169. *The Relation between the Coefficient of Thermal Expansion and Structure of Solutions.*

By Robert Wright.

The coefficient of thermal expansion of a solution of a polar solute in a less polar solvent is to a large extent independent of the concentration. This phenomenon may be explained on the assumption that in concentrated solutions the molecules of the polar solute are linked together to form a continuous mesh-work which extends throughout the solution; so that the system may be compared to a porous substance containing a certain amount of free liquid inside the pores.

When a physical property of a binary solution is plotted against the composition, the resulting curve is as a rule continuous; but the coefficients of thermal expansion of certain salt solutions appear to be exceptions to this general rule, in that they are to a large extent independent of the concentrations of the solutions. Kremers in a series of papers (*Pogg. Ann.*, **100—114**) studied the relation between temperature and volume for a number of salt solutions and the following results for sodium iodide, which are typical, are taken from his work (Landolt-Börnstein, " Tabellen," 1923, 240).

Increase in volume, in c.c., of solutions of sodium iodide with temperature. (Each solution occupied 100 c.c. at 19·5°. The concentrations (*c*) are given in g.-mols./kg. of solvent.)

a.	40°.	60°.	80°.	Diff. 60°∼80°.
0 (pure water)	0·612	1·528	2·721	1·193
2	0·928	2·000	3·234	1·234
4	1·088	2·240	3·488	1·248
6	1·160	2·346	3·600	1·254
8	1·176	2·380	3·624	1·244
10	1·180	2·380	3·614	1·234

As the concentration increases, the thermal expansion of the solution tends to become constant, especially over the range 60—80°; in this region the temperature of the solution is sufficiently removed from that of maximum density, in the neighbourhood of which the thermal expansion of water and of aqueous solutions is abnormal. If therefore the coefficient of thermal expansion of the solution is plotted against the concentration, the resulting curve will show a flat, or almost flat, portion.

In the present investigation the coefficients of thermal expansion of a number of solutions have been determined between 25° and 78°. The lower temperature is not as far removed from the region of irregular aqueous expansion as is desirable, but it was employed for convenience. The higher temperature (alcohol vapour bath) is sufficiently below the boiling points of the solutions. The solvents employed were water and toluene, which are suitable for the temperature range chosen and differ widely in their physical properties. The solutes in water were of both types, electrolytes and non-electrolytes, but those in toluene were of necessity of the latter type only. The results obtained are given in the following tables and are of an accuracy of the order of 3%. The coefficient found for water was $46{\cdot}7 \times 10^{-5}$, and for toluene 119×10^{-5}.

Coefficients of Cubical Expansion ($\times 10^5$) *of Solutions between* 25° *and* 78°.

	c (g.-mols./kg. of solvent).													
Solute.	1.	2.	3.	4.	5.	6.	8.	10.	12.	14.	16.	18.	20.	100% Solute.
					Aqueous salt solutions.									
LiCl	43	40	38	36	35	34	32	31	31	31	31	31	—	—
LiBr	45	43	41	40	40	39	39	39	39	40	—	—	—	—
LiI	48	48	48	48	48	48	46	42	—	—	—	—	—	—
$LiNO_3$	50	52	53	54	54	54	54	54	—	—	—	—	—	—
NaCl	49	49	49	49	49	49	—	—	—	—	—	—	—	—
NaBr	50	51	52	53	54	54	54	—	—	—	—	—	—	—
NaI	52	54	56	59	60	60	60	60	—	—	—	—	—	—
$NaNO_3$	52	57	59	60	61	61	61	60	—	—	—	—	—	—
KCl	47	47	47	47	—	—	—	—	—	—	—	—	—	—
KBr	48	48	48	48	48	—	—	—	—	—	—	—	—	—
KI	50	51	52	52	52	52	—	—	—	—	—	—	—	—
KNO_3	50	52	54	—	—	—	—	—	—	—	—	—	—	—
KCNS	53	55	58	58	58	58	58	58	58	56	54	53	52	—
NH_4Cl	45	43	42	41	41	40	—	—	—	—	—	—	—	—
NH_4Br	44	46	45	44	43	43	—	—	—	—	—	—	—	—
NH_4I	47	48	49	50	50	50	50	50	—	—	—	—	—	—
NH_4NO_3	49	51	53	54	54	54	54	53	53	53	53	52	51	—
NH_4CNS	51	53	55	55	56	55	56	55	55	54	53	52	51	—
					Solutions of organic compounds in water.									
$CH_3{\cdot}CO_2H$	52	56	60	64	67	70	77	81	85	88	90	92	94	118
$C_2H_5{\cdot}CO_2H$	53	60	66	70	74	78	82	86	88	90	92	95	97	119
PrOH	53	60	65	69	75	80	84	87	90	92	94	97	99	113
$CH_3{\cdot}CO{\cdot}NH_2$	49	52	55	57	60	62	65	67	69	71	—	—	—	—
$CO(NH_2)_2$	49	51	53	54	55	56	58	59	60	—	—	—	—	—
C_5H_5N	54	61	65	69	73	77	82	86	91	93	95	97	99	114
					Solutions of organic compounds in toluene.									
$CH_3{\cdot}CO_2H$	122	124	123	123	123	123	124	123	123	124	123	124	123	118
$C_2H_5{\cdot}CO_2H$	121	122	—	—	123	—	—	122	—	—	123	—	122	119
PrOH	120	123	125	125	125	124	125	125	125	125	125	124	125	113
$CH_2Ph{\cdot}OH$	117	113	111	109	106	103	100	98	97	96	—	—	93	81
C_5H_5N	—	121	—	—	120	—	—	119	—	—	—	—	118	114
NH_2Ph	—	115	—	—	110	—	—	106	—	—	—	—	100	91
m-$C_6H_4Me_2$	—	118	—	—	116	—	—	113	—	—	—	—	111	109
$Ph{\cdot}NO_2$	—	115	—	110	—	106	103	—	98	—	—	—	96	89

Discussion of Results.—Considering the aqueous electrolyte solutions, we see that the coefficient of expansion at first changes as the concentration of the solute rises, but later tends to a value which remains constant over a considerable concentration range. Potassium nitrate is not soluble enough for the coefficient to reach the steady value, and with very soluble salts, such as the thiocyanates of ammonium and potassium, a change in the value of the coefficient is again to be noted at the higher concentrations. With most salt solutions the coefficients are greater than that of pure water, but with the chlorides and bromides of lithium and ammonium they are less.

Quite different results are found with aqueous solutions of non-electrolytes: here the coefficient increases continuously with concentration, the property–composition curve being of the general type obtained with binary solutions.

With toluene as solvent we find again the two types of result. Flat portions of the property–composition curve are found with the solutes acetic acid, propionic acid, and propyl alcohol, though in each of these cases the constant value of the coefficient is not far removed from that of the pure constituents. With all the other solutes the value of the coefficient changes with the composition of the solution.

Considering the results as a whole we arrive at the general conclusion: When there is a considerable difference in polarity between the two constituents of the solution, the coefficient of thermal expansion remains unchanged over a range of concentration, but if the polarities of the two constituents are approximately equal then the coefficient varies continuously with the composition of the solution.

Now if we have a concentrated solution of a polar solute in a less polar medium the polar molecules will link themselves together and—provided the concentration be high enough—will form a continuous cellular mesh-work throughout the solution. The formation of such a mesh-work, coupled with the assumption that the polar molecules solvate themselves with the molecules of the less polar solvent, may be used to explain the constant nature of the coefficient of expansion of such solutions.

If we consider a mass of porous material such as a piece of coke or a sintered-glass disc, the overall coefficient of thermal expansion of the system will not be affected by the presence of a certain amount of liquid held in the pores. This will be true even if the coefficient of the porous material is less than that of the liquid, provided only that there is not more liquid present than will fill the pores. The same reasoning will hold good even if the porous material is not rigid; for example, we may consider, instead of the piece of coke, a sponge or a test-tube containing slightly moistened coarse sand.

It will be seen that there is a similarity between the porous system described and that postulated for a concentrated solution of a polar solute such as salt in water. So long as the solution is dilute, the molecules of the solute move freely through the solution, but with higher concentration we get a cellular structure of hydrated solute molecules linked together throughout the solution, the pores being filled with free solvent. On further addition of solute it will combine with some of this free solvent, thus causing a decrease in size of the pores but not altering the coefficient of expansion. When all the free water has been used by the added solute, further addition of the latter will of necessity change the composition of the cellular mesh-work and therefore alter its physical properties. We have thus three stages in the formation of the cellular structure: (1) When there is large excess of solvent and the hydrated molecules, or ions, move freely through the liquid; during this period the coefficient of expansion changes with the concentration. (2) When the cellular structure has been formed and contains free water in its pores; during this period the further addition of solute will simply decrease the amount of free water and will not affect the coefficient of expansion. (3) When all the free water has been used up, further addition of the solute will change the composition of the porous material and hence alter its coefficient of expansion. This hypothesis of the changes in structure of a salt solution with change of concentration is not to be regarded as strictly accurate. It is probable that some change in the nature of the cellular mesh-work takes place with each addition of solute, but that the change is slight so long as there is excess of free solvent; hence, instead of there being an absolutely flat portion of the property–composition curve, there is a slightly marked maximum or minimum.

When the two constituents of the solution are non-polar or are of equal polarity the possibility of forming such a cellular structure does not exist, and hence the coefficient of expansion of such a system will vary continuously with its concentration.

Although the polar solute is postulated as forming a mesh-work throughout the solution, the latter is still homogeneous, and is not to be regarded as a two-phase liquid system; a concentrated solution differing from a dilute one only in that with the first the solute molecules are linked together, whereas with the second they are free. Since the solution is homogeneous, we do not get a discontinuity in the vapour pressure–composition curve, which is a characteristic of a two-phase liquid system. The presence of a cellular meshwork should increase the viscosity of a solution, and concentrated salt solutions are more viscous than pure water, though dilute ones often show a smaller viscosity than that of the solvent. When pure water is frozen, large ice crystals extend throughout the system, but the freezing of a salt solution results in the formation of a paste of small ice crystals. Such behaviour may be taken as additional, though not conclusive, evidence of the existence of a cellular structure in the solution.

EXPERIMENTAL.

The solutions were prepared by direct weighing, except that, lithium salts being deliquescent, the halide solutions were titrated with standard silver nitrate, and the concentration of the nitrate solution was determined from the value of its refractive index.

Measurements of thermal expansion were made by means of a small silica tube of about 5 c.c. capacity having a straight capillary stem about 2 cm. long. The rinsing and filling of the tube were carried out by means of a small separating funnel to which the silica tube was attached by a rubber stopper. The solution in use was placed in the funnel, which with the attached silica tube was submitted to a series of evacuations and readmissions of air at the filter-pump. By this means the tube was completely filled with the solution, and at the same time any air dissolved in the solution was removed. The tube, with the funnel still attached, was left in a thermostat at 25° for about ½ hour, then removed, disconnected from the funnel, dried, and weighed. The heating chamber for the higher temperature consisted of a copper test-tube (about 20 cm. long and 2 cm. in diameter), held by means of a well-fitting rubber stopper in a small copper heating-jacket. This jacket, which contained boiling ethyl alcohol, was fitted with a side tube to which was connected a reflux condenser, the upper end of which was attached to a simple form of pressure regulator by means of which the temperature of the bath could be held exactly at the desired temperature. The open end of the test-tube in the heating-jacket was closed by a cork fitted with a thermometer.

The silica tube, after its first weighing, was placed in a test-tube which was about 1 cm. shorter than the silica tube, the whole was then lowered by means of a thread into the heating chamber, the thread being held in position by means of the thermometer cork. The thermometer was now kept under observation till the temperature rose to 78°, and this was kept constant for about 20 mins. by manipulation of the pressure regulator. During this heating some of the liquid was expelled from the silica tube and collected in the glass test-tube. At the end of 20 mins.' heating at constant temperature the thermometer was removed, and the test-tube containing the silica tube raised by means of the thread till the jet of the silica tube was high enough to be wiped with a piece of filter-paper, thus removing the last drop of the expelled solution; the silica tube was then removed from the heater, cooled, and weighed.

There are two main sources of error in the process. During the filling of the tube at the filter-pump the evacuation process, as well as removing dissolved air, will also remove some solvent vapour so that the solutions become more concentrated. Secondly, if the solution is left for too long in the heating jacket loss may take place through evaporation; on the other hand, if the time is too short the system will not reach thermal equilibrium. On raising the silica tube from the heater there should always be a drop of expelled liquid remaining on the jet to be removed by the filter paper; if the level of the liquid is below the tip of the jet the result should be neglected. As a rule 20 mins.' heating at constant temperature sufficed.

In calculating the coefficient of expansion, the change of volume of the silica tube between the two temperatures was considered small enough to be neglected. If W_1 and W_2 are the weights of liquid which filled the tube at 25° and 78° respectively, and if ρ is the density of the liquid at the higher temperature, than the volume of the expelled liquid at the higher temperature is $(W_1 - W_2)/\rho$ and that of the tube is W_2/ρ. Hence the coefficient of thermal expansion of the liquid between 25° and 78° is given by the expression $(W_1 - W_2)/53W_2$.

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