[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

The Apparent Volumes and Thermal Expansions of Certain Salts in Glycol and Methanol

BY R. E. GIBSON AND JOHN F. KINCAID

Simple theoretical considerations which give at least a rough account of many of the thermodynamic properties of electrolytes in aqueous solutions become quite inadequate when applied to describe the magnitude or the dependence on concentration of the thermal expansions of these solutions. For example, in the vicinity of 25° it is possible to obtain moderately good values of the apparent volumes or apparent compressions of salts in water at infinite dilution merely by extrapolation of data at moderate concentrations with a formula, linear in the square root of the concentration, but it seems certain that such a procedure leads to erroneous results when applied to apparent expansions. Furthermore, different salts show large individual differences even in solutions as dilute as 0.5 molal. The results of an investigation of the apparent expansions of aqueous salt solutions[1] convinced us that the peculiar properties of water play a dominant role in determining the apparent expansions of salts in this solvent and, as a step toward elucidating this behavior, we have determined the apparent volumes and apparent thermal expansions of sodium iodide, sodium bromide and lithium bromide in glycol, of lithium bromide in methanol, and the apparent volumes of potassium iodide in glycol and of sodium iodide in methanol, with the object of comparing the results with those for the same salts in aqueous solution. Water, glycol and methanol are similar chemically, all being rich in oxygen, but their compressibilities and thermal expansions are quite different. Their specific compressions to 1000 bars are 0.03940, 0.02814 and 0.10180, respectively, at 25°. The dielectric constants at 20° of water, glycol and methanol[2] are 80.37, 38.66 and 32.35, respectively.

Experimental

Measurements of the specific volumes of the solutions at 25° and of the expansions corresponding to temperature changes of 2.50° between 20 and 32.5° were made with the same apparatus[1] that was used in a study of the aqueous solutions. The temperature of the dilatometer could be held constant and measured to 0.01° and a volume change of 10^{-4} ml. could be determined readily. The specific volumes at the different temperatures were known, therefore, with a relative accuracy of approximately 2 parts in 10^6. The preparation of samples of sodium iodide,[1] sodium bromide[3] and lithium bromide[1] also has been outlined. Although our purified sample of lithium bromide gave perfectly clear solutions in water and in glycol, it produced a slightly cloudy solution in methanol. As this was eliminated by evaporating the aqueous solution from which the salt was recrystallized in a platinum rather than a Pyrex glass dish we concluded that the cloudiness was due to siliceous matter. Checks of the specific volumes of the aqueous solutions indicated that these impurities were insignificant.

An account of the preparation of *methanol* has already been given.[4] *Glycol* obtained from the Eastman Kodak Company was redistilled twice in a vacuum. The different fractions varied slightly in density, but all immediately developed a yellow color when sodium iodide was added. This color was quite intense in dilute solution but died out completely when sodium iodide sufficient to make a solution stronger than 20% was added. If the concentrated solutions were diluted, the color reappeared. When the last traces of glycolaldehyde were removed from the glycol, no coloration was produced with sodium iodide and we conclude that the peroxide of glycolaldehyde was probably responsible for the oxidation of the iodide. The reason for the disappearance of the yellow coloration in the presence of large amounts of sodium iodide is still to be investigated. It may be noted that even after standing for months in air, solutions of sodium iodide in pure glycol do not develop a yellow color. In order to obtain as accurate an estimate of the specific volume of pure glycol as possible we purified it in two different ways. The addition compound of sodium iodide with glycol was crystallized from anhydrous solution and filtered by suction from the supernatant liquor. From this solid, glycol was distilled off in a high vacuum and then redistilled. The specific volume of this sample at 25.00° was 0.90101. The commercially obtained glycol was also mixed with sodium hydroxide, distilled *in vacuo* and redistilled. This procedure freed it completely from glycolaldehyde and the specific volume of the sample was 0.90102. Three different samples treated by the same method had specific volumes of 0.90102 ml. per gram. The specific volumes of samples distilled once or twice from Eastman glycol without chemical treatment varied between 0.90095 and 0.90098. A small amount of the denser glycolaldehyde seemed to account for the discrepancies.

Results

Table I summarizes the results of the specific volume measurements. At the head of each sec-

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[1] R. E. Gibson and J. F. Kincaid, THIS JOURNAL, **59**, 25 (1937).

[2] G. Åkerlöf, *ibid.*, **54**, 4129 (1932).

[3] R. E. Gibson, *ibid.*, **57**, 284 (1935).

[4] R. E. Gibson, *ibid.*, **57**, 1551 (1935).

Table I

The Specific and Apparent Volumes of Some Salts in Glycol and Methanol at 25°

100 x_2	v	ϕ_2	$(v_{\text{obsd.}} - v_{\text{calcn.}}) \times 10^5$
Sodium Iodide–Glycol			
$\phi_2 = 0.25594 + 0.08394x_2 - 0.0856x_2^2$			
0.000	0.90101		
3.352	.87949	0.2590	1
3.807	.87658	.2593	1
7.847	.85087	.2620	0
10.687	.83293	.2639	−1
15.667	.80168	.26699	0
21.523	.76521	.27004	0
30.506	.70964	.27368	3
34.879	.68263	.27489	3
39.869	.65175	.27580	0
Sodium Bromide–Glycol			
$\phi_2 = 0.26522 + 0.07303\ (x_1x_2)^{1/2}$			
1.304	0.892831	0.2731	−1
2.077	.88802	.2749	−1
4.647	.87220	.2808	1
9.361	.84348	.2863	−2
15.215	.80825	.29129	−2
19.569	.78227	.29419	0
24.983	.75011	.29696	4
Potassium Iodide–Glycol			
$\phi_2 = 0.28406 + 0.02432\ c_2^{1/2}$			
6.857	0.85918	0.2909	0
13.469	.81924	.2939	0
20.924	.77460	.2969	4
28.526	.72932	.2991	−5
Lithium Bromide–Glycol			
$\phi_2 = 0.24993 + 0.08722\ x_2^{1/2}$			
1.9962	0.888271	0.2628	1
4.069	.87524	.2676	0
8.115	.85019	.27481	0
12.360	.82430	.28034	−3
20.593	.77509	.28951	0
30.100	.71947	.29787	3
Lithium Bromide–Methanol			
0.000	1.27136		
4.033	1.22336	0.0821	
7.187	1.18679	.0952	
11.711	1.13567	.11297	
13.264	1.11835	.11806	
15.833	1.08980	.12487	
24.352	0.99772	.14779	
30.123	.93742	.16286	
35.114	.88586	.17358	
Sodium Iodide–Methanol			
$\phi_2 = 0.08542 + 0.15174\ c_2^{1/2}$			
0.000	1.27136		
7.287	1.18775	0.1242	4
14.520	1.10711	.14015	−3
22.774	1.01770	.15755	8
31.287	0.92794	.17371	5
38.209	.85682	.18642	−13

tion is written the empirical equation which best represents the data. It will be noticed that several concentration functions have been used as arguments in these equations. The choice of such functions was determined solely by which argument gave the best fit in the simplest type of equation. The last column of the table demonstrates the adequacy of the equation used.

The thermal expansion data were converted to values of $\Delta_T v$,[5] the finite changes in specific volumes for a given rise of temperature, which were expressed as quadratic functions of the temperature by a least square method.[6] Table II gives the coefficients of these equations and the deviation diagrams in Fig. 1 show how well the equations represent the observations. From the equations given in Table II the specific expansibility $(\mathrm{d}v/\mathrm{d}T)_P$ was calculated readily. The ap-

Table II

Coefficients in the Quadratic Equations Representing the Change in Specific Volume of the Solutions with Temperature over the Range from 20 to 35°

$$\Delta_T v = A + B(t - 25) + C(t - 25)^2$$

100 x_2	$A \times 10^5$	$B \times 10^5$	$C \times 10^4$
Sodium Iodide–Glycol			
0.000	0.3	57.15	0.0507
5.016	.0	53.90	.0500
10.687	.0	50.61	.0388
19.574	.0	45.67	.0354
28.578	.2	41.26	.0234
Sodium Bromide–Glycol			
5.195	0.0	53.25	0.0646
9.582	.0	50.30	.0485
14.792	.4	47.34	.0125
20.826	−.1	44.07	.0048
Lithium Bromide–Glycol			
4.069	0.0	53.09	0.0702
8.115	−.1	50.00	.0364
12.360	−.1	46.89	.0342
20.593	−.4	41.01	.0034
Lithium Bromide–Methanol			
0.000	0.0	152.54	0.3383
7.187	1.0	126.40	.1810
15.833	0.9	100.96	.1152
24.352	.1	80.42	.0366
35.114	.1	59.66	.0347

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(5) The symbols used are as follows. The subscripts 1 and 2 refer to the liquid solvent and the salt in solution, respectively; the subscripts w and s stand for pure solvent and pure solid salt, respectively. The symbol Δ_T indicates the increase with temperature of the quantity to which it is prefixed. The weight fraction is represented by x, the grams per ml. by c, the moles per liter by C, the specific volume in ml. by v, the apparent volume by ϕ, the temperature in °C. by t, the molecular weight by M. The apparent volume is defined by the relation $v = x_2\phi_2 + x_1v_w$ and the apparent expansibility at any temperature $\phi_T \equiv (\mathrm{d}\phi_2/\mathrm{d}T)_P$.

(6) H. M. Roeser, *Sci. Papers Bur. Standards*, **16**, 363 (1920).

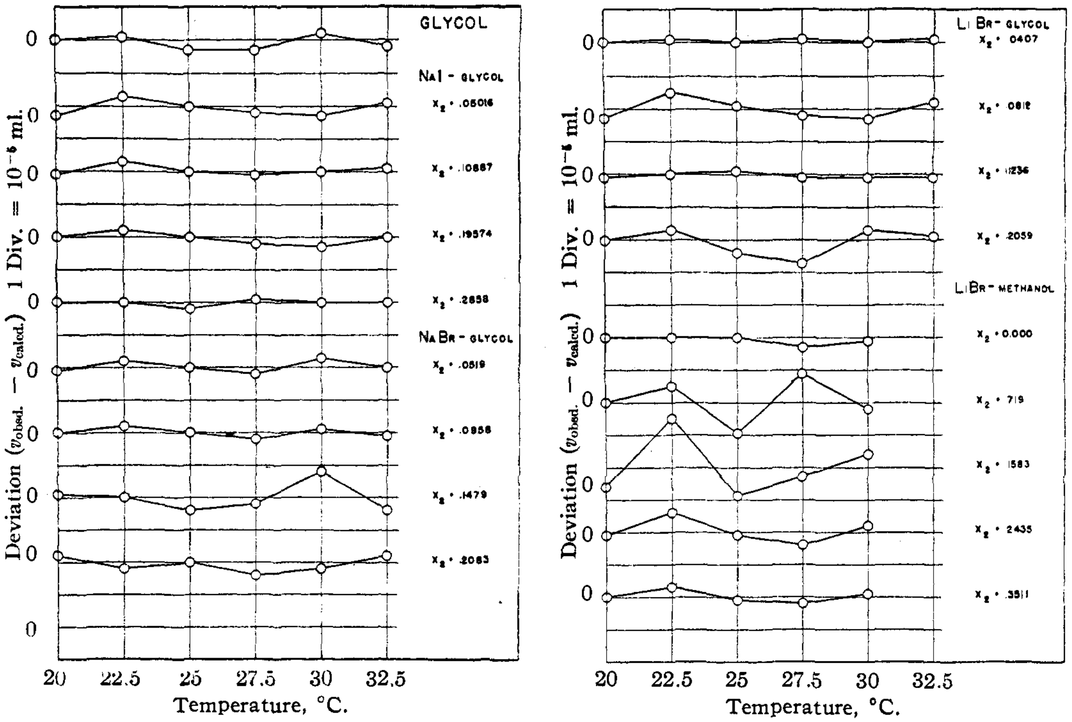
Fig. 1-A.

Fig. 1-B.

Fig. 1.—Differences between the observed specific expansions of non-aqueous solutions and those calculated by the equations in Table II.

parent expansibility was computed from the obvious relation

$$\phi_T = \frac{1}{x_2}\left[\frac{dv}{dT} - x_1\frac{dv_w}{dT}\right]$$

Discussion of Results

In Fig. 2 we have plotted $(\phi_2 - v_s)$,[7] the apparent expansion which occurs when 1 g. of salt mixes with sufficient solvent to give a solution of a given concentration, against $C_2^{1/2}$ for some of the salts in glycol, in methanol and, for purposes of comparison, in water.[1] Vosburgh, Connell and Butler[8] found that the apparent volumes of salts in dilute solutions in alcohols were linear functions of $C_2^{1/2}$ and for sodium iodide in methanol we find that this result holds in concentrated solution, but in the other cases the linear function is not adequate. It may be noted that when our results for sodium iodide solutions in methanol are extrapolated by the equation in Table I to the low concentrations investigated by Vosburgh, Connell and Butler, our specific volumes agree with theirs to within 3×10^{-5} cc.

Simple considerations lead to the conclusion that $(\phi_2 - v_s)$ should decrease algebraically with rising compressibility of the solvent for solutions of the same salt in chemically related solvents, where the forces between the solvent and the solute are roughly the same. The relative positions of the various curves in Fig. 2 are all in accord with this conclusion with one exception, namely, the curve of $(\phi_2 - v_s)$ for lithium bromide in water which lies above that of the same salt in glycol, whereas the reverse would be expected from the compressibilities of the two solvents. This phenomenon is accounted for on the now well-known hypothesis of the structure of liquid water.[9] The lithium ion in virtue of its small radius can approach close enough to a water molecule to polarize the molecule, thereby causing a strengthening of the electrostatic bonds which hold the water molecules in the less random open liquid structure (the "quartz-like" structure of Bernal and Fowler with all inference as to its exact nature removed). The effect is to cause an expansion of the water and hence to produce a smaller net contraction than if structural effects were absent. This also

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[7] Values of v_s were taken from the data of Baxter and Wallace, THIS JOURNAL, 38, 70 (1916).

[8] W. C. Vosburgh, L. C. Connell and J. A. V. Butler, *J. Chem. Soc.*, 933 (1933).

[9] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, 1, 540 (1933); S. Katzoff, *ibid.*, 2, 841 (1934).

accounts for the fact that the compressions of lithium salt solutions are abnormally high.[3] Such an effect is either absent or much less significant in glycol, as will be evident from the following discussion of apparent expansibilities. A reasonable extrapolation shows that in solutions of high concentration, where effects due to structural changes become less, the curve for the glycol solutions of lithium bromide should cross that for the aqueous solutions. This is seen without extrapolation in the differential effects. In Fig. 3 the partial volumes[10] of lithium bromide in glycol and in water are plotted against $C_2^{1/2}$; at low concentrations the partial volumes of lithium bromide are greater in the aqueous solutions, but when the concentration exceeds 4 moles per liter the partial volumes are greater in the glycol solutions. The apparent volumes of lithium bromide in glycol solutions also throw light on the puzzling phenomenon that, whereas the negative departures from Raoult's law in aqueous solutions indicate strong attractive forces between lithium salts and the water, the contraction on solution as measured by $(\phi_2 - v_s)$ is very small and even becomes an expansion in highly concentrated solutions. The quantity $(\phi_2 - v_l)$, where v_l is the volume of the pure liquefied solute at the temperature and pressure of the solution, should be taken as a measure of the electrostriction rather than $(\phi_2 - v_s)$ and the glycol solutions show that $(v_l - v_s)$ must be quite large for lithium bromide in comparison with other salts. A lower limit for v_l is given by the partial volume of the salt in the most concentrated glycol solution. This is at least 0.315 cc. per gram (see Fig. 3), indicating that the salt expands more than 9.1 per cent. on melting.

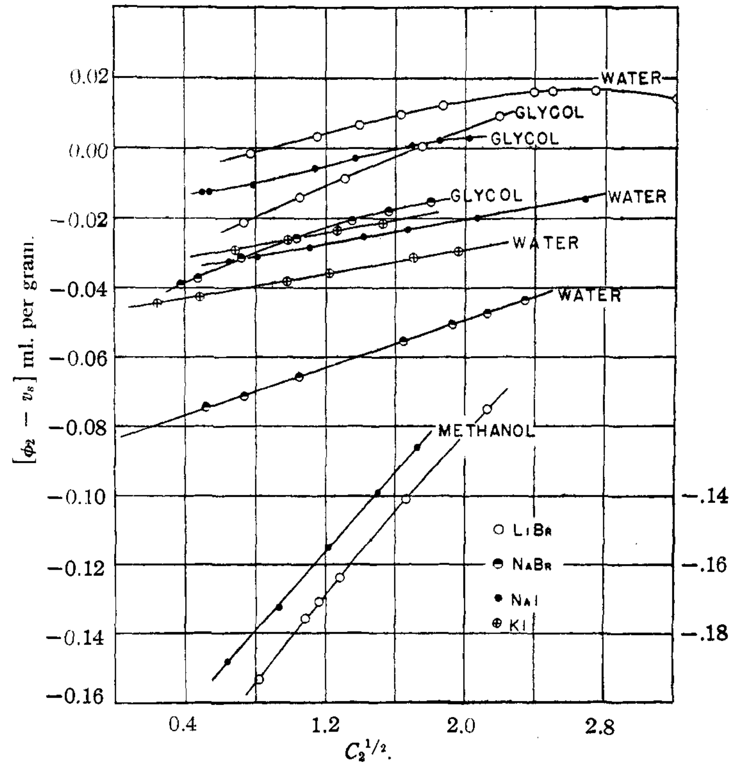

Fig. 2.—The volume changes per gram of salt accompanying the solution of salts in different solvents. The scale of ordinates on the right refers to lithium bromide in methanol.

The Apparent Thermal Expansions and Expansibilities.—In Fig. 4 the apparent molal expansibilities, $M_2\phi_T$, of the salts in different solvents are plotted against $C_2^{1/2}$. It will be seen at once that the magnitude, sign and concentration-variation of $M_2\phi_T$ for the salts in glycol and methanol are quite different from what they are in aqueous solutions. These curves for the non-aqueous solutions run in what may be regarded as a fairly normal way and by contrast bring out the abnormal behavior of similar curves for aqueous

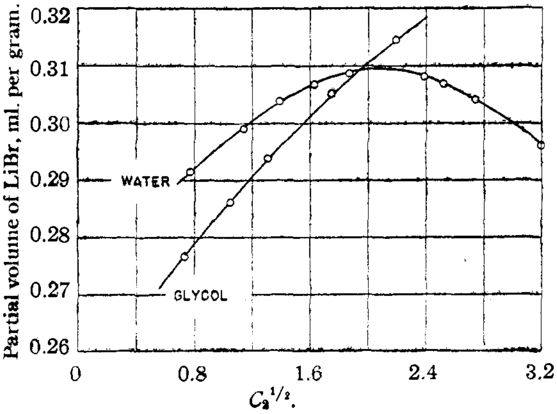

Fig. 3.—The partial volumes of lithium bromide in water and in glycol solutions as functions of the square root of the number of moles of salt per liter of solution at 25°.

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(10) The partial volumes were calculated from the apparent volumes by the formula of Adams and Gibson, This Journal, 54, 4523 (1932). For glycol solutions $d\phi_2/dx_2$ was obtained from the equation in Table II and for aqueous solutions it was determined from tabular differences.

solutions. In general $M_2\phi_T$ is negative except in the most concentrated solutions of sodium iodide, and the slopes of the curves are positive, as would be expected from the interionic attraction theory[11] and a reasonable assumption about the effect of pressure and temperature on the dielectric constant. Data necessary for calculating the magnitudes of these slopes from the theory unfortunately are lacking.

On comparing the effect of the three salts on the expansibility of glycol we note that $M_2\phi_T$ decreases algebraically as we pass from salt to salt by an amount roughly proportional to the increase in the effective pressure of the solution, P_e,[12] as determined by compression measurements.[13] Indeed, it seems possible that, when the necessary data are at hand, ϕ_T may actually be calculated quantitatively from P_e and a knowledge of the effect of pressure on the expansion coefficient of the solvent, a thing which seems quite impossible with aqueous solutions. Furthermore, the expansion coefficient of methanol changes much more rapidly with pressure than that of glycol and it will be seen that ϕ_T for lithium bromide is much greater numerically in methanol than in glycol solutions. This again suggests that P_e may be the predominant factor in determining the expansion coefficient of these non-aqueous salt solutions.

The effective pressure hypothesis does not by any means explain the thermal expansibilities of aqueous solutions. The values of $M_2\phi_T$ are too large and, moreover, when we compare aqueous solutions of different salts we see that there is not even a qualitative relationship between the effective pressures and the thermal expansibilities. The large positive values of $M_2\phi_T$ may be explained by the assumption that salts increase the randomness of the water structure and by considering the purely mechanical effect of the volume of the dissolved ions. A detailed discussion of this cannot be given here, but it is necessary to show that the assumption made in the foregoing that lithium bromide promotes the tetrahedral arrangement of the water molecules is not incompatible with the observation that although $M_2\phi_T$ for lithium bromide in water is quite small it is, nevertheless, positive.

The observed thermal expansion of water may be regarded as the resultant of (a) an expansion due to the ordinary increase of the kinetic energy of the system as a whole, and (b) a contraction resulting from the increase in randomness as produced by a loosening up of the tetrahedral arrangement of the water molecules which is well pictured by Katzoff[9] as a departure of the O–H–O angles from 180°. The magnitude of contraction (b) depends on the amount of randomness introduced by a given rise of temperature and on the amount of excess volume which the tetrahedral structure introduces into the system.

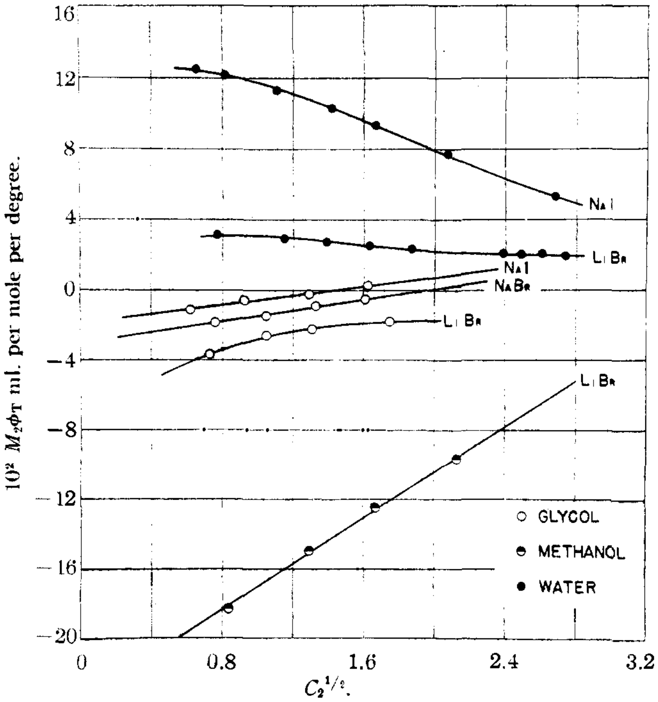

Fig. 4.—The apparent molal expansibilities at 25° of salts in different solvents as functions of the square root of the number of moles of salt per liter of solution.

Because of its polarizing power, the lithium ion, we have supposed, increases the strength of those bonds which hold the water molecules in the tetrahedral arrangement. We should, therefore, expect that a given rise of temperature would introduce less randomness into water in lithium bromide solution than in pure water and hence that contraction (b) would be diminished. This would lead to an apparent expansibility of the water in the solution larger than that of pure water and hence a positive value of $M_2\phi_T$, as is observed.

The specific volume of water is 84% greater than if the molecules of radius 1.4 Å. were packed

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(11) F. T. Gucker, Jr., This Journal, **56**, 1017 (1934).

(12) R. E. Gibson, *ibid.*, **56**, 13 (1934).

(13) Unpublished results obtained in this Laboratory.

closely together.[9] The excess volume introduced by the tetrahedral arrangement is therefore approximately 45% of the total volume. The expansion coefficient of water at 25° is 25.7 × 10^{-5} ml. per gram per degree. If it behaved as a normal liquid it would have an expansion coefficient of approximately 85 × 10^{-5} ml. per gram per degree. This difference may be accounted for if we assume that a rise of one degree introduces a randomness which corresponds to a loss of about 0.1% of the excess volume, a very reasonable amount.

Summary

We have measured the specific volumes at 25° and the expansion coefficients in the neighborhood of this temperature of solutions of some salts in methanol and glycol. A comparison of the apparent and partial volumes of lithium bromide in water, glycol and methanol gives strong evidence that this salt influences the structure of water by promoting the tetrahedral arrangement of the molecules.

Unlike the same quantities for salts in aqueous solution, the apparent molal expansibilities of the salts in glycol and methanol are negative and increase with the concentration of salt, thereby agreeing qualitatively with the predictions of the interionic attraction theory and the effective pressure hypothesis. A comparison of the behavior of the salts in water on the one hand and in glycol and methanol on the other indicates that the structural changes in water play a predominant role in determining the thermal expansions of aqueous solutions.

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The Rate of Reaction of Magnesium with Acids in Ethyl Alcohol[1,2]

BY MARTIN SCLAR[3] AND MARTIN KILPATRICK

The rate of reaction of metals with acids in aqueous solution has been the subject of many investigations. A summary of the work up to 1929 has been given by Centnerszwer.[4] In non-aqueous solvents two quantitative studies have appeared. Zecchini[5] measured the rates of reaction of zinc with hydrogen chloride in water, ethyl alcohol, methyl alcohol and acetone. Brönsted and Kane[6] sought to show that sodium amalgam reacted with molecules of carboxylic acids in benzene, and that the rate of the reaction increased with the ease with which the acid gave up its proton. In addition, several partially quantitative observations have been made, especially by Kahlenberg and his co-workers in connection with their criticism of the Arrhenius theory of electrolytic dissociation. Smith[7] gives a summary of this work. Additional investigations are desirable because comparison of the results in aqueous and non-aqueous solutions may lead to a better understanding of the problem.

In the present work ethyl alcohol was selected as the solvent and magnesium as the metal for the general study. After describing the procedure and some orientating experiments, we shall proceed to demonstrate that magnesium can displace hydrogen from the molecules of ethyl alcohol without the intermediate formation of solvated proton. We shall also show that this reaction predominates when magnesium dissolves in alcoholic solutions of acids. It will be seen that the observed rate of this reaction shows great variations. Experiments with solutions of acids containing chloride ion, organic chlorine compounds and small amounts of water, respectively, will be described, which indicate that the variations in the observed rates probably are due to differences in the amount of metal surface available for reaction. The results of experiments to determine the effect of temperature and the rate at which the magnesium cylinder is rotated will then be presented. Finally some miscellaneous experiments will be described.

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(1) Abstracted from the dissertation of Martin Sclar presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy, April, 1935.

(2) An abstract of this paper was presented at the eighty-ninth meeting of the American Chemical Society held at New York, April, 1935.

(3) George Leib Harrison Fellow in Chemistry, 1934–1935.

(4) Centnerszwer, *Z. physik. Chem.*, **141A**, 297 (1929).

(5) Zecchini, *Gazz. chim. ital.*, **27**, 466 (1897).

(6) Brönsted and Kane, THIS JOURNAL, **53**, 3624 (1931).

(7) Smith, "The Effects of Moisture on Chemical and Physical Changes," Longmans, Green and Co., London, 1929, Chap. 14.