

The Compressibility of Aqueous Solutions II

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(Communicated by A. W. Porter, F.R.S.—Received April 17, 1934)

Introduction

In an earlier communication, Perman and Urry* described the measurement, by a direct method, of the compressibility coefficients of aqueous solutions of urea, cane sugar, potassium chloride, and calcium chloride, over a range of temperatures and concentrations. Their work was over the pressure range 0–200 atmospheres excess pressure. They were able to apply their results together with other data obtained by their co-workers, to an extension of Porter's theory of compressible solutions, and thus obtained values for the osmotic pressures of those solutions which agreed very well with the values obtained by more direct methods.

The present work is a continuation of this and subsequent work (unpublished by these authors). It was intended, especially, to investigate the effect of the nature of the solute molecule upon the compressibility, and, for this reason, the choice of solutes was particularly important. A number of series of chemically related compounds were used where only one part of the molecule varied in a progressive manner from substance to substance. In another series there was no chemical relationship, but the members had the same empirical formula and their molecular weights were therefore simple multiples of each other.

Finally it was intended to use as fully as possible the experimental results of Perman and Urry.

Experimental Procedure

The experimental procedure was, fundamentally, the same as that of Perman and Urry, but the results were obtained at one temperature only, namely, 30° C, at which temperature the thermostat was very accurately maintained at all times. The thermostatic arrangements were superior to those of the earlier workers. Electrical immersion heaters in the bath were controlled by a thermo-regulator-relay system, but, contrary to the usual

* 'Proc. Roy. Soc.,' A, vol. 126, p. 44 (1929).

procedure, the relay, when activated, did not cut off the current supply to the heaters; it introduced, in series, a resistance which was so adjusted that the current supply to the heaters was reduced until it was just insufficient to maintain the bath at constant temperature. When the relay was inactive, this resistance was short-circuited, and the current in the heaters was regulated by another resistance until it was only slightly in excess of that required to maintain the bath at 30° C. The variation of current in the heaters was, therefore, very small, whereas, in the customary method, the variation was from its maximum to zero. This arrangement also assisted greatly in reducing sparking at the relay contacts.

A further increase in accuracy was considered necessary in the calibration of the capillary tubes. It was noted that the equation $V = \pi r^2 (L - 2/3r)$, giving the radius of the tube in terms of the length and volume of the mercury thread used in the calibration, did not admit direct solution. If the effect of hemispherical ends were ignored, as is usual in such calibrations, where the length of the thread is great compared with its radius, there would be an error of nearly 4% in the value of r^2 , since L cannot be greater than 15 mm and r is about 0.75 mm for the tubes used. Furthermore, the ends are not spherical, as was assumed in deriving the above equation. An alternative method of procedure was therefore adopted. A very long thread was introduced into the tube and its length L_1 measured. A small portion (about 1.3 cm) was run out into a tared weigh-tube and the length of the remainder L_2 measured. During the measurements of L_1 and L_2 , one end of the long thread was adjusted to coincide accurately with the etched mark on the tube. Then the portion of thread which had been removed was considered as an equivalent cylinder with one end concave and the other convex (not necessarily spherical, but some definite constant shape), having a volume $V = \pi r^2 (L_1 - L_2)$, its mean position being $\frac{1}{2}(L_1 + L_2)$ from the etched mark. This procedure was repeated, small lengths of mercury being run out and weighed until the whole tube was emptied.

This method of calibration was also considered very suitable because it bore a great resemblance to the method of measuring volume changes in the capillaries due to pressure during actual experiments. In practice, r need not be calculated, but a graph may be plotted for each capillary tube showing its internal volume (*i.e.*, the weight of the mercury thread divided by density of mercury) against the distance from the etched calibration mark.

With these exceptions, the general experimental procedure was the same as that of Perman and Urry, and, since the same kind of glass was used in the

construction of the piezometers, use could be made of the elastic constants for glass obtained by them.*

The Solutions Studied

Three series of compounds were considered, care being taken that the compounds selected were sufficiently soluble to give a good range of concentration.

The first, consisting of potassium chloride, potassium bromide, and potassium iodide, gave an example of an inorganic salt series where the acid radicals varied from salt to salt, but themselves belonged to a chemically related series.

The second series was chosen where the metallic radicals varied from salt to salt, but which were all members of the same periodic series, and consisted of the bromides of calcium, strontium, and barium. The values for the solutions of calcium chloride studied by Perman and Urry were compared with those for this series.

The third series consisted of very soluble organic compounds having the same empirical formula but having no close chemical resemblances. Formalde-

Table I—Series I

Grams per 100 grams	Grams per 100 cc	n/N	D_4^{20}	Compressibility (0–100 atmospheres)
Potassium Chloride (Perman and Urry)				
2.59	2.62	0.0063	1.011	428×10^{-7}
5.37	5.53	0.0134	1.029	412
10.40	11.04	0.0276	1.062	385
12.23	13.15	0.0337	1.075	375
17.92	19.95	0.0526	1.113	347
22.19	25.38	0.0690	1.144	328
Potassium Bromide				
3.23	3.32	0.0050	1.027	430×10^{-7}
9.60	10.34	0.0161	1.077	401
14.60	16.39	0.0259	1.123	378
19.51	22.77	0.0367	1.166	358
25.51	30.98	0.0519	1.218	337
31.16	39.42	0.0685	1.265	317
32.10	40.70	0.0716	1.268	314
Potassium Iodide				
6.32	6.62	0.0073	1.048	422×10^{-7}
12.41	13.66	0.0154	1.101	399
19.86	23.14	0.0268	1.165	374
31.02	39.68	0.0488	1.279	336
38.76	53.46	0.0687	1.379	313
47.53	62.09	0.0983	1.476	302

* 'Proc. Phys. Soc.,' vol. 40, p. 186 (1928).

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hydral acetic acid formed this series which was compared with the sugar solution of Urry (see Appendix).

Table I-III give the experimental results, the concentrations being expressed as (a) grams of solute per 100 grams of solution, (b) grams of solute per 100 cc of solution, and (c) the ratio of the number of molecules of solute n to the number of molecules of solvent, N .

Table II—Series II

Grams per 100 grams	Grams per 100 cc	n/N	D_4^{30}	Compressibility (0-100 atmospheres)
Calcium Bromide				
1.29	15.04	0.0138	1.132	382×10^{-7}
2.84	34.77	0.0331	1.295	322
4.36	59.74	0.0610	1.480	272
5.76	87.74	0.1007	1.663	221
6.04	109.76	0.1354	1.798	204
Strontium Bromide				
1.03	14.67	0.0109	1.126	388×10^{-7}
2.70	31.17	0.0239	1.262	342
3.98	47.13	0.0375	1.387	309
4.17	64.01	0.0531	1.518	279
6.24	80.66	0.0735	1.655	248
4.60	97.97	0.0912	1.763	226
Barium Bromide				
1.74	9.40	0.00581	1.075	412×10^{-7}
1.85	18.25	0.01142	1.151	382
1.19	30.07	0.01934	1.243	351
1.87	40.44	0.02836	1.341	322
1.93	64.44	0.04560	1.502	283
1.01	92.40	0.06839	1.743	246

Table III—Series III

Gms per 100 grams	Grams per 100 cc	n/N	D_4^{30}	Compressibility (0-100 atmospheres)
Formaldehyde				
1.95	8.11	0.0518	1.020	416×10^{-7}
1.5	11.82	0.0780	1.028	406
3.4	17.06	0.1177	1.040	379
2.1	25.42	0.1703	1.055	361
3.0	31.12	0.2460	1.073	340
3.1	35.68	0.2970	1.078	326
0.2	43.70	0.4034	1.087	303
Acetic Acid				
0.0	10.05	0.0334	1.005	433×10^{-7}
0.5	20.83	0.0774	1.016	417
0.7	31.50	0.1329	1.026	395
2.6	44.13	0.2227	1.036	381
7.3	59.89	0.4028	1.045	351

Fig. 1 shows the compressibility-concentration curves drawn from these figures, but, owing to the smallness of the scale of plotting, the individual curves for each member of any series cannot be distinguished from those of the other members of the same series; accordingly, the curve for the middle member of each series only is given except for Series III where the curves are sufficiently spaced to allow separate plotting.

The values for solutions of calcium chloride (Perman and Urry) would, if plotted on the same diagram, almost coincide with the curve for Series I which includes calcium bromide.

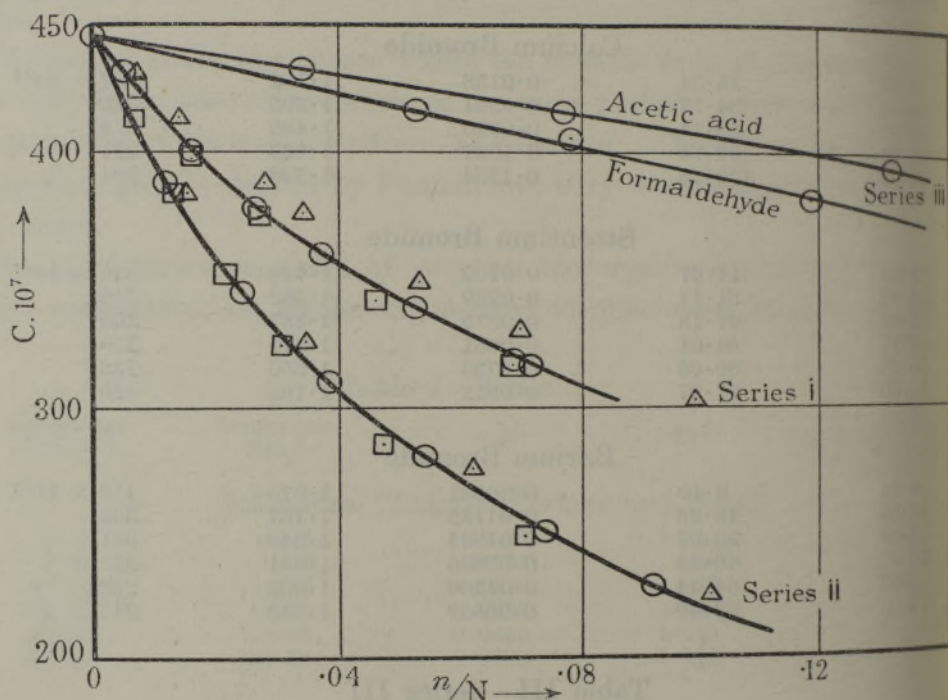


FIG. 1

Discussion

Inspection of small scale graphs at once suggests that the compressibility curves for substances closely related chemically lie very close to each other, whereas, when there are few or no chemical resemblances, as in Series III, the curves are widely spaced. In this connection, compare the diagram on p. 64 of Perman and Urry's earlier paper showing compressibility-concentration (molecular) curves at 30° C for potassium chloride, calcium chloride, urea, and cane sugar solutions. There, too, no relationship is suggested between the curves of chemically unlike substances.

A more careful plotting of the results on a larger scale reveals further information for the series of chemically related substances.

In Series I, the molecular weights differ by steps of about 45 units. It would be expected that an increase of this amount to the molecular weight of the chloride would cause a greater effect than the same addition to that of the bromide. This is, in fact, seen to be so, since the curve of potassium bromide lies slightly closer to that of the iodide than it does to the chloride curve.

This effect is also seen in the large scale diagram for Series II. In Series I, the weight variation between the compounds was greater than the weight of the common radical; in Series II, the heavier part of the molecules, the bromine radical, is fixed and the variation is small in comparison. Hence the curves for this series should lie closer than those of Series I. This is so, and moreover it can be seen that the curves for the two heavier bromides, barium and strontium, are more closely related than those of the lighter pair, calcium and sodium.

On this basis, too, it would be anticipated that the curves for solutions of calcium chloride (Urry) and calcium bromide should resemble one another more than those of potassium chloride and potassium bromide. The experimental results amply confirm this.

According to the electron theory, the members of these series differ amongst themselves by the number of electron orbits completed, the valency group upon which the chemical properties largely depend being common in any series. It is known that usually an increase in the number of completed orbits means an increase in the general stability of the compound and so, on this basis too, the differences between the properties of the chloride and bromide solutions should be greater than the differences between the properties of the bromide and iodide solutions. A similar statement might be made for the other series.

The compounds of Series III consisted of the same elements in exactly the same proportions by weight, but no obvious chemical properties are common to the compounds. Accordingly, no similarity was expected, worthy of mention between the compressibility curves for the series, and none was observed. In connection may be made here of a series of results obtained by Urry (private communication) for three sugars, a monosaccharide, a disaccharide, and a trisaccharide, namely, glucose, sucrose, and raffinose (see Appendix). The curves drawn from the data do not lie so close as those of Series I or II above, but are sufficiently close to indicate that there is some relationship between them. The compounds, being sugars, have many chemical resemblances, and we suppose that the molecules are built up of very similar units. The general

symmetry of the whole molecule would, however, differ very much along the series and it would be expected, therefore, that the curves for this series would not bear the close similarity of those of such a series as the salt series considered above, but would show a greater relationship to each other than the curves of a series such as the Series III considered above. The experimental results support this view.

Consideration of the data available, namely, that in Perman and Urry's earlier communication, Urry's unpublished results for the sugar solutions, and our own results given above, suggests, therefore, that there is some connection between the nature of the solute molecule and its effect upon the compressibility of the solvent, water.

Firstly, it is seen in all substances examined that the depression of compressibility is some function of the concentration of the solution, but, unless there is a close chemical relationship between the solutes, there is little similarity between the effects of different solutes. Where this similarity does exist, such as in one of the salt series described above, the effects are quite orderly and appear to depend directly upon the closeness of the relationship between the compounds considered. Unfortunately, however, the data available are very scanty for such a qualitative survey of so large a field; there are many indications, however, that there is a chemical as well as a physical aspect of solution and theories of solution.

It is well known that there is some chemical connection between solute and solvent, sufficient indeed to suggest a loose chemical combination between the molecules. The theories of co-ordinate linkages put forward by Sidgwick and others already furnish a mechanism for such solute-solvent combinations, and it is reasonable, therefore, to suggest that the effect of the solute upon the physical properties of the solvent depends to a greater extent upon the chemical properties of the solute than upon its molecular weight.

In the compressibility results given this is definitely confirmed.

In all the above considerations the curves studied have been those in which the molecular concentration (n/N) has been plotted against the compressibility. The method of expressing the concentrations can be varied, but, although curves for any series may then become more widely spaced, the general arguments outlined above still hold.

When, however, the concentrations are expressed in terms of the weight of solute per unit weight of solution, the curves (not reproduced here), plotted from the data, nearly always approximate to straight lines. This is mentioned in Perman and Urry's paper, pp. 62-64, but no theoretical inference was

The weight-concentration-compressibility curves for sucrose and potassium chloride are straight for all temperatures; that for urea showed very slight curvature which, the authors suggested, was due to a slight hydrolysis which is known to take place. The calcium chloride curves, however, show considerable curvature over the whole range, the explanation probably being the great and varying hydration which occurs in solution.

Weight-concentration-compressibility curves for the present results show the same fairly close approximation to the straight line. The curves for Series I show very slight curvature for potassium iodide, and even less for the bromide, whilst the chloride curve is straight. In Series II, where the curves lie even closer this is even more apparent, and a marked contrast is seen in the calcium chloride curve if this is plotted on the same diagram, although, as already stated above, it lies very close to the other curves when the concentrations are expressed as the ratio of the numbers of molecules. In Series III, the formaldehyde curve is straight whilst that for acetic acid shows but slight curvature due probably to such changes as hydration, ionization, and association.

Thus, in most substances studied, a linear equation would approximately relate the compressibility and the concentration, the latter being expressed as the weight w of solute per unit weight of solution. Hence the depression of the compressibility Δc can be defined by such an equation as $\Delta c = k \cdot w$. If n is the number of solute molecules of molar weight M , in unit weight of solution, $w = n \cdot M$. This can be substituted in the first equation giving the relationship $\Delta c = k \cdot n \cdot M$, and since, for any one solute M is normally a constant, $\Delta c = K \cdot n$, where K is a constant depending partly upon M . This final equation is also linear, and so the compressibility-concentration curves, plotted to express the concentrations in terms of moles of solute per unit weight of solution, would be straight lines too, differing from the weight (in gram) per unit weight of solution curves only in the gradient.

Provided that the concentrations are expressed in this manner, the curves for the solutions studied, with the exception of calcium chloride, are either straight lines or curves differing only very slightly from straight lines. The gradients of the curves, however, differ considerably even amongst members of the same related series, and to see best the family relationship between the members of any series, the concentrations should be expressed as the ratio of the numbers of molecules n/N .

In the series of three sugars (see Appendix), however, the three curves plotted in this way have the same gradient, i.e., are coincident straight lines. This would suggest that every raffinose molecule has exactly three times the

effect, and every sucrose molecule twice the effect of a glucose molecule. The fact that the lines are straight is to be anticipated after considering the information given above, since the sugars, as solutes, usually behave in a more orderly manner than inorganic salts, acetic acid, urea, etc. It is also to be expected that the heavier raffinose molecule would affect the compressibility more than the lighter sugars, but it is not difficult to suggest reasons for the effects following the ratio of the molecular weights.

Two explanations may be put forward to account for this, the one being purely physical, and the other purely chemical:—

(a) Polysaccharide molecules are considered as consisting of monosaccharide molecules linked to each other by single bonds. The monosaccharide molecules are assumed to be unchanged in structure, except for this link, and it is reasonable to assume, therefore, that a trisaccharide molecule would have approximately three times the volume of one of its constituent monosaccharide molecules. When a liquid suffers compression, it is assumed, after consideration of the available experimental material, that at the lower pressures at least (up to about 5000 atmospheres), the main result is to force the molecules closer together, so reducing the spaces between them. The molecules themselves are assumed to be only very slightly affected. In a solution, the solute molecules must necessarily occupy the spaces between the solvent molecules, whether attached to the latter or not. On this basis it might be assumed therefore, that, as the compressibility at the pressures we are considering depends on the change of volume of the intermolecular (solvent) spaces, the effect of a solute would depend directly on the volume of the solute molecule. Raffinose would, therefore, be expected to affect the compressibility three times, and sucrose twice as much as glucose.

(b) It has been pointed out above that the effects of a solute upon compressibility depend very largely upon the chemical structure of the molecule. Then, as raffinose has three 6-carbon units, sucrose two, and glucose one, all bearing a general resemblance to each other, it might be expected that each unit produces its own effect as if the others were not present. In the general properties of sugars, this is seen. It is known that, when monosaccharide molecules combine to form di- and tri-saccharides, their chemical properties are not submerged in a new set of properties of the di- or tri-saccharide. Accordingly, on a chemical basis, too, we might anticipate that a raffinose molecule would affect compressibility three times as much as a glucose molecule, and so the compressibility-concentration (grams/100 grams) curves would approximately coincide.

Finally, the compressibility-concentration (weight) curve for formaldehyde solutions would, if plotted upon the same diagram as those of the three sugars, bear very close relationship to the sugar curves. There is not that remarkable coincidence that is seen between the sugar curves, but the closeness suggests that, whatever explanation is put forward to explain the coincidence of the sugar curves, the same explanation must also apply to the formaldehyde solutions in which one molecule of formaldehyde would produce approximately one-sixth the effect of a molecule of glucose.

But the above reasons, chemical and physical (volumetric), can be applied if a sugar molecule be regarded as a chain or ring of formaldehyde molecules joined through the carbons, but naturally the accuracy of the coincidence of the curves cannot be expected to be as good as between the sugars themselves. Similar reasoning would suggest that the acetic acid molecule would have quite a different volume and effect from two formaldehyde molecules or one-third of a glucose molecule, and no relationship to formaldehyde or the sugars is expected, or found.

APPENDIX

We are very grateful to Dr. W. D. Urry for permission to include his values, hitherto unpublished, for the compressibility coefficients of glucose and raffinose solutions. These results are given in Table IV. The concentrations were

Table IV—Temperature 30° C. Pressure range 0–100 atmospheres

Grams per 100 grams	n/N	D_4^{30}	Compressibility
Glucose			
4.21	0.0044	1.0105	434.0×10^{-7}
8.79	0.0096	1.0279	417
15.28	0.0180	1.0526	396
26.83	0.0367	1.0973	358
36.23	0.0568	1.1369	327.5
Sucrose			
5.12	0.0027	1.016	430×10^{-7}
13.95	0.0085	1.051	400
20.62	0.0137	1.080	378
35.62	0.0293	1.150	331
47.14	0.0473	1.210	292
55.19	0.0648	1.253	268
61.67	0.0848	1.293	247
Raffinose			
6.96	0.0027	1.0233	425.5×10^{-7}
11.15	0.0045	1.0410	411
20.71	0.0093	1.0836	377
25.44	0.0122	1.1054	361

determined polarimetrically and are expressed (a) as grams of sugar per 100 grams of solution, and (b) as the ratio of the number of molecules of sugar to the number of molecules of solvent (n/N).

For purposes of comparison, the results for cane sugar solutions are also repeated here, and thus the whole series consists of a monosaccharide, a disaccharide, and a trisaccharide.

The relationship of the curves to each other has been discussed above.

Summary

(1) Slight improvements and modifications of Perman and Urry's method of measuring the compressibility of solutions are described.

(2) Results are given for solutions of potassium chloride, potassium bromide, potassium iodide, calcium bromide, strontium bromide, barium bromide, acetic acid, and formaldehyde. The measurements were made at 30° C and over the pressure range 0–100 atmospheres excess.

In an Appendix, results for solutions of glucose, sucrose, and raffinose, obtained by W. D. Urry, over the same pressure range, are given.

(3) The results are discussed with regard to compressibility in equi-molecular solutions, and to the effect upon the solvent of differently constituted solute molecules.