# The Solubility of Propylene Vapor in Water as Affected by Typical Detergents

By James W. McBain and A. M. Soldate

It has been shown[1,2] that potassium oleate added to water greatly increases the amount of hydrocarbon which can dissolve. The solubilized hydrocarbons are incorporated in or upon the colloidal particles or micelles of the soap, thus lowering the vapor pressure of the hydrocarbon and leaving the freezing point of the soap solution unaffected.

These observations are now extended to a series of typical detergents, surface active agents, and other substances in order to determine whether such solubilization always occurs with detergents, and to contrast it with the effects of salts and mixed solvents. The result is to show that all the detergents tested exhibit this property, whereas salts such as a carbonate, pyrophosphate, or a Calgon do not; and much larger quantities of an organic solvent must be added to produce a comparable effect.

## Experimental

Propylene was used in all experiments following the procedure already described.[1] Although evacuation was carried out in each case for half an hour in a Cenco Hyvac pump, the evacuation was necessarily incomplete.[3] All data refer to solutions at $25°$.

Since it was not always convenient to arrange for the same equilibrium pressure, it was assumed that Henry's law could be used within the range 500 to 700 mm. pressure. Hence all the data are expressed in terms of grams of propylene dissolved per gram of water per mm. pressure for this range.

## The Data

The observations are collected in Table I, which gives the amount of detergent, salt, or other substance added expressed as per cent. (meaning, however, grams per 100 cc. of solvent), and the values of $x/m$, multiplied by $10^5$, and a comment as to the effect noted.

## Discussion

The chief result is to show that all the detergents exhibit solubilizing action for propylene in water, as well as for otherwise insoluble dye.

(1) J. W. McBain and J. J. O'Connor, THIS JOURNAL, 63, 875 (1941).
(2) J. W. McBain and J. J. O'Connor, ibid., 62, 2855–59 (1940).
(3) J. W. McBain and M. Taylor, Z. physik. Chem., 76, 179 (1911).

TABLE I

THE SOLUBILITY OF PROPYLENE IN AQUEOUS SOLUTIONS[a] AT $25°$ IN GRAMS $\times 10^{-5}$ OF PROPYLENE PER GRAM OF WATER PER MM. PRESSURE FOR THE RANGE 500–700 MM.

| Solution | | Mean | Effect |
|---|---|---|---|
| Water only | 3.5, 3.4, 3.4, 3.3 | 3.4 | standard |
| 15% potassium oleate | | 18.7 | great |
| 12% potassium oleate | 14.3, 15.6, 14.8 | 14.9 | great |
| 9% potassium oleate | | 12.5 | great |
| 1% potassium oleate | 3.4, 3.3, 3.5, 3.9, 3.9 | 3.7 | slight |
| 15% pure Tergitol 4 | | 13.6 | great |
| 1.5% Aerosol OT | | 7.5 | fair |
| 1% Aerosol OT | 3.9, 3.0, 3.3, 3.2, 3.4 | 3.4 | none |
| 15% Aerosol MA | 11.2, 10.8 | 11.0 | good |
| 15% Mixture; 1 pt. OT, 4 pts. MA | 9.8, 10.4 | 10.1 | good |
| 15% Aerosol AY | 7.7, 8.0, 10.9 | 8.9 | good |
| 1% Aerosol AY | 2.8, 3.1 | 3.0 | none? |
| 15% Aerosol IB | 5.5, 5.8 | 5.7 | fair |
| 10% Aerosol IB | 4.9, 4.3 | 4.6 | fair |
| 15% Aerosol OS | 7.0, 7.1 | 7.1 | fair |
| 15% sodium deoxycholate | | 6.1 | fair |
| 15% sodium dehydrocholate | | 0.8 | salts out! |
| 15% Aquasol AR (Turkey Red Oil) | | 14.4 | great |
| 15% Igepon A (thixotropic) | 7.6, 7.8 | 7.7 | fair |
| 15% of 95% Triton NE | | 11.3 | good |
| 15% of 90% Alronal | 11.5, 13.3 | 12.4 | good |
| 25% Triton K 60 | | 32.6 | great |
| 15% potassium novenate | | 11.2 | good |
| 10% Nacconol NR | | 9.2 | good |
| 10% Sapamine KW | | 5.4 | fair |
| 15% diethylcarbitol | | 3.7 | slight |
| 0.4% Calgon | 3.6, 3.6, 4.1 | 3.8 | none? |
| 2% Calgon | | 3.3 | none |
| 5% Calgon | | 3.8 | none |
| 12% KO1 + 0.2% Calgon | | 14.6 | Calgon none |
| 12% KO1 + 3% Calgon | | 15.2 | Calgon none |
| 5% K₂CO₃ | | 3.0 | negative |
| 0.5% K₂CO₃ | | 3.5 | none? |
| 12% KO1 + 5% K₂CO₃ | | 15.9 | K₂CO₃ slight |
| 12% KO1 + 0.2% K₂CO₃ | | 14.1 | K₂CO₃ slight |
| 12% KO1 + 2% tetrasodium pyrophosphate | | 14.5 | phosphate none |
| 12% KO1 + 5% tetrasodium pyrophosphate | 15.0, 16.1 | 15.6 | phosphate none |

[a] For a description of the active agent in materials here designated only by trade names, see Ind. Eng. Chem., 31, 66 (1939); 33, 16, 740 (1941).

This is strikingly emphasized by the contrasting behavior between the detergent, sodium deoxycholate, and the closely similar non-detergent, sodium dehydrocholate. Whereas the former doubled the solubility of propylene in water, the latter salts out three-quarters of what would otherwise dissolve in the water alone. Frazer, Stewart and Schulman have stated[4] that bile salts form no complexes with paraffin, but this is evidently not true in solution; therefore, the solubilized paraffin may be of some significance in experiments on digestive processes.

(4) Frazer, Stewart and Schulman, Nature, 149, 167 (1942).

Salts, as such, have a definite salting out effect, although the present method is usually too insensitive to show the influence of only a few per cent. of either salt or detergent. A small amount of electrolyte may have an enormous effect upon the viscosity of such a detergent as potassium oleate without altering its solubilizing power very noticeably. 15% detergent usually increases the solubility many fold, the highest value in Table I being 18.7 for potassium oleate. Even this is only a small fraction of the amount of propylene which would dissolve in equal weight of a similar pure organic solvent.

In contradistinction to the detergents, the addition of 15% of a good organic solvent has a comparatively negligible result. Thus 15% diethyl carbitol increases the solubility of propylene by only 10% of that of water alone. This again illustrates the difference between solubilizing by detergents which can be appreciable with only a few tenths of a per cent., whereas in hydrotropy with the addition of a good miscible solvent, very high concentrations are required to get a comparable result. The difference is that in the mixed solvent the added molecules are separate and are submerged in the excess of first solvent whereas with the detergent or colloidal electrolyte the solute is segregated in colloidal particles, which themselves incorporate the solubilized material.

## Summary

A further study of the effect of added substances upon the solubility of propylene in water is to show that all the detergents tested greatly increase the amount of propylene dissolved, in spite of any salting out action which they may otherwise possess. This solubilizing effect is shown by anion active, cation active, and nonelectrolytic detergents.

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# The Effect of Temperature and Solvent Type on the Intrinsic Viscosity of High Polymer Solutions

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According to hydrodynamics, the specific viscosity of a Newtonian liquid containing a small amount of dissolved material should depend in first approximation only upon the volume concentration and the shapes of the suspended particles. By suitable application of such hydrodynamical considerations to solutions of long chain molecules, it is possible in a rough fashion to derive the Staudinger–Kraemer equation, denoting proportionality between specific or intrinsic viscosity and molecular weight. It is an experimental fact, however, that the proportionality constant, $K_m$, is dependent not only upon the type of polymer concerned, but also upon the temperature and the nature of the solvent. Even in the dilute range, where specific viscosity is linear with concentration, these variations are often quite considerable. This paper tries to treat such variations in a systematic fashion, and to advance for them an explanation which is based upon changes in the average geometrical shape of the particles. A relationship between intermolecular and intra-molecular agglomeration tendency is presented.

**Theoretical Considerations.**—According to Burk,[1a] Eyring,[2] Flory,[3] Guth,[4] Huggins,[5] Kuhn,[6] Mark,[7] and Meyer,[8] a long chain hydrocarbon molecule in solution takes on a somewhat kinked or curled shape, intermediate between a tightly rolled up mass and the rigid linear configuration assumed by Staudinger.[9] Presumably all possible degrees of curling are represented, owing to the internal Brownian movement of the flexible chains, but the configurations of intermediate extension predominate statistically. The average or effec-

(1a) R. E. Burk and L. Laskowsky, J. Chem. Phys., 7, 465 (1939).

(2) H. Eyring, R. E. Powell and W. E. Roseveare, THIS JOURNAL, 60, 3113 (1940); Ind. Eng. Chem., 33, 430 (1941).

(3) P. J. Flory, THIS JOURNAL, 61, 3334 (1939); 62, 1057 (1940).

(4) E. Guth and H. Mark, Monatsh., 65, 94 (1934); E. Guth and H. M. James, Ind. Eng. Chem., 33, 624 (1941).

(5) M. L. Huggins, J. Phys. Chem., 42, 911 (1938); 43, 439 (1939); J. Appl. Phys., 10, 700 (1939).

(6) W. Kuhn, Koll. Z., 68, 2 (1934); 76, 258 (1936); 87, 3 (1939); Z. physik. Chem., A161, 427 (1932).

(7) H. Mark and E. Valko, Kautschuk, 6, 210 (1930); H. Mark, Koll. Z., 53, 32 (1930).

(8) K. H. Meyer, G. V. Susich and E. Valko, ibid., 59, 208 (1932); K. H. Meyer, ibid., 95, 70 (1941).

(9) H. Staudinger and collaborators, Ber., 68, 707 (1935); ibid., 70, 1565 (1937); Melleand, 18, 681 (1937); 20, 693 (1939).