CLVIII.—*The Solubility of Picric Acid in Mixed Solvents. Part I. Water–Alcohol and Water–Acetone Mixtures.*

By JAMES COOPER DUFF and EDWIN JOHN BILLS.

WE have previously indicated (J., 1929, 2789; 1930, 1331) the differences in behaviour of mononitrophenols in aqueous methyl and ethyl alcohol. The trinitrophenol, picric acid, has now been studied in a similar manner. Methyl, ethyl, *iso*propyl, and *n*-propyl alcohols were used, as these four alcohols are miscible with water in all proportions. As a contrast to the results obtained in the aqueous alcohol series, the solubility of picric acid in mixtures of acetone and water at 25° is also recorded.

Dolinski (*Ber.*, 1905, **38**, 1836) and Findlay (J., 1902, **81**, 1219) found a normal solubility curve for picric acid in water between 0° and 100°. Only a few isolated values (mainly at room temperature) are available for the solubility of picric acid in ethyl alcohol, and none for the other alcohols. Angelescu and Dumitrescu (*Z. physikal. Chem.*, 1928, **132**, 217) have examined the behaviour of picric acid in several mixed solvents, in all cases at 12° only. Their results for water–ethyl alcohol and for water–acetone differ considerably from ours (see pp. 1197, 1199).

We have included a number of electrical conductivity values for picric acid in the solvents (p. 1200). These were determined to see if they had any relation to the solubility data obtained, and the principal result is to show that acetone, which possesses the highest solvent power, gives the lowest conductivity although, among the alcohols, solvent power and conductivity run parallel.

EXPERIMENTAL.

Methyl and the two propyl alcohols were dried over calcium and distilled before use. Kahlbaum's 99·8% pure ethyl alcohol, and acetone of A.R. quality (British Drug Houses) were used as received. The mixed solvents were made from definite weights of each and of water. Picric acid was recrystallised from water and dried over sulphuric acid.

Stoppered weighing bottles, containing the solvents and excess of finely powdered picric acid, were maintained at the desired temperature in a thermostat for 5 hours with frequent shaking. About 5 g. of clear solution were decanted in each case, weighed, and (except for *n*-propyl alcohol mixtures) evaporated in the weighing bottle at 80°. The picric acid was then weighed and the result also checked by titration of the acid in aqueous solution with 0·1*N*-baryta, thymolphthalein being used as indicator. For the *n*-propyl alcohol mixtures, only the titration method was applied to the weighed solution. In no case was saturation of the solution hastened by heating above the temperature selected for the series. It is mainly in this respect that our method differs from that of Angelescu and Dumitrescu (*loc. cit.*). In the tables below, *S* represents g. of picric acid in 100 g. of solvent.

Water–Methyl Alcohol.

MeOH, %	0	30	40	50	60	70	80	90	100
$S^{0°}$	0·7	1·1	1·6	2·6	3·9	5·5	7·6	10·6	13·8
$S^{14°}$	1·1	1·8	2·4	3·5	5·3	7·3	9·6	12·3	16·3
$S^{25°}$	1·3	2·4	3·3	4·9	7·1	9·6	12·4	16·0	21·1

Curve BF (Fig. 1) is plotted from the results at 25°. The curves at the other two temperatures are similar.

Water–Ethyl Alcohol.

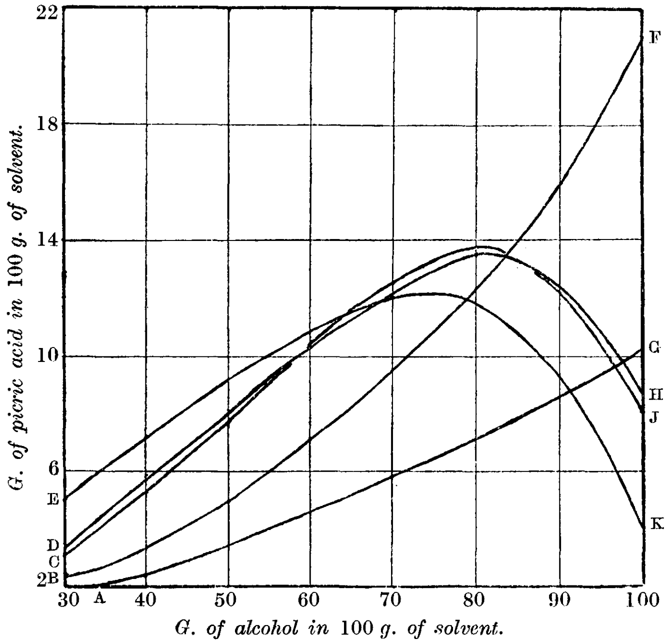
Values of *S* at given temperatures.

EtOH, %.	0°.	14°.	25°.	40°.	50°.	12°.*
0	0·7	1·1	1·3	1·9	2·4	2·93
20	1·0	1·4	2·1	3·1	4·25	1·4
30	1·2	1·9	3·1	4·6	6·5	2·0
40	2·0	3·8	5·3	7·35	10·0	2·9
50	3·8	5·5	7·8	10·3	13·6	3·9
60	5·6	7·6	10·5	13·5	17·4	4·9
70	7·6	9·7	12·6	16·3	20·7	6·0
78	8·9	11·1	13·6	17·95	22·5	6·8
80	9·1	11·5	13·8	18·3	22·8	7·1
81	9·3	11·4	13·8	18·3	22·8	7·3
85	9·0	11·0	13·2	17·6	22·3	7·9
90	8·1	10·2	12·3	16·6	21·1	8·6
95	7·0	8·8	10·2	14·8	19·2	9·4
100	4·5	6·0	8·0	11·0	14·8	10·4

* The results at 12° are taken from the curve given by Angelescu and Dumitrescu (*loc. cit.*) and are plotted as the curve AG.

Our results show a maximum solubility when the alcohol concentration in the solvent is 80—81% for each temperature from 0° to 50°. The curve CJ (Fig. 1) represents the results at 25°. For the other temperatures the curves are similar. Behrend (*Z. physikal. Chem.*, 1892, **10**, 265) found at 12·3°, $S = 5·85$, and at 14·8°, $S = 6·3$ in ethyl alcohol.

FIG. 1.



BF *Aqueous methyl alcohol at* 25°.
CJ ,, *ethyl* ,, ,, 25°.
DH ,, iso*propyl* ,, ,, 25°.
EK ,, n-*propyl* ,, ,, 25°.
AG ,, *ethyl* ,, ,, 12° (Angelescu and Dumitrescu).

Water-iso*Propyl Alcohol.*

Alcohol, %.	0°.	25°.	40°.	50°.
0	0·7	1·3	1·9	2·4
30	1·5	3·8	4·9	6·4
40	3·3	5·9	8·0	9·5
50	5·2	8·1	10·8	13·9
60	6·9	10·3	13·7	17·8
70	8·5	12·0	16·0	20·1
75	9·1	12·7	16·8	20·8
80	9·7	13·4	17·4	21·3
82	9·6	13·4	17·5	21·5
85	9·5	13·1	17·0	21·2
90	9·2	12·6	16·4	20·4
95	7·8	11·1	15·0	18·0
100	5·8	8·7	12·0	15·4

Maximum solubility at each temperature occurs in solvent containing 80—82% of *iso*propyl alcohol. Curve DH (Fig. 1) represents the results for 25°. The curves for the other temperatures are similar.

*Water–*n-*Propyl Alcohol.*

Alcohol, %.	0°.	25°.	50°.	Alcohol, %.	0°.	25°.	50°.
0	0·7	1·3	2·4	75	8·1	12·2	19·1
30	2·8	5·0	9·7	80	8·2	12·0	19·0
40	4·5	7·2	12·4	85	7·9	10·8	17·4
50	5·8	9·2	15·3	90	6·0	9·4	15·7
60	7·1	10·9	18·0	95	4·4	7·0	12·6
70	8·0	12·0	19·0	100	2·4	3·7	7·5

Maximum solubility at each temperature occurs in solvent containing about 75% of propyl alcohol. Curve EK (Fig. 1) represents the results at 25°. For 0° and 50° similar curves apply.

Water–Acetone.

Acetone, % ...	0	30	40	50	60	70	80	90	100
$S^{25°}$	1·3	9·5	18·9	31·3	46·7	65·8	87·8	110·8	134·3
*$S^{12°}$	2·9	7·9	12·1	20·0	29·0	44·0	70·0	107·0	194·2

* These figures are from the curve given by Angelescu and Dumitrescu (*loc. cit.*).

Our results give a smooth curve of simple type.

Methyl Alcohol–Ethyl Alcohol.

MeOH, %	0	20	40	60	80	100
$S^{25°}$	8·0	9·8	12·3	14·9	17·6	21·1

These results give a curve which is almost a straight line, showing that the alcohols do not affect each other's solvent power.

Discussion.

The curves CJ, DH, and EK in Fig. 1 indicate that at 25° ethyl, *iso*propyl, and *n*-propyl alcohols each produce a maximum solubility for picric acid when there is a definite proportion of the alcohol in the mixed solvent. This proportion has not been found to vary noticeably between 0° and 50°. Methyl alcohol, on the other hand, has not this effect, the solubility (between 0° and 25°) of picric acid increasing continuously from that in water alone to that in anhydrous methyl alcohol, as exemplified by curve BF for 25°. Picric acid thus makes a more definite distinction between methyl alcohol and the higher alcohols in the presence of water than was found with *p*-nitrophenol (*loc. cit.*), which gave maximum solubilities in different concentrations of aqueous ethyl alcohol depending on temperature.

The behaviour of picric acid appears to be exceptional for an acid. The solubility data for numerous carboxylic acids in aqueous ethyl alcohol are known (" International Critical Tables," vol. 4), and in all cases the results show no maximum in the mixed solvent.

There is no chemical union between picric acid and the alcohols, but an important factor affecting the solubility appears to be the existence in solution of two molecular forms, one of which yields yellow and the other colourless solutions. This is particularly noticeable in the aqueous mixtures containing acetone or *n*-propyl alcohol; with increasing concentration of these solvents in the mixtures the yellow colour diminishes, and finally disappears in the anhydrous solvent.

The solvent powers of the alcohols on picric acid are in the same order as their dielectric constants (see *D* below) and as the specific conductivities (κ below), which were determined in a Kohlrausch cell at 25° for 2% picric acid solutions. Acetone, although having nearly the same value for *D* as *n*-propyl alcohol, has a much lower value for κ.

	H_2O.	MeOH.	EtOH.	Pr$^\beta$OH.	Pr$^\alpha$OH.	Acetone.
$^{25°}$	81·3	30·3	25	25	22	21
$\kappa^{25°} \times 10^3$...		0·91	0·43	0·48	0·25	0·032

Although the values for κ are influenced by degree of association and the viscosity of the solvents, they serve to emphasise a marked difference between acetone and the alcohols in their solvent action on picric acid in the presence of water.

The high solvent action of acetone on picric acid suggests that there may be a connexion between solubility and the dipole moments of the solvent molecules. It is hoped to discuss this possibility more fully when data have been obtained from other solvent mixtures.

A feature of the water–alcohol series of solvents is the fact that, for mixtures containing less than 60% of alcohol, *n*-propyl alcohol has the greatest and methyl alcohol the least influence on the solubility of picric acid, while the reverse holds for the anhydrous alcohols. This is probably the result of the dissociating action of water on associated alcohol molecules, with subsequent association of the simple alcohol molecules with water. Such an association is probably most marked for *n*-propyl alcohol, thus agreeing with its hygroscopic character and the large amount of water (28·31%) present in the constant-boiling mixture of these two solvents. That alcohols do not affect each other noticeably is illustrated by the solubility values found for picric acid in mixtures of methyl and ethyl alcohols (p. 1199).

There are not yet sufficient experimental data to warrant discussion of the causes of the fall in the solubility of picric acid after a definite concentration of ethyl, *iso*propyl, and propyl alcohol in the aqueous mixtures is reached. The influence of non-associated equids on the solvent action of the alcohols is under investigation, and the results may enable us to discuss the matter more definitely.

In our opinion, the great difference between the shape of our curve for aqueous ethyl alcohol and that of Angelescu and Dumitrescu is due to the possibility that some of their picric acid solutions were supersaturated when analysed. The results they obtained for picric acid in mixtures of alcohol or acetone with other organic solvents will be considered with our results in Part II of this investigation.

THE TECHNICAL COLLEGE,
BIRMINGHAM.

[*Received, February* 17*th*, 1931.]