The Cryoscopic Behaviour of Polynitro-compounds in Sulphuric Acid.

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The effects are reported of various additional solutes upon the molecular depressions of picric acid, $1 : 3 : 5$-trinitrobenzene, and $2 : 4 : 6$-trinitrotoluene in sulphuric acid. The value of θ/m_2 varies more or less with the concentration (m_2) of the polynitro-compound and with the concentration (m_3) of the third component, but is in general (for $m_2{\sim}0.04$) greater than the cryoscopic constant (K_f) with water and less than K_f with potassium hydrogen sulphate, ammonium hydrogen sulphate, or disulphuric acid as third component. Nitromethane differs from the polynitro-compounds in giving θ/m_2 greater than K_f in the presence of potassium hydrogen sulphate. A comparison is drawn between the behaviour of the polynitro-compounds and the variations in the solubility of sulphur dioxide near 100% sulphuric acid.

THE form in which aromatic polynitro-compounds exist in solution in anhydrous sulphuric acid has been a matter of some controversy. Since results of reasonable precision have been obtainable by the cryoscopic technique, Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1933, **55**, 1900) have regarded picric acid and $1 : 3 : 5$-trinitrobenzene as non-electrolytes, Gillespie (*J.*, 1950, 2542; 1954, 1851) has attributed deviations of the order of 10% from the ideal molecular depression for a non-electrolyte to some basic character in $2 : 4 : 6$-trinitrotoluene, and Brand, Horning, and Thornley (*J.*, 1952, 1374) could find no spectrophotometric evidence at all for the ionisation of this compound in 100% sulphuric acid. One of us (Wyatt, *J.*, 1953, 1175) attempted to reconcile the conflicting spectrophotometric and cryoscopic evidence for $2 : 4 : 6$-trinitrotoluene by reference to the variability in the cryoscopic constant (K_f) to be expected from a dissociating solvent when the extent of dissociation is altered; but the K_f values deduced were at variance with the simple theory

developed and disagreed with Kunzler and Giauque's calorimetric measurements (*J. Amer. Chem. Soc.*, 1952, **74**, 3472). A possible alternative explanation in terms of salt effects has therefore been proposed (Wyatt, *J.*, 1954, 2647).

In the work now reported, an investigation has been made of the molecular depressions of freezing-point caused by polynitro-compounds and nitromethane in the presence of potassium hydrogen sulphate and other solutes which interfere with the solvent dissociation. It appears that the suggestion that bases which suppress the solvent dissociation may be used indiscriminately in the cryoscopic method (Gillespie, Hughes, and Ingold, *J.*, 1950, 2473, see p. 2484) can be misleading, at least in the case of solutes which ionise hardly, if at all (*i.e.*, $v \sim 1$). In such cases even qualitative conclusions about basic strength are unreliable when founded upon molecular depressions in the presence of one only of the many solutes which could be used to reduce the solvent dissociation. Until the detailed behaviour of the polynitro-compounds has received an adequate, quantitative explanation no arbitrary selection of the cryoscopic data can justifiably be held to be in conflict with the spectrophotometric interpretation of these compounds as non-electrolytes.

EXPERIMENTAL

The experimental arrangements followed closely those recommended by Gillespie, Hughes, and Ingold (*loc. cit.*), except that a 6—11° solid-stem mercury-in-glass thermometer graduated in 0·01° was used (Gillespie and Leisten, *J.*, 1954, 1) and that a single-armed stirrer operated by one solenoid was found to be adequate for stirring the contents of the cryoscope. In some preliminary experiments attempts were made to use thermistors for temperature measurements (cf. Gold, Hawes, and Tye, *J.*, 1952, 2167), but with 2 volts across a bridge with 6000 ohms in each arm the readings were not reliable even to 0·01°; and, although improvements might have been possible by reducing the potential a more elaborate galvanometer system would then have been necessary for detection.

Materials.—The oleum and slightly aqueous solutions of sulphuric acid were prepared in the usual manner (Gillespie, Hughes, and Ingold, *loc. cit.*) and the molality of excess of water or disulphuric acid was estimated from the freezing-point. Potassium sulphate and ammonium sulphate of " AnalaR " quality were dried for 2 hr. at 105°. Commercial 1 : 3 : 5-trinitro-benzene and picric acid were twice recrystallised from glacial acetic acid or methylated spirits respectively and dried at 100°. Commercial 2 : 4 : 6-trinitrotoluene was recrystallised three times from chloroform, dried between filter-papers, and kept for two days in a vacuum-desiccator. Nitromethane was dried ($CaCl_2$) and distilled just before use. Technical acetone was purified by means of the sodium iodide addition compound (Shipsey and Werner, *J.*, 1913, **103**, 1255), dried (K_2CO_3), and distilled.

Results.—The results are collected in Tables 1—4, in which m_2 indicates the molality of the nitro-compound and $(\theta/m_2)'$ gives the value of the molecular depression corrected slightly as described below. θ represents the depression of freezing-point from that of the solvent after treatment with the third component, the concentration of which was so arranged that the initial freezing-point was roughly 9·5°, 8·5°, or 7·5°. Variations in the molecular depression due to the usual imperfections in the simple cryoscopic formula were allowed for by a correction term similar to that of Hammett and Deyrup (*loc. cit.*) and Gillespie, Hughes, and Ingold, (*loc. cit.*). To simplify the presentation here, all molalities in the Tables were calculated from the solvent weight *after* allowance for reaction to form solutes of the types $M^+HSO_4^-$ and $H_2S_2O_7$ with the third component, and possible solvation of any particles present was ignored. The relationship between the corrected, $(\theta/m_2)'$, and the observed molecular depression, $(\theta/m_2)_{obs.}$, is

$$(\theta/m_2)' = (\theta/m_2)_{obs.} \{1 + 0.00350 + (\bar{m}_2 + 2m_3)/m_1\}$$

where the symbols in the correction term have the same significance as in Gillespie's formula. The correction term does not affect the general trend of the results, being usually less than 1·03, and it has not been applied in the case of disulphuric acid solution in view of the uncertainties in v_3 and s_3 due to the possible formation of higher polyacids (Gillespie, *loc. cit.*, p. 2516). Since 2 : 4 : 6-trinitrotoluene solutions slowly reddened on exposure to sunlight, the cryoscope was exposed to ultraviolet radiation from a high-pressure quartz-mercury arc after the final addition of the trinitrotoluene in the runs quoted in Tables 3*a* and 3*b*, and any possible variation in the freezing-point sought. After 2 hr. the final freezing-point of 7·816° quoted in Table 3*a* had

TABLE 1. Molecular depressions of picric acid.

(a) Molality of $(H_3O^+ \cdot HSO_4^-) = 0·093$

m_2	—	0·0223	0·0459	0·0929	0·1612
F. p. ...	9·511°	9·368°	9·221°	8·945°	8·563°
$(\theta/m_2)'$	—	6·55	6·45	6·26	6·06

(b) Molality of $(H_3O^+ \cdot HSO_4^-) = 0·173$

m_2	—	0·0186	0·0410	0·0856	0·1562
F. p.	8·643°	8·531°	8·395°	8·136°	7·732°
$(\theta/m_2)'$	—	6·21	6·30	6·19	6·12

(c) Molality of $(H_3O^+ \cdot HSO_4^-) = 0·298$

m_2	—	0·0394	0·0781	0·1375
F. p.	7·341°	7·115°	6·885°	6·561°
$(\theta/m_2)'$	—	6·15	6·27	6·11

(d) Molality of $KHSO_4 = 0·0883$

m_2	—	0·0181	0·0371	0·0762	0·1481
F. p.	9·455°	9·350°	9·241°	9·031°	8·658°
$(\theta/m_2)'$	—	5·92	5·89	5·70	5·54

(e) Molality of $KHSO_4 = 0·1528$

m_2	—	0·0170	0·0366	0·0758	0·1430
F. p.	8·668°	8·581°	8·482°	8·286°	7·944°
$(\theta/m_2)'$	—	5·30	5·28	5·24	5·29

(f) Molality of $NH_4HSO_4 = 0·0790$

m_2	—	0·0213	0·0401	0·0772	0·1378
F. p.	9·573°	9·446°	9·343°	9·137°	8·835°
$(\theta/m_2)'$	—	6·09	5·84	5·78	5·50

(g) Molality of acetone (as $BH^+ \cdot HSO_4^-$) = 0·0981

m_2	—	0·0183	0·0375	0·0714	0·1355
F. p.	9·372°	9·260°	9·145°	8·945°	8·582°
$(\theta/m_2)'$	—	6·26	6·21	6·14	6·01

(h) Molality of $H_2S_2O_7 = 0·130$

m_2	—	0·0217	0·0383	0·0821	0·1529
F. p.	9·502°	9·378°	9·294°	9·060°	8·716°
$(\theta/m_2)'$	—	5·71	5·44	5·39	5·14

(i) Molality of $H_2S_2O_7 = 0·313$

m_2	—	0·0486
F. p.	8·236°	8·024°
$(\theta/m_2)'$	—	4·36

(j) Pure acid as solvent without third component

m_2	—	0·0183	0·0356	0·0743	0·1330
F. p.	10·359°	10·241°	10·140°	9·910°	9·574°
$(\theta/m_2)'$	—	6·46(?)	6·17	6·07	5·95

TABLE 2. Molecular depressions of 1:3:5-trinitrobenzene.

(a) Molality of $(H_3O^+ \cdot HSO_4^-) = 0·089$

m_2	—	0·0428	0·0803	0·1534
F. p.	9·560°	9·290°	9·060°	8·635°
$(\theta/m_2)'$	—	6·45	6·39	6·14

(b) Molality of $(H_3O^+ \cdot HSO_4^-) = 0·168$

m_2	—	0·0269	0·0506	0·0993	0·1720
F. p.	8·708°	8·542°	8·404°	8·162°	7·696°
$(\theta/m_2)'$	—	6·41	6·26	6·24	6·17

(c) Molality of $KHSO_4 = 0·0746$

m_2	—	0·0866	0·1591
F. p.	9·558°	9·058°	8·898°
$(\theta/m_2)'$	—	5·91	5·80

(d) Molality of $KHSO_4 = 0·1524$

m_2	—	0·0200	0·0410	0·0844	0·1533
F. p.	8·684°	8·581°	8·472°	8·241°	7·896°
$(\theta/m_2)'$	—	5·34	5·37	5·46	5·37

(e) Molality of $H_2S_2O_7 = 0·116$

m_2	—	0·0239	0·0462	0·0939	0·1750
F. p.	9·612°	9·477°	9·353°	9·100°	8·679°
$(\theta/m_2)'$	—	5·64	5·61	5·45	5·33

(f) Pure acid as solvent without third component

m_2	—	0·0187	0·0355	0·0687	0·1179	0·1897
F. p.	10·354°	10·238°	10·132°	9·925°	9·637°	9·226°
$(\theta/m_2)'$	—	6·23	6·27	6·27	6·12	6·01

TABLE 3. Molecular depressions of 2:4:6-trinitrotoluene.

(a) Molality of $(H_3O^+ \cdot HSO_4^-) = 0·169$

m_2	—	0·0190	0·0424	0·0805	0·1425
F. p.	8·693°	8·577°	8·432°	8·195°	7·816°
$(\theta/m_2)'$	—	6·36	6·41	6·46	6·45

(b) Molality of $(H_3O^+ \cdot HSO_4^-) = 0·300$

m_2	—	0·0413	0·0833	0·1547
F. p.	7·312°	7·059°	6·806°	6·383°
$(\theta/m_2)'$	—	6·56	6·53	6·48

(c) Molality of $KHSO_4 = 0·0783$

m_2	—	0·0172	0·0399	0·0788	0·1350
F. p.	9·571°	9·470°	9·337°	9·112°	8·789°
$(\theta/m_2)'$	—	5·97	5·99	6·02	5·94

(d) Molality of $KHSO_4 = 0·1542$

m_2	—	0·0204	0·0388	0·0731	0·1381
F. p.	8·660°	8·555°	8·452°	8·268°	7·910°
$(\theta/m_2)'$	—	5·33	5·57	5·58	5·67

TABLE 4. Molecular depressions of nitromethane.

(a) Molality of $(H_2O^+ \cdot HSO_4^-) = 0·093$

m_2	—	0·0090	0·0466	0·0929	0·1468
F. p.	9·511°	9·453°	9·229°	8·934°	8·590°
$(\theta/m_2)'$	—	6·55	6·14(?)	6·37	6·46

(b) Molality of $KHSO_4 = 0·0821$

m_2	—	0·0183	0·0404	0·1210	0·1696
F. p.	9·543°	9·430°	9·288°	8·765°	8·462°
$(\theta/m_2)'$	—	6·30	6·45	6·60	6·56

(c) Pure acid as solvent without third component

| m_2	—	0·0909
F. p.	10·355°	9·818°
$(\theta/m_2)'$	—	6·15

fallen to 7·753°, and after 4½ hr. to 7·696° : similarly the value 6·383° (Table 3*b*) was reduced to 6·144° after 7½ hr. Thus, whatever the nature of this photochemical reaction, it is such as to cause a sufficient increase in the molecular depression to be a possible source of error in any

lengthy physical investigations involving this substance. Mr. B. J. Kirkbride has recently observed that nitromethane also undergoes some reaction in sulphuric acid since there is a slow drift of the freezing-point with time. (Dr. R. J. Gillespie informs us that he has come to the same conclusion from conductivity measurements.)

DISCUSSION

The Tables show that the value of the overall molecular depression varies with the concentration of the nitro-compound (except trinitrotoluene usually) and with that of the third component. The two values quoted by Hammett and Deyrup for picric acid, showing deviations from K_f (6·12), fit in well with this pattern. To clarify the general trends observed, values of $(\theta/m_2)'$ have been interpolated for a 0·04m-concentration of the
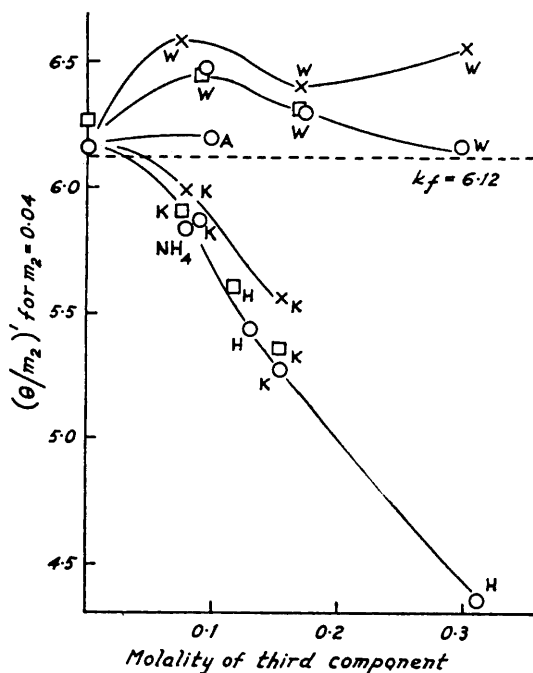
Molecular depressions of polynitro-compounds in sulphuric acid.

○ Picric acid.
□ Trinitrobenzene.
× Trinitrotoluene.

The third components are indicated by letters as follows :

K, $KHSO_4$.
NH_4, NH_4HSO_4.
W, $H_3O \cdot HSO_4$.
H, $H_2S_2O_7$.
A, $(CH_3)_2C(OH) \cdot HSO_4$.

three polynitro-compounds and plotted in the diagram against the molality of the third component : the point at 0·074m-water for trinitrotoluene has been taken from Gillespie's results (*loc. cit.*, p. 2544). If a higher molality of nitro-compound had been chosen the picture would have been similar, apart from some flattening of the water curve for picric acid and trinitrobenzene. Qualitatively, the three polynitro-compounds are seen to behave in the same way, although the trinitrotoluene curves are somewhat higher than the other two, giving rise to the general appearance of a sheaf of curves reminiscent of those found for activity effects in other solvents. The curves show clearly that the behaviour of these compounds is quite different in the presence of potassium and ammonium hydrogen sulphates from that in the presence of hydroxonium hydrogen sulphate, whilst acetone seems to have little effect at all. These facts eliminate the possibility of straightforward basic behaviour of the type considered by Gillespie, since such a hypothesis would require similar effects to be produced by all solutes which give rise to hydrogen sulphate ions. Other types of chemical reaction are still conceivable, but would have to be brought to terms with the spectrophotometric evidence of Brand *et al.* On the whole, it seems, however, that salting-out and salting-in effects could provide an adequate explanation, and must in any case always be considered in a three-component system (Wyatt, *J.*, 1954, 2647). Our data are neither extensive nor accurate enough for the calculation of activity coefficients by McKay's method (*Nature*, 1952, **169**, 464; McKay and Perring, *Trans. Faraday Soc.*, 1953, **49**, 163; Robinson, *ibid.*, p. 1411), although this method can be adapted for cryoscopic

determinations; but qualitatively it follows that salting-out of the non-electrolyte would be accompanied by an increase of $(\theta/m_2)'$, and salting-in by a decrease. Thus, if the differences of behaviour persist up to the limit of solubility, the solubilities of the polynitro-compounds should be less in slightly aqueous sulphuric acid than in dilute oleum or solutions of potassium and ammonium hydrogen sulphates; and this aspect of the problem is being investigated further. There is some evidence that non-electrolytes do in fact behave in this way; for sulphur dioxide, which has been regarded as undergoing no chemical reaction in sulphuric acid (Gold and Tye, *J.*, 1950, 2932), has been shown to have an inflection in its solubility near, but not at, 100% sulphuric acid (Miles and Carson, *J.*, 1946, 786). At 20° a minimum solubility occurs at 80·64—80·81% sulphur trioxide (*i.e.*, 98·79—99·00% sulphuric acid), after which the solubility rises steadily through 81·63% sulphur trioxide (100% sulphuric acid) and so becomes larger on the sulphur trioxide side than on the water side of 100% sulphuric acid. [A similarly displaced minimum in the density recorded by Lichty (Landolt–Börnstein's " Tabellen," Hauptwerk I, 399, footnote) does not seem to have been substantiated in the recent work of Gillispie and Wasif, *J.*, 1953, 215.]

The measurements on picric acid and trinitrobenzene at low molalities suggest that the molecular depression does not agree with Raoult's law even in the pure solvent. This is not unexpected for dilute solutions of non-electrolytes in dissociating solvents, since the solute would generally be expected to interact differently with the various species present in the pure solvent, especially where differences of polarity are possible [see *e.g.*, Rushbrooke, " Introduction to Statistical Mechanics, " O.U.P., London, 1949, p. 226, condition (*b*)].

Nitromethane differs from the polynitro-compounds in giving similar results in the presence of $KHSO_4$ and $H_3O^+ \cdot HSO_4^-$. Here, it seems, the possibility of basic behaviour cannot be ruled out, but would presumably be superimposed on salt effects in such a way that the two phenomena would be difficult to disentangle.