

TABLE 1

Series or Mixed	%Tri- iso- buty- lene	Specific retention volume				No. of Theoretical Plates for injection for Propy- lene	Reten- tion time from injection for Propy- lene min.
		Ethane	Ethy- lene	Pro- pane	Propy- lene		
—	nil	0.14	10.4	0.14	15.6	—	—
—	100	5.2	3.2	22.1	20.5	—	—
Series	49.3	2.5	6.8	10.7	17.3	1012	8.4
Mixed	47.2	2.5	7.6	10.6	17.9	1134	8.8
Series	27.2	1.3	9.0	5.7	17.0	990	7.1
Mixed	23.5	1.2	9.8	5.1	17.3	1075	7.1

of the column(s) immediately after use. Operating conditions: support, 85–100 mesh 'Celite'; stationary phase, 1 part approximately to 4 of support; column temperature, 12°C. (tap water); inlet pressure, 5 cm. of mercury (gauge) for single 4-ft. columns, 10 cm. for combined 8-ft. columns; outlet pressure, atmospheric; carrier gas, nitrogen, approximately 20 ml. per min.; detector, hydrogen flame (temp.)

The ethylene glycol/silver nitrate contained 27 per cent by weight of silver nitrate. A saturated solution at 12°C. contains about 42 per cent w/w. The triisobutylene was old stock and contained approximately 5 per cent of an acid calculated as C₁₂. A study of Fig. 1 and Figs. 1a and 1b in Barnard and Hughes¹ communication suggests that their 'series' column contained practically no triisobutylene and that their "mixed" column contained about 10 per cent triisobutylene and 90 per cent ethylene glycol/silver nitrate. Triisobutylene is appreciably volatile, and in our experiments it was found that the mixing operations caused a loss of about 10 per cent on a total of 2.5 gm. Our experiments were done at 12°C. merely to allow more precise measurement of the rather short retention times. A check at 25°C. showed that the differences from relative retention volumes at 12°C. for the same column were not very great, but ethane and hydrogen were not well separated which made precise measurement difficult.

I wish to thank the Directors of the Distillers Company Limited for permission to publish this communication.

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¹ Barnard J. A., and Hughes, H. W. D., *Nature*, **183**, 250 (1959).

Use of Tritium to Study the Solubility of Water in Hydrocarbons

THE use of tritiated water as a radioactive tracer to study the solubility of water in hydrocarbons clearly offers many advantages, especially the fact that low concentrations of water in a hydrocarbon can be easily and accurately assayed by liquid scintillation counting. We have adopted this technique to make a closer study of how well Henry's Law is obeyed for such a system. Black, Joris and Taylor^{1,2} used tritium with a gas counting technique for a similar investigation and assumed, along with others³, that Henry's Law was followed up to saturation point. In the discussion of the latter paper³ some evidence was put forward to suggest that substantial deviations from Henry's Law were observed for water dissolved in hydrocarbon fuels. More recently Englin *et al.*⁴ have published results substantiating the original assumptions. The work described below using the more sensitive techniques of liquid scintillation counting of HTO as a tracer is claimed to be the most accurate study of the water-hydrocarbon system to date.

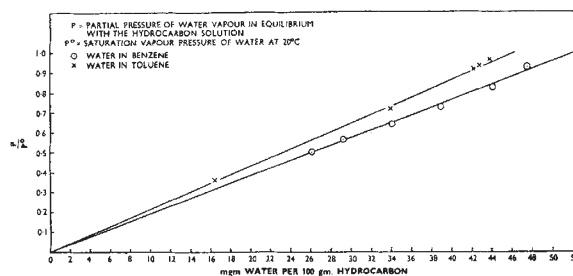


Fig. 1. Solubility of Water in Benzene and Toluene at 20°C.

A stream of dry air was saturated with tritiated water at temperature T_1 and was allowed to come to equilibrium with the hydrocarbon liquid at temperature T_2 ($T_2 > T_1$). Samples were taken of the hydrocarbon after equilibration and counted after dissolving in a liquid phosphor.

By varying T_1 and keeping T_2 constant it was possible to obtain a series of values of equilibrium water solubilities corresponding to different water vapour partial pressures. It is convenient to express the vapour pressure data as the function p/p_0 where p = water vapour pressure at T_1 and p_0 = water vapour pressure at T_2 . These values were calculated having ascertained experimentally that the saturator and the air steam velocity were such as to ensure saturation at temperature T_1 . Typical results are given for benzene and toluene in Fig. 1 showing that there is virtually no deviation from Henry's Law up to saturation. Saturation solubilities at 20°C. of water in benzene and toluene are found to be 52 mgm./100 gm. and 46 mgm./100 gm. respectively. The value for toluene compares very favourably with that obtained by Englin *et al.*⁴ (48 mgm./100 gm.).

Precautions were taken to ensure that equilibrium conditions were established during the experiments. For calibration purposes the specific activity of the air stream in equilibrium with the hydrocarbon was determined. This was done by condensing out the water vapour and counting it under identical conditions to those pertaining to the counting of the hydrocarbon samples. Under these conditions it was lower by 15 per cent than that of the original water in the saturator; this was due to the isotope effect of tritium. The data given in Fig. 1, however, refer to the behaviour of water, which of course assumes that any isotope effect of water and tritiated water, when dissolved in a hydrocarbon, is negligible.

The liquid scintillation counter used was a single channel instrument. By giving special attention to the design of the sample cell used to contain the liquid phosphor it was possible to operate at room temperature for all the experiments described above. The maximum counting efficiency for non-quenching tritium samples was 12 per cent over a background of 300 c.p.m.

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¹ Joris, G. G., and Taylor, H. S., *J. Chem. Phys.*, **16**, 45 (1948).

² Black, C., Joris, G. G., and Taylor, H. S., *J. Chem. Phys.*, **16**, 537 (1948).

³ Davies, P. L., Fourth World Petroleum Congress Section V/E, 427 (1955).

⁴ Englin, B. A., Tuglulukov, V. M., Sakodinskaya T. P., *Khimiya i Tekhnologiya Topliva*, **11**, 43 (1956).