432. *Solubility and Heat of Solution of* 2 : 4 : 6-*Trinitrotoluene in Sulphuric Acid at* 25°.

By B. J. KIRKBRIDE and P. A. H. WYATT.

The solubility of 2 : 4 : 6-trinitrotoluene in sulphuric acid at 25° in the presence of disulphuric acid, water, or potassium hydrogen sulphate up to concentrations of about 0·4m was measured. It is increased by addition of disulphuric acid and decreased by addition of water; in the latter case irregularities appear near 0·2m-H_3O,HSO_4 similar to those observed in cryoscopy. Potassium hydrogen sulphate increases the ratio of trinitrotoluene to sulphuric acid in the solution but hardly affects the mole fraction of the nitro-compound. The heat of infinite dilution of a saturated solution of trinitrotoluene is less than 100 cal. mole^{-1}, and the heat of solution of the solid, 4·6 kcal. mole^{-1}, is close to the heat of fusion. These observations help in a discussion of the magnitude of the solubility of this compound in sulphuric acid, which is 13·15 g. per 100 g. of H_2SO_4 at 25°.

ELECTROLYTES exert specific influences upon the cryoscopic behaviour of polynitro-compounds in the solvent sulphuric acid and an explanation in terms of " salting-out " and " salting-in " was suggested,[1] to test which we have investigated the solubility of 2 : 4 : 6-trinitrotoluene in sulphuric acid with and without the addition of other electrolytes. Heats of dilution and solution of this solute were also determined to obtain a broader picture of the nature of solutions of non-electrolytes in this solvent.

EXPERIMENTAL

All materials were prepared or purified as described by Brayford and Wyatt.[1]

Solubilities.—The solubility was measured of trinitrotoluene in pure sulphuric acid and in sulphuric acid containing hydroxonium hydrogen sulphate (*i.e.*, in aqueous acid), disulphuric acid, or potassium hydrogen sulphate as third component. Since freezing-point measurements were used to prepare the sulphuric acid solutions, it was convenient to carry out the equilibration with solid trinitrotoluene in a cryoscope. A sample (about 120 g.) of sulphuric acid containing the third component was first prepared therein, and an excess of solid trinitrotoluene then added. The thermometer (a 10-junction copper–constantan thermocouple) was replaced by a glass stopper, and the cryoscope was allowed to equilibrate for 40—80 hr. at 25·1°, the contents being continuously stirred. Samples were then taken with the simple filter and suction device shown in Fig. 1. Each sample was delivered directly into a weighed weighing bottle and analysed for trinitrotoluene by the titanous sulphate–ferric alum procedure.[2,3,4] (Alcohol was used in the dilution of the samples to keep the trinitrotoluene in solution.) Pure 2 : 4 : 6-trinitrotoluene was used to standardize the titanous sulphate solution.

Heats of Solution.—The apparatus for thermal measurements has been described.[5] With pure sulphuric acid in the calorimeter, the heat changes were measured as successive amounts of trinitrotoluene were added, both as a *ca.* 0·5m-solution in sulphuric acid and as a solid.

Results.—In Fig. 2 the results of the solubility measurements are shown in terms of the number of moles of trinitrotoluene dissolved per 1000 g. of sulphuric acid. Determinations were reproducible to about 0·5%. When converting the results into mole fractions for Table 1, allowance was made for the ionization of potassium and hydroxonium hydrogen sulphates into two particles, but disulphuric acid was treated as a non-electrolyte—its partial ionization[6] would not affect the calculated value for the mole fraction of trinitrotoluene, provided that no attempt was made to allow for ionic solvation, since the ionization involves no change in the

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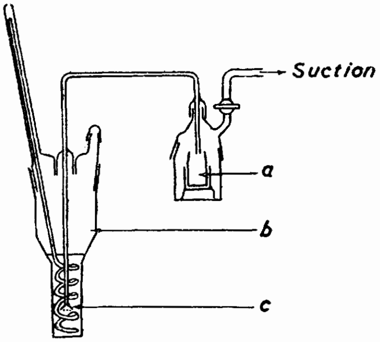
[1] Brayford and Wyatt, *J.*, 1955, 3453.
[2] Knecht and Hibbert, " New Methods of Volumetric Analysis," Longmans Green, London, 1918.
[3] Callan and Henderson, *J. Soc. Chem. Ind.*, 1922, **41**, 157T.
[4] Hammett and Chapman, *J. Amer. Chem. Soc.*, 1934, **56**, 1282.
[5] Kirkbride and Wyatt, *Trans. Faraday Soc.*, 1958, **54**, 483.
[6] Gillespie, *J.*, 1950, 2493.

number of particles: $H_2S_2O_7 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HS_2O_7^-$. Similarly, the self-dissociation of the solvent does not affect the solute mole fraction.

Table 2 contains the thermal results. The small heat changes observed when trinitrotoluene is added in solution are just greater than the probable error (estimated [5] as 50 cal. mole^{-1}). The experimental error was probably rather larger when the solid was added, however, since it was difficult to correct [5] for the difference between the temperatures of the solid and the calorimeter contents before the addition was made. Experience with the addition of liquids under the same conditions showed that this difference seldom exceeded 2°, but a correction based on this figure would imply that the values recorded for the heat of solution (Table 2) could be 150 cal. mole^{-1} low. An error of this magnitude does not affect the subsequent discussion.

FIG. 1. *Sampling device.*



a, Weighing bottle in wire cradle; *b*, cryoscope; *c*, No. 2 sintered filter disc.

FIG. 2. *Solubility of* 2 : 4 : 6-*trinitrotoluene in sulphuric acid solutions at* 25°.

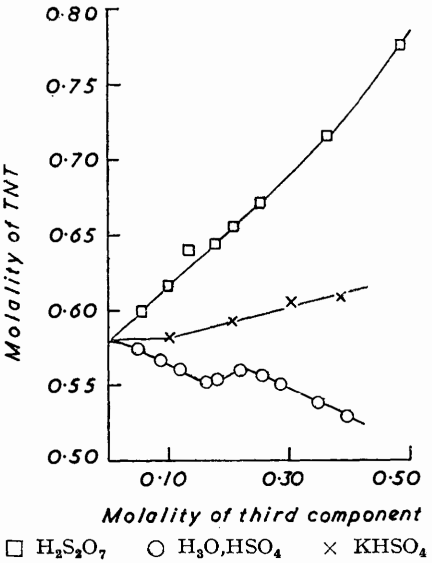


TABLE 1. *Composition (mole fractions) of saturated trinitrotoluene solutions at* 25°.

(*a*) Water as third component

T.N.T.	H_3O^+ + HSO_4^-	H_2SO_4
0·0537	0·000	0·9463
0·0529	0·00884	0·9383
0·0519	0·01422	0·9339
0·0509	0·02170	0·9274
0·0500	0·02878	0·9212
0·0498	0·03243	0·9178
0·0501	0·03841	0·9115
0·0494	0·04470	0·9059
0·0488	0·04939	0·9018
0·0471	0·06023	0·8927
0·0460	0·06842	0·8856

(*b*) $H_2S_2O_7$ as third component

T.N.T.	$H_2S_2O_7$	H_2SO_4
0·0553	0·00525	0·9395
0·0564	0·00905	0·9346
0·0583	0·01204	0·9297
0·0585	0·01593	0·9256
0·0592	0·01872	0·9221
0·0603	0·02247	0·9172
0·0635	0·03231	0·9042
0·0678	0·04187	0·8903

(*c*) $KHSO_4$ as third component.

T.N.T.	K^+ + HSO_4^-	H_2SO_4
0·0530	0·01813	0·9289
0·0529	0·03644	0·9107
0·0532	0·05296	0·8938
0·0526	0·06648	0·8809

The presence of trinitrotoluene seems to produce very little change in the specific heat of sulphuric acid. At molalities of 0·0055, 0·0111, 0·0165, 0·0266, and 0·0318 values of $0{\cdot}337_7$, $0{\cdot}338_4$, $0{\cdot}337_2$, $0{\cdot}337_5$, and $0{\cdot}336_9$ cal. deg.$^{-1}$ g.$^{-1}$ respectively were recorded (cf. the corresponding value of 0·3373 cal. deg.$^{-1}$ g.$^{-1}$ for the pure solvent [5]).

TABLE 2.

(*a*) Relative partial molar heat content of trinitrotoluene in sulphuric acid solutions at 25°.
Trinitrotoluene added as a 0·4989m solution.

Mean molality	0·00277	0·00832	0·01382	0·01922
$\bar{H}_2$ relative to 0·5m (cal. mole^{-1})	83	76	0	68

(*b*) Heat of solution of crystalline trinitrotoluene in sulphuric acid at 25°.

Mean molality	0·02272	0·02923
$\bar{H}_2$ relative to pure crystals (cal. mole^{-1})	4574	4535

DISCUSSION

A striking feature of the curves shown in Fig. 2 is their similarity to the curves obtained in the cryoscopic work, apart from the expected change in direction of the effects; *i.e.*, a decrease in solubility is associated with an increase in the molecular depression of the solvent freezing-point. In spite of the tenfold difference in trinitrotoluene concentration between the two sets of experiments, therefore, the solubilities support the general conclusions [1, 7] about "salting-out" effects in this solvent.

The effects of potassium hydrogen sulphate are puzzling. On the basis of the cryoscopic data it was concluded that this compound should "salt-in" trinitrotoluene. Although the amount of trinitrotoluene dissolved per 1000 g. of sulphuric acid does increase appreciably (Fig. 2), recalculation of the results on a mole-fraction basis shows that the solubility of the nitro-compound is practically constant (Table 1). In this case, the discrepancy probably arises from the difference in concentration of trinitrotoluene in the cryoscopic and solubility experiments, since some indication of an increase in the molecular depression with increasing trinitrotoluene concentration was actually observed in potassium hydrogen sulphate solutions [see ref. 1, Table 3 (*d*)].

When water is the third component, the irregularities recorded previously in the molecular depression of the freezing-point of the solvent in the neighbourhood of 0·2m are also reflected in the solubilities. Comparison with the similar effects of water upon the solubility of sulphur dioxide [8] in this solvent, and upon the density, leads us to suppose that the causes for the changes in non-electrolyte activity coefficients reside in modifications in the structure and constitution of the solvent itself rather than in any specific chemical involvement of the non-electrolyte (chemical solvation).

The magnitude of the solubility in the pure solvent (mole fraction 0·0537) can be interpreted from thermal data. The very small heat absorption upon dilution of a 0·5m solution shows that the heat of infinite dilution of a saturated solution must be negligible (less than 100 cal. mole^{-1}). It is also significant that the heat of solution of the solid is very similar to the heat of fusion of trinitrotoluene. Unfortunately there is no record of a direct determination of the heat of fusion, but the values obtained from melting curves [9-12] of trinitrotoluene in mixtures with compounds of similar structure have usually been quoted as 4·6 or 4·9 kcal. mole^{-1}. This again provides evidence that the non-electrolyte probably exists in solution as simple molecules and not in chemically solvated form.

Although the absence of marked thermal changes indicates that departures from ideality in these solutions are mainly due to entropy effects, the standard theory of athermal solutions is not in itself sufficient to account for all the properties because it accounts for *negative* deviations from Raoult's law,[13] *i.e.*, for a solubility greater than the ideal value

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[7] Wyatt, *J.*, 1954, 2647.

[8] Miles and Carson, *J.*, 1946, 786.

[9] Auwers, *Z. phys. Chem.*, 1899, **30**, 300.

[10] Pastak, *Bull. Soc. chim. France*, 1926, **39**, 82.

[11] Timmermans, *Bull. Soc. chim. Belg.*, 1935, **44**, 17.

[12] Rinkenbach and Hall, *J. Amer. Chem. Soc.*, 1924, **46**, 2637.

[13] Hildebrand and Scott, "The Solubility of Non-electrolytes," Reinhold, New York, 3rd edn., Chap. 6.

(and effects in the same direction would also be required by a chemical solvation treatment). A heat of fusion[12] of 4·6 kcal. mole^{-1} and m. p. 80·5° would require an ideal solubility at 25° of 0·30 in mole-fraction terms. Thus we have a considerable *positive* deviation from Raoult's law. Qualitatively the reduced solubility can be accounted for by supposing that sulphuric acid behaves as an " associated " solvent towards non-electrolytes of lower polarity. In view of the small changes of heat content, the positive excess free energy of solution must be associated with a negative excess entropy, as is the case for non-electrolytes in water; and theories of this loss of entropy on solution could obviously be applied to both solvents. For example, according to Frank and Evans,[14] the non-electrolyte would be pictured as inducing a greater " crystallinity " of sulphuric acid in its vicinity.

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SHEFFIELD UNIVERSITY.

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[14] Frank and Evans, *J. Chem. Phys.*, 1945, **13**, 507.