

XCIV.—*The Volume of a Solute in Solution. Part II.
The Influences of Molecular Association, Solvate
Formation and Ionisation.*

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IN a previous communication (Trans., 1910, **97**, 2620) it was shown that the volume of a solute in a solvent is constant, independent of the concentration, and differing but slightly from solvent to solvent.

With this rule established, it becomes possible to study systematically the influences of molecular association, solvate formation, and ionisation on the specific volume of the solute in solution. These are points which have been rather neglected by previous investigators, whose work has been almost wholly confined to aqueous solutions where all three factors may come into play. Traube (*Annalen*, 1896, **290**, 43), for example, studied a large number of aqueous solutions, and although he eliminated the influence of ionisation by considering non-electrolytes, the other two factors played an unknown part, vitiating to some extent the accuracy of his conclusions. It is impossible to generalise with safety from results for aqueous solutions, unless the influences of these secondary factors are properly understood.

By taking, in the first place, cases in which the solute polymerises in solution and does not combine with the solvent, we can determine the influence of molecular association on the specific solution volume of the solute. In the second place, by taking cases where the solute is known to combine with the solvent, we can study the effect of solvate formation. The influence of ionisation can be determined by a study of aqueous solutions of electrolytes and by a comparison of the behaviour of these with that of non-electrolytes. The method

of working consists simply in determining the specific volumes of solutions of known concentrations, the specific volume of the dissolved substance being then calculated by means of the formula

$$v = \frac{(100 + A)S_1 - 100S_0}{A},$$

where v is the specific volume of the solute in solution, A is the percentage concentration of the solution (grams of solute per 100 of solvent), S_1 the specific volume of the solution, and S_0 the specific volume of the pure solvent at the same temperature.

Measurements were made by means of a quartz pyknometer.

The specific volume determinations were made to within a mean error not greater than one unit in the fifth place. All the measurements were made at the constant temperature of 12.87° , obtained in a bath of running water, the temperature of which could be controlled to within 0.005° . The details of the working are described in the previous paper (*loc. cit.*).

All the substances used were carefully purified; as a rule, Kahlbaum's chemicals were further purified by redistillation or crystallisation.

The Influence of Molecular Association.

In the following tables are given the specific volumes, v , of some hydroxyl compounds dissolved in normal solvents. In all cases the solute exists in solution as complex molecules, the complexity of which increases with the concentration (see Beckmann, *Zeitsch. physikal. Chem.*, 1882, **2**, 715; Auwers and Orton, *ibid.*, 1896, **21**, 337).

The results are for the constant temperature of 12.87° .

<i>Phenol in Toluene</i> ($S_0 = 1.14636$).			<i>Phenol in Chloroform</i> ($S_0 = 0.66587$).		
<i>A.</i>	S_1 .	<i>v.</i>	<i>A.</i>	S_1 .	<i>v.</i>
2.136	1.14152	0.915	4.029	0.67562	0.917
4.446	1.13656	0.916	7.450	0.68324	0.916
10.916	1.12376	0.917	13.637	0.69591	0.916
23.042	1.10326	0.916	28.251	0.72106	0.916
40.428	1.08047	0.917			

<i>Benzoic Acid in Benzene</i> ($S_0 = 1.12819$).			<i>Benzoic Acid in Chloroform.</i>		
<i>A.</i>	S_1 .	<i>v.</i>	<i>A.</i>	S_1 .	<i>v.</i>
2.158	1.12251	0.859	1.555	0.66861	0.845
4.528	1.11649	0.858	3.659	0.67227	0.847
7.279	1.10992	0.859	9.207	0.68105	0.846

<i>Monochloroacetic Acid in Benzene.</i>			<i>Monochloroacetic Acid in Toluene.</i>		
<i>A.</i>	S_1 .	<i>v.</i>	<i>A.</i>	S_1 .	<i>v.</i>
4.129	1.11216	0.724	2.615	1.13530	0.713
9.176	1.09405	0.722	8.852	1.11099	0.712
12.183	1.08395	0.721	12.359	1.09851	0.711

<i>o</i> -Cresol in Benzene.			<i>o</i> -Cresol in Nitrobenzene ($S_0=0\cdot82600$).		
<i>A.</i>	S_1	<i>v.</i>	<i>A.</i>	S_1	<i>v.</i>
3·757	1·12164	0·947	3·178	0·82985	0·951
5·456	1·11886	0·948	10·552	0·83808	0·952
12·418	1·10810	0·946	19·361	0·84644	0·952
28·659	1·08772	0·947			
<i>Acetic Acid in Benzene.</i>			<i>Acetic Acid in Toluene.</i>		
<i>A.</i>	S_1	<i>v.</i>	<i>A.</i>	S_1	<i>v.</i>
4·220	1·12270	0·952	3·111	1·14133	0·979
8·715	1·11704	0·989	7·548	1·13456	0·978
24·060	1·10006	0·983	13·792	1·12587	0·976
30·548	1·09368	0·981	16·862	1·12182	0·976
<i>Methyl Alcohol in Benzene</i> ($S_0=1\cdot12842$).			<i>o</i> -Nitrophenol in Benzene.		
<i>A.</i>	S_1	<i>v.</i>	<i>A.</i>	S_1	<i>v.</i>
1·900	1·13075	1·253	3·127	1·11691	0·755
7·883	1·13748	1·252	7·089	1·10354	0·755
16·375	1·14574	1·252	12·916	1·08546	0·754
24·426	1·15252	1·251	33·521	1·03418	0·754
27·270	1·15466	1·251			
62·162	1·17546	1·251			

It will be seen from the above tables that the specific volume of the solute in solution is, in all cases, with the exception of acetic acid in benzene, independent of the concentration. Now in all the above cases the solute is associated in solution, and the degree of association increases with increase of concentration. For example, Beckmann (*loc. cit.*) found that phenol in benzene at a concentration of 0·34 per cent. has a molecular weight of 143, and at a concentration of 2·5 per cent. the molecular weight is 161, the normal molecular weight being 94.

It may be concluded, therefore, from these experiments that the specific volume of a solute in solution is independent of its degree of association.

It will be noticed that in those cases given above where determinations have been made for a given solute in two different solvents, that the specific volume of the solute is not the same in both. The slight difference is merely the normal effect of the solvent which was studied in the previous paper (*loc. cit.*). In regard to the exceptional case of acetic acid and benzene, this might be explained (as will presently be seen) by supposing that the acetic acid combines to some extent with the benzene, although there is no other evidence to support this.

The Influence of Solvate Formation.

There appears to be few cases where there is certain evidence that the solute (which must not be ionised) combines with the solvent when dissolved. From what has just been established, it follows that it does not matter whether the solute is associated or not.

One case of this class was mentioned in the previous paper, namely, that of triphenylmethane in benzene, and it was found that the specific volume of the solute in this solution is not sensibly different from the values in other normal solvents. In this case evidently, solvate formation does not influence the apparent volume of the solute. This is supported by a few other cases given below, but, as will be seen, the rule is not general.

Calcium Chloride in Methyl Alcohol
($S_0=1\cdot25078$).

<i>A.</i>	<i>S₁.</i>	<i>v.</i>
1·006	1·23642	-0·19
2·114	1·22192	-0·143
6·877	1·16564	-0·072
9·348	1·13992	-0·046

Calcium Chloride in Ethyl Alcohol
($S_0=1\cdot25651$).

<i>A.</i>	<i>S₁.</i>	<i>v.</i>
1·729	1·23446	0·120
3·815	1·21288	0·143
4·842	1·20272	0·149

Calcium chloride combines with methyl alcohol, forming a compound of the formula $\text{CaCl}_2\cdot 4\text{CH}_3\text{O}$, and a similar compound with ethyl alcohol. There can be little doubt that these compounds exist also in solution, and that the amount formed will decrease with the concentration. This change is shown by a constant increase in the value of the specific solution volume. In the case of methyl alcohol, the volume of the solution is less than the volume of methyl alcohol it contains.

m-Dinitrobenzene in Toluene Solutions of Naphthalene.

m-Dinitrobenzene crystallises with naphthalene like picric acid. As picric acid itself is too sparingly soluble, it was considered of interest to determine the specific volume of *m*-dinitrobenzene in solutions of naphthalene in toluene, and to compare them with values found in other solvents.

Solution A.

1·259 per cent. of naphthalene
($S_0=1\cdot14396$).

<i>A.</i>	<i>S₁.</i>	<i>v.</i>
2·637	1·13156	0·661
4·563	1·12296	0·663
7·846	1·10905	0·664
11·903	1·09304	0·665

Solution B.

5·334 per cent. of naphthalene
($S_0=1\cdot13678$).

<i>A.</i>	<i>S₁.</i>	<i>v.</i>
2·618	1·12482	0·667
5·651	1·11161	0·666
9·961	1·09411	0·666

Solution C.

7·825 per cent. of naphthalene
($S_0=1\cdot13265$).

<i>A.</i>	<i>S₁.</i>	<i>v.</i>
1·060	1·12778	0·668
3·306	1·11772	0·666

Solution D.

25·449 per cent. of naphthalene
($S_0=1\cdot10852$).

<i>A.</i>	<i>S₁.</i>	<i>v.</i>
3·250	1·09455	0·665
23·051	1·02633	0·669

In Pure Toluene.

<i>A.</i>	<i>S₁.</i>	<i>v.</i>
3·123	1·13153	0·660
10·478	1·10051	0·663

It is clear from the above that the formation of a compound of naphthalene with *m*-dinitrobenzene has but little effect on the apparent specific solution-volume of the latter.

Trinitrotoluene in Benzene Solutions of Naphthalene.

Like dinitrobenzene, trinitrotoluene also crystallises with naphthalene from a mixed solution of the two. The specific volumes of trinitrotoluene have been determined in two different solutions of naphthalene in benzene, and for the sake of comparison in pure benzene and also in chloroform, the latter being also used in case the solute combined with benzene as well as with the naphthalene.

<i>Solution A.</i>			<i>Solution B.</i>		
2.423 per cent. of naphthalene ($S_0=1.12428$).			9.642 per cent. of naphthalene ($S_0=1.11352$).		
<i>A.</i>	S_1 .	<i>v.</i>	<i>A.</i>	S_1 .	<i>v.</i>
2.507	1.11219	0.630	5.289	1.08922	0.630
6.795	1.09296	0.632	6.262	1.08502	0.631
14.856	1.06062	0.632	10.701	1.06690	0.631
<i>Trinitrotoluene in Pure Benzene.</i>			<i>Trinitrotoluene in Chloroform.</i>		
<i>A.</i>	S_1 .	<i>v.</i>	<i>A.</i>	S_1 .	<i>v.</i>
4.211	1.10818	0.633	1.628	0.66516	0.622
7.833	1.09219	0.633	2.622	0.66468	0.619
12.840	1.07185	0.633	3.202	0.66454	0.623
15.462	1.06184	0.633			

In this case, as in the previous example, the apparent volume of the solute is unaltered by its combination with a portion of the solvent.

Acetic Acid in Aniline ($S_0=0.97295$).

<i>A.</i>	S_1 .	<i>v.</i>
4.015	0.96986	0.893
6.119	0.96824	0.891
11.293	0.96401	0.885
14.356	0.96168	0.814

If these values of *v* be compared with those found in toluene, it will be seen that they are considerably less; hence, in this case, combination with the solvent causes a marked contraction in volume.

Benzoic Acid in Aniline.

<i>A.</i>	S_1 .	<i>v.</i>
1.810	0.97046	0.832
5.603	0.96543	0.832
9.885	0.96008	0.830
13.854	0.95543	0.829

On comparing these values with those found in benzene, it will be seen that they are decidedly lower, but that the difference is not so well marked as in the previous case.

Results Calculated from Measurements of Other Observers.

A few cases have been selected from work of previous investigators which have a bearing on the present question. They are all in aqueous solution, from which the solute crystallises with water of crystallisation. It is therefore tolerably certain that these substances form hydrates in aqueous solution, and any appreciable deviation from constancy of the specific volumes of these substances, as the concentration varies, can only be attributed, from what has so far been established, to the influence of solvate formation, or, rather, to the variation in the degree of hydration. A few of the cases below are weak electrolytes, but the amount of ionisation is negligibly small.

Dextrose. ¹ $C_6H_{12}O_6 + H_2O$.		Lactose. ¹ $C_{12}H_{22}O_{11} + H_2O$.		Maltose. ¹ $C_{12}H_{22}O_{11} + H_2O$.		Gallotannic Acid. ² $C_{14}H_{10}O_9 + 2H_2O$.		Citric Acid. ² $C_6H_8O_7 + H_2O$.	
A.	v.	A.	v.	A.	v.	A.	v.	A.	v.
5.19	0.614	2.52	0.608	8.11	0.599	4	0.562	9.14	0.588
10.09	0.624	10.44	0.624	16.98	0.597	8	0.564	18.29	0.593
15.85	0.626	21.97	0.628	28.25	0.611	10	0.566	27.43	0.596
32.35	0.627	—	—	—	—	18	0.574	40.71	0.605

¹ Kannonikoff, *J. pr. Chem.*, 1894, [ii], **49**, 170.

² See Traube, *Annalen*, 1896, **290**, 66, 92.

It will be noticed that there is a gradual increase in the specific volume of the solute with increase of concentration. This can only mean that in these cases hydration takes place, the degree of which decreases as the concentration increases. This increase of the solution volume with increase of concentration is the behaviour of practically all non-electrolytes in aqueous solution. The above cases were selected for illustration simply because hydrates of these substances actually exist. We have seen that the rule for normal substances is the independence of the specific solution volume on the concentration, and, further, that this rule is equally true for cases where the solute is polymerised in solution. But as has just been stated, in aqueous solution very few substances (non-electrolytes) obey this rule. The well known case of sugar in water is only in approximate agreement with the rule. This well-marked difference between the behaviour of aqueous solutions and solutions in normal solvents can only be satisfactorily explained on the supposition that in practically all aqueous solutions of non-electrolytes, hydration to some extent takes place. It must be pointed out that non-electrolytes which are soluble even only to a small extent in water, are almost wholly substances which, in the pure state, are associated, such as the hydroxyl compounds, amino-compounds, and the lower ketones. It is not, then, very surprising to find evidence that these substances form solvates in their solutions in associated

solvents. That the behaviour is true for other solvents than water is shown by the following few examples.

<i>Phenol in Ethyl Alcohol.</i>			<i>o-Nitrophenol in Ethyl Alcohol.</i>			<i>Glycerol in Ethyl Alcohol.</i>		
<i>A.</i>	<i>S₁.</i>	<i>v.</i>	<i>A.</i>	<i>S₁.</i>	<i>v.</i>	<i>A.</i>	<i>S₁.</i>	<i>v.</i>
3·784	1·23993	0·875	2·491	1·24235	0·674	3·261	1·23975	0·726
6·082	1·23214	0·876	6·920	1·22095	0·707	4·829	1·23231	0·731
9·856	1·22012	0·879	12·349	1·19643	0·709	13·575	1·19442	0·737
17·159	1·19931	0·882	12·626	1·19531	0·711	36·471	1·12085	0·749
25·838	1·17810	0·885	—	—	—	—	—	—

It will be noticed that the values of *v* increase in a regular manner as the concentration increases, and if these values in the cases of phenol and nitrophenol be compared with their values in normal solvents, it will be seen that they are considerably lower. There can be little doubt that in these solutions solvates are formed.

Summarising the data given above, the following conclusion may be drawn in regard to influence of solvate formation on the volume of the solute in solution. When a dissolved substance forms an unstable compound or solvate with the solvent, the specific volume of the former is not generally constant, but increases as the concentration of the solution increases. This is, however, not always the case, as has been shown. The variation of the specific solution volume can, however, only conceivably take place when solvates are formed. The increase with increase of concentration runs parallel with the decrease of the amount of solvate formed. It does not, however, necessarily happen, although it probably holds in the majority of cases, that the amount of solvate formed decreases with increase of the concentration. There is the well known case of alcohol and water, which gives a minimum value for the specific volume of the alcohol in solution. In such a case, there exists a solvate with an unusually great stability, which is the principal product of the reaction over a wide range of concentration. In any case, whether a decrease or increase of the solution volume of a solute (non-electrolyte) takes place when the concentration increases, its variation may be regarded as a true criterion of solvate formation.

The Influence of Ionisation.

A large amount of experimental data has been accumulated on densities and specific volumes of aqueous solutions of electrolytes. Yet no generalisations of importance have resulted. This is due, no doubt, to the complexity of factors which come into play. We have to deal with the following possibilities, all of which may vary with the concentration :

- (1) Ionisation.
- (2) Association of molecules of solute.
- (3) Association of molecules of solvent.
- (4) Hydration of undissociated solute.
- (5) Hydration of ions.

We have seen that molecular association does not affect the volume of the solute in solution, and therefore factor (2), if it exists, can be neglected. In regard to factor (3), we have seen that when two substances form a homogeneous mixture, the specific volume of the one is constant, whether it exists in the mixture in the form of simple molecules, or in the form of associated molecules. It clearly cannot matter which of the two substances is associated, or whether both are associated in the mixture. The rule will hold in any case. We can, therefore, neglect factor (3).

It has been found that in almost all cases the volume of the solute in solution in the cases of electrolytes decreases as the concentration decreases. There are very few exceptions to this rule. Ammonia, hydrobromic acid, and hydriodic acid give fairly constant values over moderately wide ranges of temperature (Carius and Topsøe, *Zeitsch. anal. Chem.*, 1869, **8**, 279). This change persists also even at extremely dilute solutions. The following example, taken from measurements of Kohlrausch (*Ann. Phys. Chem.*, 1895, [iii], **56**, 185) and Mendeléeff (*Zeitsch. physikal. Chem.*, 1887, **1**, 273), is typical.

Sulphuric Acid.

Concentration per cent.	Molecular volume of H_2SO_4 in solution at 6° (Kohlrausch).	Concentration per cent.	Molecular volume of H_2SO_4 in solution at 0° (Mendeléeff).
0.002	5.9	1.34	25.7
0.01	7.71	5.16	29.8
0.05	10.75	17.88	33.3
0.1	12.03	30.34	36.6
1.0	15.54	52.13	41.4
5.0	17.57	83.05	46.3

The volume of an electrolyte in solution shows no tendency to assume a constant value, but goes on decreasing as the dilution increases, and in many cases becomes negative. In such cases, the volume of the solution is less than the volume of water it contains. Obviously a contraction or condensation of the water by the electrolyte has taken place. Cameron and Robinson (*J. Physical Chem.*, 1910, **14**, 1) have measured the amount of this condensation for a few cases, but no regularities have been discovered. Negative solution volumes at small concentrations have been observed in the following cases: sodium hydroxide (Kohlrausch, *Ann. Phys. Chem.*,

1879, [iii], 6, 1); sodium sulphide (Boch, *ibid.*, 1887, [iii], 30, 638); magnesium sulphate (Kohlrausch, *ibid.*, 1895, [iii], 56, 185). There can be no doubt that in many other cases also, the solution volumes would assume negative values at sufficiently great dilution. But this is by no means a general property, for even with some strong electrolytes in very dilute solution, the solution volume of the solute has a comparatively large positive value. For example, sodium chloride at a concentration of 0.3 per cent. has a molecular volume of 17.8, and at 20 per cent. its molecular volume is 20.4 (Schütt, *Zeitsch. physikal. Chem.*, 1890, 5, 536). In this case the variation with concentration is very small. It is clear, then, that a complexity of factors comes into play. The simple effect of dissociation fails to explain why the ions assume a negative value for the specific solution volumes. There is, indeed, no relation whatever between the degree of ionisation and the solution volume. Obviously, condensation of water by the ions takes place: yet this does not necessarily mean that the ions are hydrated, for it may simply mean that the water molecules are attracted into closer proximity around each ion, and in this connexion it is interesting to observe that the charged particles in colloidal solutions condense or contract the solvent in a similar manner. The formation of a hydrate in the case of a colloidal solution would be, of course, impossible, and it would seem to suggest that the condensation of the solvent is a property of charged particles of the solute. This explanation does not, however, cover all the facts, for it would follow that particles carrying the same charge would produce equal contractions, which is not the case. The simple effect of ionisation, then, fails to explain all the facts, and since in extremely dilute solutions, when almost all the salt is ionised, the decrease of the volume of the solute in solution with decrease of the concentration still persists, we can only conclude that the ions become hydrated, the degree of hydration varying with the concentration, and depending also on the nature of the ion.

In strong solutions, as in the case of non-electrolytes, the volume of the solute in solution varies with the concentration, and there can be little doubt, therefore, that hydrates of varying complexity are formed.

Summary.

The results of this work may be summarised as follows:

- (1) In solutions in which no chemical changes of any kind occur, the specific volume of the solute is constant, independent of the concentration. Its value varies slightly for different solvents.
- (2) Molecular association of the solute in solution is without

influence on the apparent volume of the solute. The behaviour is the same as if the molecules were normal.

(3) Solvate formation, that is, combination of the solvent and solute, generally causes a contraction in the apparent volume of the solute, and, further, the volume of the solute in solution generally decreases with decrease of concentration. But in some of the cases investigated, the formation of a solvate appears to be without influence on the solution volume of the solute.

(4) Variation of the specific solution volume of a non-electrolyte with variation of the concentration may be regarded as a true criterion of solvate formation. From this it follows that in almost all cases of aqueous solutions of non-electrolytes hydrates are formed.

(5) With aqueous solutions of electrolytes it is probable that in strong solutions the undissociated molecules are hydrated, and in dilute solutions the ions are also probably hydrated.

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