CLXXII.—*The Solubilities of Nitrophenols in Aqueous Ethyl-alcoholic Solutions.*

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It was shown by one of us (Duff, J., 1929, 2789) that *p*-nitrophenol in aqueous methyl-alcoholic solutions at 25° and 40° had solubility curves in which critical points occurred where the solvent was composed of methyl alcohol and water in simple molecular proportion. The positions of the critical points varied with the temperature. *o*-Nitrophenol gave no indication of an alcohol hydrate at 25°, and only one ($3CH_4O,H_2O$) was indicated at 40°.

The behaviour of *o*-, *m*-, and *p*-nitrophenols in aqueous ethyl-alcoholic solutions has now been examined. Solubilities for *m*-nitrophenol were determined at 0°, 12·5°, and 25°; and these three temperatures and also 40° were used for *p*-nitrophenol, since this isomeride yielded the most characteristic results. *o*-Nitrophenol was considered only at 25°, this being sufficient for comparison with the results obtained from the other two isomerides.

The solubilities of the three nitrophenols in water have been determined by Sidgwick, Spurrell, and Davies (J., 1915, **107**, 1202); and those in absolute ethyl alcohol over a wide range of temperature by Carrick (*J. Physical Chem.*, 1921, **25**, 628). His method, synthetic in character, differs from ours, but our results for absolute alcohol agree with his.

Solubilities are expressed as g. per 100 g. of solvent throughout.

EXPERIMENTAL.

Kahlbaum's ethyl alcohol of 99·8% purity was used. The nitrophenols were recrystallised by the usual methods before use. The solubilities were determined for *o*- and *p*-nitrophenols in the same way as for aqueous methyl-alcoholic solutions (Duff, *loc. cit.*). The results for *m*-nitrophenol were obtained by the same synthetic method as that previously used for *p*-nitrophenol.

o-*Nitrophenol* (Fig. 1).—The solubility was determined at 25° in aqueous-alcoholic solutions over the range 0—100% alcohol. The results are given below, and the resulting curve (AB) presents no unusual features. During solution at 25° the *o*-nitrophenol did not form any oily liquid phase.

EtOH, % ...	0	30	40	50	60	70	80	90	100
S	0·25	0·7	1·7	3·9	7·4	12·2	21·0	32·5	46·0

m-*Nitrophenol* (Fig. 1).—(a) *Solubilities at* 0°. No oily phase was formed. The solubility curve (CDEF) is a straight line between D and E, points which correspond approximately to 33% and 90% of alcohol in the solvent.

EtOH,%	0	20	30	40	50	60	70	80	90	100
S	0·9	1·6	5·0	19·8	36·8	53·7	71·5	89·5	106·6	115·5

(b) *Solubilities at* 12·5°. The results for the curve CKHM are given in Table I. In solvents ranging from 24 to 46% of ethyl alcohol, *m*-nitrophenol produces two liquid phases, and saturation with this phenol ended with two liquid phases in contact with the solid. Determinations of these end points gave the straight line GLH, the results for which are in Table II. Since GLH is a straight line, the two saturated liquid phases are evidently the saturated aqueous solution for solvent containing 24% of alcohol and the oily saturated solution for solvent of 46% alcohol. The area GLHKG is the field in which two liquid phases co-exist.

FIG. 1.

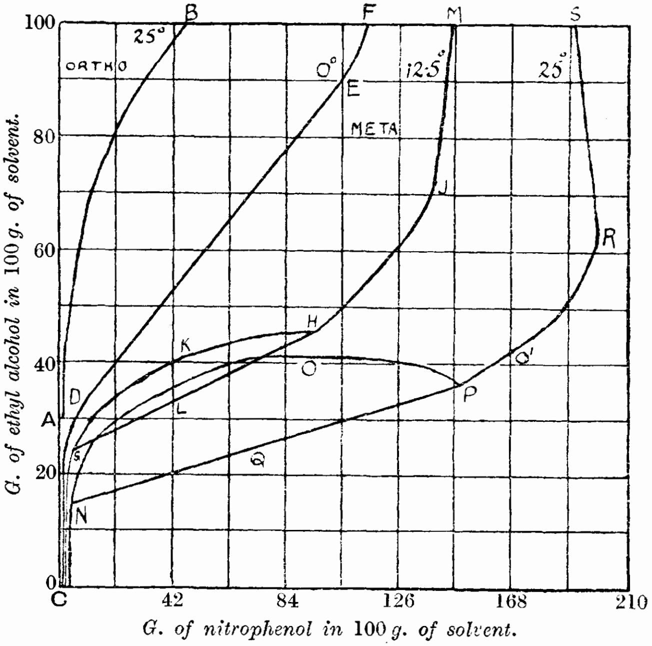

TABLE I.

EtOH, %.	S.	EtOH, %.	S.	EtOH, %.	S.	EtOH, %.	S.
0	1·2	35	27·2	46	96·0	70	139·5
20	2·5	40	41·0	50	106·2	80	143·5
25	6·8	42	52·1	60	126·2	90	146·0
27·5	8·9	45	74·4	63	131·0	100	148·0
30	12·8						

TABLE II.*

EtOH, %	25	27·5	30	35	40	42	45
S	10·3	17·9	30·5	51·0	71·5	80·5	92

* Two liquid phases remain at end-point.

(c) *Solubilities at* 25°. The results for the curves CNO and O'RS are given in Table III. In solvents ranging from 15 to 42% of ethyl alcohol, *m*-nitrophenol produces two liquid phases, which co-exist in the area NOPQN. The results yielding the lines NP and PO are given as S_1 in Table IV. Along the line PO the two liquid phases become one on addition of sufficient *m*-nitrophenol.

The minimum alcoholic content of solvent in which this occurs is 36% (P) and the maximum is 42% (O). By saturation of the solutions which gave PO, the values S_2 (Table IV) and hence the curve PO′ were obtained. Along the line NP are two saturated liquid phases which, since NP is a straight line, are composed of the saturated aqueous solution for 15% alcoholic and the saturated oily solution for 36% alcoholic solvent. At 25° *m*-nitrophenol was more soluble in 63% alcohol (R) than in absolute alcohol, whereas at the lower temperatures no maximum occurred.

TABLE III.

EtOH, %.	S.	EtOH, %.	S.	EtOH, %.	S.	EtOH, %.	S.
0	1·35	35	43·5	44	174·0	63	204·0
10	1·7	37·5	52·2	45	179·0	70	202·0
15	4·0	39	59·8	46	186·0	80	200·0
20	6·5	40	65·9	50	189·0	90	197·5
25	11·0	41	81·5	60	201·0	100	195·0
30	25·0	42	171·0				

TABLE IV.

EtOH, %	15	20	25	30	35	36	37·5	39	40	41
S_1	5·9*	38·8*	76·5*	106·3*	147·0*	150†	142†	140†	135†	122·5†
S_2	—	—	—	—	—	150	156	162	165	167

* Two liquids remain at end-point.

† Two liquids became miscible at end-point.

p-*Nitrophenol* (Fig. 2).—(a) *Solubilities at* 0°. The results are given in Tables V (curve ACG) and VI (straight line BED). The curve as a whole resembles that obtained for *m*-nitrophenol at 12·5°. The alcohol limits in the solvent for producing two liquid phases (co-existing in the area BCDEB) are 25% and 51%. Along the straight line BED two saturated liquids are in equilibrium with solid *p*-nitrophenol. These liquids are respectively aqueous saturated solution in 25% alcohol and oily saturated solution in 51% alcohol.

TABLE V.

EtOH, %.	S.	EtOH, %.	S.	EtOH, %.	S.	EtOH, %.	S.
0	0·5	35	12·5	51	82·0	70	120·0
10	0·6	40	25·0	54	96·0	80	118·0
25	1·4	45	41·0	56	101·0	90	117·0
30	5·2	50	58·5	60	108·0	100	116·4

TABLE VI.*

EtOH, %	27·5	30	35	40	45	50
S	9·2	15·2	30·0	44·8	61·0	76·0

* Two liquids remain at end-point.

(b) *Solubilities at* 12·5°. The results are given in Tables VII (curves AHJ and J′MN) and VIII (S_1, straight line HLK and curve KJ; S_2, curve KJ′). For solvents containing between 17·5 and 45% of alcohol, it is possible to have two liquid phases co-existing (area HJKLH); 41% is the minimum alcoholic content to enable two liquid phases to become miscible (K) by saturation with *p*-nitrophenol at 12·5°.

FIG. 2.

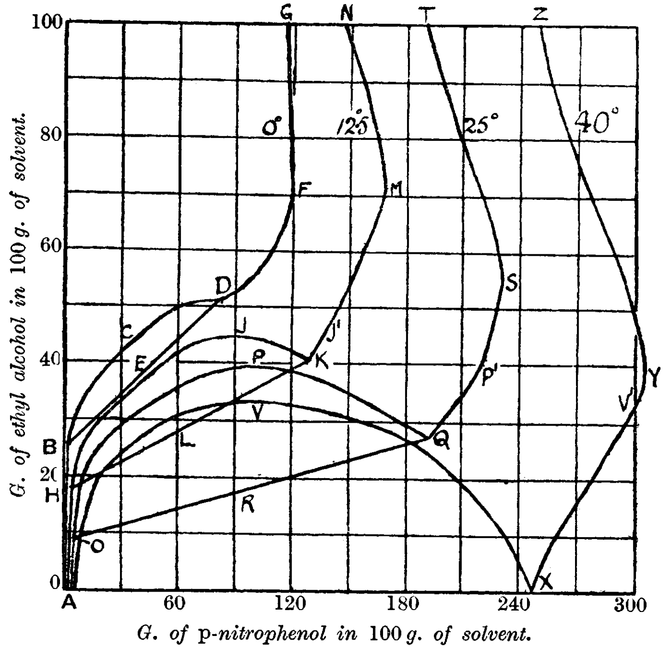

TABLE VII.

EtOH, %.	*S*.	EtOH, %.	*S*.	EtOH, %.	*S*.	EtOH, %.	*S*.
0	1·1	35	33·5	45	135·5	72	169·0
15	1·8	40	53·2	46	137·0	75	167·0
17·5	3·6	41	56·1	50	144·0	80	164·0
20	5·8	42	63·5	60	156·0	90	157·0
25	8·8	44	80·8	70	168·0	100	147·0
30	17·4						

TABLE VIII.

EtOH, %.	17·5	20	25	30	35	40	41	42	44	45
S_1	4·0*	18·0*	41·0*	68·6*	92·5*	127·0*	127·8†	124·0†	108·8†	—
S_2	—	—	—	—	—	—	127·8	130·3	133·0	135·5

* Two liquids remain at end-point.

† Two liquids become miscible at end-point.

(c) *Solubilities at* 25°. The results are given in Tables IX (curves AOP and P′ST) and X (S_1, straight line ORQ and curve QP; S_2, curve QP′). For solvents containing between 8 and 39% of ethyl alcohol, two liquid phases can co-exist (area OPQRO) and they can become miscible if the alcoholic content of the solvent is not less than 27% (point Q). Along the line ORQ exist two saturated solutions which are aqueous saturated solution in 8% alcohol and oily saturated solution in 27% alcohol.

TABLE IX.

EtOH, %.	*S*.	EtOH, %.	*S*.	EtOH, %.	*S*.	EtOH, %.	*S*.
0	1·6	25	19·2	38·5	80·5	60	227·0
10	3·4	27·5	26·2	39	220·0	70	220·0
15	5·2	30	34·9	40	220·5	80	208·9
17·5	6·0	32·5	45·7	46	223·0	90	199·0
20	8·5	35	57·8	50	226·1	100	189·5
22·5	13·7	37·5	70·1	56	230·4		

TABLE X.

EtOH, %...	9	10	12·5	15	17·5	20	22·5	25	26·5
S_1	7·8*	17·5*	42·5*	65·6*	95·6*	118·7*	141·6*	169·1*	186·2*

* Two liquids remain at end-point.

EtOH, %	27	27·5	30	32·5	35	37·5	38·5
S_1............	192†	191†	177·1†	160·5†	147·9†	132·7†	117·6†
S_2	192	194	198	206·1	210·5	217·9	218·7

† Two liquids become miscible at end-point.

(d) *Solubilities at* 40°. At this temperature two liquid phases can co-exist (area AVXA) in solvents containing between 0 and 33·8% of ethyl alcohol. The two liquids can become miscible along the line XV on addition of sufficient *p*-nitrophenol. The results at 40° are given in Tables XI (curves AV and V′YZ) and XII (S_1, curve XV; S_2, curve XV′).

TABLE XI.

EtOH, %.	*S*.	EtOH, %.	*S*.	EtOH, %.	*S*.
0	2·9	32·5	79·5	50	298
10	5·5	33·3	95·0	60	289
15	9·0	33·8	300·5	70	276
20	19·0	35	303·0	80	265
25	36·5	39	306·0	90	255
30	55·1	40	305·0	100	250·0

TABLE XII.

EtOH, % ...	0	10	15	20	25	30	32·5	33·3	33·8
S_1..............	246*	233*	220*	206*	190*	149*	114*	101*	—
S_2	246	258	268	277	286	296	299	—	300·5

* Two liquids become miscible at end-point.

The above results show that in aqueous ethyl-alcoholic solutions *p*-nitrophenol has a maximum solubility at 0° and 12·5° in 72% alcohol, at 25° in 56% alcohol, and at 40° in 39% alcohol.

Discussion of Results

The results obtained for the solubility of *o*-nitrophenol serve to emphasise the special features of the solubility curves of the *m*- and *p*-isomerides. The last two exhibit a marked tendency to form oily solutions at low temperatures, therein differing from *o*-nitrophenol, although this isomeride has a much lower m. p. (44° as against 116° for *p*-nitrophenol) than the others. The greatest tendency to produce two liquids during solution in dilute alcoholic solutions is shown by *p*-nitrophenol : this is possibly connected with the greater ease with which this isomeride forms addition compounds with weak bases and with its own metallic derivatives; moreover, the salts of *p*-nitrophenol show the highest degree of hydration, whilst those of *o*-nitrophenol are, in general, the least hydrated. It seems probable, therefore, that the additive powers of *m*- and *p*-nitrophenol enable them to produce the oily liquid phases which characterise the looped portions of their solubility curves. The curves show that, as the temperature rises, there is a fall in the maximum alcohol concentration of the solvent determining the area in which two liquid phases co-exist.

Some of the curves show as many as four significant points; *e.g.*, in the curve (Fig. 2) for *p*-nitrophenol at 25°, the point S shows maximum solubility, points P and O are the upper and lower limits, respectively, for the co-existence of two liquids, and point Q indicates the minimum alcohol concentration of solvent in which two liquid phases can be made completely miscible. The occurrence of maximum solubility for *m*- and *p*-nitrophenol at temperatures above 12° in aqueous ethyl-alcoholic solutions was unexpected, since this was not the case for methyl alcohol (Duff, *loc. cit.*). In considering the direction changes of the curves in Figs. 1 and 2, it is noteworthy that McCombie and his co-workers (J., 1921, **119**, 970; 1922, **121**, 243, 2308), studying the rates of saponification of esters by potassium hydroxide in aqueous ethyl-alcoholic solutions, found significant points in the resultant curves at which the alcohol and water in the solvent were present in simple molecular proportions. These points, however, were not all evident at any one temperature. Dexter, McCombie, and Scarborough (J., 1923, **123**, 1229) studied an example of isomeric change in aqueous ethyl-alcoholic solutions and obtained a curve changing in direction at three points corresponding to alcohol–water complexes.

Since the significant points of the curves now recorded vary with temperature and differ for the two nitrophenols, there is no evidence for the existence of alcohol hydrates in the solutions. It is more probable that the points are of eutectic character. In view of the results obtained by McCombie and his co-workers (*loc. cit.*), it is a remarkable coincidence that so many of the significant points in Figs. 1 and 2 occur where the alcohol and water in the solvent are in simple molecular proportion, as Table XIII shows.

TABLE XIII.

Fig 1.					
Point	H	J	P	O	R
EtOH, %	46	72	36	42	63
Ratio EtOH : H_2O	1 : 3·00	1 : 0·993	2 : 9·08	2 : 7·06	2 : 3·00
Fig. 2.					
Point	D	F	K	J	M
EtOH, %	51	70	41	45	72
Ratio EtOH : H_2O	2 : 4·91	1 : 1·09	2 : 7·23	1 : 3·12	1 : 0·993
Point	Q	P	S	V	Y
EtOH, %	27	39	56	33·8	39·0
Ratio EtOH : H_2O	1 : 6·91	1 : 4·00	1 : 2·00	1 : 5·00	1 : 4·00

Although the presence of alcohol–water complexes in the solvent is improbable, it seems necessary to assume that *m*- and *p*-nitrophenols are both capable of association with the solvent. This especially applies to the co-existence of two saturated liquids along, *e g.*, the straight line NP for 25° in Fig. 1. In this case, if the solvent used is 24% in alcoholic content, it will be induced, by addition of *m*-nitrophenol, to act as an equilibrium mixture of 15% alcohol (point N) and of 36% alcohol (point P), and with the requisite amount of *m*-nitrophenol, it will produce the two saturated liquid phases. The results found for the line NP agree with those calculated from the foregoing assumption, and this applies to the corresponding sections of the other curves.

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