Vapor–Liquid Equilibria in the Systems Aniline–Pseudocumene, *o*-Toluidine–*n*-Decane, and *m*-Xylidine–*n*-Dodecane at Atmospheric Pressure

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Vapor–liquid equilibria were investigated at atmospheric pressure in the systems aniline–pseudocumene, *o*-toluidine–*n*-decane, and *m*-xylidine–*n*-dodecane. The equilibrium data were correlated by the Wilson equation.

In the literature there is little information available on vapor–liquid equilibria in systems formed by higher boiling constituents of coal tar including those of aniline and its derivatives with paraffin (*3*, *6*, *12*) and aromatic hydrocarbons (*4*, *7*, *13*, *15*). Only binary azeotropes of aniline with one-ring aromatics and *n*-paraffins (*8*, *9*, *14*) and those of *o*-toluidine and *m*-xylidine with *n*-paraffins (*9*) were examined systematically. In order to fill the gap in this field, it seemed useful to investigate vapor–liquid equilibria in some systems of this type. The systems in which vapor–liquid equilibria were examined were aniline–pseudocumene, *o*-toluidine–*n*-decane, and *m*-xylidine–*n*-dodecane. The investigation of vapor–liquid equilibria in these systems is of practical importance because aniline and its derivatives as well as aromatics and *n*-paraffins are found in some organic raw materials of the coal tar type, particularly in low-temperature coal tar. In addition, the binary vapor–liquid equilibrium data can also be used for predicting with Wilson's equations the vapor–liquid equilibria in some ternary and multicomponent systems.

Experimental Section

The aniline, *o*-toluidine, and *m*-xylidine (all research grade) were fractionated in the presence of zinc dust through a 40 theoretical plate laboratory fractionating column. *n*-Decane and *n*-dodecane (all research grade) from Phillips Petroleum Co. were subjected to fractional distillation, and narrow-boiling fractions containing pure hydrocarbons were collected. Pseudocumene was carefully fractionated using the above column.

A simple modified Swietoslawski's ebulliometer (*16*) was used for determination of the equilibrium parameters (composition of vapor and liquid and of temperature). To observe small changes in atmospheric pressure during measurements, Swietoslawski's simple ebulliometer filled with double-distilled water was used. The temperature was measured with the aid of calibrated mercury-in-glass thermometers (0.1° division). The contents of the respective components in the liquid and in the vapor condensate were taken from the standard refractive index–composition curves at 20 °C. In the case of the system aniline–pseudocumene, aniline was also determined volumetrically (*10*).

In Table I are given some physical properties of amines and hydrocarbons.

Table I. Physical Properties of Amines and Hydrocarbons

substance	bp, °C	$n^{20}{}_D$	ebulliometric degree of purity[a]
aniline	183.9	1.5862	IV
o-toluidine	200.2	1.5726	IV
m-xylidine	217.4	1.5602	III
pseudocumene	169.35	1.5048	IV
n-decane	174.6	1.4118	IV
n-dodecane	216.5	1.4206	IV

[a] A substance is characterized by IV ebulliometric degree of purity when the difference between the boiling and condensation temperatures is in the range of 0.02–0.005 °C. For III degree of purity that difference range is 0.05–0.02 °C (*17*).

Table II. Vapor–Liquid Equilibrium Data for the System Aniline–Pseudocumene at Atmospheric Pressure[a]

x_1	y_1	T, °C	$y_{1\,(\text{calcd})}$	Δy_1
0.0085	0.041	182.7	0.041	0.0
0.03	0.092	180.8	0.127	0.035
0.046	0.177	178.9	0.175	−0.002
0.077	0.282	176.8	0.25	−0.032
0.135	0.348	175.2	0.355	0.007
0.203	0.398	173.6	0.434	0.036
0.352	0.489	171.4	0.542	0.053
0.407	0.526	170.5	0.571	0.045
0.582	0.667	169.6	0.667	0.0
0.693	0.75	169.2	0.742	−0.008
0.769	0.80	168.8	0.79	−0.01
0.856	0.852	168.6	0.853	0.001
0.906	0.888	168.8	0.895	0.007
0.964	0.957	169.1	0.943	−0.014

[a] $\Delta y_1 = y_{1(\text{calcd})} - y_{1(\text{obsd})}$; $\Lambda_{12} = 0.8093$; $\Lambda_{21} = 0.3361$; $|\Delta y_1|_{\text{mean}} = 0.0178$; $|\Delta T|_{\text{mean}} = 1.14$ °C.

Results

The vapor–liquid equilibrium data in the systems aniline–pseudocumene, *o*-toluidine–*n*-decane, and *m*-xylidine–*n*-dodecane were used for computing the Wilson equation parameters Λ_{12} and Λ_{21}. The parameters were evaluated from the values of the activity coefficients of the respective components in the systems at infinite dilution using the Newton–Raphson method. At infinite dilution the activity coefficients $\gamma_1{}^0$ and $\gamma_2{}^0$ are related to the Wilson parameters by the expressions

$$\ln \gamma_1{}^0 = -\ln \Lambda_{12} + 1 - \Lambda_{21}$$

and

$$\ln \gamma_2{}^0 = -\ln \Lambda_{21} + 1 - \Lambda_{12}$$

The infinite-dilution activity coefficients were found for each system as a result of graphical extrapolation of the activity coefficient–composition curves to infinite dilution. (The nonlinear least-squares method gave similar values for the Wilson parameters.) The values of the Antoine equation constants were taken from the tables compiled by Hala et at. (*5*) and by Dreisbach (*2*).

The corrections for vapor-phase imperfections in these systems, computed by Pitzer's method (*11*), were found to be well within the errors of graphical extrapolation of the activity coefficients to infinite dilution. Therefore as such they were insignificant in calculations.

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Table III. Vapor-Liquid Equilibrium Data for the System *o*-Toluidine–*n*-Decane at Atmospheric Pressure[a]

x_1	y_1	T, °C	$y_{1(\text{calcd})}$	Δy_1
0.019	0.143	197.25	0.144	0.001
0.052	0.269	192.9	0.31	0.041
0.079	0.381	189.2	0.382	0.001
0.114	0.46	185.2	0.441	−0.019
0.192	0.57	180.6	0.514	−0.056
0.22	0.595	179.1	0.525	−0.07
0.532	0.655	176.0	0.692	0.037
0.671	0.727	174.6	0.742	0.015
0.844	0.835	173.8	0.843	0.008
0.909	0.894	174.0	0.895	0.001
0.958	0.942	174.2	0.947	0.005

[a] $\Lambda_{12} = 0.2781$; $\Lambda_{21} = 0.6705$; $|\Delta y_1|_{\text{mean}} = 0.023$; $|\Delta T|_{\text{mean}} = 2.14$ °C.

Table IV. Vapor-Liquid Equilibrium Data for the System *m*-Xylidine–*n*-Dodecane at Atmospheric Pressure[a]

x_1	y_1	T, °C	$y_{1(\text{calcd})}$	Δy_1
0.034	0.096	215.6	0.083	−0.013
0.064	0.16	214.1	0.143	−0.017
0.098	0.214	212.5	0.188	−0.026
0.124	0.241	211.8	0.219	−0.022
0.145	0.272	211.0	0.236	−0.036
0.338	0.435	210.1	0.387	−0.048
0.542	0.538	209.9	0.512	−0.026
0.673	0.62	211.1	0.621	0.001
0.818	0.762	213.1	0.764	0.002
0.883	0.82	214.0	0.832	0.012
0.95	0.918	215.5	0.929	0.011

[a] $\Lambda_{12} = 0.2961$; $\Lambda_{21} = 1.0987$; $|\Delta y_1|_{\text{mean}} = 0.0195$; $|\Delta T|_{\text{mean}} = 2.86$ °C.

In Tables II, III, and IV are listed the results of vapor-liquid equilibrium measurements in the systems aniline–pseudocumene, *o*-toluidine–*n*-decane, and *m*-xylidine–*n*-dodecane, along with the deviations in the vapor phase between the calculated and experimental (observed) compositions, Δy_1. The compositions x_1 and y_1 are expressed in mole fractions of the more volatile components, viz., hydrocarbons.

The quantities $|\Delta y_1|_{\text{mean}}$ and $|\Delta T|_{\text{mean}}$ (see Tables II–IV) are defined as

$$|\Delta y_1|_{\text{mean}} = \frac{\sum |y_{1(\text{calcd})} - y_{1(\text{obsd})}|}{n}$$

and

$$|\Delta T|_{\text{mean}} = \frac{\sum |T_{\text{calcd}} - T_{\text{obsd}}|}{n}$$

where n is the number of experimental points and T is the equilibrium boiling temperature.

In addition, it became interesting to show how the Wilson parameters vary with the chemical nature of the components for the systems examined. The values of interaction energy, $\lambda_{12} - \lambda_{11}$, were found to be 621 ± 18 (*n*-decane (1)–*o*-toluidine (2)), 606 ± 2 (*n*-dodecane–*m*-xylidine), and −168 ± 3 cal/mol (pseudocumene–aniline), respectively. While the values of $\lambda_{12} - \lambda_{11}$ are of similar magnitude for the systems containing *n*-paraffins, there is an indication that would suggest a strong interaction between the NH_2 group and the methyl groups in the aniline–pseudocumene system.

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A New Total Pressure Vapor–Liquid Equilibrium Apparatus. The Ethanol + Aniline System at 313.15, 350.81, and 386.67 K

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A new multicell apparatus for the measurement of total pressure vapor–liquid equilibrium data is described. Fifteen cells provide thirteen mixture and two pure compound points on the *P* vs. *x* isotherm. Multiple freezing–evacuation–thawing cycles are used to degas the loaded cells. The number of isotherms measured with one loading of the cells is limited only by chemical stability; usually three are measured in a typical 5-day run (including loading, degassing, and isotherm measurements). The method of Mixon, Gumowski, and Carpenter is used to reduce the data. Data are reported on the ethanol + aniline system at 313.15, 350.81, and 386.67 K and the effect of the equation of state used is explored.

Introduction

The fact that any one of the four experimental variables (P, T, x_1, and y_1) in binary vapor–liquid equilibrium (VLE) measurements can be calculated from the other three permits us to exclude from our experimental measurements that variable most subject to error. In high-temperature systems where chemical reaction rates are not negligible, the pressure may be the variable whose measurement is least reliable and it may be advisable to measure *Txy* data and calculate the equilibrium pressure. When chemical reactions are not a factor, the equilibrium vapor composition is usually most difficult to measure accurately and it is advisable to measure *PTx* (total pressure) data.

The *PTx* approach eliminates analyses of the phase compositions, thereby eliminating two of the major sources of error

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