Extended Xylene Solubility Studies

ROGER S. PORTER[1] and JULIAN F. JOHNSON
Chevron Research Co., Richmond, Calif.

Xylene solubility data previously reported from this laboratory have been extended using an improved procedure. New paraxylene solubility data have been obtained in the temperature ranges of −20° to +50° and −70° to −120° F. The solubility of metaxylene was also measured at −100° F. in xylene solutions of several compositions. All results suggest ideal solution behavior. Metaxylene, however, can supersaturate up to at least 12% absolute above its equilibrium value even though liquid paraxylene can be in equilibrium with its crystals in the same solution.

IN THIS STUDY, solubility tests were made principally on paraxylene with supplemental measurements on metaxylene. Measurements were made on enriched mother liquors from a commercial paraxylene plant and on synthetic blends. These tests represent a high and low temperature extension of earlier paraxylene solubility tests developed in this laboratory (*2*). Saturated solutions of paraxylene were obtained by equilibrating excess solid paraxylene with the mother liquor in a constant temperature bath. At the desired test temperatures, liquid aliquots were withdrawn from the solution and analyzed by gas chromatography for the content of nonaromatics, the three xylenes, toluene, and ethylbenzene. The improved gas chromatographic procedure and integration system (*1*) employed a Perkin-Elmer Model 800 gas chromatograph with a 300-foot, 0.02-inch I.D. capillary column of Type 347 stainless steel coated with UCON 50-LB-550X, (Varian Aerograph, Walnut Creek, Calif.).

Since the isothermal tests were generally performed in order of increasing temperature, it was necessary to upgrade the solution periodically by adding pure paraxylene. At each test temperature, the solution was allowed 2 hours to reach equilibrium. This was proved to be sufficient by two additional experiments at lesser times which were used to check for rate of approach to equilibrium (Table I). The solutions were vigorously stirred continuously. Liquid aliquots of about 0.25 ml. were withdrawn with a hypodermic syringe through a sintered glass filter. Tests with filters of different porosity confirmed visual observations that the solution withdrawn was free of crystals. The improved apparatus in which excess paraxylene and mother liquor were equilibrated consisted of a 200-ml. capacity U-tube with crossarm, stirrer, and sintered glass filter stick equipped with a squeeze bulb and syringe. Measurements from −92° to +50° F. were conducted in a low temperature viscosity bath used in the previous study (*2*). Below −92° F., a silvered Dewar flask was used and the coolant was acetone with controlled additions of solid carbon dioxide. Temperature regulation of the baths was continuously monitored with a recording platinum resistance thermometer. Bath regulation was ±0.05° F. and better.

RESULTS

The mole per cent of paraxylene soluble in mother liquor as a function of temperature is given in Table I. The high reproducibility of measurements is indicated. The alphabetical listings represent analyses of aliquots withdrawn separately after the 2-hour equilibrium time. Results in Table I are shown graphically in Figure 1. Log mole per cent soluble paraxylene is plotted against the reciprocal of the absolute temperature on the centigrade scale.

Measurement in the upper temperature range, −20° to +50° F., for paraxylene solubility indicated rather good agreement with the solubility curve published by Humble (*3*) (Figure 1). The Humble curve was calculated from the theory for ideal solution behavior and was derived from data only at the higher temperatures, > −90° F. In the lower temperature range, there is a significant deviation from this theoretical curve in the commercially important range below −85° F. Other curves can be calculated which agree with data and differ from the one calculated at Humble (Figure 1). The experimental paraxylene solubility data have standard deviations of about ±0.4% absolute and are close to data obtained earlier by Haddon and Johnson (*2*) with the deviation in the direction of the theoretical curve calculated at Humble (*3*). The theoretical curve is based in part on specific heats which are not known to high precision. An integrated form of the van't Hoff equation was used for calculation.

The possibility of differences in paraxylene solubility owing to differences in the composition of solutions has been tested. Table II shows equivalent paraxylene solubility results at −100.0° F. on solutions of two compositions which differ from the mother liquor evaluated in Table I, which is described as system III in Table III. Metaxylene readily supersaturates, in one case up to 59% absolute (Table II), even though paraxylene is in equilibrium with its crystals.

Tables III and IV report tests on metaxylene solubility equilibria. Significantly, the 46% metaxylene solubility, top

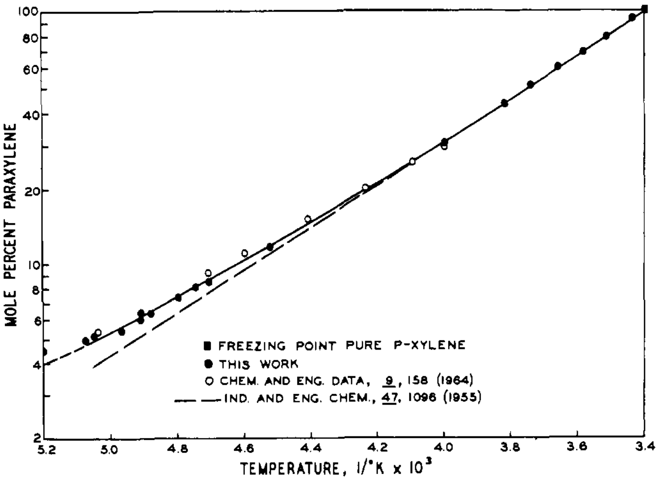

Figure 1. Paraxylene solubility as a function of temperature

---

[1] Present address: Polymer Science and Engineering Program, University of Massachusetts, Amherst, Mass.

Table I. Analysis of Solutions at Equilibrium with Paraxylene Crystals

Temp., ° F.	Solution Sample	Paraxylene, Mole %	Temp., ° F.	Solution Sample	Paraxylene Mole %	Temp., ° F.	Solution Sample	Paraxylene, Mole %
−120.24	A[a]	4.58	−88.00	A[a]	7.85	+10.00	A	50.65
	B[a]	4.45		B[a]	8.09		B	51.08
	C[a]	4.42		C[a]	7.95		C	51.05
−111.86	A	4.97	−84.74	A	8.68	+20.00	A	59.00
−110.24	A[a]	5.28		B	8.52		B	59.56
				C[a]	8.45		C	59.05
				D[a]	8.51			
−104.58	A[a, b]	5.27	−70.00	A[a]	11.56	+30.00	A	68.07
	B[a, c]	5.63		B[a]	11.79		B	69.36
	C[a]	5.21		C	11.76		C	68.23
	D[a]	5.49						
−98.21	A[a, b]	6.35	−20.00	A	30.23	+40.00	A	78.75
	B[a, c]	6.87		B	30.53		B	78.96
	C[a]	6.24		C	30.56		C	78.04
	D[a]	6.46						
92.00	A[a]	7.30	− 0.00	A	41.59	+50.00	A	91.24
	B[a]	7.50		B	43.09		B	92.45
	C[a]	7.26		C	43.12		C	92.64

[a] Sample withdrawn through a medium sintered-glass filter (10–15 microns), all others were withdrawn through a coarse sintered-glass filter (170–220 microns). [b] Sample withdrawn after ¾ hour. [c] Sample withdrawn after 1½ hours, all others first aliquots after 2 hours and successive aliquots at 15-minute intervals.

Table II. *p*-Xylene Solubility Tests at −100.0° F. on Original Solutions of Different Compositions

	Analyses of Original Solution			Analyses of Equilibrium Solution			
Toluene	1.91	2.14	1.88	2.10	1.99	1.97	
Ethylbenzene	33.24	32.50	32.76	34.37	34.82	34.82	
Paraxylene	10.12	10.41	10.18	6.02	6.02	5.94	
Metaxylene	49.34	49.29	49.70	51.75	51.59	51.53	
Orthoxylene	5.39	5.66	5.47	5.75	5.56	5.70	
Toluene	4.40	4.04	4.04	4.16	4.13	4.36	4.28
Ethylbenzene	20.18	20.57	20.20	21.81	21.83	21.05	21.02
Paraxylene	11.27	11.28	11.16	5.87	6.37	6.33	6.50
Metaxylene	55.70	55.53	56.02	59.23	58.68	59.42	59.19
Orthoxylene	8.44	8.58	8.57	8.92	8.99	8.84	9.01

Table III. Test for Metaxylene Solubility and Supersaturation

		Composition of Original Mother Liquor, Mole %	Equilibrium Solution, Mole %	Temp., ° F.
Toluene		1.81	2.12 ± 0.05	−100.00
Ethylbenzene		37.44	43.35 ± 0.14	
Paraxylene		5.15	5.68 ± 0.09	
Metaxylene	I	53.29	46.15 ± 0.20	
Orthoxylene		2.31	2.70 ± 0.12	
Toluene		1.84	1.79 ± 0.05	−100.00
Ethylbenzene		35.96	35.36 ± 0.16	
Paraxylene		4.91	4.87 ± 0.07	
Metaxylene	II	51.99	52.52 ± 0.25	
Orthoxylene		5.28	5.46 ± 0.14	
Nonaromatic, C_5		1.00	3.34 ± 0.09	−98.21
Toluene		4.21	3.39 ± 0.07	
Ethylbenzene		22.65	22.72 ± 0.22	
Paraxylene		7.84	6.48 ± 0.20	
Metaxylene	III	56.45	55.79 ± 0.16	
Orthoxylene		7.84	8.28 ± 0.06	
Nonaromatic, C_5		1.00	2.46 ± 0.50	−104.58
Toluene		4.21	3.54 ± 0.11	
Ethylbenzene		22.65	23.43 ± 0.30	
Paraxylene		7.84	5.40 ± 0.16	
Metaxylene	III	56.45	56.82 ± 0.33	
Orthoxylene		7.84	8.36 ± 0.10	

Table IV. Tests for the Dependence of *m*-Xylene Solubility on Solution Composition

Both tests at −100.0° F.

	Analyses of Original Solutions			Analyses of Equilibrium Solutions		
Toluene	1.93	2.13		2.81	2.92	2.79
Ethylbenzene	25.82	25.84		34.89	35.35	35.62
Paraxylene	4.87	4.75		6.74	6.65	6.63
Metaxylene	61.40	61.17		47.53	47.05	46.87
Orthoxylene	5.97	6.09		8.03	8.03	8.08
Toluene	2.00	2.26	2.09	2.64	2.62	2.52
Ethylbenzene	24.82	24.38	24.61	32.28	31.93	32.08
Paraxylene	4.57	4.86	4.64	5.81	5.91	5.94
Metaxylene	58.95	59.20	58.99	46.90	47.14	47.54
Orthoxylene	9.55	9.30	9.66	12.37	11.99	12.31

sample, Table III, is distinctly less than the 56% metaxylene soluble at the same temperature, −100° F., using the bottom mother liquor described in Table III. This difference between 46 and 56% metaxylene solubility at −100° F. is the result of supersaturation. Theory and experiment suggest that each xylene exhibits its own unique solubility independent of other compounds which may be in either the liquid or solid phase (*3*). Table IV gives additional data at −100° F., which may show the metaxylene can be in equilibrium with crystals while paraxylene is supersaturated. The reverse can clearly be achieved. A comparison of the two tests in Table IV with the top analysis in Table

III indicates that metaxylene solubility is 46 to 47% at −100° F., independent of the composition of the solution. The 46% metaxylene solubility at −100° F. is just on previously reported theoretical solubility charts as mole percentages of 46 to 48 are given in (*3, 4*).

ACKNOWLEDGMENT

The authors express appreciation to A.R. Bruzzone for help with the experimental work.

LITERATURE CITED

(1) Gardiner, K.W., Klaver, R.F., Baumann, F., Johnson, J.F., *Gas Chromatog. Intern. Symp.* 3, 349 (1961) Academic Press, New York, 1962.
(2) Haddon, W.F., Jr., Johnson, J.F., J. CHEM. ENG. DATA **9**, 158 (1964).
(3) Haines, H.W., Jr., Powers, J.M., Bennet, R.B., *Ind. Eng. Chem.* **47**, 1096 (1955).
(4) Hauthal, H.C., Moll, K.K., *Chem. Tech. (Berlin)* **16**, 395 (1964).

RECEIVED for review August 12, 1966. Accepted March 13, 1967.

Properties of Superheated Liquids

Density and Compressibility of CCl_4

VERNON E. DENNY and RONALD L. SMITH[1]
Department of Engineering, University of California, Los Angeles, Calif.

A capillary tube pycnometer has been developed which enables study of *PVT* behavior of superheated liquids. Experiments were conducted for superheats as high as 42° C., and data for the density and compressibility of CCl_4 are reported for superheats up to 13.1° C. The results are in close agreement with an earlier study by Gibson and Loeffler of CCl_4 under subsaturated conditions.

ALTHOUGH the phenomenon of liquid superheating accompanies a variety of natural as well as industrial processes, the technical literature contains very little information about the behavior of liquids under superheated conditions. The purpose of this paper is to discuss experimental techniques for studying the superheated liquid state and to report the *PVT* behavior of pure CCl_4 at low pressures under modest superheats.

EXPERIMENTAL CONSTRAINTS

According to the nucleation theory of Volmer (*8*), the probability of formation of a critically sized vapor phase embryo in a homogeneous liquid under superheated conditions increases as the volume of the liquid phase increases. Thus, one could, at least in principle, prevent vapor phase nucleation at very high superheats by reducing the effective volume of the liquid phase, as has been observed by several investigators under rather specialized circumstances (*2, 5*). Since, however, there are practical limits to the minimum size of an experimental system, and since nucleation also can occur (and, in practice, usually does occur) at the interface between the liquid and its container, it is necessary to constrain a superheated system in additional ways. In this study, retardation of vapor phase nucleation was effected by eliminating pre-existing vapor phase nuclei at solid-liquid interfaces, promoting interfacial wetting, and reducing thermomechanical fluctuations. The first and second constraints were accomplished by degassing both the experimental apparatus and the test liquid using high vacuum techniques. The effect of thermomechanical shock was arrested by mounting the apparatus on specially designed shock mounts embedded in massive concrete walls.

APPARATUS AND PROCEDURE

A schematic diagram of the over-all apparatus appears in Figure 1. Principal components include a high vacuum system, *HVS*, a liquid degasser, *LD*, a Torricellian barometer, *TB*, a nitrogen reservoir, *NR*, a dust trap, *DT*, and the pycnometer itself, *CP*. Additional details of the pycnometer system appear in Figure 2.

The liquid to be superheated was stored in a spherical quartz bulb, *QB*, which was blown from vitreous silica and connected to the rest of the borosilicate glass pycnometer by means of a graded seal. The total superheated volume (*QB* and adjacent stem) was determined gravimetrically using pure mercury (3.244106 cc. at 24° C.). The effect of pressure and temperature on this volume was calculated from the physical properties of pure SiO_2 using standard equations from the literature (*6, 7*).

Changes in volume of the liquid stored in *QB*, produced by changes in temperature or pressure, were calculated from displacements of the N_2 - CCl_4 interface in the small bore capillary tube, *SBC*, whose mean radius (0.01011 cm.) was determined according to a technique described by Giddings (*4*). The bypass valve, *BPV*, and associated reservoir, *BPR*, were included because the volumetric capacity of *SBC* was too small to accommodate the over-all changes in volume produced during an isobaric run.

The experimental program was begun by assembling the glassware as in Figure 1, using one-shot glass break-out valves (*V1, V3*) to separate *LD* and *NR* from *CP*. The internal surfaces of the apparatus then were degassed by raising their temperature to 350° C. under a high vacuum of 10^{-7} mm. of Hg. (Since the conductance of capillary tubing is small under high vacuum conditions, *QB* was exhausted through a bypass line which was later sealed off at *S1*.) Degassing was continued for about 10 days, during which time the liquid degasser was set in operation. (Spectroscopic grade CCl_4 charged to *LD* was freed from dissolved gases by operating the unit as a fractionating

---

[1] Present address: California Institute of Technology, Pasadena, Calif.