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# THE SOLUBILITY AND HEAT OF SOLUTION OF SUCCINIC ACID IN WATER AND THE PARAFFIN ALCOHOLS.

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The following is the report of an investigation undertaken for the purpose of collecting further information concerning the influence of solvent upon certain specific properties of solutions. The solvents chosen, including water, represent the lower homologues of the paraffin alcohol series.

## MATERIALS AND APPARATUS.

Ordinary 95 per cent ethyl alcohol which had been standing for several months over quicklime was decanted and distilled. The distillate was then allowed to stand over anhydrous copper sulphate for several days, then decanted and again distilled. This distillate was next refluxed over metallic calcium for several hours and again distilled into glass-stoppered bottles, being protected during the final distillation by a tube of phosphorus pentoxide.

The remaining alcohols were of Kahlbaum's "C. P." grade. Except for the preliminary treatment with lime, they were subjected to exactly the same treatment as was the ethyl alcohol. In every distillation a Glinsky fractionating still-head was used and only the constant-boiling middle fraction was collected for use. The boiling points of the fractions taken were.

| | | |
|---|---|---|
| Methyl Alcohol | 64°.5—64°.7 at | 750.6 mm. |
| Ethyl Alcohol | 77.7 | 747.2 |
| n—Propyl Alcohol | 96.0— 96.2 | 743.1 |
| n—Butyl Alcohol | 115. —115.2 | 745.6 |
| iso—Butyl Alcohol | 105.9—106. | 733.1 |
| ter—Butyl Alcohol | 81.2— 81.5 | 741.7 |

*Succinic Acid.*—A high grade of the "C. P." acid was further purified by the rapid cooling of a hot saturated aqueous solution. The fine white crystals were filtered on a Hirsch funnel, sucked dry, then allowed to dry on a porous plate and finally allowed to stand over phosphorus pentoxide in a desiccator for at least three weeks before being used.

*Benzoic Acid.*—Kahlbaum's "C. P." acid was first fractionally resublimed, then fused and preserved in a desiccator until it was needed.

*Sodium Hydroxide Solutions.*—The solubility was determined by titrating weighed portions of the saturated solutions with a standard solution of sodium hydroxide, using phenolphthalein as indicator. For this purpose two aqueous solutions of sodium hydroxide were prepared, approximately .5N and .10N, respectively. A slight excess of solid barium hydroxide was added to each to remove any carbonates present. After being allowed to stand for some time they were quickly filtered into ceresin-coated stock-bottles. Each of these stock-bottles was connected with the upper end of a certified burette by means of a ceresin-coated glass tube, thus forming a single piece of apparatus. The burettes were filled by suction. Entrance of carbon dioxide into the apparatus was prevented by trains of test-tubes containing the respective standard solutions.

The alkaline solutions were standardized (Morey's Method[1]) by titrating against weighed portions of benzoic acid, care being taken to insure complete neutrality of the alcohol used. Here as elsewhere in the work only hot redistilled water was used.

The saturation apparatus consisted of a large glass test-tube (22 x 150 mm.) provided with a tight-fitting, one-hole rubber stopper. Into this hole was pressed a metal sleeve through which passed the axle of the stirrer and to which was attached a stout spiral of heavy platinum wire. The only possible opening into the test-tube was kept effectually sealed by the flange of the axle which rotated upon the metal sleeve. The stirrer was driven at the rate of 1,200 to 1,600 revolutions per minute by means of a small electric motor. The saturation apparatus thus arranged was immersed in the constant temperature bath which was electrically heated and electrically controlled at the desired temperature to within $\pm 0.02°$.

While preliminary experiments showed that saturation is complete in two hours, the time allowed for saturation was rarely less than four hours. After saturation the stirrer was stopped, the crystals allowed to settle and several portions of the clear saturated solution were withdrawn by means of certified 5 cc. pipettes. To prevent the entrance of fine crystals into the

[1]Bureau of Standards, Scientific Paper, No. 183, 1912.

pipettes the tips were protected by small muslin filters. These portions were transferred to tarred glass-stoppered weighing bottles and the weight of the solution was determined. The samples were then transferred to small Erlenmeyer flasks, boiled water added and then titrated to a faint pink color by means of the standard alkali. In every case the final titration was made with the dilute sodium hydroxide. From the data thus obtained were calculated the solubilities.

The heats of solution of succinic acid in the solvents used have been calculated by means of the well-known van't Hoff isochore,

$$\ln C_2 - \ln C_1 = \frac{Q}{R} \frac{T_2 - T_1}{T_2 \cdot T_1}$$

where R is the gas constant (1.985 cals.). $C_2$ and $C_1$ are the solubilities at the absolute temperatures $T_2$ and $T_1$, respectively, and Q is the molar heat of solution produced by dissolving one gram-mole of the acid in one hundred grams of the solvent. By a mathematical rearrangement,

$$Q = \frac{2.3026 \times 1.985 \times T_2 \times T_1}{T_2 - T_1} \log_{10} \frac{C_2}{C_1} \text{ cals.}$$

Succinic acid is but slightly dissociated in water and practically not at all in the alcohols. This relation will give, therefore, a close approximation to the heats of solution of the acid in the solvents under consideration.

The results obtained are given .in the accompanying table. Each solubility value given is the mean of three or four separate values which do not differ by more than a few hundredths of a gram per one hundred grams of solvent.

TABLE I.

SOLUBILITY OF SUCCINIC ACID.

| Solvent | In Grams Per 100 Grams of Solvent | | | In Moles Per 100 Moles of Solvent | | | Molar Heat of Solution | |
|---|---|---|---|---|---|---|---|---|
| | 25° | 30° | 35° | 25° | 30° | 35° | $Q_1$ | $Q_2$ |
| Water | 8,368 | 10.295 | 12.821 | 1.277 | 1.571 | 1.956 | 7442.5 | 8142.6 |
| Methyl Alcohol | 20.460 | 23.076 | 26.260 | 5.552 | 6.262 | 7.125 | 4320.4 | 4796.9 |
| Ethyl Alcohol | 9.996 | 11.492 | 13.185 | 3.899 | 4.483 | 5.143 | 5230.7 | 5101.0 |
| n—Propyl | 4.806 | 5.665 | 6.664 | 2.445 | 2.882 | 3.391 | 5905.4 | 6027.4 |
| n—Butyl | 3.179 | 3.817 | 4.464 | 1.995 | 2.395 | 2.801 | 6572.7 | 5804.4 |
| tert—Butyl | 8.504 | 9.687 | 10.949 | 5.336 | 6.079 | 6.871 | 4680.0 | 4542.1 |
| Iso—Butyl | 2.532 | 3.062 | 3.646 | 1.589 | 1.921 | 2.288 | 6825.7 | 6478.7 |
| Iso—Amyl | 2.146 | 2.570 | 3.133 | 1.601 | 1.918 | 2.338 | 6474.3 | 7352.0 |

$Q_1$ and $Q_2$ represent the molar heats of solution calculated for the intervals ($25°$-$30°$) and ($30°$-$35°$), respectively.

### SUMMARY.

As might be expected, the solubility of succinic acid increases with rise in temperature in all of the solvents studied. Considering the alcohols alone, the solubility at all temperatures is greatest in the methyl alcohol and decreases rapidly with the increase in the molecular weight of the alcohol. Methyl, ethyl, *n*-propyl and *n*-butyl alcohols have the simple molecular chain structure. *n*-Butyl ($CH_3CH_2CH_2CH_2OH$), iso-butyl ($(CH_3)_2CHCH_2OH$) and tert-butyl) ($(CH_3)_3COH$) are isomeric compounds whose molecular structures differ simply in the grouping of the atoms within the molecules. The effect of these structural differences upon the solubility of succinic acid is to be seen from the table, the solubility being greatest in the tertiary-butyl and least in the iso-butyl alcohol.

The effect of solvent upon the heat of solution is apparently just the reverse of that upon the solubility. For the normal alcohols the heat of solution increases as the molecular weight of the alcohol increases. Likewise, for the isomeric butyl alcohols the heat of solution is greatest in the iso-butyl and least in the tertiary-butyl alcohol.

For the temperature intervals studied the heat of solution shows a decided increase with rise in temperature for solutions in water, methyl alcohol and iso-amyl alcohol. The reverse is equally true for solutions in iso-butyl alcohol. For the other alcohols the heat of solution may be considered as practically independent of the temperature. Obviously, the heat of solution of a given substance is a specific property of the solvent. These deductions are based entirely upon the assumption of the validity of the van't Hoff isochore when applied to solubility methods.

Hints as to interesting relations between the solubility of the solute and the surface tension, compressibility and the association of the solvent have been observed. Before any generalizations can be made regarding these relations the work will have to be extended to higher alcohols and these we do not have.

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