114. *The Solubility of Picric Acid in Mixed Solvents. Part II. Benzene–Alcohol Mixtures.*

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In Part I (J., 1931, 1196) we considered the solubility of picric acid in mixtures of water and alcohols, in which both solvents contain associated molecules. We now deal with its solubility in mixtures of benzene with various alcohols. It was expected that the former solvent, since it contains non-associated molecules, would differ from water in its effect upon the solubility in the alcohol.

Angelescu and Dumitrescu (*Z. physikal. Chem.*, 1928, **132**, 217) determined the solubility of picric acid in a number of mixtures of benzene and ethyl alcohol at 12°, but we have not been able to confirm all their values, as shown by our results at 12·5°. Apart from calculated values recorded by Findlay (J., 1902, **81**, 1220), no series of solubility results for picric acid in benzene could be found for temperatures between 5° and 25°.

We have used five series of benzene–alcohol mixtures, in which the alcohols were respectively methyl, ethyl, *n*- and *iso*-propyl, and butyl. Solubility determinations were made at 0°, 12·5°, and 25°.

EXPERIMENTAL.

The alcohols used were purified as described in Part I. Benzene of A.R. quality was fractionally crystallised and distilled. For the solubility determinations the method described in Part I was used. Although most of the results were obtained by saturation at the selected solubility temperature, with avoidance of preliminary overheating, yet a number of determinations were made by saturating the solutions at about 10° higher than the desired solubility temperature, and then leaving them for 4 to 5 hours at the latter temperature in the thermostat to attain equilibrium. Angelescu and Dumitrescu used this latter method. We obtained concordant results by both methods. In the tables below, S represents g. of picric acid in 100 g. of solvent. The calculated values for S are from the corresponding equations which are discussed below. All the results for 25° (except those for benzene–*iso*propyl alcohol) are represented in the diagram.

Benzene–Methyl Alcohol.

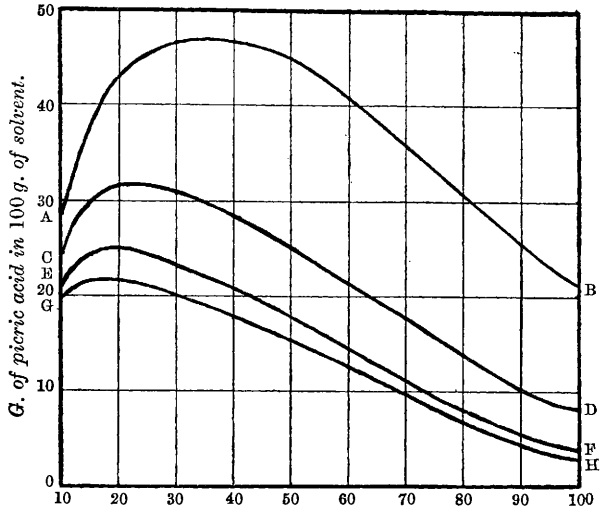
MeOH, % ...	0	10	20	30	40	50	60	70	80	90	100
$S^{0°}$, found ...	—	10·0	13·3	15·4	17·2	18·5	19·8	20·5	18·2	16·2	13·8
$S^{0°}$, calc.....	—	9·0	12·6	15·4	17·4	18·8	19·7	19·8	19·1	16·6	—
$S^{12·5°}$, found..	5·6	14·5	21·0	26·4	29·2	29·8	29·2	26·5	23·1	19·8	16·0
$S^{12·5°}$, calc....	—	19·3	24·2	27·1	28·7	29·3	28·7	27·0	23·7	18·3	—
$S^{25°}$, found ...	10·4	28·5	42·9	46·5	46·5	44·6	40·6	36·0	30·6	25·6	21·1
$S^{25°}$, calc.....	—	38·6	44·2	46·3	46·2	44·3	41·0	36·1	29·3	19·9	—

Benzene–Ethyl Alcohol.

EtOH, % ...	0	10	20	30	40	50	60	70	80	90	100
$S^{0°}$, found ...	—	9·3	10·0	10·7	11·0	10·8	10·3	9·5	8·2	6·6	4·5
$S^{0°}$, calc.....	—	8·0	9·8	10·6	11·0	10·9	10·6	9·7	8·3	6·1	—
$S^{12·5°}$, found	5·6	13·4	16·6	18·3	18·1	17·6	16·0	14·0	11·1	8·2	5·8
$S^{12·5°}$, calc. ...	—	15·4	17·4	18·2	18·1	17·3	16·0	14·1	11·5	7·3	—
$S^{25°}$, found ...	10·4	24·5	31·4	30·6	28·2	25·0	21·7	17·8	13·7	10·1	8·0
$S^{25°}$, calc. ...	—	30·1	31·0	29·9	27·8	25·1	21·7	17·8	13·3	7·9	—
*$S^{12°}$, found	6·9	12·2	16·6	19·0	19·5	19·0	17·7	16·2	14·0	11·0	10·4

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

FIG. 1.



AB *Benzene–methyl alcohol at* 25°. EF *Benzene–*n*-propyl alcohol at* 25°.
CD *Benzene–ethyl* ,, ,, ,, GH *Benzene–butyl* ,, ,,

The results obtained by Angelescu and Dumitrescu at 12° are somewhat higher than ours for 12·5°, particularly for pure alcohol and pure benzene.

*Benzene–*iso*Propyl Alcohol.*

Pr$^{\beta}$OH, % ...	0	10	20	30	40	50	60	70	80	90	100
$S^{0°}$, found ...	—	6·6	8·2	8·8	8·8	8·6	8·0	7·4	6·8	6·2	5·8
$S^{0°}$, calc.	—	6·7	8·0	8·6	8·8	8·7	8·2	7·5	6·3	4·6	—
$S^{25°}$, found ...	10·4	22·5	25·4	25·0	22·5	20·0	17·0	13·8	11·3	9·8	8·7
$S^{25°}$, calc.....	—	25·4	25·6	24·6	22·7	20·3	17·5	14·2	10·5	6·2	—

*Benzene–*n*-Propyl Alcohol.*

Pr$^{\alpha}$OH, % ...	0	10	20	30	40	50	60	70	80	90	100
$S^{0°}$, found ...	—	6·5	7·6	7·8	7·4	6·9	6·1	5·2	4·3	3·4	2·4
$S^{0°}$, calc.	—	7·3	7·8	7·8	7·5	6·9	6·1	5·2	4·0	2·5	—
$S^{25°}$, found ...	10·4	21·0	25·0	23·0	20·7	17·7	14·5	11·2	7·8	5·4	3·7
$S^{25°}$, calc.....	—	26·0	24·8	22·7	20·2	17·5	14·5	11·3	7·9	4·3	—

Benzene–Butyl Alcohol.

BuOH, % ...	0	10	20	30	40	50	60	70	80	90	100
$S^{0°}$, found ...	—	5·8	6·5	6·8	6·5	5·9	5·0	4·2	3·4	2·7	1·8
$S^{0°}$, calc.....	—	6·5	6·8	6·7	6·4	5·9	5·1	4·3	3·3	2·0	—
$S^{25°}$, found ...	10·4	19·6	21·5	19·9	17·8	15·4	12·6	9·9	6·9	4·4	2·9
$S^{25°}$, calc.....	—	21·8	21·6	19·8	17·7	15·3	12·7	9·9	7·0	3·8	—

The approximate alcoholic contents of the solvents giving maximum solubility at the various temperatures are shown by the following table.

	MeOH.	EtOH.	Pr$^{\beta}$OH.	Pr$^{\alpha}$OH.	BuOH.
At 0°	70%	>40%	35%	30%	30%
,, 12·5°	50	35	—	—	—
,, 25°	35	25	25	20	20

Discussion.

In Part I it was found that between 0° and 50° there was no noticeable variation in the alcoholic concentration of the solvent mixtures in which maximum solubility of picric acid occurred. The results found for benzene–alcohol mixtures indicate that in the solvents having the greatest solvent action on picric acid the content of alcohol decreases with increasing temperature. Both at 0° and at 25°, in these particular solvents, the content of alcohol is greatest for methyl and least for *n*-propyl and butyl alcohol. In the first place, this agrees with the order of the proportions of the alcohols found in the constant-boiling mixtures they give with benzene, *viz.*, 39·55% MeOH, 32·36% EtOH, 33·3% Pr$^{\beta}$OH, and 16·9% Pr$^{\alpha}$OH. Secondly, methyl alcohol has the greatest and propyl and butyl alcohol the smallest dissociating action on picric acid (see Part I). The presence of alcohol, especially methyl alcohol, in the solvent develops the yellow modification of picric acid. Benzene probably associates more readily with this yellow modification and enhanced solubility of the picric acid becomes possible until a sufficiently high concentration of alcohol is present for the alcohol to dissociate the associated molecules of benzene and picric acid.

Methyl alcohol, having the greatest dissociating and solvent action, of the alcohols, on picric acid, can thus be present to the greatest extent in the solvent possessing maximum solvent action. As the temperature rises, the dissociating effect of the alcohol on associated molecules of picric acid and benzene will increase, and thus maximum solubility is attained with a lower proportion of alcohol in the mixed solvent.

Above 20% (10% at 0°) concentration of alcohol in the mixed solvents, the influence of the alcohol is regular, and a relation between the increased solubility of picric acid and the amount of

alcohol present with each 100 g. of benzene can be expressed by the equation

$$S_C - S_0 = KC^p$$

where S_0 = solubility of picric acid in 100 g. of benzene,

S_C = solubility of picric acid in a mixture of 100 g. of benzene + C g. of alcohol,

and K and p are constants which can be calculated from the experimental results.

The values found for K and p for the different series and different temperatures are as follows :

	C_6H_6 + MeOH.			C_6H_6 + EtOH.			C_6H_6 + PrβOH.		C_6H_6 + PrαOH.		C_6H_6 + BuOH.	
	0°.	12·5°.	25°.	0°.	12·5°.	25°.	0°.	25°.	0°.	25°.	0°.	25°.
K	1·4	4·2	12·4	1·9	4·2	12·8	1·55	10·0	2·6	13·5	2·3	10·6
p	0·7	0·55	0·44	0·505	0·42	0·246	0·49	0·24	0·32	0·13	0·3	0·14

Since benzene is solid at 0°, an assumed value of 2·5 for S_0 was used in order to calculate values for K and p in the equations for 0°. Solubility results from the above values have been calculated for S and are given for comparison with the experimental results in the respective tables. Close agreement is shown for solvents containing from 20 to 80% of alcohol. The agreement is somewhat better at 0° than at 25°.

Angelescu and Dumitrescu (*loc. cit.*) proposed the above type of equation for the solubility of picric acid in mixed solvents generally, but their results failed to agree with the equations over a wide range. For benzene–ethyl alcohol at 12° they give the equation $S_C - S_0 = 1{\cdot}63C^{0{\cdot}666}$ and this only agrees with the results found for S in solvents having 16 to 40% alcoholic concentration. Our equation for these solvents at 12·5° is $S_C - S_0 = 4{\cdot}2C^{0{\cdot}42}$, which agrees with the major portion of the experimental results.

The influence of alcohols on the solubility of picric acid in chloroform and in ether is under investigation.

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