$$\rho(n_D, x_1) = \sum_{i=0}^4 A_i x_1^i \quad (2)$$

The results of the fitting are the following: for the mixture toluene (1)-acetonitrile (2), $A_0 = 0.270140$, $A_1 = 0.182074$, $A_2 = -0.19374$, $A_3 = 0.110298$, $A_4 = -0.03213$, the relative sum of squares (RSS) of the fitting is 0.3310^{-6} , and the maximum deviation (MD) $n_D^{\text{expt}} - n_D^{\text{calcd}}$ is 0.00036; for the mixture benzene (1)-acetonitrile (2), $A_0 = 0.270025$, $A_1 = 0.135707$, $A_2 = -0.081026$, $A_3 = 0.0077236$, $A_4 = 0.00309267$, with a RSS of the fitting of 0.4810^{-6} , and the MD $n_D^{\text{expt}} - n_D^{\text{calcd}}$ is 0.00030. The true equilibrium molar fractions are then obtained by solving iteratively eq 2 by using the Newton-Raphson method and stopping the iterative procedure when $|x_i - x_{i+1}| < 10^{-6}$. This procedure gives a stated resolution of 0.003 for the measured molar fraction.

Results and Discussion

Results and Consistency Criteria. The raw P - x - y data measured for the two systems along with γ_1 and γ_2 values are reported in Tables II and III. To check for the thermodynamic consistency, we used the calculated vapor composition obtained from the collocation method developed by Christiansen and Fredenslund (6). A detailed description of the computational procedure appears also in the work of Grausø (7). As the vapor-liquid composition y_1 has been measured, it is possible to compare the experimentally obtained values of y_1 with calculated values; these results appear in Table IV. The consistency test evaluated in terms of the quantities Δy and ΔP did not show any systematic trend relative to the dispersion of Δy or ΔP vs. the liquid composition. We used for this punctual test vapor pressures of the pure components obtained by an extrapolation of the smooth P - x values obtained from a least-squares cubic spline fit of the experimental data.

The VLE data are presented in Figures 2 and 3 for the benzene (1)-acetonitrile (2) mixture and in Figures 4 and 5 for the toluene (1)-acetonitrile (2) mixture. The benzene (1)-acetonitrile system forms an azeotrope with 52.0 mol % benzene whereas the toluene (1)-acetonitrile system forms an azeotrope with 10.5 mol % toluene.

Data Reduction with Molecular Solution Models. The Wilson molecular, NRTL, and UNIQUAC equations were also used to calculate the γ_i .

[†] Present address: Ecole Nationale d'Ingénieurs, Gabes 8018, Tunisia.

Table I. Chemicals Used and Physical Properties of Pure Components

| component | vendor | stated purity, % | ρ , mol/cm ³ | | n_D | |
|--------------|-------------------------|------------------|------------------------------|-------------------|--------|-------------------|
| | | | exptl | lit. ^b | exptl | lit. ^a |
| acetonitrile | Baker, HPLC | 99.8 | 0.7805 | 0.780 15 | 1.3420 | 1.341 6 |
| benzene | Merck, UVASOL | 99.9 | 0.8731 | 0.873 70 | 1.4978 | 1.497 92 |
| toluene | Baker, analyzed reagent | 99.7 | 0.8650 | 0.862 31 | 1.4941 | 1.494 13 |

^a Experimental and literature values at 298.15 K. Reference: acetonitrile, Weast, R. C., Ed. "Handbook of Chemistry and Physics", 57th ed.; CRC Press: Boca Raton, FL, 1978-1979; benzene and toluene, Thermodynamic Research Center Hydrocarbon Project, Thermodynamic Research Center, Table 52, April 30, 1956. ^b Experimental and literature values at 293.15 K. Reference: API, Research Project 44.

Table II. Experimental P vs. $x_1, y_{1,\text{exptl}}$ Values and Calculated Isothermal Vapor-Liquid Equilibrium Results for the Toluene (1)-Acetonitrile (2) Mixture at 343.15 K

| x_1 | $y_{1,\text{exptl}}$ | P_{exptl} , torr | activity coeff | |
|--------|----------------------|---------------------------|----------------|------------|
| | | | γ_1 | γ_2 |
| 0.0023 | 0.0035 | 523.32 | 3.8404 | 1.000 |
| 0.0043 | 0.0060 | 523.81 | 3.8100 | 1.000 |
| 0.0072 | 0.0106 | 524.15 | 3.7660 | 1.0001 |
| 0.0155 | 0.0201 | 525.90 | 3.6402 | 1.0005 |
| 0.0282 | 0.0360 | 528.29 | 3.4521 | 1.0017 |
| 0.0503 | 0.0596 | 531.43 | 3.1486 | 1.0055 |
| 0.0840 | 0.0887 | 533.16 | 2.7623 | 1.0149 |
| 0.1347 | 0.1254 | 532.54 | 2.3481 | 1.0352 |
| 0.1872 | 0.1545 | 529.49 | 2.0697 | 1.0604 |
| 0.2576 | 0.1873 | 522.92 | 1.8213 | 1.0997 |
| 0.3353 | 0.2179 | 512.82 | 1.6139 | 1.1572 |
| 0.3641 | 0.2297 | 508.80 | 1.5461 | 1.1842 |
| 0.4778 | 0.2704 | 490.76 | 1.3218 | 1.3223 |
| 0.5849 | 0.3154 | 464.93 | 1.2026 | 1.4784 |
| 0.7488 | 0.4118 | 410.78 | 1.0727 | 1.8747 |
| 0.9314 | 0.6493 | 301.86 | 0.9838 | 2.7427 |
| 0.9851 | 0.9401 | 225.56 | 0.9986 | 1.7851 |
| 0.9919 | 0.9611 | 215.54 | 0.9994 | 1.6631 |
| 0.9966 | 0.9699 | 210.00 | 0.9995 | 1.6327 |

Table III. Experimental P vs. $x_1, y_{1,\text{exptl}}$ Values and Calculated Isothermal Vapor-Liquid Equilibrium Results for the Benzene (1)-Acetonitrile (2) Mixture at 343.15 K

| x_1 | $y_{1,\text{exptl}}$ | P_{exptl} , torr | activity coeff | |
|--------|----------------------|---------------------------|----------------|------------|
| | | | γ_1 | γ_2 |
| 0.0014 | 0.0049 | 526.60 | 2.728 | 1.0000 |
| 0.0027 | 0.0100 | 527.36 | 2.7193 | 1.0000 |
| 0.0088 | 0.0212 | 533.14 | 2.6775 | 1.0000 |
| 0.0356 | 0.0862 | 558.22 | 2.5073 | 1.0016 |
| 0.0589 | 0.1300 | 574.41 | 2.3868 | 1.0040 |
| 0.0963 | 0.1927 | 596.75 | 2.1919 | 1.0111 |
| 0.1688 | 0.2830 | 628.29 | 1.9099 | 1.0325 |
| 0.2918 | 0.3825 | 661.27 | 1.5825 | 1.0919 |
| 0.3685 | 0.4337 | 673.44 | 1.4404 | 1.1436 |
| 0.4143 | 0.4615 | 677.92 | 1.3709 | 1.1806 |
| 0.4213 | 0.4669 | 677.01 | 1.3610 | 1.1867 |
| 0.5040 | 0.5134 | 681.87 | 1.2598 | 1.2683 |
| 0.5391 | 0.5325 | 685.67 | 1.2236 | 1.3093 |
| 0.6088 | 0.5740 | 679.97 | 1.1615 | 1.4045 |
| 0.6524 | 0.6049 | 678.98 | 1.1284 | 1.4755 |
| 0.6825 | 0.6219 | 673.66 | 1.1079 | 1.5307 |
| 0.7794 | 0.6958 | 656.26 | 1.0540 | 1.7536 |
| 0.8672 | 0.7725 | 631.94 | 1.0206 | 2.0396 |
| 0.9338 | 0.8640 | 602.22 | 1.0053 | 2.3382 |
| 0.9630 | 0.9168 | 582.01 | 1.0017 | 2.4995 |
| 0.9955 | 0.9824 | 556.24 | 1.0000 | 2.7079 |

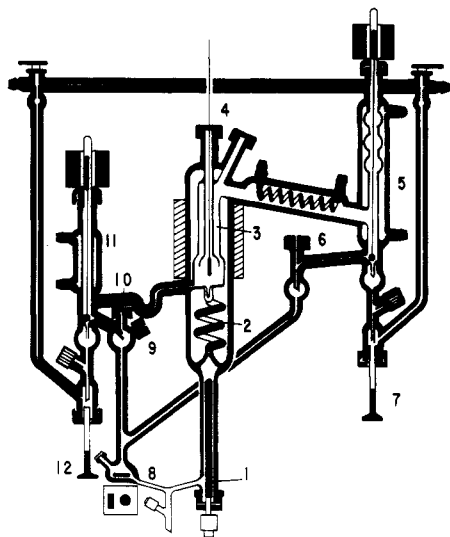


Figure 1. Schematic diagram of the ebulliometer: (1) quartz heating, (2) cottrell pump, (3) equilibrium chamber, (4) platinum sensor, (5) vapor-phase condenser, (6) vapor sampling, (7) sampling vial for condensed vapor phase, (8) mixing chamber, (9) liquid sampling, (10) liquid introduction to the ebulliometer, (11) liquid-phase condenser, (12) sampling vial for liquid phase.

The liquid-phase activity coefficients were obtained from the following equation which takes into account the vapor-phase imperfections:

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^s} + \frac{(B_{ii} - V_i^L)(P - P_i^s)}{RT} + \frac{P \delta_{ij}}{RT} (1 - y_i)^2 \quad (3a)$$

where

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (3b)$$

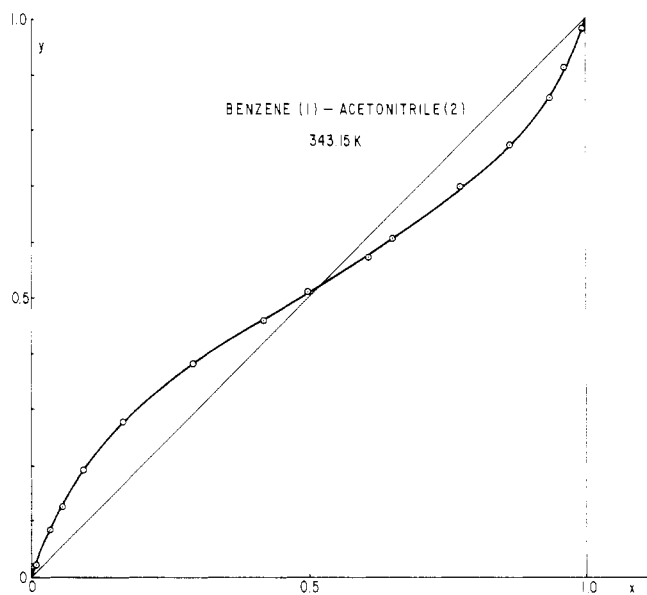


Figure 2. Plot of vapor composition y vs. liquid composition x_1 for the benzene (1)-acetonitrile (2) system at 343.15 K: (O) experimental data, (—) fitted curve.

The second virial coefficients of the compounds were calculated with the O'Connell and Prausnitz correlation (δ). The energy parameters obtained by correlating the VLE data using the previously mentioned equations appear in Table IV along with the results of the optimizing procedure. These equations, derived from the molecular solution models, are well-known and

Table IV. Solution Model Parameters for Binary Mixtures from Wilson's Equation and NRTL and UNIQUAC Equations, and Results of Thermodynamic Consistency

| mixture | T, K | G_{12}^a , cal/mol | G_{21} , cal/mol | MRD ^b | Δy^c | ΔP^c , atm |
|------------------------------|----------|----------------------|---|------------------|--------------|--------------------|
| toluene (1)-acetonitrile (2) | 343.15 K | -84.30 | -943.68 | 0.52 | 0.004 | 0.0004 |
| | | 370.85 | 661.44 ($\alpha_{\text{NRTL}} = 0.5$) | 0.53 | | |
| | | -441.27 | -7.82 | 0.54 | | |
| benzene (1)-acetonitrile (2) | 343.15 K | 138.55 | -847.99 | 0.10 | 0.002 | 0.001 |
| | | 577.87 | 58.03 ($\alpha_{\text{NRTL}} = 0.2$) | 0.09 | | |
| | | -544.48 | 168.89 | 0.10 | | |
| | | | | | | |

^a In the following order: Wilson molecular $G_{12} = -(g_{12} - g_{11})$, $G_{21} = -(g_{12} - g_{22})$; NRTL $G_{12} = g_{12} - g_{22}$, $G_{21} = g_{21} - g_{11}$; UNIQUAC $G_{12} = -(g_{12} - g_{22})$, $G_{21} = -(g_{12} - g_{21})$. ^b Where $\text{MRD} = (1/n) \sum_i 100 F_i$ and $F_i = (1/n) \sum_j \{ (P_{i,\text{calcd}} - P_{i,\text{exptl}}) / P_{i,\text{exptl}} \}^2 + \{ (y_{i,\text{calcd}} - y_{i,\text{exptl}}) / y_{i,\text{exptl}} \}^2$; see ref 8 for the optimization procedure. ^c $\Delta y = (1/\text{ND}) \sum_i |y_{i,\text{calcd}} - y_{i,\text{exptl}}|$; $\Delta P = (1/\text{ND}) \sum_i |P_{i,\text{calcd}} - P_{i,\text{exptl}}|$ where ND is the number of data points.

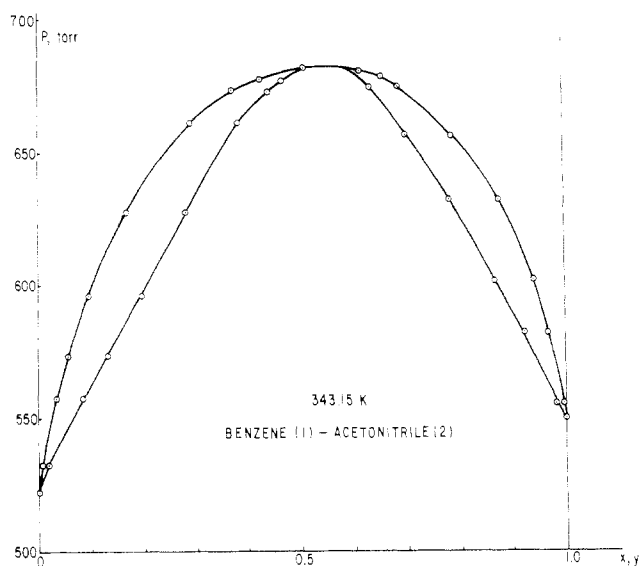


Figure 3. Plot of P vs. liquid and vapor compositions for the benzene (1)-acetonitrile (2) system at 343.15 K: (O) experimental data, (—) fitted curve.

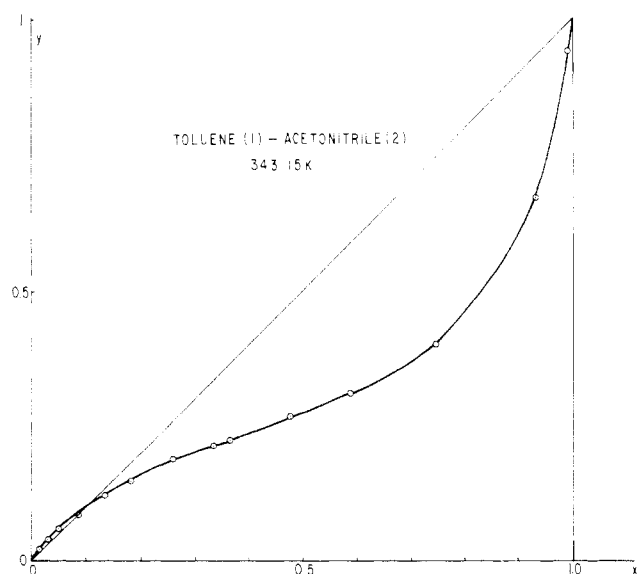


Figure 4. Plot of vapor composition y vs. liquid composition x_1 for the toluene (1)-acetonitrile (2) system at 343.15 K: (O) experimental curve, (—) fitted curve.

can be found in the literature (9).

Calculation of Infinite-Dilution Activity Coefficients. The γ_i^∞ have been calculated by using the thermodynamic scheme proposed by Ellis and Jonah (10) which has also been discussed

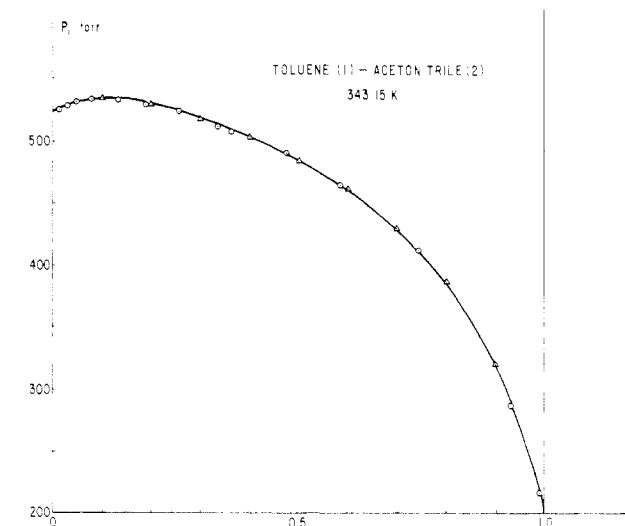


Figure 5. Plot of P vs. liquid composition for the toluene (1)-acetonitrile (2) system at 343.15 K: (O) this work, (Δ) data of Muthu et al. (1), (—) fitted curve.

in recently published works (11, 12). The equation for isothermal VLE data is

$$\gamma_1^\infty = \frac{1}{P_1^S \nu_1^0} \left(\frac{\partial P}{\partial x_1} \right)_{x_1=0} (1 - P_2^S \epsilon_2) + P_2^S \quad (4a)$$

with

$$\nu_1^0 = [(P_2^S - P_1^S)(V_1^L - B_{11})/RT] \exp(-\delta_{12} P_2^S/RT) \quad (4b)$$

$$\epsilon_2 = (V_2^L - B_{22})/RT \quad (4c)$$

From symmetrical consideration γ_2^∞ is obtained by rotating the subscripts 1 and 2.

The limiting quantity $(\partial P / \partial x_1)_{x_1=0}$ has been calculated by using a simple algebraic expression to fit the experimental quantity $P - (P_1^S x_1 + P_2^S x_2) / (x_1 x_2)$ and extrapolating at $x_1 = 0$. The results obtained were as follows: benzene (1)-acetonitrile (2) mixture, $\gamma_1^\infty = 3.09$ and $\gamma_2^\infty = 3.56$; toluene (1)-acetonitrile (2) mixture, $\gamma_1^\infty = 3.36$ and $\gamma_2^\infty = 3.49$.

Acknowledgment

We thank A. Soria, who performed the experimental measurements, and Professor A. Fredenslund, who kindly provided the computer programs for the thermodynamic consistency test.

Glossary

| | |
|-----|---|
| A | coefficients of the orthogonal polynomial, see eq 2 |
| B | second virial coefficient, cm^3/mol |
| n | refractive index |
| P | total pressure or saturated vapor pressure of pure components, torr |

R gas constant, $\text{cm}^3 \text{ torr}/(\text{mol K})$
 T temperature, K
 V liquid molar volume, cm^3/mol
 x, y liquid and vapor molar fractions, respectively

Greek Letters

γ activity coefficients
 ρ density $1/V$, mol/cm^3

Subscripts

1, 2 components 1 and 2, respectively
 i, j components i and j , respectively
 exptl, experimental or calculated quantity, respectively
 calcd

Superscripts

L liquid-phase property
 V vapor-phase property
 ∞ at infinite diluted conditions

Literature Cited

- (1) Muthu, O.; Maher, P. J.; Smith, B. D. *J. Chem. Eng. Data* **1980**, *25*, 163.
- (2) Krishna, C.; Tripathi, R. P.; Rawat, B. S. *J. Chem. Eng. Data* **1980**, *25*, 11.
- (3) Raghunath, P.; Tripathi, R. P.; Asselineau, L. *J. Chem. Eng. Data* **1975**, *20*, 33.
- (4) Palmer, D. A.; Smith, B. D. *J. Chem. Eng. Data* **1972**, *17*, 71.
- (5) Stage, H.; Fisher, W. G. *GIT Fachz. Lab.* **1968**, *12*, 1167.
- (6) Christiansen, L. J.; Fredenslund, Aa. *AIChE J.* **1975**, *21*, 49.
- (7) Grausø, L. Ph.D. Dissertation, Institutet for Kemiteknik Danmarks Tekniske Højskole, Lyngby, Denmark, 1977.
- (8) O'Connell, J. P.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1967**, *6*, 246.
- (9) Monfort, J. P.; Rojas, L. *Fluid Phase Equilib.* **1976**, *2*, 181.
- (10) Ellis, S. R. M.; Jonah, D. A. *Chem. Eng. Sic.* **1962**, *17*, 971.
- (11) Eckert, C. A.; Newman, B. A.; Nicolaidis, G. L.; Long, T. C. *AIChE J.* **1981**, *27*, 33.
- (12) Maher, P. J.; Smith, B. D. *Ind. Eng. Chem. Fundam.* **1979**, *18*, 354.

Received for review July 23, 1981. Accepted June 14, 1982. I appreciate the partial financial support provided for this work by CONACYT under project 1333.

Isothermal Vapor-Liquid Equilibria in Binary Systems Formed by Esters with Alkenes

Jürgen Gmehling

Lehrstuhl für Technische Chemie B, Universität Dortmund, D 4600 Dortmund, Federal Republic of Germany

Since no vapor-liquid equilibrium (VLE) data are available for ester-alkene systems, isothermal vapor-liquid equilibrium data have been measured for the binary systems methyl acetate-1-hexene (50 °C), 1-hexene-ethyl acetate (60 °C), ethyl acetate-1-octene (75 °C), and butyl acetate-1-decene (90 °C). Thermodynamic consistency was checked by two methods and the data were correlated by using different expressions for the excess Gibbs energy. The data were used for the determination of the C=C-CCOO interaction parameters of the UNIFAC method, which are important, e.g., for the prediction of the VLE behavior of vinyl acetate systems.

Introduction

Design of distillation columns requires the knowledge of vapor-liquid equilibria. With the recent expressions for the excess Gibbs energy (e.g., Wilson (18), NRTL (19), UNIQUAC (20)) multicomponent systems can be described by using binary data alone. Although a lot of binary data have been published (1-3), there is often a lack of data. In these cases the real behavior of the missing binary data must be estimated by using prediction methods, such as the group contribution methods ASOG (4, 5) or UNIFAC (6-9). In these methods, the mixture is assumed to consist not of molecules but of the functional groups which, when added, form the parent molecules. This has the advantage that a large number of mixtures of interest in chemical technology can be described in terms of relatively few parameters characterizing the interaction between the groups.

These parameters have to be determined from experimental information. In the case of the UNIFAC method, the whole information of the Dortmund Data Bank (10, 11) has been used. In spite of the large data base there are a lot of gaps

Table I. Pure Components

| component | supplier | type of column | grade of purification, % |
|----------------|----------------|----------------|--------------------------|
| 1-hexene | EGA Chemie | a | >99.99 |
| 1-octene | Merck AG | a | >99.99 |
| 1-decene | Merck AG | a | >99.99 |
| methyl acetate | DEGUSSA | b | >99.99 |
| ethyl acetate | Merck AG | b | >99.99 |
| butyl acetate | Riedel de Haen | b | >99.99 |

^a Wire band column (length, 1000 mm; number of theoretical plates, approximately 55). ^b Packed column (diameter, 30 mm; length, 1000 mm; SS 316-helix packing).

in the parameter table for group combinations where no data (or no reliable data) are available in the literature.

The purpose of this investigation was to enable determination of the interaction parameters between the C=C and the CCOO group and thus fill one of the gaps in the UNIFAC parameter table. Therefore, the above-mentioned binary systems have been measured.

Experimental Section

Purification of the Components. All chemicals were obtained from commercial sources and were further purified by rectification in a packed or a wire band column, and the purity was tested by gas chromatography. Table I shows the supplier of the different chemicals and the grade of purification.

Analysis. Liquid and vapor compositions were determined with a digital densimeter (DMA02D by Heraeus/Paar). It was calibrated by using air and doubly distilled water. The density measurement was carried out at 20 ± 0.01 °C. The precision at this temperature was better than 10^{-4} g/cm³. The calibration curves were attained by measuring weighed samples of the