Solubility of *m*- and *p*-Xylene in Water and in Aqueous Ammonia from 0° to 300° C.

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THE SOLUBILITY of the isomeric xylenes in water at elevated temperatures is of considerable interest, and yet the best data used mixed xylenes and are fairly old (5). These data were redetermined by observing the formation and disappearance of a cloud of finely dispersed xylene. The solubility of xylene in concentrated aqueous ammonia was also measured.

EXPERIMENTAL

Materials. The *m*-xylene was 99.1% pure and the *p*-xylene was 99.8% pure (by freezing point using ASTM D 1016-55). Main impuritier are isomeric xylenes in both cases. The aqueous ammonia was Baker and Adamson C.P., 14.6*N*.

Procedure. Solvent and xylene were carefully weighed into glass ampoules. The ampoules were sealed, allowing just enough space for thermal expansion. This was estimated from a few preliminary experiments, and after practice the vapor space was reduced until it was about 0.1 cc. at the cloud point. The ampoule, observed through a telescope from behind a safety barrier, was suspended in a 4-liter, stirred silicone oil bath, and the bath was heated until the xylene dissolved. On cooling a cloud of fine xylene droplets appeared, making the suspension opaque. The temperature was raised until the cloud disappeared. The cycle was repeated three to four times until reliable appearance and disappearance temperatures for the cloud were recorded (Table I).

The mole fraction of xylene, x_2, is calculated as follows:

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Table I. Solubility of *m*- and *p*-Xylene in Water and Aqueous Ammonia

Isomer	Grams: Xylene	Grams: Solvent	Mole Fraction Xylene × 10^3	Cloud Point, ° C.: Forms	Cloud Point, ° C.: Disappears	Midpoint, ° C.	$10^3/°$ K.
			Water				
Para	0.0212	82.70	0.0434	42.8	43.3	43.0	3.164
	0.0286	95.10	0.0510	54.4	58.3	56.4	3.035
	0.0275	81.00	0.0576	61.7	68.3	65.0	2.958
	0.0328	84.70	0.0656	73.9	76.7	75.3	2.870
	0.0248	53.969	0.0779	85.0	89.4	87.2	2.775
	0.1293	51.424	0.4264	161.7	163.3	162.5	2.296
	0.0439	9.6845	0.7686	186.7	189.5	188.1	2.168
	0.1536	8.7930	2.9555	241.6	244.9	243.2	1.937
	0.1225	2.7060	7.6238	280.5	284.4	282.5	1.800
	0.1174	2.6220	7.5407	291.6	298.3	294.9	1.760
Meta	0.0295	84.80	0.0590	64.4	71.1	67.7	2.934
	0.0558	84.00	0.1127	105.6	109.0	107.3	2.629
	0.0958	92.90	0.1749	122.7	125.6	124.2	2.517
	0.1262	50.190	0.4265	162.7	165.6	164.2	2.287
	0.0434	9.4040	0.7825	185.6	187.3	186.4	2.176
	0.0444	9.6990	0.7762	187.8	190.0	189.9	2.160
	0.0855	2.9130	4.956	264.4	268.9	266.6	1.853
	0.1540	5.1988	5.00	...	270.6	270.6	1.839
Mixed	0.0247	51.458	0.0814	87.2	...	89	2.762
			Aqueous Ammonia, 14.6*N*				
Para	0.0586	88.457	0.1123	10.6	13.9	12.2	3.505
	0.0869	87.300	0.1688	31.1	33.3	32.3	3.274
	0.0733	45.920	0.2707	54.4	57.8	56.1	3.038
	0.0296	5.681	0.8833	101.1	103.3	102.3	2.664
	0.0455	6.7439	1.143	116	120	118.0	2.557
	0.1141	4.4193	4.36	176	177	176.5	2.224
	0.1140	2.2541	8.51	199	204	201.5	2.107
	0.1141	1.7839	13.52	212	216	214.0	2.053
	0.1830	2.2375	13.69	233	241	237.0	1.960
Meta	0.0476	88.457	0.0912	0	1.7	0.83	3.651
	0.0501	49.212	0.1727	33.3	36.1	34.7	3.249
	0.0421	51.986	0.1373	33.9	37.8	35.8	3.237
	0.0386	47.900	0.1367	33.9	36.1	35.0	3.246
	0.0507	51.498	0.1670	34.4	38.9	36.7	3.228
	0.0220	6.0115	0.6205	96.1	98.3	97.2	2.700
	0.0487	6.7851	1.216	112	115	113.5	2.587
	0.0487	6.7836	1.217	119	120	119.5	2.547
	0.1109	4.2745	4.38	171	175	173.0	2.242
	0.0988	2.2218	7.49	192	199	195.5	2.134
	0.0998	2.2385	7.51	194	199	196.0	2.132
	0.1830	2.2285	13.74	...	226	224	2.012
	0.1455	1.7605	13.83	212	218	215.0	2.049
	0.2259	2.1051	17.89	239	240	239.5	1.951
	0.0637	5.4720[a]	1.87	131	133	132	2.467
	0.0788	5.1907[b]	2.24	146	148	147	2.378

[a] Solution 0.3*M* in NH_4ClO_4. [b] Solution 1.0*M* in NH_4ClO_4.

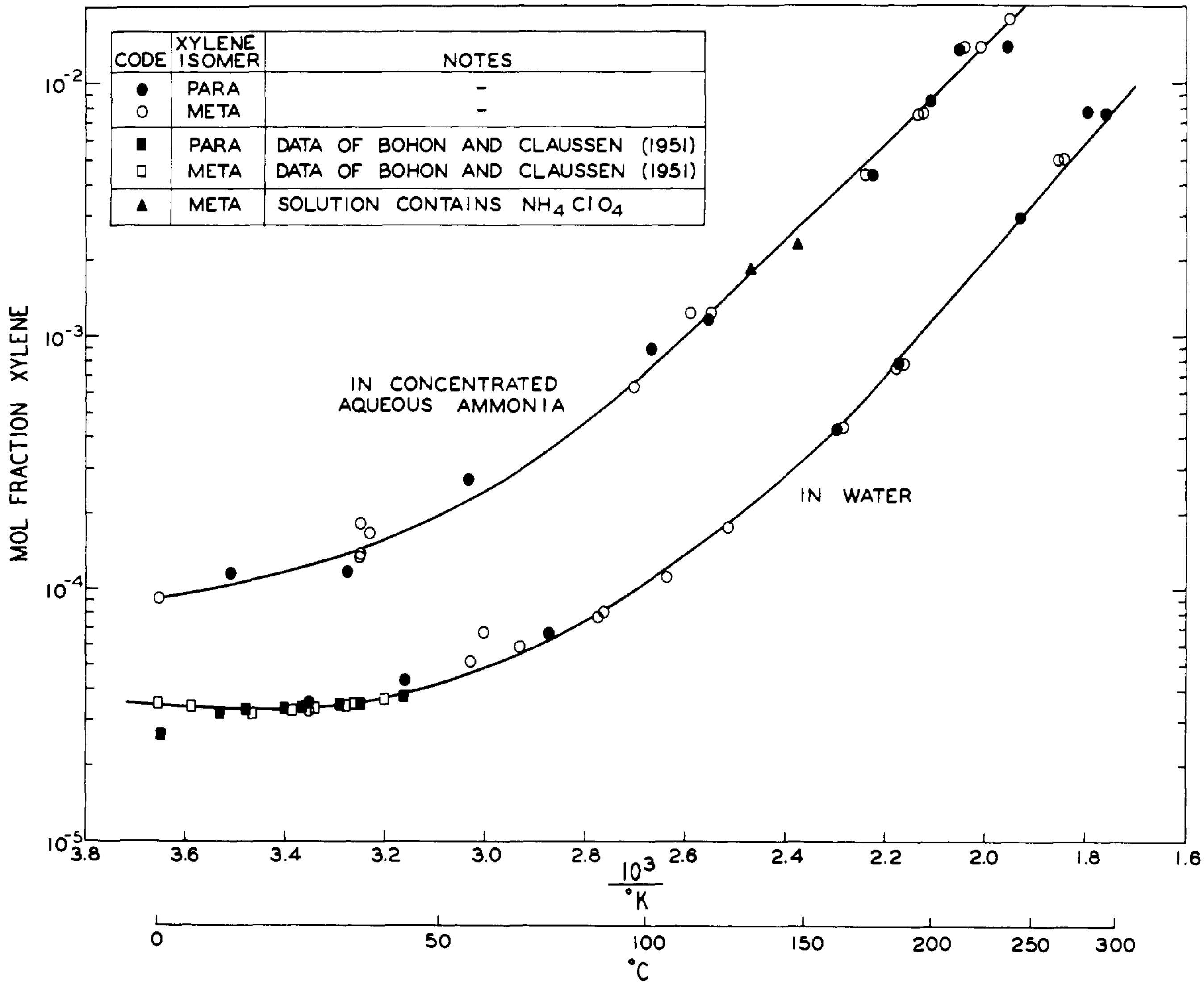

Figure 1. Solubility of *m*- and *p*-xylene in water and in aqueous ammonia

in water, x_2 = (moles of xylene)/(moles of water + moles of xylene). Concentrated aqueous ammonia is 30% by weight of ammonia and therefore contains 0.30/17.03 +0.70/18.02 = 0.05642 total mole per gram of solvent. (Because of the similar molecular weight of water and ammonia, the total number of moles per gram is relatively insensitive to the per cent ammonia—i.e., 28% aqueous ammonia contains 0.05634 mole per gram). Therefore, in aqueous ammonia, x_2 = (moles of xylene)/[(grams of aq. NH_3) (0.0564) + (moles of xylene)].

CONCLUSIONS

Figure 1 shows all of the data recorded in Table I, and also the data of Bohon and Claussen (*2*) which cover the region from 0° to 40° C. and were determined using a sensitive spectrophotometric technique. Within the experimental uncertainty, both isomeric xylenes have the same solubility and are four to seven times more soluble in aqueous ammonia than in water.

The data of Bohon and Claussen show that the solubility of xylene in water goes through a minimum at 18° C., and explanations for this were examined by those authors. Alexander (*1*) repeated and substantiated the measurements of Bohon and Claussen on the solubility of benzene in water, and also found a minimum in the solubility curve. The present results also agree with the data of Bohon and Claussen. The curve of the solubility for the xylenes in aqueous ammonia appears to be similar to that for water and may have a minimum which lies below the lowest temperature studied.

The increased solubility of xylene in aqueous ammonia relative to water is not due to the ammonium ion. This was shown by two experiments in which 0.3 and 1.0*M* ammonium perchlorate was added to the aqueous ammonia and found to have no effect on solubility. The perchlorate anion was chosen, since it has relatively little effect on benzene solubility in water (*6*) and therefore probably affects the solubility of xylene very little.

Hildebrand (*3, 4*) believes the greater solubility of toluene in liquid ammonia relative to water results from the larger dispersion force of the ammonia molecule. It is probable that these large London forces enable the ammonia molecule to coordinate with xylene and solubilize it in aqueous ammonia as well.

ACKNOWLEDGMENT

The authors are grateful to A.J. Duschka for assistance in making the measurements.

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RECEIVED for review December 15, 1958. Resubmitted July 15, 1960. Accepted October 31, 1960.