The anomalous behavior of the heat capacity of methyl alcohol vapor, showing first a decrease with a minimum at about 120° and then a normal increase of heat capacity with temperature, can be explained by assuming that part of the energy is required for the dissociation of associated methyl alcohol molecules. Vapor densities of methyl alcohol determined by Young[12] are probably of sufficient reliability to calculate the order of magnitude of the association. Assuming dimer formation, the fraction, x, of the molecules which were associated was calculated (Table III). A mixture of dimers and trimers is probably formed at higher pressures. Upon the assumption that trimers were formed, the fraction, x', was also calculated. By glancing at the tabulated results it is evident that association of the vapor occurs at the boiling point under atmospheric pressure. An extrapolation of the calculated values for 120 and 160° to one atmosphere of pressure shows that 0.8 and 0.3% of the molecules are associated at these temperatures as contrasted with about 9% at the boiling point. In view of the above discussion a new apparatus has been built to determine the heat capacity of the vapor at temperatures above 200° and at pressures less than one atmosphere.

TABLE III

DEGREE OF ASSOCIATION OF METHYL ALCOHOL VAPOR

t, °C.	Pressure in mm.	Mol. wt.	x	x'
20	96.0	32.3	0.016	
40	260.5	32.9	.054	
60	625.0	33.4	.083	0.062
70	927	33.8	.105	.079
80	1341	34.2	.128	.096
100	2621	35.3	.187	.140
120	1520	32.54	.031	.023
120	3040	34.16	.125	.094
120	4560	36.52	.245	.188
160	1520	32.11	(.004)	(.003)
160	3040	32.86	.050	.038
160	4560	33.63	.095	.071

Summary

The heat capacity of methyl alcohol vapor was determined at selected temperatures in the interval from 75 to 170°, using a Scheel and Heuse flow calorimeter. The vapor was heated electrically and the increase in temperature was measured with a ten-junction copper–constantan thermel. There is a flat minimum in the heat capacity curve from approximately 110 to 150°. This minimum can be explained by assuming the presence of associated molecules in the vapor state.

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[12] Landolt–Börnstein, "Tabellen," 5th ed., Vol. I, p. 278, Vol. II, p. 1361; "International Critical Tables," Vol. III, p. 436.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DUKE UNIVERSITY]

Solubility Studies. VI. The Solubility of Nitrobenzene in Deuterium Water and in Ordinary Water

BY HERBERT E. VERMILLION,[1] BURTON WERBEL, JOHN H. SAYLOR AND PAUL M. GROSS

In connection with our investigations of the solubilities of organic compounds in aqueous solutions, it was thought to be of interest to compare the solubilities of nitrobenzene in deuterium water and in ordinary water.

Experimental

The solubilities of nitrobenzene in deuterium water were determined both by the use of a Zeiss liquid–gas interferometer and by an analytical method.

The interferometer method previously described[2] was modified so that small samples could be used. An 8-cm. gold-plated interferometer cell was employed in the measurements. While the total capacity of the cell is about 25 ml., a cross section of only approximately 4 sq. mm. in each compartment is needed to permit passage of the light beam through the cell. Therefore a brass insert channelled to pass the light beam was fitted into each compartment of the cell to reduce the volume until a 5-ml. sample completely filled the cell.

Standard solutions for the calibration of the interferometer were prepared by weighing on a microbalance a droplet of nitrobenzene placed in the center of a weighed capillary tube. The tube and its contents were then dropped into a weighed Pyrex vial with a constricted neck and the desired amount of water (about 6 g.) added. The vial was then sealed off and weighed. The vials were then shaken until the nitrobenzene was in solution. Any transfer of deuterium water was always made in a special cabinet capable of maintaining a dry atmosphere.

The saturated solutions were prepared by shaking an excess of nitrobenzene with about 5 ml. of the solvent in

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[1] This paper was taken in part from the thesis submitted by Herbert E. Vermillion to the Graduate School of Duke University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1939.

[2] Gross and Saylor, THIS JOURNAL, 53, 1744 (1931).

TABLE I

THE SOLUBILITIES OF NITROBENZENE IN ORDINARY WATER AND IN DEUTERIUM WATER

	Interferometer method				Analytical method			
Temp., °C.	G./1000 g. H_2O	Moles/mole H_2O	G./1000 g. D_2O	Moles/mole D_2O	G./1000 g. H_2O	Moles/mole H_2O	G./1000 g. D_2O	Moles/mole D_2O
0	1.66[a][7]	0.000243						
6	1.70[b]	.000249	1.46	0.000238			1.43	0.000233
30	2.06[b] 2.06[c]	.000302	1.67	.000272	2.06	0.000302	1.70	.000277
50					2.64	.000387	2.13	.000347
60	3.12[b]	.000457						

[a] Supercooled liquid nitrobenzene. [b] Unpublished measurements of Dr. J. M. Stuckey. [c] The value of 2.06 g./1000 g. H_2O at 30° is in good agreement with that of 2.05 g./1000 g. H_2O obtained by Gross and Saylor.[2]

sealed Pyrex tubes placed in a constant temperature-bath. Dilutions were made in a 5-ml. flask in a manner similar to that previously described.[2]

The analytical method employed involved the reduction of the nitrobenzene in the saturated solutions to aniline, bromination of the aniline by the addition of a standard bromate solution plus an excess of bromide and acid, and the determination of the excess bromine iodometrically.

Some attempts were made to reduce the nitrobenzene solutions with zinc amalgam as suggested by Perrier and Lobunetz[3] and with $TiCl_3$ as used by Kolthoff.[4] However, these reducing agents did not give as consistent results and were not so easy to handle as zinc dust which has been used by Callan, Henderson and Strafford[5] and Kurtz, Headington and Zieber.[6]

A special sampling technique was employed in order to prevent contamination of the sample by the small amount of nitrobenzene present on the surface of the saturated solution. The vial was broken open and a tube with its end blown out to a thin bulb was inserted nearly to the nitrobenzene layer. The vial was closed by means of a piece of rubber tubing slipped over the tube and the neck of the vial. After a short time the bulb was broken by tapping it with a stiff wire and the tube stoppered. After fifteen minutes a 5-ml. pipet with a drawnout tip was inserted through the tube and a 5-g. sample removed to a weighed 25-ml. glass-stoppered reduction flask.

After the flask and the sample were weighed, 0.5 g. of zinc dust was added, the flask attached to a small reflux condenser and 4 ml. of 12 *M* hydrochloric acid added through the condenser in three portions at intervals of about one minute. After the second addition of acid, the flask was placed on a water-bath at 50°. After standing for a half hour, the contents of the flask were filtered and transferred quantitatively to an iodine flask. This filtration was found to be very important for when it was omitted the results obtained were often high.

Five ml. of 20% potassium bromide and 25 ml. of 0.025 *N* potassium bromate were added to the solution in the iodine flask. The lip of the flask was filled with freshly prepared 40% potassium iodide solution and the flask was kept below 15°. After fifteen minutes the flask was shaken, cooled in an ice-bath and 5 ml. of 40% potassium iodide added. The liberated iodine was immediately titrated with 0.025 *N* sodium thiosulfate, starch solution being added near the end-point.

The nitrobenzene was distilled under reduced pressure in a Hickman still and the best fraction further purified by fractional crystallization. The freezing point of the substance used was 5.6–5.7°. Different samples of deuterium water obtained from the California Isotope Company and from the Norsk Hydro-Elektrisk Kvaelstofaktieselskab were used. They contained 99.5–99.6% deuterium water.

Results

The experimental results are listed in Table I together with some measurements by Dr. J. M. Stuckey of the solubilities of nitrobenzene in ordinary water. In these cases the saturated solutions were analyzed by means of the interferometer using our previously described procedure.[2] Every result is the mean of at least two individual determinations.

The fact that the solubilities of nitrobenzene in deuterium water are found to be always less than those in ordinary water might be interpreted as originating from or at least paralleling structural differences in the solvents. However, such differences in solubility have not been adequately explained in terms of the structural constants of the two molecules.

Acknowledgment.—We wish to acknowledge the help of Charles N. Miles in working out the analytical method used in these determinations.

Summary

The solubilities of nitrobenzene in deuterium water have been determined at 6, 30 and 50° by two different methods and compared with those in ordinary water.

DURHAM, N. C.

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(3) Perrier and Lobunetz, *Bull. Sci. Univ. Kiev*, **2**, 73 (1936).

(4) Kolthoff, *Chem. Weekblad*, **22**, 558 (1925).

(5) Callan, Henderson and Strafford, *Soc. Chem. Ind.*, **39**, 88T (1920).

(6) Kurtz, Headington and Zieber, *Ind. Eng. Chem., Anal. Ed.*, **8**, 3 (1936).

(7) Saylor, Stuckey and Gross, THIS JOURNAL, **60**, 373 (1938).