

Solubility Data for *p*-Xylene

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The solubility of *p*-xylene in a mixture of C₆-C₈ aromatics was determined over a temperature range of -109° to -20° F. The mixture of aromatics approximated feed stocks to commercial *p*-xylene plants. The method used equilibrated excess solid *p*-xylene with feed stock liquid at constant temperatures after which aliquots were withdrawn and the *p*-xylene content determined from gas chromatography.

COMMERCIALY, one method to prepare *p*-xylene is to separate it from mixtures of xylenes by low-temperature fractional crystallization, because *p*-xylene is the least soluble component in a mixture of C₈ isomers present in typical feed stock liquids.

Low-temperature *p*-xylene solubility data were published in 1955 as part of a comprehensive report covering significant *p*-xylene developments to that date (2). This solubility curve, calculated theoretically from the integrated Van't Hoff equation, compared favorably with freezing point data on mixtures of pure xylene isomers.

From recent solubility measurements on a mixture approximating actual feed stocks, a solubility curve, lying above that previously reported, has been obtained. The technique employed permits direct measurement of *p*-xylene solubility by a gas chromatographic method and is applicable to any feed stock mixture without modification.

EXPERIMENTAL

Saturated *p*-xylene solutions at different temperatures were obtained by equilibrating excess solid *p*-xylene with feed stock liquid in a constant temperature bath. Small aliquots withdrawn from these solutions were analyzed for *p*-xylene content by gas chromatography.

Solubility measurements were conducted at six temperatures between -20° and -85° F. using 50-ml. samples of feed stock in an acetone bath. Temperature regulation, as monitored on a constant-recording platinum resistance thermometer, was $\pm 0.05^\circ$ F. at -20° F. and $\pm 0.1^\circ$ F. at -85° F. Above -40° F., feed stock was enriched with pure *p*-xylene to give excess solid at the equilibrium temperature. One additional measurement was obtained at -109.3° F. in an acetone-dry ice slurry.

Solution mixtures were stirred frequently and given a minimum of two hours to reach equilibrium. Three ¼-ml. aliquots were withdrawn at 15-minute intervals with a 1-ml. syringe. Liquid was first drawn through a coarse sintered glass filter stick to remove solid *p*-xylene. A small positive pressure prevented liquid from rising into the filter stick before sampling. At very low temperatures appreciable amounts of ice built up in the sintered glass disk, but this can be prevented by using dry nitrogen or dry air to blanket liquid and sampling tube.

Instrument Co., Walnut Creek, Calif.), with a 60-foot, ¼-inch O.D. copper column, packed with 40/60 mesh Chromosorb GC-22 (Johns-Manville). Solid substrate was

Mole per cent soluble *p*-xylene was determined at each temperature by gas chromatography. The unit employed was an Aerograph Model 600 gas chromatograph (Wilkins coated with 4.9% by weight of oxy-bis-2-ethylbenzoate.

The temperature was 90° C. Chromatograms were integrated automatically on a unit described previously (1).

Duplicate analyses were performed for each temperature on the first and third samples withdrawn.

RESULTS

Table I gives mole per cent composition data on the feed stock mixture used in this work. Amounts of the four principal constituents (ethylbenzene and the three xylene isomers) are similar to those present in typical feed stock mixtures reported previously (2).

p-Xylene temperature-solubility data are shown in Table II as mole per cent soluble *p*-xylene. At temperatures where regulation was best, -20° and -109.3° F., precision of duplicate analyses was better than $\pm 0.5\%$. Results at intermediate temperatures are precise to better than $\pm 2.1\%$. If nonequilibrium conditions had existed during the sampling periods, trends in changes of per cent solubility with time should be evident. At temperatures below -40° F., where *p*-xylene precipitated from feed

Table I. Composition of a Typical *p*-Xylene Feed Stock

Component	Mole %
Nonaromatic C ₈	0.42
Benzene	0.29
Toluene	3.38
Ethylbenzene	14.31
<i>p</i> -Xylene	20.72
<i>m</i> -Xylene	46.28
<i>o</i> -Xylene	13.20
Aromatic and Nonaromatic C ₉	1.40
Total	100.00

Table II. *p*-Xylene Temperature Solubility Data

Temp., ° F.	Sample	Mole %, <i>p</i> X	Mole %, <i>p</i> X
-20.0	A-1	29.28	
	A-3	29.37	29.33 \pm 0.05
-30.0	B-1	25.44	
	B-2	25.47	
	B-3	26.11	25.67 \pm 0.33
-44.0	C-1	20.40	
	C-2	19.67	20.03 \pm 0.36
-60.0	D-1	15.10	
	D-3	14.86	14.98 \pm 0.12
-76.0	E-1	10.87	
	E-3	11.32	11.10 \pm 0.22
-85.0	F-1	9.18	9.18
-109.3	G-3	5.38	
	G-4	5.34	5.36 \pm 0.02

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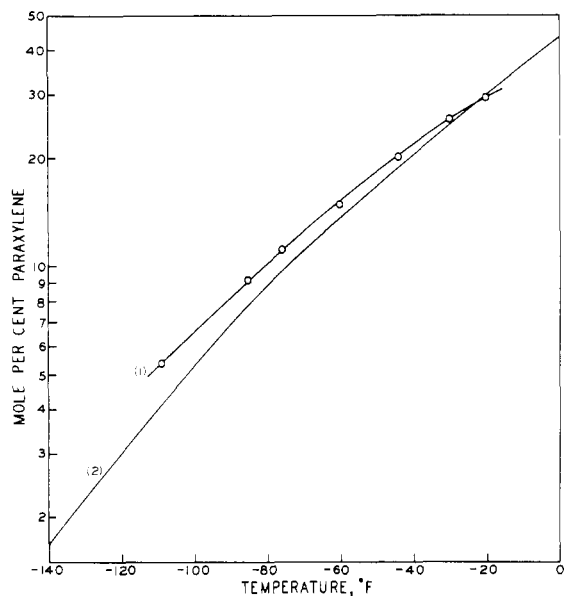


Figure 1. *p*-Xylene solubility in feed stock vs. temperature. Curve (1): this report; Curve (2): *Ind. Eng. Chem.* **47**, 1100 (1955).

stock liquid, measured *p*-xylene solubility should decrease with time under nonequilibrium conditions; and above -40°F . it should increase. These trends were not observed on samples withdrawn at 30-minute intervals; therefore, it was concluded that equilibrium was attained.

Solubility results are shown graphically in Figure 1, where they are compared with the solubility curve published in 1955. Present data lie considerably above this curve in the range -109.3° to -20°F .

The published curve was based on integration of the Van't Hoff equation using heat of fusion and extrapolated specific heat data on pure xylene isomers. The curve was supported by freezing points of mixed xylenes. It is, therefore, not surprising that our experimental data do not agree completely with the published curve.

LITERATURE CITED

- (1) Gardiner, K.W., Klaver, R.F., Baumann, F., Johnson, J.F., *Gas Chromatog. 3rd Intern. Symp.*, East Lansing, Mich., 1961; Academic Press, New York, 1962.
- (2) Haines, H.W., Jr., Powers, J.M., Bennett, R.B., *Ind. Eng. Chem.* **47**, 1096 (1955).

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