

Liquid–Liquid Equilibria for Aniline + Cyclohexane + Water

Valerii P. Sazonov,* Vyacheslav V. Filippov, and Nikolai V. Sazonov

Department of General and Inorganic Chemistry, Technical University, Samara 443100, Russia

Liquid–liquid equilibria and mutual solubility for aniline + cyclohexane + water have been measured in the temperature range 29 °C to 45.6 °C with analysis by gas chromatography. Phase diagrams, including tie lines and plait point, are reported at some temperature. The form of the solubility curve in the vicinity of the critical end point is discussed.

The ternary system aniline + cyclohexane + water is a convenient system to study. MacQueen et al.¹ and Rice and MacQueen² noted a large increase in the upper critical solution temperature (T_c) of mixtures of aniline and cyclohexane with the addition of water. Once an excess of water was added, T_c from the three-phase to a two-phase system at 45.5 °C remained essentially independent of the addition of further water. Sazonov³ carried out a study of the phase transformations in this ternary system in the temperature range (28.9 to 45.6) °C by a synthetic method. They established that 45.6 °C was the maximum temperature of existence of equilibrium between the three liquid phases. In the present paper our results for the mutual solubility and compositions of the liquid equilibrium phases of the system aniline + cyclohexane + water at (29.0, 39.0, and 45.6) °C are reported.

Experimental Section

Twice-distilled water, pure grade aniline (Reakhim, Russia, 99 mass % purity), and cyclohexane for chromatography (Reakhim, Russia, 99.8 mass % purity) were used. Aniline was dried with KOH and vacuum-distilled twice. The measured density and refractive index are $\rho(20\text{ °C}) = 1021.7\text{ kg}\cdot\text{m}^{-3}$ and $n(20\text{ °C, D}) = 1.5860$. Cyclohexane was not purified and $\rho(20\text{ °C}) = 778.5\text{ kg}\cdot\text{m}^{-3}$ and $n(20\text{ °C, D}) = 1.4263$.

The solubility curves and the border of the three-phase region were determined by a titration method. Heterogeneous mixtures of two components were prepared in 15-mL flat-bottomed glass vessels. The total mass of the mixture was (8 to 11) g, depending on the overall composition. The vessels were put into a 30-L water thermostat with transparent sides. A sealed magnetic stirrer was used for continual agitation of the mixtures. The temperature variations at a specified temperature were $\pm 0.02\text{ °C}$, according to thermometers with 0.01 °C scale divisions. The heterogeneous mixtures of the two substances were titrated by the third component until the second or third liquid phase appeared. The addition of a component was made with a microsyringe, the needle of which was pushed through the hermetic rubber stopper. The relative error in determinations of the solubility curves did not exceed 1%.

Composition analysis of each phase was carried out by gas chromatography, employing a thermal conductivity

detector. The column was coated with 10 mass % Apieson L on Polychrom-1. The thermostat temperature was 145 °C and the carrier gas was helium, flowing at $25\text{ cm}^3\cdot\text{min}^{-1}$. The sample volume was 1 μL . The initial mixtures were kept for (3 to 3.5) h in a water thermostat at a given temperature to attain equilibrium and complete phase separation. Analytical samples (3 to 5 samples from each liquid phase) were taken by a microsyringe through a rubber stopper. The areas of the chromatographic peaks and the emergence times of the components were measured with the aid of the digital automatic integrator.

Calibration measurements carried out on the pure components and on homogeneous solutions showed that aniline and cyclohexane mole fractions could be determined with an uncertainty of better than 0.001 while, for water, the uncertainty was found to be better than 0.002.

Results and Discussion

Liquid–liquid equilibrium and mutual solubility data were obtained for the system aniline + cyclohexane + water at (29.0, 39.0, and 45.6) °C, and their values are shown in Tables 1 and 2. In Table 2 composition values corresponding to the plait point of an aniline-rich and cyclohexane-rich phase determined by Hand's method are also included. Compositions are always expressed in molar fractions x_{iA} , x_{iB} , or x_{iC} where the first index refers to the component and the second to the phase (A = aniline-rich phase, B = cyclohexane-rich phase, and C = water-rich phase). The water-rich phase contains only traces of aniline and cyclohexane; thus, this phase is practically one-component, while the cyclohexane-rich phase contains only very small quantities of water.

The binary boundary subsystems in the aniline + cyclohexane + water system have limited miscibility, with upper critical solution temperatures. At the temperature 29.0 °C, components of these binary systems show limited solubility, and in the ternary system there is an equilibrium of three liquid phases geometrically represented by a unsymmetrical triangle.

The region of the three-phase liquid state occupies more than half the area of the triangle of compositions. The areas of equilibrium of two liquid phases are adjacent to three parts of the phase triangle. Near the top of the triangle of compositions the one-phase areas can be found.

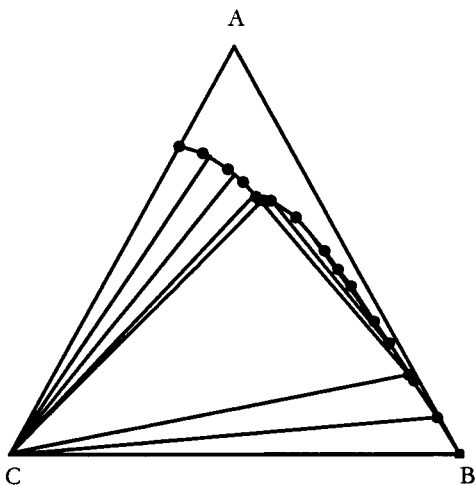
In Figure 1, the isothermal diagram at 39.0 °C is characterized by the binary system aniline + cyclohexane, which at this temperature is homogeneous, while the two other systems have limited solubility.

* To whom correspondence should be addressed. E-mail: sazonov@sstu.samara.ru.

Table 1. Mutual Solubility Data for the System Aniline (A) + Cyclohexane (B) + Water (C) at Several Temperatures^a

x_A	x_B	x_C	x_A	x_B	x_C
$t = 29.0\text{ }^\circ\text{C}$					
0.772	0.000	0.228	0.675*	0.187*	0.138*
0.749	0.062	0.189	0.477*	0.432*	0.091*
0.703	0.138	0.159	0.437*	0.483*	0.080*
0.695	0.156	0.149	0.266*	0.695*	0.039*
0.690	0.166	0.144	0.178*	0.805*	0.017*
0.690	0.178	0.132	0.077*	0.020*	0.903*
0.693	0.191	0.116	0.102*	0.025*	0.873*
0.687	0.256	0.057	0.157*	0.039*	0.804*
0.675	0.291	0.034	0.288*	0.073*	0.639*
0.625	0.373	0.002	0.018*	0.082*	0.900*
0.597	0.403	0.000	0.030*	0.171*	0.799*
0.301	0.699	0.000	0.051*	0.316*	0.633*
0.279	0.720	0.001	0.001 ₉	0.000 ₁	0.998
0.183	0.812	0.005	0.005 ₉	0.000 ₁	0.994
0.091	0.904	0.005		0.000	0.993
$t = 39.0\text{ }^\circ\text{C}$					
0.757	0.000	0.243	0.091	0.904	0.005
0.740	0.061	0.199	0.611*	0.262*	0.127*
0.700	0.137	0.163	0.556*	0.332*	0.112*
0.669	0.185	0.146	0.480*	0.429*	0.091*
0.634	0.231	0.135	0.401*	0.529*	0.070*
0.625	0.244	0.131	0.308*	0.646*	0.046*
0.624	0.255	0.121	0.270*	0.697*	0.033*
0.624	0.269	0.107	0.073*	0.029*	0.898*
0.582	0.347	0.071	0.274*	0.109*	0.617*
0.501	0.450	0.049	0.026*	0.082*	0.892*
0.456	0.503	0.041	0.046*	0.168*	0.786*
0.415	0.551	0.034	0.077*	0.307*	0.616*
0.327	0.647	0.026	0.001 ₉	0.000 ₁	0.998
0.274	0.706	0.020	0.005 ₈	0.000 ₂	0.994
0.183	0.807	0.010	0.008	0.000	0.992
$t = 45.6\text{ }^\circ\text{C}$					
0.751	0.000	0.249	0.333	0.626	0.041
0.734	0.061	0.205	0.276	0.694	0.030
0.693	0.136	0.171	0.182	0.804	0.014
0.633	0.234	0.133	0.090	0.904	0.006
0.563	0.337	0.100	0.005 ₈	0.000 ₂	0.994
0.485	0.437	0.078	0.001 ₉	0.000 ₁	0.998
0.415	0.525	0.060	0.008	0.000	0.992

^a Values marked with asterisks correspond to composition of ternary mixtures with transition of the equilibrium of two liquid phases in equilibrium of the three liquid phases. x_i is the mole fraction of component i in the mixture.

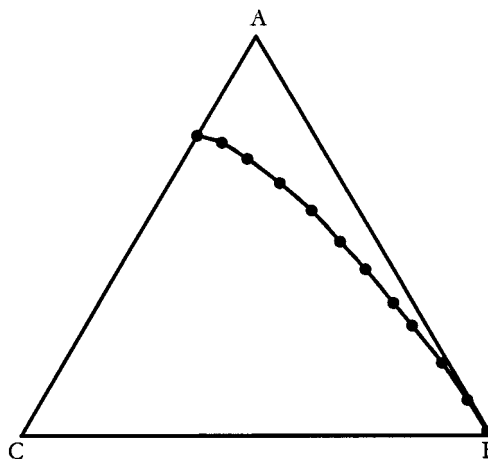
**Figure 1.** Ternary phase diagram for the system aniline + cyclohexane + water at 39.0 °C.

With an increase in temperature from 29.0 °C up to 39.0 °C, the area of equilibrium of the three liquid phases decreases basically at the expense of the moving tops of a

Table 2. Liquid–Liquid Equilibrium Data for the System Aniline (A) + Cyclohexane (B) + Water (C)^a

x_{AA}	x_{BA}	x_{AB}	x_{BB}	x_{AC}	x_{BC}
$t = 29.0\text{ }^\circ\text{C}$					
0.689	0.142	0.138	0.858	0.003 ₉	0.000 ₁
0.762	0.032			0.006 ₈	0.000 ₂
0.753	0.058			0.005 ₈	0.000 ₂
0.734	0.090			0.005 ₈	0.000 ₂
0.718	0.121			0.004 ₉	0.000 ₁
0.698	0.153			0.003 ₉	0.000 ₁
0.661	0.319	0.278	0.721		
0.678	0.281	0.253	0.745		
0.685	0.253	0.226	0.772		
0.690	0.228	0.204	0.793		
0.692	0.205	0.176	0.821		
0.691	0.184	0.148	0.848		
$t = 39.0\text{ }^\circ\text{C}$					
0.621	0.249	0.196	0.788	0.004 ₉	0.000 ₁
0.749	0.038			0.007 ₉	0.000 ₁
0.731	0.081			0.007 ₉	0.000 ₁
0.712	0.115			0.006 ₉	0.000 ₁
0.686	0.158			0.006 ₉	0.000 ₁
0.663	0.192			0.005 ₉	0.000 ₁
0.637	0.226			0.004 ₉	0.000 ₁
0.624	0.258	0.227	0.755		
0.623	0.272	0.261	0.719		
0.611	0.298	0.282	0.694		
0.585	0.340	0.308	0.666		
0.548	0.392	0.336	0.636		
0.433*	0.528*	0.433*	0.528*		

^a Values marked with asterisks correspond to plait points calculated by Hand's method. x_{iA} is the mole fraction of component i in the aniline-rich phase; x_{iB} is the mole fraction of component i in the cyclohexane-rich phase; x_{iC} is the mole fraction of component i in the water-rich phase.

**Figure 2.** Saturation line (organic-rich branch only) for the system aniline + cyclohexane + water system at 45.6 °C.

phase triangle appropriately aniline-rich and cyclohexane-rich phases. The region of aniline-rich and cyclohexane-rich phases is limited by the binodal curve with a critical point. The coordinates of this point are determined by Hand's method and are given in Table 2.

In Figure 2 the phase diagram of the ternary system is shown at 45.6 °C. This temperature is the maximum temperature for the existence of three-phase liquid equilibrium ($T_{3L \rightarrow 2L}$) for this ternary system. At this temperature three liquid phases pass to a two-phase system. From the geometrical point of view, this phenomenon is expressed in the transformation of an indefinitely small triangle of three liquid phases in the tie line, as aniline-rich and cyclohexane-rich phases become identical in structure and properties and are united in a critical point.

For this reason one tie line of the two-phase equilibrium has special properties at 45.6 °C; namely, this tie line characterizes equilibrium of a critical solution with a water-rich phase. The condition of the system with $P = \text{const}$ is nonvariant. The existence of an “opened type” region of two-phase equilibrium is characteristic of an isothermal condition $T_{3L \leftrightarrow 2L} + \Delta T$; thus, the branched binodal curve lacks special points. At $T_{3L \leftrightarrow 2L} - \Delta T$ on the isothermal diagram there is an indefinitely small triangle of equilibrium of three liquid phases; the region of two-phase equilibrium with a critical point adjoins to one of which parts.

At $T = T_{3L \leftrightarrow 2L}$ the bottom branch of the binodal curve and the spinodal curve join to form a critical point. According to thermodynamic rules given by Storonkin et al.,⁴ in a vicinity of a critical point the binodal curve should be convex toward the one-phase condition. This is illustrated by the phase diagram at 45.6 °C as shown in Figure 2.

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