



XIX. The molecular volumes of salt-solutions

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XIX. *The Molecular Volumes of Salt-Solutions.* By W. W. J. NICOL, M.A., B.Sc., F.R.S.E., &c., Lecturer on Chemistry, Mason College, Birmingham*.

HITHERTO but little attention has been paid to the molecular volumes of salt-solutions; the phrase, so far as I am aware, occurs only in the papers of Berthelot, Thomsen, and Ostwald. The first of these examined the relation of the heat evolved by the solution of the haloid acids in water to the molecular volume of the resulting solutions†; while Thomsen, in addition to experiments with iodic acid similar to those of Berthelot, has pointed out the close connexion existing between the molecular heat and molecular volume of various salt-solutions‡. The experiments of Ostwald§, quoted by Thomsen (*loc. cit.*) in support of the theory of the "Avidity of Acids," are misleading, as the solutions he employed contained two equivalents of the salt or acid in every 1000 grms.; as a consequence, they contained different quantities of water, and therefore did not really admit of comparison.

The molecular volume of a solution is a measure of the space occupied by the molecules of salt and water forming the unit of the solution, along with the intermolecular spaces separating them. It is obtained by dividing the molecular weight of the unit of the solution by its specific gravity; or, generally,

$$\text{Mol. vol.} = \frac{xM + n18}{\delta},$$

where M is the molecular weight of the salt, x and n the numbers respectively of salt and water molecules, and δ the specific gravity of the solution.

I hope in the following pages to be able to show that an exact and extended knowledge of the molecular volumes of salt-solutions will throw much light on the constitution of such solutions, and will probably prove a powerful instrument in investigating the constitution of the salts themselves. With this object in view, I give first the results of the more complete and important of my experiments in this direction, and shall then proceed to state the conclusions I feel warranted in drawing from them. My method of experiment is the same as that described in my former paper||; but, inasmuch as

* Communicated by the Author.

† *Comptes Rendus*, lxxvi. p. 679.

‡ *Thermochemische Untersuchungen*, Band i. p. 52, ii. p. 427.

§ Wiedemann's *Annalen*, ii. p. 429.

|| *Phil. Mag.* 1883, xv. p. 91.

these data are to be used for mutual comparison, I have in many cases taken the mean of two or more independent determinations, as likely to possess greater accuracy than the results of single experiments.

Table I. contains a complete list of the solutions experimented on, with their specific gravities and molecular volumes. For convenience of reference these are numbered.

TABLE I.

Water at $20^{\circ}=1$. Strength x molec. salt to 100 H_2O .

No.	x .	Salt.	δ .	Molec. vol.	Remarks.
1.	5.0	KCl	1.11445	1949.84	
2.	4.0	"	1.09415	1917.84	
3.	2.0	"	1.04959	1857.12	Mean of 2.
4.	1.0	"	1.02568	1827.67	" 3.
5.	0.5	"	1.01310	1813.54	" 2.
6.	5.0	NaCl	1.10276	1897.42	" 6.
7.	4.0	"	1.08408	1876.23	" 3.
8.	2.0	"	1.04393	1836.29	" 3.
9.	1.0	"	1.02255	1817.52	" 5.
10.	0.5	"	1.01145	1808.54	" 2.
11.	5.0	KNO_3	1.14888	2006.74	" 2.
12.	4.0	"	1.12264	1963.53	" 2.
13.	2.0	"	1.06524	1879.58	
14.	1.0	"	1.03373	1839.07	" 4.
15.	0.5	"	1.01730	1819.03	
16.	5.0	NaNO_3	1.13813	1954.96	
17.	2.0	"	1.05980	1858.85	
18.	1.0	KClO_3	1.04122	1846.49	
19.	1.0	NaClO_3	1.03844	1835.93	
20.	1.0	K_2SO_4	1.06744	1840.10	Mean of 2.
21.	0.5	"	1.03758	1818.76	" 2.
22.	1.0	Na_2SO_4	1.06744	1819.31	
23.	0.5	"	1.03466	1808.32	Above diluted.
24.	2.0	KHO	1.05325	1815.52	From K.
25.	2.0	NaHO	1.04712	1795.40	From Na.
26.	0.5	MgSO_4 7 aq.	1.03201	1863.35	
27.	0.5	FeSO_4 7 aq.	1.04050	1863.53	
28.	0.5	NiSO_4 7 aq.	1.04296	1860.43	
29.	0.5	CoSO_4 7 aq.	1.04303	1860.30	
30.	0.5	CuSO_4 5 aq.	1.04268	1863.22	101 H_2O .
31.	0.5	ZnSO_4 7 aq.	1.04367	1862.18	

When a salt is in the solid state, its molecular volume evidently expresses the space occupied by its molecule along

with that fraction of the intermolecular space that clearly belongs to that molecule. Only, therefore, on the supposition that the intermolecular spaces, in different salts in the solid state, are coextensive, or nearly so, does the molecular volume give any clue to the constitution of the salt; but I venture to submit that the molecular volumes of salt-solutions do more than this, and that it is possible, by the comparison of similarly constituted solutions, and the effect of heat and concentration on their molecular volumes, to determine, not only the molecular volumes of the salts themselves, but also that of each of their constituents, as has, to some extent, been accomplished in the case of organic liquids.

If we compare the molecular volumes (Table I.) of the salts of the same acid-radical with different metals, and also those of the same metal with different acid-radicals, we obtain the following results :—

A. The Alteration in the Molecular Volume of a Salt-Solution resulting from the replacement of Potassium by Sodium.

(1) *In Combination with Chlorine.*

Table II. contains the data necessary for this comparison. It is evident from it that, when solutions of the same strength are compared, the volume-change as above is 10 to 10·48, or

$$(K-Na)Cl = 10\cdot0 \text{ to } 10\cdot48 = \Delta.$$

TABLE II.

No. in Table I.	<i>x.</i>	KCl.	NaCl.	Diff.	Δ .
1—6.	5·0	1949·84	1897·42	52·42	10·48
2—7.	4·0	1917·84	1876·23	41·61	10·40
3—8.	2·0	1857·12	1836·29	20·83	10·41
4—9.	1·0	1827·67	1817·52	10·15	10·15
5—10.	0·5	1813·54	1808·54	5·00	10·00

It is to be noted here that Δ increases with the concentration. I shall return to this later.

(2) *In Combination with (SO₄).*

$$(K-Na)\left(\frac{SO_4}{2}\right) = 10\cdot39 \text{ to } 10\cdot44 = \Delta.$$

TABLE III.

No. in Table I.	<i>x.</i>	K ₂ SO ₄ .	Na ₂ SO ₄ .	Diff.	Δ .
20—22.	1·0	1840·10	1819·31	20·79	10·39
21—23.	0·5	1818·77	1808·32	10·44	10·44

The effect of concentration is here the reverse of that in the case of the chlorides.

(3) *In Combination with NO₃.*

$$(K-Na) NO_3 = 10.36 = \Delta.$$

(4) *In Combination with (ClO₃).*

$$(K-Na) ClO_3 = 10.56 = \Delta.$$

(5) *In Combination with (OH).*

$$(K-Na) OH = 10.06 = \Delta.$$

Table IV. contains all the above.

TABLE IV.

No. in Table I.	x .	KNO ₃ .	NaNO ₃	Diff.	Δ .
11-16.	5.0	2006.74	1954.96	51.78	10.36
13-17.	2.0	1879.58	1858.85	20.73	10.36
		KClO ₃	NaClO ₃		
18-19.	1.0	1846.49	1835.93	10.56	10.56
		KOH.	NaOH.		
24-25.	2.0	1815.52	1795.40	20.12	10.06

The above results may be summed up as follows :—The value of $(K-Na) R$, where $R = Cl, \left(\frac{SO_4}{2}\right), NO_3, ClO_3$, or OH , is a number lying between 10.0 and 10.56; and it is to some extent dependent on the strengths of the solutions compared.

B. The Alteration in the Molecular Volume of a Salt-Solution resulting from the replacement of one Acid-radical by another.

(α) *The replacement of NO₃ by Cl.*

(1) In combination with Potassium.

$$K(NO_3-Cl) = 10.98 \text{ to } 11.4 = \Delta.$$

(2) In combination with Sodium.

$$Na(NO_3-Cl) = 11.28 \text{ to } 11.51 = \Delta.$$

TABLE V.

No. in Table I.	x .	KNO ₃ .	KCl.	Diff.	Δ .
11-1.	5.0	2006.74	1949.84	56.90	11.40
12-2.	4.0	1963.53	1917.84	45.69	11.42
13-3.	2.0	1879.58	1857.12	22.46	11.23
14-4.	1.0	1839.07	1827.67	11.40	11.40
15-5.	0.5	1819.03	1813.54	5.49	10.98
		NaNO ₃ .	NaCl.		
16-6.	5.0	1954.96	1897.42	57.54	11.51
17-8.	2.0	1858.85	1836.29	22.56	11.28

(β) *The replacement of Cl by $\left(\frac{\text{SO}_4}{2}\right)$.*

(1) In combination with Potassium.

$$\text{K} \left(\text{Cl} - \frac{\text{SO}_4}{2} \right) = 8.55 \text{ to } 8.91 = \Delta.$$

(2) In combination with Sodium.

$$\text{Na} \left(\text{Cl} - \frac{\text{SO}_4}{2} \right) = 8.49 \text{ to } 9.2 = \Delta.$$

TABLE VI.

No. in Table I.	x .	(KCl) ₂ .	K ₂ SO ₄ .	Diff.	Δ .
3-20.	1.0	1857.12	1840.10	17.02	8.50
4-21.	0.5	1827.67	1818.76	8.91	8.91
		(NaCl) ₂ .	Na ₂ SO ₄		
8-22.	1.0	1836.25	1819.31	16.94	8.49
9-23.	0.5	1817.52	1808.32	9.20	9.20

Finally :—

(γ) *The replacement of (ClO₃) by Cl.*

(1) In combination with Potassium.

$$\text{K} (\text{ClO}_3 - \text{Cl}) = 18.82 = \Delta.$$

(2) In combination with Sodium.

$$\text{Na} (\text{ClO}_3 - \text{Cl}) = 18.41 = \Delta.$$

Thus we find, in all the above cases, that the substitution of one metal for another in combination with the same acid-radical, or the replacement of one acid-radical by another under the same conditions, is attended by an alteration in the molecular volume of the solution, which, in each case, is nearly

Phil. Mag. S. 5. Vol. 16. No. 98. August 1883. L

a constant quantity. The volumes, therefore, of the above elements and groups of elements are independent of the manner in which they may be combined together, provided only they be determined in solution in water and under the same conditions. Now such is not the case in the solid state. Taking the molecular volumes of the above salts, calculated by Schröder* from the most reliable determinations of the specific gravity of the solid salts, we have the following :—

$$(K-Na) Cl = 37.4 - 27.1 = 10.3,$$

$$(K-Na) NO_3 = 48.5 - 37.6 = 10.9,$$

$$(K-Na) \left(\frac{SO_4}{2} \right) = \left(\frac{32.8 - 26.7}{2} \right) = 3.1.$$

$$K \left(Cl - \frac{SO_4}{2} \right) = 37.4 - 16.4 = 21,$$

$$Na \left(Cl - \frac{SO_4}{2} \right) = 27.1 - 13.3 = 13.8.$$

$$K (NO_3 - Cl) = 48.5 - 37.4 = 11.1,$$

$$Na (NO_3 - Cl) = 37.6 - 27.1 = 10.5.$$

All attempts to extend the experiments of Kopp on liquids to the case of solid salts have, I believe, failed, or at the best been attended by only partial success, owing doubtless to the impossibility of obtaining these under such conditions that their molecular interspaces are even approximately comparable. This, however, is not the case with some isomorphous salts examined by Thorpe† and others; but I shall return to this point later on. Meanwhile I believe that I am justified in concluding, from my experiments above, that, *when salts are dissolved in water, the molecular interspaces in various solutions are approximately coextensive*. Hence it is possible to ascertain the relative molecular volumes of the salts themselves with a degree of accuracy equal, at least, to that with which the molecular volumes of liquids have been determined.

I will now consider the causes which lead to the variations in the difference between the molecular volumes of two salt-solutions, and which thus affect the accuracy of the above determinations. Putting the errors of experiment on one side, we have the main cause in the effect of concentration on the volumes of the solutions compared, or, what is the same thing (as I hope to be able to show), in the different solubilities of the two salts. Among the best-marked instances given above, we find two cases in which Δ increases with the concentration,

* Poggendorff's *Annalen*, cvi. p. 242.

† Journal of Chemical Society, 1880, p. 102.

viz. Tables II. and V., where the values of $(K-Na)Cl$ and $K(NO_3-Cl)$ are least with the most dilute solution; and two cases where the reverse is the case, Table VI., where $K\left(Cl-\frac{SO_4}{2}\right)$ and $Na\left(Cl-\frac{SO_4}{2}\right)$ have the greatest value when the solution is most dilute. If we compare the most concentrated and the most dilute solutions of the same salt, we can ascertain what effect concentration has on the molecular volume of the salt. This is done in Table VII., where the volume of the water is assumed constant = 1800.

TABLE VII.

x .	Mol. vol. KCl.	Diff.	Mol. vol. NaCl.	Diff.	Mol. vol. KNO ₃ .	Diff.	Mol. vol. KCl.	Diff.
0.5	27.08		17.08		38.06		27.08	
5.0	29.97	2.89	19.48	2.40	41.35	3.29	29.97	2.89
	Mol. vol. KCl.		Mol. vol. $\left(K, \frac{SO_4}{2}\right)$.		Mol. vol. NaCl.		Mol. vol. $\left(Na, \frac{SO_4}{2}\right)$.	
1.0	27.67		18.76		17.52		8.32	
2.0	28.56	0.89	20.05	1.29	18.14	0.62	9.66	1.34

The numbers in the columns headed Mol. vol. are the molecular volumes of *one* molecule of the salt in a solution which contains x molecules to $100H_2O$; the difference is the increase of the molecular volume of each molecule produced by the increase in concentration shown by the column headed x .

A glance at these differences will show the immediate reason of the increase or the diminution, as the case may be, of the differences between the pairs of salts, when the solution is concentrated. In the first two cases, $(K-Na)Cl$ and $K(NO_3-Cl)$, the salt with the larger molecular volume has it increased by concentration at a rate faster than that of the other; and the converse is true with regard to $K\left(Cl-\frac{SO_4}{2}\right)$ and $Na\left(Cl-\frac{SO_4}{2}\right)$, for here it is the one with the smaller molecular volume on which the effect of concentration is more marked.

To find, however, the real cause of this we must bear in mind that, in the first instances, it is the first member of each pair of salts that is least soluble in water, while in the latter it is the second member of each pair of which this is true. The solubilities in terms of salt-molecules to 100 water-molecules are approximately:—

KCl.....	8.4,	NaCl.....	10.99,
KNO ₃	5.6,	K ₂ SO ₄	1.0 +,
Na ₂ SO ₄ ...	2.0 +.		

All at 20° C.

We have therefore arrived at the following :—

In the case of salts when compared in pairs, the increase of molecular volume by concentration is greatest with the less-soluble salt. Why is this? When viewed in the light of the theory of solution which I recently stated in a paper* read before the Royal Society of Edinburgh, the reason is evident. In that paper I suggested that the solubility of a salt in water was due to “the attraction of the molecules of water for a molecule of salt exceeding the attraction of the molecules of salt for one another;” and that “as the number of dissolved salt-molecules increases, the attraction of the *dis-similar* molecules is more and more balanced by the attraction of the *similar* molecules;” and that this last increases until the two forces balance, when saturation takes place. I also showed that the rate of increase in the density of a salt-solution is less than the rate at which it becomes more concentrated, but that when a solution is sufficiently dilute no further dilution affects its specific gravity; as a consequence, the molecular volume of the salt dissolved is constant. It is evident from the above that the effect of concentration in increasing the molecular volume of a solution is due to the molecules of salt coming more and more within the sphere of one another’s attraction, and being thus brought nearer and nearer to the point at which crystallization takes place. Now what is true of the same salt in solutions of different strengths is equally true of solutions of the same strength of salts whose solubilities are different; and it follows that the less soluble salt will have its molecular volume increased by concentration faster than the more soluble salt. Such, I believe, is the explanation of the variations in the differences above observed; and, as a consequence, if the salt-solution be sufficiently dilute, the differences between their molecular volumes are constant.

The next point to be considered is the influence of rise of temperature on the molecular volumes of salt-solutions. Table VIII. contains the requisite data. These are the results of single experiments, and are therefore not of equal accuracy with the data in Table I., nor, in consequence, do the values at 20° correspond exactly with those given in that table; but they are accurate in general to ± 0.0005 in the specific gravity.

The column headed Difference contains the increase of molecular volume due to heating from 20° to 40°. This refers to the salt alone; for water = 1, both at 20° and 40°.

* Phil. Mag. 1883, xv. p. 91.

TABLE VIII.

<i>x.</i>	Salt.	<i>t</i> °.	<i>δ</i> .	Mol. vol.	Diff.	D.
5.0	NaCl	20	1.10292	1897.25		
"	"	40	1.10032	1901.73	4.48	0.89
2.5	"	20	1.05426	1846.09		
"	"	40	1.05270	1848.82	2.73	1.09
2.0	"	20	1.04396	1836.29		
"	"	40	1.04266	1838.57	2.28	1.14
1.0	"	20	1.02259	1817.44		
"	"	40	1.02190	1818.68	1.24	1.24
5.0	KCl	20	1.11445	1949.84		
"	"	40	1.11278	1952.77	2.93	0.58
2.0	"	20	1.04961	1857.08		
"	"	40	1.04864	1858.80	1.72	0.86
1.0	"	20	1.02561	1827.79		
"	"	40	1.02507	1828.76	0.97	0.97
5.0	NaNO ₃	20	1.13790	1955.37		
"	"	40	1.13359	1962.79	7.42	1.48
2.5	"	20	1.07366	1874.42		
"	"	40	1.07086	1879.34	4.92	1.97
2.0	"	20	1.05980	1858.85		
"	"	40	1.05738	1863.09	4.24	2.12
5.0	KNO ₃	20	1.14917	2006.23		
"	"	40	1.14556	2012.55	6.32	1.26
2.0	"	20	1.06524	1879.58		
"	"	40	1.06333	1882.95	3.37	1.63
1.0	"	20	1.03373	1839.07		
"	"	40	1.03233	1841.56	2.49	2.49
2.0	Na ₂ SO ₄	20	1.06744	1819.31		
"	"	40	1.06594	1821.87	2.56	1.28
1.0	"	20	1.03466	1808.32		
"	"	40	1.03385	1809.74	1.42	1.42
2.0	K ₂ SO ₄	20	1.07286	1840.12		
"	"	40	1.07172	1842.08	1.96	0.98
1.0	"	20	1.03762	1818.69		
"	"	40	1.03694	1819.87	1.18	1.18
5.0	NH ₄ Cl	20	1.03880	1990.27		
"	"	40	1.03814	1991.55	1.28	0.25
2.5	"	20	1.02130	1893.43		
"	"	40	1.02093	1894.12	0.69	0.28
2.0	"	20	1.01741	1874.36		
"	"	40	1.01711	1874.93	0.57	0.29
5.0	NH ₄ NO ₃	20	1.07685	2043.00		
"	"	40	1.07372	2049.00	6.00	1.20
2.5	"	20	1.04137	1920.54		
"	"	40	1.03957	1923.87	3.33	1.33
2.0	"	20	1.03389	1895.76		
"	"	40	1.03238	1898.53	2.77	1.39

The last column (D) contains the difference divided by x , and thus gives the increase of volume for each molecule of salt present.

A glance at the table will show that, in every case, the increase of the molecular volume by heating from 20° to 40° is inversely proportional to the strength of the solution. In other words, the more dilute a solution is the greater the increase of its molecular volume by heat per molecule of dissolved salt. This is, I believe, inexplicable by the hydrate theory of solution. It appears impossible that a solution which contains only *one* molecule of salt to 100 molecules of water should experience a greater change of molecular volume per salt-molecule than a solution of the same salt containing *two* salt-molecules. This is, however, in accordance with the theory* of expansion of salt-solutions which I put forward at the end of my paper on the Nature of Solution. At that time the only data at my disposal were the results obtained by Kremers and others, whose experiments were made with non-molecular solutions. The above table, however, fully bears out my previous statement that the expansion of a solution is the result of the action of heat on the resultant of the three forces—the attraction of water for water, that of water for salt, and that of salt for salt, the last two being inversely proportional to one another.

In the cases considered in the first part of this paper, it is clear that a variation in the composition of the salt necessitates a corresponding change in the molecular volume of the solution containing that salt. This, however, holds true only of salts non-isomorphous in the strict sense of the term—that is, of heteromorphous and homeomorphous salts. When, however, two salts are strictly isomorphous, that is isotomous, they preserve their isotomy in solution. The last six salts given in Table I. come under this head; they are the members of the so-called magnesian-sulphate group, which crystallize (except CuSO_4) with $7\text{H}_2\text{O}$, and then possess approximately identical molecular volumes†. This is also true to some extent of their solutions, which have nearly the same molecular volumes. What the slight variations may be due to I am not in a position at present to prove; but enough has been said to show that the intermolecular spaces in isomorphous salts are comparable, and that true isomorphism is conditioned by the molecule itself; while with salts which are isomorphous in the wider sense (homeomorphous), such as the chlorides, bromides,

* Phil. Mag. 1883, xv. p. 99.

† Thorpe, Journ. of Chem. Soc. 1880, p. 102.

&c. of sodium and potassium, the apparent isomorphism is the result, not of the isomorphism of the molecules themselves, but of the mutual relations of the molecules and intermolecular spaces being such as to produce the same crystalline form.

In conclusion, I may be allowed to point out that this method of investigating the molecular volumes of salts is, in all probability, capable of extension to organic substances; and that, by comparing solutions of various organic bodies which differ by one or more CH_2 -groups, or in other respects, it may be possible to determine the volume of these differences. Such solutions need not necessarily be aqueous. At present, I have made only a few experiments in this direction; these were with formiate, acetate, and butyrate of sodium; the results are given in Table IX. Analysis showed that, while the formiate and acetate of sodium were pure, the butyrate contained 21.7 p. c. of sodium, theory requiring 20.9 p. c. All attempts to purify the small quantity at my disposal were vain; the impurity was probably acetate; this would tend to reduce the molecular volume by increasing the specific gravity.

TABLE IX.

<i>x.</i>	Salt.	t° .	δ .	Mol. vol.	Diff. per CH_2 .
2.0	Butyrate	20 ^o	1.04349	1935.82	
2.0	Acetate	20	1.04380	1881.58	13.74
2.0	Formiate	20	1.04561	1851.58	15.00
1.0	Butyrate	20	1.02278	1867.46	
1.0	Acetate	20	1.02280	1840.05	13.70
1.0	Formiate	20	1.02345	1825.19	14.86
2.0	Butyrate	40	1.04173	1939.08	
2.0	Acetate	40	1.04279	1883.41	13.92
2.0	Formiate	40	1.04436	1853.82	14.81
1.0	Butyrate	40	1.02184	1869.18	
1.0	Acetate	40	1.02218	1841.16	14.07
1.0	Formiate	40	1.02276	1826.44	14.72

I hope soon to be able to carry out further experiments in the field of inquiry thus opened up.