[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF YALE UNIVERSITY]

# The Solubility of Some Strong, Highly Soluble Electrolytes in Methyl Alcohol and Hydrogen Peroxide–Water Mixtures at 25°

BY GÖSTA ÅKERLÖF AND HARLOW E. TURCK

**Introduction.**—The solubility of strong electrolytes in organic solvent–water mixtures has been the subject of a considerable number of investigations. Our knowledge of this field is, however, as yet somewhat incomplete and a study of the experimental data available shows that a large share of them without much doubt is too seriously in error to be of much value for the building up of systems of higher order or for the testing of quantitative relationships. With regard to hydrogen peroxide–water mixtures, "International Critical Tables" give in Volume IV a single series of measurements with potassium sulfate, which show an enormous increase in solubility with increasing peroxide concentration. This fact was considered to be of such interest that some preliminary measurements were carried out with a number of different salts to serve as a basis for a following study of certain quaternary systems with mixtures of strong electrolytes present.

## Experimental Method

As a rule the "analyzed" salts employed were carefully recrystallized and dried according to commonly accepted methods except in the case of ammonium chloride and potassium iodide, which two salts were analyzed gravimetrically and found to be sufficiently pure for our purposes without further purification. Only salts forming anhydrous solid phases in pure aqueous or in methyl alcohol–water solutions at 25° were employed for the solubility measurements in order to avoid complications due to the changing activity of the solvent. The methyl alcohol used was an "analyzed" acetone-free product unusually free from impurities. Batches of three liters each of this alcohol were fractionated slowly in a very efficient 1.8-meter high column. The first 500 cc. distilled was discarded and an appreciable quantity always left undistilled. The fractionated alcohol was stored in 2-liter Pyrex bottles with carefully ground stoppers. As source for hydrogen peroxide Merck 30% Superoxol was used without further purification. The chief impurity was sulfuric acid at a concentration of less than 0.001 molal, but the influence of this impurity was considered to be well within the other errors of the solubility measurements.

Alcohol–water mixtures in quantities of about 800 cc. were made up by adding an approximately weighed amount of methyl alcohol to a carefully determined amount of water and the exact amount of alcohol added was found after the two solvents had been mixed. Separate portions of about 200 cc. of the alcohol–water mixtures thus made up were poured into 250-cc. glass-stoppered Pyrex bottles containing a sufficient amount of salt to leave several grams undissolved as solid phase. The stoppers to the bottles were carefully ground in and tightly clamped down by a strip of heavy elastic held by a wire around the neck of the bottles. The concentration of hydrogen peroxide in the original Superoxol was calculated from its density using the data given in Volume III of "International Critical Tables." The amount of peroxide–water mixture used for a single solubility determination varied between 50 to 100 cc. In the presence of the alkali chlorides, nitrates and sulfates the decomposition of the peroxide over a period of twenty-four hours was found to be practically negligible and the determination of the proper solubility correction could thus also be neglected.

The solubility bottles were mounted in a shaking machine and rotated at a rate of about 10 r. p. m. over a period of about twenty hours in a water thermostat regulated to 25° with a precision of 0.01° and controlled with the same accuracy. A few hours after the shaking had been finished, duplicate samples were taken from each bottle by applying gentle suction to the outlet tube from a small Erlenmeyer flask fitted with a two-holed rubber stopper provided with a short inlet tube coming from the bottle containing the solution to be sampled. As a rule the weighed sample was then evaporated to dryness, ignited over a small flame or heated in a drying oven, the residue of pure salt weighed, reheated and reweighed to assure constant weight. In the case of measurements with ammonium chloride and potassium iodide the amount of salt in the sample was determined as the corresponding silver salts according to standard analytical procedure.

## Experimental Results

These are given in Tables I and II. All alcohol and peroxide concentrations are expressed as weight per cent. or mole fraction of the pure solvent mixture and all salt concentrations are given in molality per 1000 g. of the solvent mixture. The weighings have been corrected to vacuum and all the solubility data given represent the mean of at least two entirely separate determinations.

## Discussion

A large-scale graphical representation of the solubility data for sodium and potassium chloride in Table I is shown in Fig. 1 where the logarithms of the solubilities given have been plotted against their respective mole fractions of methyl alcohol, this being the most rational method. A very slight break in each of the two curves is indicated

TABLE I

SOLUBILITY MEASUREMENTS AT 25° WITH METHYL ALCOHOL–WATER MIXTURES AS SOLVENT AND (1) SODIUM CHLORIDE, (2) POTASSIUM CHLORIDE, (3) SODIUM NITRATE, (4) POTASSIUM NITRATE, (5) POTASSIUM BROMIDE, (6) POTASSIUM IODIDE, (7) POTASSIUM SULFATE, (8) AMMONIUM CHLORIDE AND (9) LEAD NITRATE AS SOLUTES

| Methyl alcohol W., % | Methyl alcohol Mol. fr. | s |
|---|---|---|
| (1) Sodium chloride | | |
| 0.00 | 0.000 | 6.162 |
| 10.59 | .0625 | 5.038 |
| 20.49 | .1266 | 4.096 |
| 30.16 | .1954 | 3.273 |
| 39.80 | .2712 | 2.552 |
| 50.65 | .3661 | 1.896 |
| 60.10 | .4587 | 1.328 |
| 70.83 | .5774 | 0.8656 |
| 80.45 | .6983 | .5544 |
| 89.29 | .8241 | .3685 |
| 100.00 | 1.0000 | .2367 |
| (2) Potassium chloride | | |
| 0.00 | 0.0000 | 4.826 |
| 11.10 | .0656 | 3.638 |
| 20.11 | .1240 | 2.820 |
| 29.87 | .1933 | 2.077 |
| 39.93 | .2721 | 1.476 |
| 50.65 | .3661 | 0.9561 |
| 59.28 | .4502 | .6487 |
| 69.74 | .5645 | .3766 |
| 78.98 | .6787 | .2193 |
| 80.45 | .6983 | .2005 |
| 90.04 | .8248 | .1135 |
| 100.00 | 1.0000 | .0707 |
| (3) Sodium nitrate | | |
| 0.00 | 0.0000 | 10.825[b] |
| .... | .... | .... |
| 21.30 | .1321 | 7.111 |
| .... | .... | .... |
| 40.10 | .2735 | 4.172 |
| .... | .... | .... |
| 59.94 | .4570 | 2.076 |
| 70.05 | .5682 | 1.364 |
| 78.96 | .6786 | 0.893 |
| 89.45 | .8265 | .543 |
| 100.00 | 1.0000 | .485[a] |
| (4) Potassium nitrate | | |
| 0.00 | 0.0000 | 3.774 |
| 4.98 | .0286 | 3.046 |
| 9.45 | .0554 | 2.503 |
| 21.04 | .1303 | 1.522 |
| 40.30 | .2752 | 0.7130 |
| 59.94 | .4570 | .3125 |
| 70.05 | .5682 | .1898 |
| 78.96 | .6786 | .1123 |
| 89.45 | .8265 | .0607 |
| (5) Potassium bromide | | |
| 0.00 | 0.0000 | 5.784[b] |
| 20.00 | .1233 | 3.711 |
| 40.82 | .2795 | 2.180 |
| 59.56 | .4530 | 1.182 |
| 72.39 | .5959 | 0.7697 |
| 80.03 | .6927 | .4625 |
| 89.79 | .8311 | .2629 |
| 94.76 | .9103 | .2049 |
| 100.00 | 1.0000 | .1805 |
| (6) Potassium iodide | | |
| 0.00 | 0.0000 | 8.962[b] |
| 20.00 | .1233 | 6.776 |
| 40.82 | .2795 | 4.845 |
| 60.21 | .4597 | 3.333 |
| 72.39 | .5959 | 2.473 |
| 80.03 | .6927 | 1.970 |
| 89.79 | .8311 | 1.412 |
| 94.76 | .9103 | 1.187 |
| 100.00 | 1.0000 | 0.965 |
| (7) Potassium sulfate | | |
| 0.00 | 0.0000 | 0.6905 |
| 9.74 | .0572 | .3049 |
| 15.09 | .0909 | .1933 |
| 21.30 | .1321 | .1134 |
| 29.99 | .1941 | .0536 |
| 40.10 | .2735 | .0221 |
| 59.94 | .4570 | .00342 |
| (8) Ammonium chloride | | |
| 0.00 | 0.0000 | 7.384[b] |
| 20.00 | .1233 | 5.580 |
| 40.82 | .2795 | 3.893 |
| 60.21 | .4597 | 2.657 |
| 72.39 | .5959 | 1.731 |
| 80.03 | .6927 | 1.357 |
| 89.79 | .8311 | 0.9305 |
| 94.76 | .9103 | .7691 |
| 100.00 | 1.0000 | .6612[a] |
| (9) Lead nitrate | | |
| 0.00 | 0.0000 | 1.799[c] |
| 20.08 | .1236 | 0.8768 |
| 30.00 | .1941 | .6730 |
| 40.00 | .2725 | .5151 |
| 50.05 | .3612 | .3820 |
| 60.00 | 0.4574 | 0.2800 |
| 70.00 | .5672 | .1905 |
| 80.10 | .6948 | .1237 |
| 90.02 | .8351 | .0752 |
| 100.00 | 1.0000 | .0423 |

[a] According to data in "International Critical Tables," Volume IV.

[b] According to Armstrong and Eyre, *Proc. Roy. Soc.* (London), **A84**, 123 (1911).

[c] According to Richards and Schumb, THIS JOURNAL, **40**, 1403 (1918).

at an alcohol mole fraction between 0.3 and 0.4 but stronger deviations from linearity do not occur until at alcohol concentrations above 95%. Practically the same general result is obtained from the measurements with potassium bromide and iodide, ammonium chloride and sodium nitrate, the curves for which are given in Fig. 2. They are plotted in the same manner as those in Fig. 1 although on a smaller scale since the experimental errors appear to be somewhat larger.

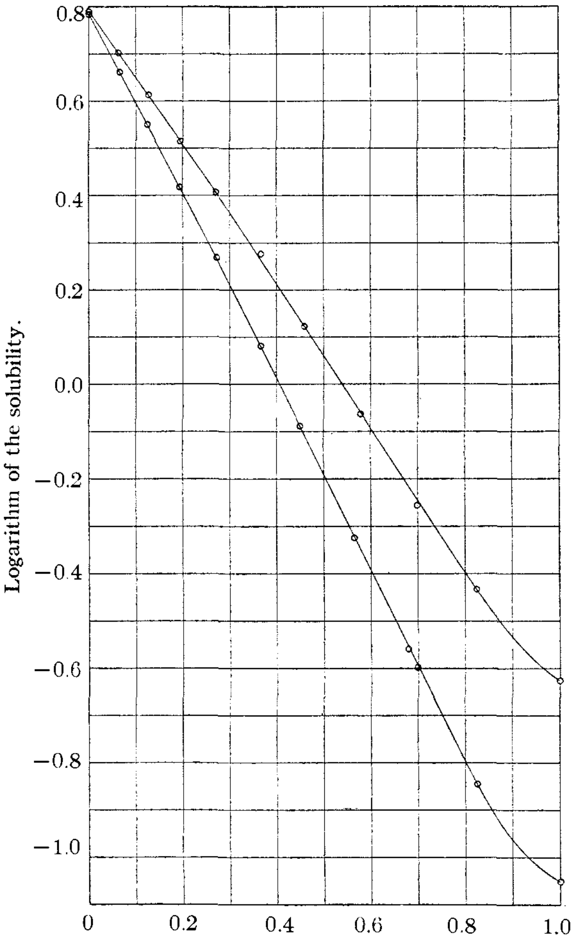

Fig. 1.—Curves for the logarithm of the solubility of sodium and potassium chlorides in methanol–water mixtures as plotted against the alcohol mole fraction. The potassium chloride curve has been moved up two spaces.

A slightly different picture is found in the case of potassium nitrate and sulfate, whose solubility curves are shown in Fig. 3, together with, as a com-

TABLE II

SOLUBILITY MEASUREMENTS AT 25° WITH HYDROGEN PEROXIDE–WATER MIXTURES AS SOLVENT AND (1) SODIUM CHLORIDE, (2) POTASSIUM CHLORIDE, (3) SODIUM NITRATE, (4) POTASSIUM NITRATE, (5) POTASSIUM SULFATE, (6) POTASSIUM PERCHLORATE AND (7) SODIUM FLUORIDE AS SOLUTES

| Hydrogen peroxide W., % | Hydrogen peroxide Mol. fr. | (1) | (2) | (3) | (4) | (5) | (6) | (7) |
|---|---|---|---|---|---|---|---|---|
| 0.00 | 0.0000 | 6.162 | 4.826 | 10.825 | 3.774 | 0.6905 | 0.149[a] | 0.9989 |
| 5.30 | .0288 | 6.028 | 4.835 | .... | ... | .... | ... | .... |
| 10.73 | .0599 | 5.792 | 4.974 | .... | ... | .... | ... | .... |
| 15.72 | .0899 | 5.539 | 5.093 | 9.252 | 4.710 | 1.287 | .175 | 1.216 |
| 21.17 | .1270 | 5.292 | 5.263 | .... | ... | .... | .... | .... |
| 26.24 | .1585 | 5.058 | 5.362 | .... | ... | .... | ... | .... |
| 31.43 | .1955 | 4.823 | 5.534 | 7.554 | 5.762 | 1.945 | .199 | 1.457 |

[a] According to "International Critical Tables," Volume IV.

parison, the curve for silver bromate in the same alcohol–water mixtures according to the measurements of Owen.[1] The curvature of the lines in Fig. 3 seems to become less pronounced with increasing alcohol concentration which is shown particularly in the case of lead nitrate as shown in Fig. 4. At alcohol concentrations above 20% a strictly linear variation is found for the logarithm of its solubility as plotted against the mole fraction of the alcohol. In the case of silver bromate Owen has shown that the logarithm of its solubility in a whole series of different organic solvent–water mixtures varies in an individual manner approximately linearly with the dielectric constant of the medium. At such high concentrations as most of those represented by the data in Table I, a comparison is no longer possible since we do not know the extent of the change of the dielectric constant of the medium due to the influence of the strong ionic field.

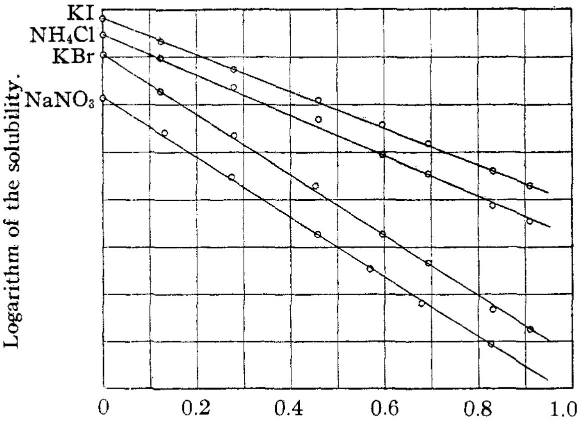

Fig. 2.—Curves for the logarithm of the solubility of potassium iodide and bromide, ammonium chloride and sodium nitrate in methanol–water mixtures as plotted against the alcohol mole fraction. The ordinates have been shifted to save space as far as possible.

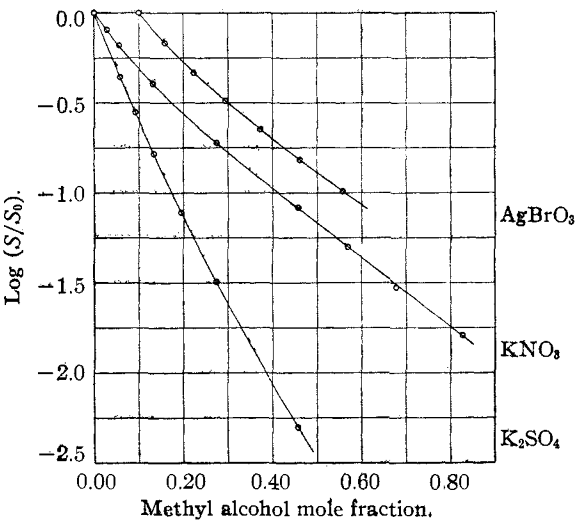

Fig. 3.—Curves for the logarithm of the ratio of the solubilities of silver bromate, potassium nitrate and sulfate in methanol–water mixtures and in pure water as plotted against the alcohol mole fraction. To separate the silver bromate and potassium nitrate curves the zero point of the former has been shifted one step to the right.

If we compare the data in Table I with the corresponding ones recorded in the literature for other organic solvent–water mixtures, we obtain

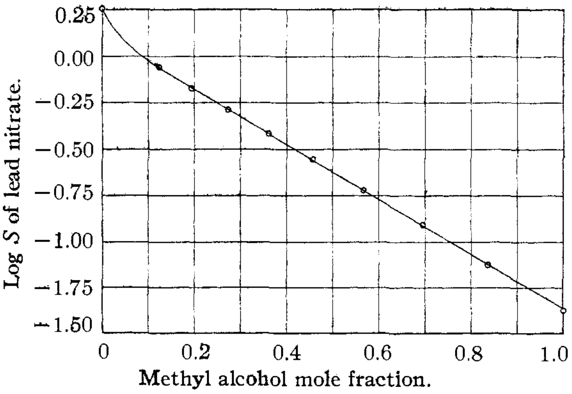

Fig. 4.—Curve for the logarithm of the solubility of lead nitrate in methanol–water mixtures as plotted against the alcohol mole fraction.

---

(1) Owen, THIS JOURNAL, 55, 1922 (1933).

on the whole exactly the same picture. In Fig. 5 have been plotted on a very large scale the data of Armstrong and Eyre[2] for the solubility of a number of different salts in ethyl alcohol–water mixtures. As shown in part I of Table III, at least at low alcohol concentrations, the ratios of the slopes for corresponding solubility curves in methyl and ethyl alcohol–water mixtures are approximately constant, as also might be expected from theoretical reasons. The dielectric polarization of methyl and ethyl alcohol–water mixtures varies linearly with the mole fraction of the components and the average of the ratios given[3] in Table III happens to be about the same as the ratio of the slopes for the dielectric polarization curves of the solvent mixtures.

TABLE III

PART I

SLOPES AT LOW ALCOHOL CONCENTRATIONS OF THE CURVES FOR THE LOGARITHM OF THE SOLUBILITY OF VARIOUS SALTS IN METHANOL AND ETHANOL–WATER MIXTURES AS PLOTTED AGAINST THE MOLE FRACTION OF THE ALCOHOL

| Salt | Methanol–water mixtures | Ethanol–water[a] mixtures | Ratio |
|---|---|---|---|
| Sodium chloride | 1.31 | 2.12 | 0.62 |
| Potassium chloride | 1.89 | 2.82 | .67 |
| Potassium bromide | 1.59 | 2.29 | .69 |
| Potassium iodide | 0.97 | 1.66 | .58 |
| Potassium nitrate | 3.06 | 5.08 | .60 |
| Potassium sulfate | 5.95 | 9.55 | .63 |
| Sodium nitrate | 1.57 | 2.45 | .64 |
| Ammonium chloride | 1.06 | 1.65 | .64 |

PART II

SLOPES OF THE SOLUBILITY CURVES FOR POTASSIUM AND SODIUM CHLORIDES AND POTASSIUM SULFATE IN DIFFERENT ORGANIC SOLVENT–WATER MIXTURES

| Organic solvent | NaCl | KCl | $K_2SO_4$ | Ratios NaCl/KCl | NaCl/$K_2SO_4$ |
|---|---|---|---|---|---|
| Methyl alcohol | 1.31 | 1.89 | 5.95 | 0.69 | 0.22 |
| Ethyl alcohol | 2.12 | 2.82 | 9.55 | .75 | .24 |
| *n*-Propyl alcohol[b] | 2.80 | 3.65 | .. | .77 | .. |
| Ethylene glycol[b] | .. | .. | 4.5 | .. | .. |
| Glycerol[b] | 1.62 | 1.92 | 4.7 | .84 | .34 |
| Acetone[b] | 2.45 | .. | 10.1 | .. | .24 |

[a] According to data of Armstrong and Eyre. Ref. 2.

[b] According to data given in Volume IV of "International Critical Tables" and Landolt-Börnstein, "Physik.-chemische Tabellen," 5th Ed.

The solubility data available for water mixtures with organic solvents other than methyl and ethyl alcohol are comparatively few and their accuracy is as a rule difficult to judge, but in several cases about the same general result seems to be indicated as that obtained for the two alcohols provided new solid or liquid phases do not appear in the system. In part II of Table III are given a few values for the slopes of the solubility curves at low solvent concentrations and the ratios of these slopes with each other in the case of sodium and potassium chlorides and potassium sulfate dissolved in various organic solvent–water mixtures. The table shows that in most cases the values of the slopes follow the variation of the slopes for the dielectric polarization curves but exceptions are apparently present and a definite rule does not exist.

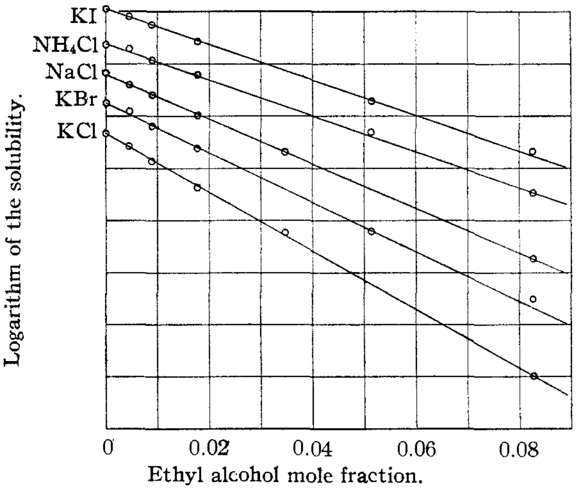

Fig. 5.—Curves for the logarithm of the solubility of sodium, potassium and ammonium chlorides, potassium bromide and iodide in ethanol–water mixtures as plotted against the alcohol mole fraction. The ordinates have been shifted to save space as far as possible.

A comparison of the data in Table I with those in Table II for the solubility of various salts in hydrogen peroxide–water mixtures is of the greatest interest. As is a well-known fact from the measurements of Cuthbertson and Maass,[4] the dielectric constant of these mixtures increases rapidly with the hydrogen peroxide concentration. Thus the dielectric constant of 30% hydrogen peroxide is, according to the authors mentioned, about 123 at 0° while that of water at the same temperature is 88.3. However, as shown by the data in Table II and the curves in Fig. 6, while the solubility of potassium chloride, nitrate and sulfate increases with increasing peroxide concentration, that of the corresponding sodium salts

---

(2) Armstrong and Eyre, *Proc. Roy. Soc.* (London), **A84**, 123 (1911).

(3) Wyman, *Phys. Rev.*, **35**, 623 (1930); compare also Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

(4) Cuthbertson and Maass, THIS JOURNAL, **52**, 489 (1930).

decreases at about the same rate. Neither the increases nor the decreases in solubility are due to the formation of new solid phases caused by the presence of the hydrogen peroxide since they remain the same as in pure water. Further, the sign of the solubility change does not depend on the cation alone since sodium fluoride contrary to the behavior of the other sodium salts studied rapidly increases its solubility with increasing peroxide concentration.

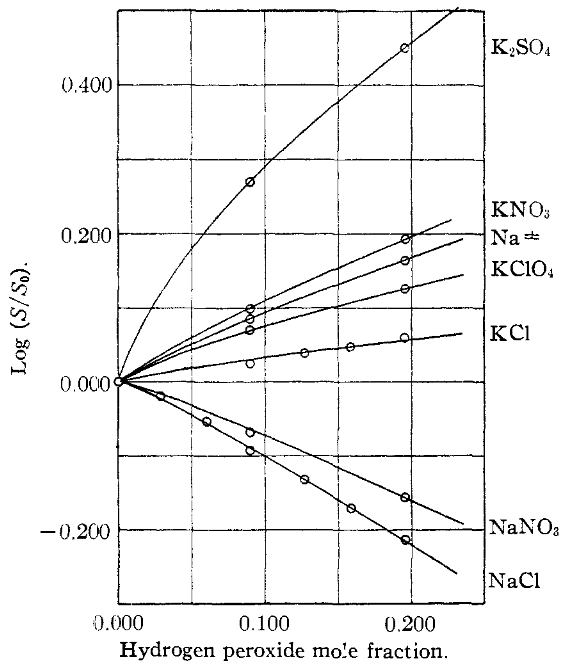

Fig. 6.—Curves for the logarithm of the ratio of the solubilities of various salts in hydrogen peroxide–water mixtures and in pure water as plotted against the peroxide mole fraction.

A complete explanation of these solubility changes would necessarily have to take into consideration a large number of different factors. Since in the case of alcohol–water mixtures with decreasing dielectric constants we always have found decreasing solubilities the opposite or increasing solubilities were to be expected in the case of hydrogen peroxide–water mixtures with increasing dielectric constants. Thus the solubility changes found for the potassium salts and sodium fluoride would represent the normal behavior. The most significant difference between sodium and potassium ions is the difference in ionic diameter. Applying the theory of Hückel[5] for concentrated solutions of strong electrolytes, it has been found that in the case of cations the smaller the ion the larger the lowering of the dielectric constant of the medium would have to be. In the case of sodium chloride and nitrate this calculated lowering may be sufficiently large to counteract the increase in dielectric constant that otherwise would have taken place due to the presence of the hydrogen peroxide, and thus actually cause a lowering of the solubility of these salts. This explanation may cover one of the more important factors and it appears reasonable in the case of solubility changes of typical strong electrolytes. However, other important factors must be present which become apparent in the behavior of salts like lead nitrate. The solubility of lead nitrate at 25° in pure water is 1.799 molal and in 31.4% hydrogen peroxide about 0.530 *m* (only three hours allowed for equilibrium due to fairly rapid peroxide decomposition). The decrease in solubility in peroxide–water mixture is thus even larger than in methanol–water mixtures (Table I) although the dielectric constants of the solvents change in opposite directions.

## Summary

The solubility has been determined for various salts in methyl alcohol– and hydrogen peroxide–water mixtures at 25°. A short discussion and comparison of the data obtained for methyl alcohol–water mixtures with the corresponding measurements recorded in the literature for other organic solvent–water mixtures has been given. In the case of the data for hydrogen peroxide–water mixtures a partial, tentative explanation of the solubility changes observed as due to changes of the dielectric constant of the medium has been attempted.

NEW HAVEN, CONNECTICUT

RECEIVED JULY 5, 1935

---

(5) Hückel, *Physik. Z.*, **26**, 93, 1925; compare also Harned and Åkerlöf, *ibid.*, **27**, 411 (1926).