As$_4$–As$_5$ and As$_4'$–As$_5'$ being broken. Atom As$_4$ would then have to be bonded to an atom As$_3''$ of a molecule related to the unprimed molecule by a screw axis, as described earlier, and similarly As$_4'$ to an atom As$_3'''$. The unprimed and primed molecules thus would be at the end and beginning of chain segments which are tied together by an As$_5$–As$_5'$ bond. It is not likely that such interruptions of the chains described earlier occur with the regularity required by the periodicity of a crystal and the formation of bonds As$_5$–As$_5'$ is thus presumed rare.

While the molecular structure of the yellow form of arsenomethane is that of a puckered substituted five-ring as described in the foregoing, a crystal structure investigation of the related substance arsenobenzene[19] has shown it to consist of hexameric molecules, As$_6$(C$_6$H$_5$)$_6$, the As atoms forming a puckered six-ring of symmetry $\bar{3}$ m and each carrying a phenyl group. No explanation for this difference between the two compounds has been found.

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HOUSTON, TEXAS

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[19] K. Hedberg, E. W. Hughes and J. Waser, reported at the San Francisco, Calif., Meeting of the American Chemical Society, March, 1949.

[CONTRIBUTION FROM THE RICHARD BENBRIDGE WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

The Solubility of Water in Aromatic Halides[1]

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The solubilities of water in benzene, toluene, fluorobenzene, chlorobenzene, bromobenzene, iodobenzene and *o*-dichlorobenzene were measured by an isotopic dilution technique using tritiated water as the tracer and counting as acetylene. Hildebrand's solubility formula was applied to the experimental results and values of the solubility parameter δ_2 were obtained. The high values of δ_2 in the case of the halides were explained in terms of the polarity effect on solubility.

Although numerous measurements have been reported for the solubility of water in organic liquids, the solvents were in most cases nonpolar.[3–11] In 1948 Taylor, *et al.*, determined the solubilities of water in various hydrocarbons using tritium hydroxide as a tracer.[3,4] In the present paper a series of measurements are reported for the solubilities of water in various polar organic liquids using tritium as a tracer. A new method was developed for counting tritiated water involving a simple one-step conversion to acetylene.[12]

The sensitivity of modern radiochemical methods have a natural application to the measurement of small solubilities.[13] In the case of water in benzene, the value obtained in the present work is compared with those reported by six previous investigators.

Hildebrand's solubility formula[14] was applied to the experimental solubilities of water in benzene, toluene, fluorobenzene, chlorobenzene, bromobenzene, iodobenzene and *o*-dichlorobenzene. The high values of δ_2 indicate a polarity effect on solubility.

Experimental

Reagents.—Tritiated water with an activity of approximately 1 mc. per ml. was supplied by Tracerlab, Inc. The organic solvents, chemical grade, were redistilled in a column of 50 theoretical plates. The iodobenzene was purified by the Esso Research and Engineering Company by means of distillation in an 80-plate column with stainless steel Helipak packing. Following purification, this solvent appeared slightly pink due to the presence of a trace of free iodine. The iodine was removed by extraction with 0.1 *F* sodium sulfite solution; the iodobenzene phase was rinsed with water, dried with calcium hydride overnight and filtered.

Solubility Measurements.—In each measurement a small amount of tritiated water was equilibrated with 20 ml. of organic liquid using a Teflon stirrer in a 100-ml. flask in a Sargent constant temperature bath maintained to ±0.02°. At the end of two hours, the mixture was poured into a test-tube immersed in the bath and the organic phase separated from water by gravitation. The efficiency of this separation was reasonably established by the excellent reproducibility of the measurements. The determination of THO in the organic phase was done by isotopic dilution with a large excess of H$_2$O. A 5.0-ml. aliquot of the equilibrated solvent was removed and mixed with 5.00 ml. of distilled water for two hours at the same temperature. After the two phases were again separated, aliquots of the water phase were withdrawn and analyzed for tritium content.

Measurement of Tritium Activity.—The tritium activities in the tritiated water samples were determined by the acetylene method previously described by the authors.[12] The essential procedure was to pass the tritiated water as a gas through a previously evacuated calcium carbide column, introduce the product acetylene into an evacuated Geiger counter, accurately measure the pressure, add argon gas and count with an ordinary scaler. As previously reported, the fractionation in this reaction was 0.53, *i.e.*, the specific activity of the acetylene was 53% of the specific activity of the original water sample.[12] In studying this fractionation it

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[1] (a) Taken in part from a thesis submitted by James Wing to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) This work was supported in part by the U. S. Atomic Energy Commission under contract At(11-1)-166 with Purdue University.

[2] Purdue Research Foundation Fellow, 1955.

[3] C. Black, G. G. Joris and H. S. Taylor, *J. Chem. Phys.*, **16**, 537 (1948).

[4] G. G. Joris and H. S. Taylor, *ibid.*, **16**, 45 (1948).

[5] C. W. Clifford, *Ind. Eng. Chem.*, **13**, 631 (1921).

[6] E. Groschuff, *Z. Elektrochem.*, **17**, 348 (1911).

[7] A. E. Hill, THIS JOURNAL, **45**, 1143 (1923).

[8] J. A. K. Staveley, J. H. E. Jeffes and J. A. E. Moy, *Trans. Faraday Soc.*, **39**, 5 (1943).

[9] A. J. Staverman, *Rec. trav. chim.*, **60**, 836 (1941).

[10] N. D. Tarassenkow and E. N. Poloshinzewa, *Zhur. Obshchei Khim.*, **1**, 71 (1931); *Ber.*, **65**, 186 (1932).

[11] C. K. Rosenbaum and J. H. Walton, THIS JOURNAL, **52**, 3571 (1930).

[12] J. Wing and W. H. Johnston, *Science*, **121**, 674 (1955).

[13] W. H. Johnston, *ibid.*, **124**, 801 (1956).

[14] J. H. Hildebrand, *J. Chem. Phys.*, **17**, 1346 (1949).

was shown that acetylene exchanged tritium with hydrated calcium hydroxide by a complex kinetic process. Part of the observed fractionation undoubtedly was due to this exchange reaction. Nevertheless, the method is quantitative since this fractionation was demonstrated to be easily reproducible.

Results and Discussion

Experimental Solubilities.—The experimental measurements of solubility are summarized in Table I. The solubilities are expressed in cc. of water per 100 cc. of solution. The deviations are empirical per cent. standard deviations of each set of measurements.

TABLE I

MEASURED VALUES FOR THE SOLUBILITIES OF WATER IN VARIOUS SOLVENTS AT 25.0°

Solvent	No. of measurements	Solubility $\times 10^2$	Stand. dev., %
Benzene	6	5.54	0.9
Toluene	5	3.34	0.8
Fluorobenzene	6	3.16	2.5
Chlorobenzene	5	3.60	2.8
Bromobenzene	5	4.24	2.3
Iodobenzene	5	5.03	1.6
o-Dichlorobenzene	5	3.09	1.5

In Table II the result for benzene is compared with the reported values of six previous workers.

TABLE II

COMPARISON OF SOLUBILITY[a] OF WATER IN BENZENE AT 25°

This work	0.0635
Clifford[5]	.053[b]
Groschuff[6]	.065[b]
Hill[7]	.073
Rosenbaum[11]	.067
Tarassenkow[10]	.069
Taylor[4]	.053[b]
Av. (excluding this work)	.063

[a] Cc. water in 100 g. benzene. [b] Interpolated value.

The value in the present work is close to the average value of the other six measurements. Taylor's value is low possibly due to complications in the measurement of the tritium activity. In his method tritiated water was absorbed on calcium oxide and the tritium was extracted for counting by isotopic exchange with ethanol vapor at 250°. Incomplete exchange or isotopic fractionation would tend to give low results by this technique.

The solubility data in the present work were substituted into Hildebrand's semi-empirical formula[14]

$$0 = \ln \varphi_2 + \varphi_1 \left(1 - \frac{V_2}{V_1}\right) + V_2 \varphi_1^2 (\delta_2 - \delta_1)^2 / RT, \quad (1)$$

where

φ = volume fraction
V = molar volume
δ = solubility parameter = $\left(\frac{\Delta H - RT}{V}\right)^{1/2}$
ΔH = heat of vaporization

The values of δ_2 calculated from this equation are listed in Table III. The values of ΔH were obtained from the vapor pressures in Lange's[15] Handbook for benzene and toluene and from Stull[16] for the other compounds. It is interesting to note that Stull's data give ΔH values of 9.15 and 9.35 for benzene and toluene in disagreement with Lange's values corresponding to 8.06 and 9.00 for these compounds, respectively. The lower values were used by Hildebrand and appear more reasonable in view of the low polarity of these molecules. Stull's values of ΔH for chlorobenzene, bromobenzene and iodobenzene, however, agree well with Lange's values.

The aromatic halides give an average value of 24.9 ± 0.1 for δ_2, which is significantly higher than the value of 23.5. The hydrocarbons exhibit slightly lower value for δ_2 of around 24.0. (Values of δ for other hydrocarbons can be found in reference 14). The high values of δ_2 for the halides is a result of their high δ and low φ_2 values in eq. 1. This may be expected for the aromatic halides, which possess some degree of dipole moment, from the following considerations.

The dipole–dipole attraction in a pure polar solvent generally requires a large heat of vaporization, which means high δ. Fluorobenzene with low ΔH has high δ due to its small molar volume.

There is a general decrease in solubility as the polarity of the solvent increases (Table III). This may be the result of the difference in polarity interaction between the polar solvent and water. In the pure liquid form, the polar solvent (or solute) is in an oriented stable state. When a polar solute is brought in contact with this solvent, the stronger polar solvent will show a larger difference in the interaction (orientation) of the solute and solvent dipoles, a condition for reducing the solubility as implied in eq. 1 by the term $(\delta_2 - \delta_1)$.

Thus, the increased ΔH and the reduced φ_2 as the result of dipole interaction give rise to high values of δ_2 in the aromatic halide series. It is suggested that a possible improvement in Hildebrand's solubility formula may be based upon these polarity effects.

TABLE III

SOLUBILITY PARAMETERS

Solvents	$10^4\varphi_2$	$10^4 x_2$	V_1	ΔH_1	$\delta_2 - \delta_1$	δ_1	δ_2
C_6H_5H	5.54	27.4	89.4	8.06	14.8	9.1	23.9
$C_6H_5CH_3$	3.34	19.7	106.4	9.00	15.3	8.9	24.2
C_6H_5F	3.16	19.6	93.8	8.72	15.4	9.3	24.7
C_6H_5Cl	3.60	20.3	101.7	9.90	15.3	9.6	24.9
C_6H_5Br	4.24	24.6	105.0	10.78	15.1	9.8	24.9
C_6H_5I	5.03	31.2	111.8	11.23	14.9	9.8	24.7
$C_6H_5Cl_2$	3.09	19.3	112.6	11.47	15.5	9.8	25.3
H_2O				10.49			23.5

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(15) N. A. Lange, "Handbook of Chemistry," 7th Ed., Handbook Publishers, Inc., Sandusky, Ohio, pp. 1442, 1460. See also "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," The American Petroleum Institute, Carnegie Press, 1953, p. 490.

(16) Dr. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).