nearly equal—a result which was still more conspicuous in previous experiments.[6]

Thus the empirical formula for the activity coefficient of different ions $\log f = 3.8_2 \sqrt{\mu}$ found previously for ethyl alcoholic solutions with $\epsilon T = 7325$ is essentially the same ($3.7_6$) for isopropyl water mixtures with $\epsilon T = 7380$. This fact makes it probable that the activity coefficient is hardly influenced by the individual properties of the ions (diameter, etc.) and of the solvent, apart from its dielectric constant.

Similarly a certain range of concentration was found[7] in aqueous solutions in which the limiting law of Debye and Hückel is not valid, but in which the individual properties of the ions play no essential part. In aqueous solutions this range of concentration joins that in which the limiting law is fulfilled. It seems that, in general, there exists a range of concentration in which the limiting law is not fulfilled, but in which the individual properties of the ions are of inferior significance, and that this range follows immediately the range of the limiting law. If that is the case all our experiments carried out with solvents of dielectric constants of about 25 at room temperature fall in this range. Further experiments, first in still more dilute solutions, and second in other different solvents of the same dielectric constant, will show whether our results are verified by further material and if there exists in media of small dielectric constants a range in which the limiting law is at all valid. Such experiments are being carried out in Vienna.

## Summary

The influence of additions of silver nitrate, sodium nitrate and sodium benzene sulfonate on the solubility of silver bromate in mixtures of water and isopropyl alcohol of the dielectric constant 25.6, and of additions of lithium chloride on the solubility of potassium bromate in ethyl alcohol of the dielectric constant $25.7_8$ has been investigated within a range of concentration between $10^{-3}$ and $10^{-4}$ mole per liter. The results show approximately linear dependence of the logarithm of the activity coefficient on the square root of the ionic strength $\log f = 3.7_6 \sqrt{\mu}$. They can be explained by the approximation of Gronwall, La Mer and Sandved, taking ion radii of the size of 2.5 to 2.8 Å. The experiments make it obvious that in the considered range of concentration neither the individual properties of the ions (radius) nor the specific properties of the solvent, except its dielectric constant, are of appreciable significance to the activity coefficient.

VIENNA, AUSTRIA RECEIVED SEPTEMBER 15, 1937

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[6] Ph. Gross, *Z. Elektrochem.*, **36**, 786 (1930).

[7] H. v. Halban and G. Kortüm, *Z. physik. Chem.*, **A170**, 351 (1934).

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[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, U. S. DEPARTMENT OF AGRICULTURE]

# The Solubility of Rotenone. II. Data for Certain Additional Solvents

BY HOWARD A. JONES AND SOLOMON LOVE

In a previous publication the solubility of rotenone at 20° in twenty-one organic solvents was reported.[1] The purpose of the work described herein was to obtain similar data on a large number of additional solvents, many of which are used at present or may find use in the commercial handling of rotenone and rotenone preparations. A temperature of 25° was adopted because it was maintained more readily with the equipment at hand than was the temperature of 20° used in the earlier work. The solubility in a few solvents was also determined at higher temperatures.

**Methods Used.**—It was desired to employ a method that would make use of smaller quantities of solvent and give more accurate results on materials of low solvent power than the method involving optical rotatory power previously used. At first a procedure utilizing the refractive index of solutions of rotenone was employed, as follows.

Several solutions of known graded concentrations in a given solvent were prepared and their refractive indices determined at 25°, after which a graph showing the relation of the two properties was constructed. Saturated solutions were then prepared at 25°, the equilibrium condition being approached from both sides. A minute amount of seed crystals was used to initiate crystallization in the supersaturated solution. All mixtures were shaken for twenty-four hours, and then their refractive indices were determined. If the values agreed, no further shaking was done; if not, the shaking was continued until equilibrium was established. The value for concentration corresponding to the refractive index of the saturated solution was read from the graph.

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[1] H. A. Jones and C. M. Smith, THIS JOURNAL, **52**, 2554 (1930).

This method was found to be rapid and convenient but not sufficiently accurate, because of the small changes of refractive index encountered. Accordingly it was used only as a rapid means of establishing the approximate solubility value of a large number of the solvents tested.

A simple synthetic method was finally adopted as follows.

A series of mixtures of rotenone and solvent ranging around the condition of approximate saturation were shaken at 25° for at least twenty-four hours, or until equilibrium was established. The solutions were then examined to determine whether the rotenone was dissolved completely. The concentrations used were narrowed down successively until the result was within the desired degree of accuracy. To prove that the value so obtained was that of the equilibrium condition, a new solution, at slightly above the supposed solubility value, was prepared by warming. Upon cooling to 25°, seeding with rotenone crystals and shaking at 25°, the separation of a small amount of crystalline material was taken as evidence that the value determined did not differ appreciably from the true solubility value.

Most of the solutions were kept at 25° in a constant-temperature air cabinet. Values at 35° were determined by the same method, as was the value in carbon tetrachloride at 28°. Approximate values at 65° in carbon tetrachloride and at 100° in a few solvents were determined by a similar method, but the tubes were suspended in a liquid bath at the temperature desired and shaken frequently by hand. The value in carbon tetrachloride at 0° was obtained by a similar method, with the use of an ice-bath. Carbon tetrachloride was studied more extensively than other solvents because of its use in the crystallization method for the determination of rotenone. An approximate value for the solubility of rotenone in water at 100° was obtained by boiling various quantities of rotenone in large volumes of water under a reflux condenser, and noting at which concentration complete solution occurred. With some materials of low solvent power, larger quantities of solvent were used than with those of high solvent power, in order that the accuracy of the results would be comparable.

## Results

Table I gives the values obtained for solubility at 25, 35, and 100°, in grams of rotenone per 100 g. of solvent. Table II gives values for carbon tetrachloride at several temperatures.

TABLE I

SOLUBILITY OF ROTENONE IN VARIOUS SOLVENTS AT 25 AND 100°

| Solvent and density[a] at 25° | Soly., in g. per 100 g. of solvent 25° | 100° |
|---|---|---|
| Acetophenone | 21.0 | |
| Amylene dichloride (tech.), 0.940 | 1.7 | |
| Aniline | 17.7 | |
| Anethole | 9.1 | |
| Anisole | 16.6 | |
| Benzaldehyde | 30.2 | |
| Benzyl alcohol | 20.3 | |
| *n*-Butylmesityl oxide oxalate | 7.6 | |
| β-*p*-*t*-Butylphenoxyethanol | 2.8 | |
| α-Chloronaphthalene | 7.2 | |
| α-Chloropropionic acid | 22.5 | |
| Citral | 4.8 | |
| Cottonseed oil, 0.916 | 0.2 | 2.5 |
| Cresol (U. S. P.), 1.034 | 48.7 | |
| Cyclohexane | < 0.1 | |
| Cyclohexanol | 0.8 | |
| Cyclohexanone | 16.8 | |
| Decahydronaphthalene | < 0.1 | |
| Diacetone alcohol | 3.3 | |
| Dichloroacetic acid (80% in water), 1.431 | 19.0 | |
| Dichlorobenzene (*o*- and *m*-mixt.), 1.363 | 9.0 | |
| Dioxane | 10.8 | |
| Dipentene | 0.5 | |
| β-Ethoxyethyl acetate | 6.5 | |
| Ethylbenzene | 5.9 | |
| Ethyl carbonate | 5.6 | |
| Ethyl cinnamate | 8.9 | |
| Fenchyl alcohol | 1.8 | |
| Formamide | 0.2 | |
| Formic acid (90% in water), 1.191 | 0.9 | |
| Furfural | 24.7 | |
| Isopropyl ether | 1.1 | |
| Kerosene (fly-spray base), 0.776 | 0.01 | 0.35 |
| Kerosene (regular run), 0.805 | 0.05 | 1.3 |
| Menhaden oil, 0.923 | 0.3 | |
| Mesityl oxide | 10.0 | |
| Methyl acetate | 10.4 | |
| Methyl ethyl ketone | 10.6 | |
| Methyl isobutyl ketone | 4.1 | |
| Methyl salicylate | 8.6 | |
| Methylene chloride | 58.2 | |
| Nitrobenzene | 26.4 | |
| Oil camphor sassafrassy, 0.970 | 4.4 | |
| Olive oil, 0.910 | 0.2 | 2.2 |
| Pine oil (steam-distilled), 0.933 | 1.9 | 25.0 |
| Piperitone | 6.9 | |
| Propionic acid | 4.2 | |
| Propylene dichloride | 18.1 | |
| Pyridine | 38.9 | |
| Safrole | 10.2 | |
| α-Terpineol | 1.2 | |
| Tetrahydronaphthalene | 15.1 | |
| 1,2,4-Trichlorobenzene | 7.0 | |
| Turpentine (steam-distilled), 0.898 | 0.3 | |
| Water | | 0.0015 |

[a] Densities are given only for impure materials and mixtures.

Benzene and carbon tetrachloride already have been shown to combine with rotenone to form solvates.[2] From more recent work it is also known that propionic acid, α-chloropropionic acid, and dichloroacetic acid form solvates with rotenone under certain conditions. It is not

[2] H. A. Jones, THIS JOURNAL, **53**, 2738 (1931).

TABLE II

SOLUBILITY OF ROTENONE IN CARBON TETRACHLORIDE AT SEVERAL TEMPERATURES

| Temp., °C. | Soly. g. per 100 g. of solvent |
|---|---|
| 0 | 0.17 |
| 20 | .4[a] |
| 25 | .52 |
| 28 | .57 |
| 35 | .83 |
| 65 | 3.3 |

[a] From previous publication.[1]

known whether the other solvents tested form solvates, nor was any effort made to determine whether the solid phase at equilibrium was a solvate. In those cases in which a solvate forms under the conditions of the test, it is, of course, this addition product that is in equilibrium with the saturated solution. However, in the absence of more complete information the results have been expressed in terms of rotenone.

Values for solubility below 1.0 g. per 100 g. of solvent are subject to an error of about 30% except in the cases of carbon tetrachloride, water, and the two grades of kerosene, for which somewhat more accurate values were obtained by using larger volumes of solvent. Solubility values between 1 and 5 g. per 100 g. of solvent are correct within about 5%, those from 5 to 25 g. per 100 g. of solvent to within about 2%, and those above 25 g. per 100 g. of solvent to within about 1%.

## Discussion of Results

It will be noted that the saturated hydrocarbons tested are all of low solvent power. On the other hand, unsaturated compounds in general have a fair degree of solvent power. This may explain the difference in solubility in the two grades of kerosene tested, for most of the unsaturated compounds had been removed from the fly-spray base. The terpenes tested are all of low solvent power.

The generally high solvent power of benzene derivatives is apparent. The solubility in benzyl alcohol, for instance, is high compared with that in the aliphatic alcohols, which, as reported in the previous paper,[1] was only a few tenths of a gram per 100 g. of solvent. In general, ketones and esters appear to be good solvents. As in the earlier work, the addition of chlorine to a compound improves its solvent power in some cases but not always. The solvent powers of benzaldehyde, cresol, methylene chloride, and pyridine are rather high. Methylene chloride has perhaps the highest solvent power for rotenone of any solvent thus far tested. The best solvent found in the previous work was chloroform, in which the solubility was 49.3 g. per 100 g. of solvent at 20°. The value obtained for methylene chloride at 25° is sufficiently higher than this to indicate that this material may be somewhat superior.

The solvent power increases rapidly with increase in temperature. When the logarithms of the solubilities in carbon tetrachloride (Table II) were plotted against the reciprocals of the absolute temperatures, an approximately straight line was obtained, indicating the heat of solution of the solvate to be nearly constant over this range of temperature. The heat of solution of the rotenone–carbon tetrachloride solvate obtained in this way was about 8400 calories per mole. If this value is assumed for the heat of solution of rotenone in water and calculation based on the solubility at 100°, it leads to a value of about 1 part per million for the solubility of rotenone in water at 25°.

## Summary

The solubility of rotenone at 25° has been determined in fifty-five solvents not hitherto reported, and in some solvents at other temperatures.

The heat of solution of the rotenone–carbon tetrachloride solvate in carbon tetrachloride was calculated from solubility data.

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