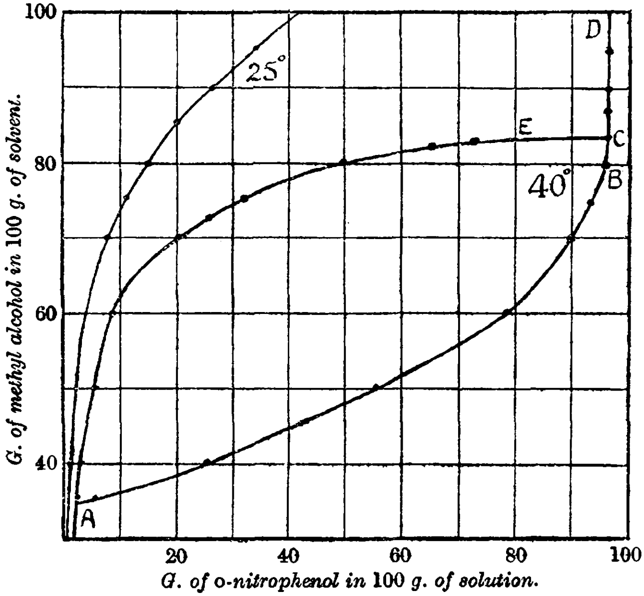
# CCCLXXVII.—*The Solubilities of* o- *and* p-*Nitrophenols in Aqueous Methyl-alcoholic Solutions at 25° and 40°. Formation of β*-p-*Nitrophenol.*

By JAMES COOPER DUFF.

DURING the course of another investigation, it was found that at room temperature *p*-nitrophenol was very soluble in aqueous formaldehyde solutions (20—40%), whereas *o*-nitrophenol dissolved only sparingly. This behaviour was traced to the presence of methyl alcohol in the formalin used, and as no data were available for the solubilities of these nitrophenols in aqueous methyl alcohol, they were investigated for the entire range of these mixed solvents at 25° and 40°.

Sidgwick, Spurrell, and Davies (J., 1915, **107**, 1202) determined the solubilities of the three isomeric nitrophenols in water, and expressed the view that *o*-nitrophenol behaves abnormally in comparison with the *m*- and *p*-isomerides. In aqueous methyl alcohol, a distinct difference is now found in the behaviour of *o*- and of *p*-nitrophenol.

FIG. 1.



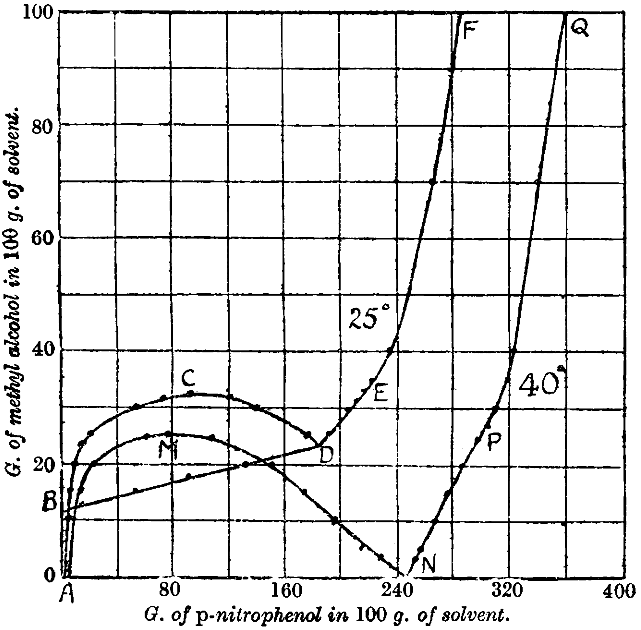
A new method for preparing the β-form of *p*-nitrophenol is described.

## EXPERIMENTAL.

The methyl alcohol used was of AR quality (British Drug Houses, Ltd.). The *o*-nitrophenol was recrystallised from methyl alcohol, and the *p*-nitrophenol from water. A series of solvents was made from definite weights of the alcohol and water. For many of the determinations the following synthetic method was used, especially for those alcoholic solutions which yielded two or three solubility points.

A weighed quantity of the solvent in a stoppered weighing bottle was maintained at 25° (or 40°) in a thermostat; nitrophenol was added until a trace remained undissolved, and from the increase in weight the solubility at that stage was calculated. Under certain conditions, an oily phase began to appear and two cases then arose. (1) Addition of *o*-nitrophenol was continued until some solid remained in the presence of the two layers after shaking, and the increase in weight was determined, the area ABCEA (Fig. 1) being thus obtained. (2) In the case of *p*-nitrophenol, addition of solute was continued either as in case (1) or until it just effected complete miscibility of the two layers, corresponding to areas BCDB and AMNA (Fig. 2), and in the latter event, by still further addition up to the limit of solubility in the homogeneous mixture, the values represented by the curves CD and MN were increased to those on curves DE and NP, respectively. Some of the final results were checked by heating the requisite proportion of aqueous methyl alcohol and the nitrophenol in sealed tubes at the selected temperature. For some sections of the solubility curves certain modifications are described under the appropriate headings.

FIG. 2.



o-*Nitrophenol*.—(a) *Solubilities at* 25°. Excess of *o*-nitrophenol was shaken with the aqueous-alcoholic solutions at 25° in a thermostat. A weighed quantity of each saturated solution was allowed to evaporate at room temperature in a desiccator, first over calcium chloride and finally over phosphoric oxide, and the residue weighed. To prevent the *o*-nitrophenol volatilising, a considerable quantity of this compound was kept in the desiccator to saturate the air space with its own vapour. The results obtained are in Table I (where *S* is the solubility as g./100 g. of solution), and the corresponding curve in Fig. 1 presents no unusual features. During solution at 25° the *o*-nitrophenol did not form any oily liquid phase.

TABLE I.

Temp. = 25°.

| MeOH, % | 0 | 30 | 40 | 70 | 75 | 80 | 85 | 90 | 95 | 100 |
|---|---|---|---|---|---|---|---|---|---|---|
| *S* | 0·25 | 0·8 | 0·97 | 8·25 | 11·15 | 15·1 | 19·9 | 26·9 | 34·1 | 42·3 |

(b) *Solubilities at* 40°. For concentrations of methyl alcohol up to 30%, the same method as for 25° was used. For solvents containing 35—83% of methyl alcohol, the synthetic method (p. 2791) was used, and for those containing 84—100% of alcohol the solubility of *o*-nitrophenol was so great as to necessitate the use of the following method : no separation into two liquid phases occurs in the last range. 5 G. of *o*-nitrophenol and 0·12 g. of alcoholic solution were heated in a sealed tube at 45° until most of the solid had liquefied, and then maintained at 40° for several hours until the liquid was completely in equilibrium with the solid. A weighed quantity of the liquid was then evaporated as described for the 25° estimations.

The results at 40° are in Tables II (Curve AECD) and III (Curve ABC). Since Table III refers mainly to two liquid phases, the results would have been expressed more correctly as g. of *o*-nitrophenol in 100 g. of solvent, but owing to the high values, the data in their present form are more suitable for plotting the curves in Fig. 1.

TABLE II.

Temp. = 40°.

| MeOH, % | 0 | 30 | 35 | 40 | 50 | 60 | 70 | 75 | 80 | 82 | 83 | 84 | 87 | 90 | 95 | 100 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *S* | 0·3 | 2·1 | 2·5 | 3·1 | 5·6 | 8·4 | 21·6 | 32·5 | 50·5 | 63·2 | 72·5 | 96·4 | 96·3 | 96·3 | 96·3 | 96·6 |

TABLE III.

Temp. = 40°.

| MeOH, % | 35* | 40* | 50* | 60* | 70* | 75* | 80† | 83† |
|---|---|---|---|---|---|---|---|---|
| *S* | 5·5 | 25·3 | 55·0 | 78·5 | 90·0 | 93·3 | 96·3 | 96·3 |

* Two liquid phases remain at end-point.
† Two liquids become miscible at end-point.

From Fig. 1 it will be seen that the area ABCA represents the field in which two liquid phases can exist, and their formation appears to be limited (at 40°) to solvent with a range of 35—84% of methyl alcohol.

p-*Nitrophenol.*—(a) *Solubilities at* 25°. For solutions containing 0—12% of methyl alcohol, weighed portions of the prepared saturated solutions were evaporated at 80° and finally in a desiccator. In solutions ranging from 12·5 to 32·5% of methyl alcohol, *p*-nitrophenol produces two liquid phases, and the synthetic method (p. 2791) was used for the determinations which give the area BCDB in Fig. 2. For the range 33—100% of alcohol no oily layer appears during solution of *p*-nitrophenol, and the same method was used. The complete results for 25° are in Tables IV, V, and VI, which relate respectively to curves ABC and EF, BD and CD, and DE in Fig. 2; *S′* is the solubility as g./100 g. of solvent.

TABLE IV.

| | Solubility. | | | Solubility. | |
|---|---|---|---|---|---|
| MeOH, %. | *S*. | *S′*. | MeOH, %. | *S*. | *S′*. |
| 0 | 2·4 | 2·5 | 30 | 35·9 | 56·1 |
| 5 | 2·6 | 2·7 | 31·5 | 42·1 | 72·4 |
| 10 | 3·0 | 3·1 | 32·5 | 48·1 | 92·3 |
| 12·5 | 3·7 | 3·9 | 33 | 68·2 | 215·0 |
| 15 | 4·6 | 4·8 | 35 | 68·6 | 219·5 |
| 17·5 | 5·7 | 6·1 | 40 | 70·0 | 233·1 |
| 20 | 8·7 | 9·5 | 70 | 72·5 | 265·6 |
| 23 | 13·0 | 15·0 | 100 | 74·1 | 285·3 |
| 25 | 16·6 | 20·0 | | | |

TABLE V.

| MeOH, % ... | 12·5* | 15* | 17·5* | 20* | 23† | 25† | 30† | 31·5† | 32·5† |
|---|---|---|---|---|---|---|---|---|---|
| *S′* ............ | 14·1 | 51·5 | 93·2 | 134·5 | 182·6 | 176·0 | 138·3 | 123·9 | 92·3 |

* Two liquid phases at end-point. † One liquid phase at end-point.

TABLE VI.

| MeOH, % ............ | 23 | 25 | 30 | 31·5 | 32·5 |
|---|---|---|---|---|---|
| *S* ........................ | 64·5 | 65·5 | 67·3 | 67·4 | 68·0 |
| *S′* ........................ | 182·6 | 190·2 | 205·3 | 207·1 | 211·6 |

It will be seen that, at 25°, the formation of two liquid phases by *p*-nitrophenol in aqueous methyl alcohol only occurs in solvents containing between 12 and 32·5% of methyl alcohol. The 23% methyl-alcoholic solution is the weakest solvent in which two liquid phases can be made completely miscible at 25° (point D) by further addition of *p*-nitrophenol. Since BD is a straight line (see Table V), the two saturated liquid phases are composed of the saturated aqueous solution for 12% alcohol and the oily saturated solution for 23% alcohol. Thus a 20% alcoholic solution will behave, at 25°, on addition of sufficient *p*-nitrophenol, as an equilibrium mixture of 12 and 23% alcoholic solutions. The two liquid phases are both saturated along the line BD. The area BCDB is the field in which two liquid phases coexist.

(b) *Solubilities at* 40°. For 0—15% methyl-alcoholic solutions, the results in Table VII were obtained by evaporation of saturated solutions, formation of an oily phase being avoided. All other solubility results (Tables VII, VIII, and IX) were obtained by the synthetic method already described. Table VII gives the results for saturated solutions formed without a second liquid phase first appearing.

TABLE VII.

(Curves AM and PQ, Fig. 2.)

| | Solubility. | | | Solubility. | |
|---|---|---|---|---|---|
| MeOH, %. | *S*. | *S'*. | MeOH, %. | *S*. | *S'*. |
| 0 | 2·8 | 2·9 | 25·5 | 43·1 | 75·4 |
| 3 | 3·1 | 3·2 | 26 | 75·0 | 296·8 |
| 4 | 3·2 | 3·3 | 27·5 | 75·4 | 304·8 |
| 5 | 3·4 | 3·5 | 30 | 75·7 | 310·5 |
| 10 | 5·1 | 5·35 | 35 | 76·1 | 318·3 |
| 15 | 8·0 | 8·7 | 40 | 76·3 | 322·0 |
| 20 | 18·1 | 22·1 | 70 | 77·2 | 339·8 |
| 25 | 37·8 | 60·5 | 100 | 78·0 | 359·3 |

TABLE VIII.

(These results indicate the minimum amount of *p*-nitrophenol required to make two liquid phases miscible. See curve MN, Fig. 2.)

| | Solubility. | | | Solubility. | |
|---|---|---|---|---|---|
| MeOH, %. | *S*. | *S'*. | MeOH, %. | *S*. | *S'*. |
| 0 | 71·1 | 246·0 | 15 | 63·7 | 176·0 |
| 3 | 69·8 | 228·5 | 20 | 60·6 | 153·8 |
| 4 | 68·8 | 220·5 | 25 | 51·6 | 106·3 |
| 5 | 68·2 | 215·0 | 25·5 | 49·7 | 99·0 |
| 10 | 66·2 | 196·2 | | | |

TABLE IX.

(These results were obtained by saturation of the solutions of Table VIII. See curve NP, Fig. 2.)

| | Solubility. | | | Solubility. | |
|---|---|---|---|---|---|
| MeOH, %. | *S*. | *S'*. | MeOH, %. | *S*. | *S'*. |
| 0 | 71·1 | 246·0 | 15 | 73·3 | 275·8 |
| 3 | 71·5 | 250·2 | 20 | 74·1 | 286·1 |
| 4 | 71·7 | 253·4 | 25 | 74·8 | 296·4 |
| 5 | 71·9 | 256·3 | 25·5 | 74·9 | 297·0 |
| 10 | 72·7 | 266·1 | | | |

From Fig. 2, it will be seen that the area AMNA is the field within which two liquid phases are possible at 40°. When the solvent contains more than 26% of methyl alcohol, only one liquid phase is possible, but when it contains less alcohol there are two solubility values for *p*-nitrophenol at this temperature. The lowest temperature at which there can be two solubility values for *p*-nitrophenol in water was found by Sidgwick, Spurrell, and Davies (*loc. cit.*) to be 39·6°.

### *Discussion of Results.*

The fact that *o*-nitrophenol in aqueous methyl-alcoholic solution behaves quite differently at 40° and at 25° may be largely due to the temperature of 40° being close to the melting point (44·3°) of this compound. Unlike *p*-nitrophenol, the *o*-isomeride at 40° forms two liquid phases only in higher concentrations of aqueous methyl alcohol. The maximum solubility is reached in 84% methyl alcohol, a solvent agreeing in composition with $3CH_4O,H_2O$ (Calc.: $CH_4O$, 84·1%).

The evidence for hydrates of methyl alcohol is supported by the work of Dunstan and Thole (J., 1909, **95**, 1559) and of Varenne and Godefroy (*Compt. rend.*, 1904, **138**, 990). On the other hand, Pushin and Glagoleva (J., 1922, **121**, 2813) give evidence against hydrate formation.

It is possible that *p*-nitrophenol in aqueous methyl-alcoholic solution may be capable of combining with definite molecular proportions, depending on temperature, of water and methyl alcohol. The following table of instant points from Fig. 2 illustrates this possibility.

| Point. | MeOH, %. | Possible hydrate. |
|---|---|---|
| C | 32·5 | $CH_4O,4H_2O$ = 31·0% $CH_4O$ |
| M | 25·5 | $CH_4O,5H_2O$ = 26·2% ,, |
| D | 23·0 | $CH_4O,6H_2O$ = 23·9% ,, |
| B | 12·0 | $CH_4O,12H_2O$ = 12·9% ,, |

The behaviour of *p*-nitrophenol in aqueous solutions of other organic solvents is under investigation and may lead to more definite conclusions.

The curves in Fig. 2 are similar in character to that obtained by Sidgwick, Spurrell, and Davies (*loc. cit.*) for the solubility of *p*-nitrophenol in water over a wide range of temperature. Increase of temperature, therefore, has the same influence as increase in the methyl alcohol concentration.

β-p-*Nitrophenol.*—During the solubility experiments with *p*-nitrophenol, it was found that when the saturated oily solutions were left to cool in the thermostat very slowly from 25° or 40°, the resulting crystals were rhombic. They were apparently the β-form, since on exposure to sunlight they rapidly turned red. This method of preparation is more convenient than those mentioned by Barker (P., 1911, **27**, 158) and by Sidgwick (J., 1915, **107**, 672). If the oily solutions are cooled quickly, it is mainly the α-form which separates. Whether the existence of α- and β-forms of *p*-nitrophenol can account for the special character of its solubility curves requires further investigation.

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