

The System *o*- and *p*-Toluenesulfonamides and Water at 20° and 95° C.

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DURING CRYSTALLIZATION studies the mutual solubilities of *o*- and *p*-toluenesulfonamides in water were determined at 20° and 95° C. Interest concerning the unexpected appearance of an amide-rich liquid phase culminated in the definition of the complete ternary phase diagram at 95° C.

Previously reported work on the phase equilibria of the toluenesulfonamide isomers has been limited to freezing point curves for the binary system, *o*- and *p*-toluenesulfonamides, which is composed of two branches intersecting at a eutectic point (1, 3). According to Dobrienskii (1) the eutectic point occurs at 108° C. and corresponds to a mixture containing 42.5% *o*-amide and 57.5% *p*-amide. Using amides that had been purified by recrystallization and sublimation, McKie (3) reported the composition of the eutectic mixture as 61.25% *p*-amide with a melting point of 110.25° C. Determinations made in this laboratory with recrystallized amides confirm the data of McKie. No reference was found for the mutual solubility effects nor for the ternary system involving the *o*- and *p*-amides and water.

EXPERIMENTAL

Materials. Samples of zone refined *o*- and *p*-toluenesulfonamides were used to calibrate the analytical methods. Their respective melting ranges, as determined by the U.S.P. method, were 156.0–156.6° and 138.4–139.0° C. McKie (3) reported melting points of 156.3° C. and 137.45° C. after vacuum sublimation.

The *o*- and *p*-toluenesulfonamides used for experimentation were high purity Monsanto production materials. By analysis, they contained less than 0.1% impurities, other than water or the relevant *o*- and *p*-isomer, and were not subjected to further purification.

Apparatus. Isothermal equilibration of mixtures and selective withdrawal of specific phases were accomplished with the apparatus shown in Figure 1. A 250-ml. Erlenmeyer flask was modified with a length of 5 mm. I.D. borosilicate glass tubing, containing a stopcock and a 5-cm. detachable section, A. Agitation was provided by a motor-driven glass stirrer fitted through a modified ground glass adapter. The adapter was equipped with a glass bearing to reduce evaporation losses and tubulated to permit venting through a short length of rubber tubing with a pinch clamp. The assembled apparatus was immersed to the top of the flask in an oil bath, the temperature of which was regulated to $\pm 0.2^\circ$ C.

Sampling of the amide-rich liquid, when in equilibrium with aqueous solution, was accomplished by the use of the detachable section, A. Otherwise, liquid samples were removed by means of a modified 5-ml. pipet, B equipped with a short length of rubber tubing and pinch clamp at one end and a flared delivery tube of 4 mm. I.D. at the other end. To ensure exclusion of suspended solids during sampling, the flared tip was indented to accommodate a small plug of glass wool.

Procedure. Each weighed mixture was heated, with occasional venting, in the assembled apparatus to a temperature 2 to 3° C. above the experimental temperature. With the vent sealed the mixture was agitated 2 to 3 hours before reducing the bath temperature to 20 or 95° C.

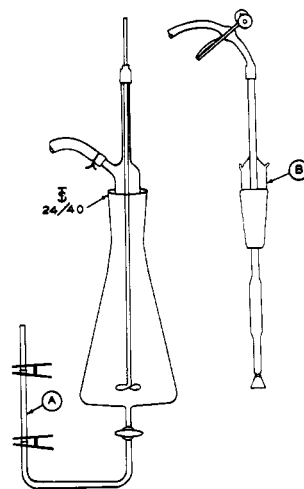


Figure 1. Apparatus used for isothermal equilibration and phase sampling

After an additional 3 to 4 hours of agitation, the stirrer head was removed and the sampling pipet inserted with its attached rubber tubing sealed. Rotary agitation was manually provided during the 30 minute interval allowed for thermal equilibrium to be re-established. At 95° C. a slight pressure developed in the flask which permitted sampling by manipulation of the pinch clamp on the sampling pipet. A slight vacuum was applied to obtain samples at 20° C. The pipet was withdrawn and, after instant removal of the glass wool, the sample was immediately transferred to a tared volumetric flask and reweighed.

When in equilibrium with aqueous solution, the amide-rich liquid was sampled by opening the stopcock beneath the flask and withdrawing a portion through a plug of glass wool into the detachable section. After removing the apparatus from the bath and cooling to room temperature, the amide-rich liquid solidified, allowing the previously tared detachable section to be uncoupled and reweighed.

Samples of wet residue were obtained by Schreinemaker's method (4).

Analysis. Samples of aqueous solution at 20° C. were collected in 50-ml. volumetric flasks, diluted to volume with 0.1N hydrochloric acid, and the *o*- and *p*-amides determined by the ultraviolet absorption method of Stewart, Caldwell, and Uelner (5). Samples of aqueous solution at 95° C. were collected in 100-ml. volumetric flasks, dissolved, and diluted to volume with 1% sodium hydroxide. After appropriate dilution and acidification the *o*- and *p*-amides were determined as above.

Samples of both wet residue and amide-rich liquid were dissolved and diluted to volume with anhydrous methanol in 100-ml. volumetric flasks. Aliquot portions were used for the following determinations: water by the Karl Fischer method, total amide by titration in a pH 9.7 carbonate buffer with 0.7M sodium hypochlorite to a platinum/saturated calomel potentiometric endpoint, and the isomer ratio by ultraviolet absorption after appropriate dilution with water and acidification. Iodometric standardizations of the sodium hypochlorite solution were made daily. Additive agreement of the water plus total amide was generally within $\pm 1\%$ of the sample weight.

RESULTS

The mutual solubilities of the *o*- and *p*-toluenesulfonamides in water at 20° and 95° C. are shown in Figures 2 and 3, in which the data are plotted according to the method of van't Hoff (2). At 20° C. the solubility of each isomer is nearly independent of the other. At 95° C., however, each isomer enhances the solubility of the other until the total amide concentration in water is approximately 11.7 grams per 100 grams of solution. Further addition of the enhancing isomer results in the formation of a second amide-rich liquid phase and causes suppression of the aqueous solubility of the other isomer.

The sample compositions (in wt. %) of the aqueous solutions and their conjugate amide-rich liquids obtained at 95° C. are given in Table I. Similar data for the sample compositions of amide-rich liquid and the corresponding wet residues are given in Table II.

Table I. Analysis of Aqueous Solutions and Conjugate Amide-Rich Liquids at 95° C.

Aqueous Soln., Wt. %		Amide-Rich Liquids, Wt. %		Solid Phase
<i>o</i> -Amide	<i>p</i> -Amide	<i>o</i> -Amide	<i>p</i> -Amide	
3.75	0.00			<i>o</i> -Amide
4.55	1.92			<i>o</i> -Amide
5.56	3.62			<i>o</i> -Amide
6.74	5.27	46.2 ^a	36.1 ^a	<i>o</i> -Amide
6.05	5.76	41.2	40.3	None
4.88	6.80	33.3	47.3	None
3.32	8.31	22.8	56.5	None
2.98	8.48			None
2.30	9.38	15.4	64.8	None
1.56	10.00			None
1.14	10.48			None
0.80	10.88	5.5 ^a	74.5 ^a	<i>p</i> -Amide
0.54	9.98			<i>p</i> -Amide
0.00	9.23			<i>p</i> -Amide

^a Value obtained by multiplying the corresponding solution compositions by 6.85.

Table II. Analysis of Amide-Rich Liquids and Wet Residues at 95° C.

Amide-Rich Liquids, Wt. %		Wet Residues Wt. %		Solid Phase
<i>o</i> -Amide	<i>p</i> -Amide	<i>o</i> -Amide	<i>p</i> -Amide	
44.0	41.0			<i>o</i> -Amide
43.3	40.3	62.4	26.5	<i>o</i> -Amide
42.6	44.5			<i>o</i> -Amide
41.1	47.5	65.4	28.4	<i>o</i> -Amide
40.9	51.2	61.6	33.6	<i>o</i> -Amide
36.9	58.3			<i>o</i> - and <i>p</i> -Amide
30.5	62.9			<i>p</i> -Amide
23.4	67.3			<i>p</i> -Amide
20.4	67.0	12.4	79.2	<i>p</i> -Amide
16.0	69.1			<i>p</i> -Amide
11.0	71.7	7.4	81.0	<i>p</i> -Amide

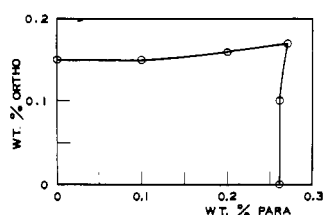


Figure 2. Mutual solubility of *o*- and *p*-toluenesulfonamide in water at 20° C.

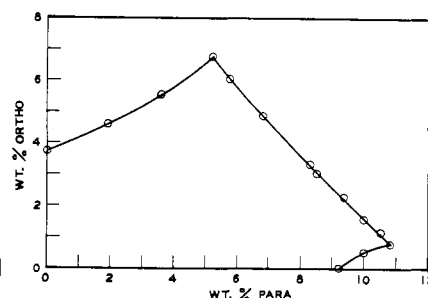


Figure 3. Mutual solubility of *o*- and *p*-toluenesulfonamide in water at 95° C.

The ternary phase diagram at 95° C., constructed from these data, is shown in Figure 4. It is composed of ten fields and four phases, two liquid and two solid.

Because of manipulative difficulties we were unable to obtain uncontaminated samples of the amide-rich liquid in equilibrium with both aqueous solution and solid *o*- or *p*-amide. As a result, points *H* and *I* in Figure 4 were not determined experimentally. However, examination of the analytical data for conjugate samples of aqueous solution and amide-rich liquid showed that the *o*- and *p*-amide concentrations in the amide-rich phase were consistently 6.85 ± 0.15 times the corresponding concentrations in the aqueous phase. In consequence, the tie lines mutually converge at point *A* in Figure 4. Using the above relationship and the experimental data for points *E* and *F*, the compositions, listed in Table I, for points *H* and *I* were calculated.

In consideration of the sampling techniques, analytical methods, and the results of duplicate determinations, our best estimate of the accuracy of these data is 2 to 3% of the amounts present.

DISCUSSION

Since the ternary phase diagram represents a condensed system of three components at constant temperature, the phase rule requires that the sum of the number of phases and the degrees of freedom always equal 3. Table III lists the phases and degrees of freedom associated with each of the fields shown in Figure 4.

The simplicity of the ternary phase diagram at 20° C. may be implied from Figure 2. Its comparison with the more complex ternary phase diagram at 95° C. stimulated conjecture concerning the intermediate isothermal ternary phase diagrams. Of particular interest was the temperature at which the amide-rich liquid disappeared on cooling and

Table III. Phases and Degrees of Freedom for the Ternary Phase Diagram at 95° C.

Field	Degrees of Freedom	Phases
ADEFG	2	Aqueous solution
CDE	1	Aqueous solution + Solid <i>o</i> -amide
CEH	0	Aqueous solution of comp. E + Solid <i>o</i> -amide + Amide-rich liquid of comp. H
EFIH	1	Aqueous solution + Amide-rich liquid
BFI	0	Aqueous solution of comp. F + Solid <i>p</i> -amide + Amide-rich liquid of comp. I
BFG	1	Aqueous solution + Solid <i>p</i> -amide
BIJ	1	Amide-rich liquid + Solid <i>p</i> -amide
HIJ	2	Amide-rich liquid
CHJ	1	Amide-rich liquid + Solid <i>o</i> -amide
BCJ	0	Amide-rich liquid of comp. J + Solid <i>o</i> -amide + Solid <i>p</i> -amide

E, F, H, I, and J are isothermal invariant points.

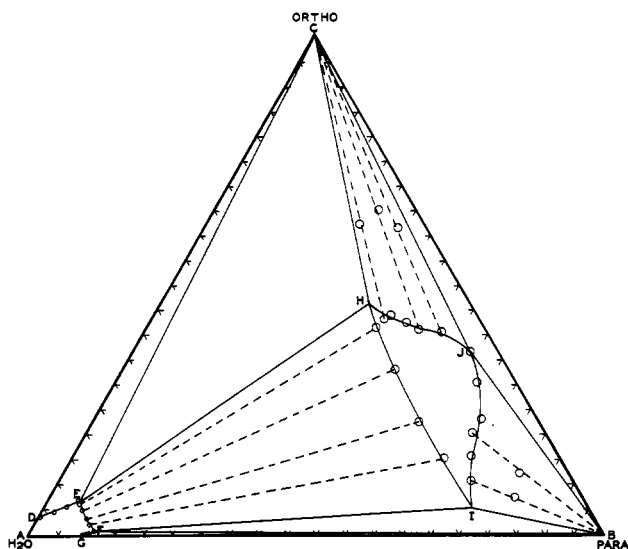


Figure 4. The System *o*-toluenesulfonamide, *p*-toluenesulfonamide, water at 95° C.

its composition. As the temperature is reduced, the field *H**I**J* will contract and disappear, while points *E* and *F* will converge and eventually merge.

The line connecting points *A* and *J*, when extrapolated, intersects *BC* at a point corresponding to the amide binary eutectic mixture and, therefore, represents mixtures of the amide binary eutectic and water. The point of intersection of the aqueous solution field boundaries in Figure 2 also corresponds to a mixture of the amide binary eutectic and water. It therefore seemed probable that the disappearance of field *H**I**J* and the mergence of points *E* and *F* would occur simultaneously at points located on line *AJ*.

To determine the temperature at which the amide-rich liquid field disappears, cooling curves were prepared for eight mixtures of various compositions within the field *H**I**J*. An apparatus similar to the Beckman freezing-point apparatus, but with a standardized Princo precision thermometer in place of the Beckman thermometer, was used. In each case, the final and longest hold temperature was $78.7 \pm 0.5^\circ \text{C}$.

To estimate the composition of the amide-rich liquid at the temperature of its disappearance, mixtures of composition *J* in Figure 4 were prepared and equilibrated at 89.6°, 84.8°, 81.9°, and 80.0° C. Samples of the amide-rich liquid were removed and analyzed. For these samples the *p*-amide to *o*-amide ratios were essentially constant, 1.59 ± 0.05 , and corresponded to the ratio, 1.58, calculated for the amide binary eutectic mixture. They contained 92.0%, 89.4%, 85.5%, and 82.6% total amide, respectively.

For extrapolative purposes in estimating the composition of the amide-rich liquid at 78.7° C., we treated these data, including those for point *J* and the melting point of the amide binary eutectic given by McKie (3), as a pseudo binary system involving the amide binary eutectic mixture and water. From the least square plot of the logarithm of the mole fraction of total amide against the reciprocal of the absolute temperature, shown in Figure 5, the predicted composition of the amide-rich liquid at 78.7° C.

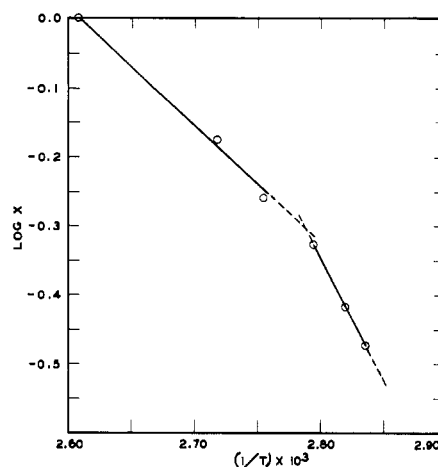


Figure 5. Solubility of the amide binary eutectic mixture as mole fraction in water

would be equivalent to a mixture containing 80.4% of the amide binary eutectic and 19.6% water. From Figure 4 the corresponding values at the intersection of line *AJ* and field boundary *HI* are 80% and 20%.

We therefore conclude that, on cooling, the amide-rich liquid field disappears at $78.7 \pm 0.5^\circ \text{C}$. and that the composition of the amide-rich liquid immediately prior to its disappearance is approximately 49% *p*-amide, 31% *o*-amide, and 20% water. On cooling from 78° to 20° we would expect a succession of simple ternary phase diagrams with progressively contracting fields of aqueous solution and with isothermal invariant points occurring along the tie line representing mixtures of amide binary eutectic and water.

Although speculative in view of the arbitrary treatment of the data, it is conceivable that the break at 85.5° C. in the solubility curve, Figure 5, may be associated with a solid phase transition. The existence of the dihydrate of *p*-toluenesulfonamide at a lower temperature was reported by McKie (3). With a total amide concentration at the point of break of 90.2%, the ternary phase diagram at 85.5° C. would be geometrically compatible with the existence of the *p*-amide monohydrate solid phase, but would probably not accommodate solid *p*-amide dihydrate.

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