[CONTRIBUTION FROM THE UNIVERSITY OF BRITISH COLUMBIA]

Systems of Sulfur Dioxide and the Isomeric Xylenes

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A number of systems of sulfur dioxide and aromatic compounds have been studied. Thus Znozzetti and De Carli measured the freezing points of sulfur dioxide and benzene solutions and claimed to have obtained evidence showing the existence of three compounds.[1] In later publications F. De Carli states he had obtained compounds of sulfur dioxide with toluene, ethylbenzene and certain other derivatives of benzene. He made no mention of having investigated the three xylenes and, as it was of interest to know whether the three xylenes behaved in a similar manner with the solvent sulfur dioxide, a series of freezing point measurements were made on the three systems.

Materials.—The organic compounds used were obtained from Kahlbaum. As the ortho, meta and para xylenes were the purest available, no further purification beyond distilling over sodium was attempted. The sulfur dioxide was the usual C. P. variety supplied by Baker and Co. in little iron tanks. Before condensation, the gas was bubbled through dilute sulfuric acid to remove any sulfur trioxide, then through several wash bottles of concentrated acid and over phosphorus pentoxide to remove any traces of water.

Procedure.—The bulb method was used throughout as it was the most convenient and was considered to be sufficiently accurate for the results desired. Various amounts of the hydrocarbons were introduced into a series of bulbs by means of a thin-stemmed thistle tube. The bulbs, whose volumes averaged about 2.5 cc. and whose stems were about 20 cm. in length, were then capped and weighed to obtain the amount of xylene. Definite quantities of sulfur dioxide were next condensed in these tubes which were then sealed and weighed. The amounts of xylene and sulfur dioxide could thus be obtained directly, and as a check, the sulfur dioxide content was always determined after the freezing point had been found, by titration with sodium hydroxide.

Sulfur dioxide was introduced into the bulbs in two ways. In the case of *p*-xylene, the apparatus described in Vol. 23, p. 327, of the *J. Ind. Eng. Chem.* was used. Bulbs, containing weighed amounts of *p*-xylene, were cooled until the contents froze and they were then sealed onto the filling line. The air was removed by a mercury vapor pump (the xylene being kept frozen in the meantime) after which the desired amounts of sulfur dioxide were condensed in each bulb. It was found that if the air were not sufficiently removed, the contents of the bulbs became red and finally dark in color when allowed to attain room temperature. In the absence of air, however, solutions of any one of the xylenes and sulfur dioxide remained clear and colorless even after standing for some months at room temperatures.

In the case of ortho and meta xylene, whose freezing points are much lower than that of the para compound, a simpler method of filling the bulbs was found to be equally successful. All that was required was to cool the bulb containing the xylene, first sweep out the air with sulfur dioxide and then by further cooling cause the gas to condense. It was found that the amount of xylene vapor lost during the removal of the air was negligible.

The next step was to determine the freezing point of the solution in each bulb. A bath, containing 95% alcohol and a little ether, was set up in a Dewar tube and connected to a container from which liquid air was blown to cool the bath. A pentane thermometer, a platinum resistance thermometer, standardized by the Bureau of Standards, and one of the bulbs were placed in the bath. The temperature was slowly lowered by the liquid air until crystals appeared in the solution in the bulb. The temperatures on the thermometers were noted and the bath was allowed to warm slowly until only one or two crystals remained. The temperature was kept at this level for several minutes, or as long as there was no apparent increase or decrease in the size or number of crystals. The bath was then allowed to warm slightly and the point at which the crystals disappeared was taken as the freezing point. Because of the viscosity of the solutions it was difficult to stir the contents of the bulbs thoroughly; this of course affected the freezing point of the solution, hence reported freezing points would vary as much as one degree. The results recorded in Table I are the averages of three determinations. The freezing point of sulfur dioxide was taken as 75.43°.

TABLE I

p-XYLENE AND SULFUR DIOXIDE

p-Xylene, g.	Sulfur dioxide, g.	Sulfur dioxide, mol %	F. p., °C.
0.3998	0.0326	11.86	+ 8.9
.9009	.0872	13.81	+ 6.9
2.4287	.2435	14.20	+ 4.8
2.3583	.2767	16.27	+ 4.3
1.1742	.2325	24.67	+ 0.8
0.6574	.1447	26.71	− 1.1
.7376	.2294	33.99	− 6.1
.7152	.3503	44.75	−12.9
.4734	.2858	49.99	−17.6
.7422	.6067	57.52	−26.3
.5409	.6001	61.36	−29.3
.8552	.9192	63.93	−34.1
.7631	1.1330	71.07	−41.4
.3963	1.0023	80.70	−51.2
.2668	0.8867	84.70	−57.6
.1087	.5693	89.90	−64.2
.1596	8.0000	98.90	−76.8
.0412	10.9005	99.77	−75.9

Freezing point of *p*-xylene +13.2°.

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(1) C. Znozzetti and F. De Carli, *Gazz. chim. ital.*, **56**, I, 34–36 (1926).

TABLE II

o-XYLENE AND SULFUR DIOXIDE

o-Xylene, g.	Sulfur dioxide, g.	Sulfur dioxide, mol %	F. p., °C.
2.6440	0.1362	7.88	−31.0
0.9209	.0466	7.73	−31.2
1.7261	.2005	16.13	−34.4
0.7073	.1086	20.27	−36.5
.7585	.1298	22.08	−36.8
.9992	.3604	37.39	−41.2
.8724	.3921	42.67	−44.3
.3944	.2238	48.44	−47.5
.8109	.6969	58.69	−51.4
.6172	.5927	61.33	−53.0
.3099	.4853	72.11	−60.0
.0894	.2537	82.58	−66.1
.2714	1.4259	89.87	−72.0
.4684	3.0402	91.50	−72.7
.0398	0.6235	97.00	−77.0
.0524	1.2478	97.70	−78.1
.0685	2.5360	98.39	−78.3
.0318	1.5661	98.82	−78.7
.0223	2.4350	99.45	−76.4

Freezing point of *o*-xylene −27.1°.

TABLE III

m-XYLENE AND SULFUR DIOXIDE

m-Xylene, g.	Sulfur dioxide, g.	Sulfur dioxide, mol %	F. p., °C.
1.1390	0.0804	10.30	−54.9
1.8307	.3257	22.52	−57.4
1.2469	.3937	34.26	−59.8
1.0973	.8057	54.82	−64.0
1.1060	.9064	57.55	−64.7
0.8079	1.2128	71.32	−68.1
.4032	0.8916	78.62	−70.7
.4172	1.9854	88.89	−73.5
.2213	1.7839	93.07	−75.5
.1949	1.9730	94.78	−76.4
.3205	4.2585	95.65	−76.6
.1032	6.1136	98.99	−76.9
.1356	9.8676	99.18	−76.2
.1063	11.9383	99.46	−75.7

Freezing point of *m*-xylene −53.6°.

The data when plotted as curves in Fig. 1 show each system to have only one eutectic. Thus there is no indication of compound formation. To further test this point crystals of the hydrocarbons which formed from solutions containing varying amounts of sulfur dioxide were analyzed but with unsatisfactory results.

By utilizing the well-known equation

$$\ln N = \frac{-L}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)$$

the values of the latent heat of fusion were calculated. These are given in Table IV and compared with those measured directly.

TABLE IV

LATENT HEAT OF FUSION OF THE XYLENES

	Calculated	Temperature range, °C.	Found
p-Xylene	3560 cal.	13.2– 0.8	4168[a] cal.
o-Xylene	3550	−27.1−−42	3333[b]
m-Xylene	6317	−53.6−−57.4	2760[b]

[a] "International Critical Tables." [b] Rossini, *Bur. Standards J. Research*, **11**, 553–559 (1933).

It thus appears that the *o*-xylene and sulfur dioxide behave very nearly as ideal solutions but this is not so in the case of the two others, the *p*-xylene deviating positively and the *m*-xylene negatively from the ideal solution.

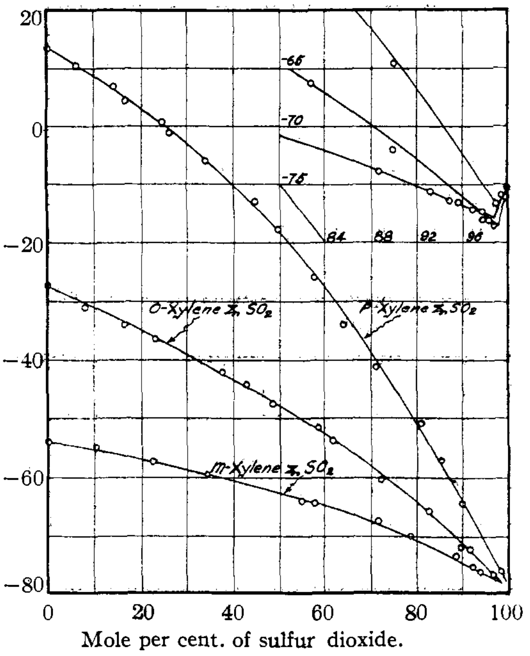

Fig. 1.

Summary

1. The freezing point curves of para, ortho and meta xylenes with sulfur dioxide have been constructed from freezing point data. There appears to be no compound formation, as there is only one eutectic in each case.

2. The calculated latent heats of fusion when compared with the experimental values show the para and meta solutions to deviate considerably from the ideal.

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