[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Apparent and Partial Molal Volumes of Sodium Perchlorate and Perchloric Acid in Mixed Solutions[1a]

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Bigeleisen,[2] using data from the literature,[3] has shown that at concentrations above 0.04 *N* the apparent molal volume of perchloric acid deviates greatly from the values predicted by the limiting Debye–Hückel law. A maximum was found at about 0.6 *N*. The apparent molal volume then decreased with increasing concentration up to 9 *N* where a minimum was observed. This behavior, which is unusual for a completely ionized solute,[4] was attributed to ion–ion and ion–solvent interactions. The present work shows that the effect is due to ion–solvent interaction.

Owen and Brinkley[5] have applied the extended Debye–Hückel theory to the extrapolation of apparent molal properties. Robinson and Stokes[6] have corrected the Debye–Hückel equation for the effects of hydration. Both viewpoints have been applied to the data presented here.

Methods.—The same type of apparatus as previously described[7] was employed to determine the densities of the solutions. The apparatus was modified to eliminate all error due to surface tension and to permit the use of larger platinum wires to support the sinkers. Each sinker was suspended from a "supplementary bob" also immersed in the solution under investigation. The supplementary bob was attached in turn to the supporting platinum wire which passed through the surface of the solution. The apparent weight change of the system with the sinker attached to the bob, and with it not attached, was a measure of the density of the solution.

The perchloric acid solutions were made up from 60% C. P. perchloric acid containing not more than 0.03% total impurity. The solutions were analyzed by weight titration as described previously[8] for solutions of hydrochloric acid.

Anhydrous sodium perchlorate was supplied by the G. Frederick Smith Chemical Company and was handled in a dry box. The moisture content, determined by vacuum drying at 250°, was found to be 0.03%. The percentage of chloride was found to be 0.002%. The material was guaranteed to be potassium free.

Solutions were made up by adding weighed amounts of anhydrous salt to weighed amounts of water or perchloric acid solution. All weights were corrected to vacuum.

Results

The results obtained with perchloric acid in water solution are given in Table I.[9] The apparent molal volume (Φ_3)[10] was calculated directly from the observed difference between the density of the solution and the density of water ($d_3 - d_1$). The observed values may be represented by the equation

$$\Phi_3 = 44.11_8 + 1.860C_3^{1/2} - 1.611C_3^{3/4} + 0.162C_3$$

where C_3 is the concentration of the perchloric acid in moles per liter of solution, with an average deviation between observed and calculated values of ±0.011 ml. The partial molal volumes of perchloric acid ($\bar{V}_3$) and of water ($\bar{V}_1$) were calculated from this equation by methods previously used.[8]

The data are in reasonable agreement with the results of Kohner and Gressmann[3] (Fig. 1). The limiting value of the apparent molal volume ($\Phi_3^0 = 44.118$) is in good agreement with the value 44.086 calculated from the values of Φ^0 for hydrochloric acid (17.830),[11] for sodium chloride (16.670),[8] and for sodium perchlorate (42.926) (see below). Bigeleisen[2] estimated the value to be 43.90 ± 0.20 ml.

The maximum value of Φ_3 was found to be 44.56 ml. at a concentration of 0.58 *N*.

The results obtained for sodium perchlorate in water solution are given in Table II[9] and may be represented by the empirical equation

$$\Phi_3 = 42.92_6 + 1.800C_3^{1/2} + 0.043C_3^2$$

with an average deviation between observed and calculated values of ±0.011 ml. The results are in good agreement with those obtained above 1 *N* by Kohner[12] (Fig. 1) which were extrapolated by Bigeleisen[2] to give a value of 42.7 ± 0.2 ml. for Φ^0_3. The partial molal volumes of sodium perchlorate and of water were calculated from this empirical equation.

In Table III[9] the results on solutions of sodium perchlorate in perchloric acid are given. The equations representing these results are

0.16 *N* $HClO_4$

$$\Phi_3 = 43.642 + 1.853X + 0.100X^4,\ \text{av. dev.} \pm 0.059\ \text{ml.}$$

[1a] For detailed tables of data order Document 2867 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $0.50 for microfilm (images 1 in. high on standard 35 mm. motion picture film) or $0.60 for photocopies (6 × 8 in.) readable without optical aid.

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[2] J. Bigeleisen, *J. Phys. and Colloid Chem.*, **51**, 1369 (1947).

[3] H. Kohner and M. L. Gressmann, *Z. physik. Chem.*, **A144**, 137 (1929); A. E. Markham, THIS JOURNAL, **63**, 874 (1941); J. N. Pearce and A. F. Nelson, *ibid.*, **55**, 3075 (1933).

[4] O. Redlich, E. K. Holt and J. Bigeleisen, *ibid.*, **66**, 13 (1944), have shown that perchloric acid is practically completely ionized even in 9 *N* solution.

[5] B. B. Owen and S. R. Brinkley, Jr., *Ann. N. Y. Acad. Sci.*, **51**, 753 (1949).

[6] R. A. Robinson and R. H. Stokes, *ibid.*, **51**, 593 (1949); R. H. Stokes and R. A. Robinson, THIS JOURNAL, **70**, 1870 (1948).

[7] H. E. Wirth, *ibid.*, **59**, 2549 (1937).

[8] H. E. Wirth, *ibid.*, **62**, 1128 (1940).

[9] Tables I, II, III and IV referred to in this paper may be obtained from the American Documentation Institute (see ref. 1).

[10] The subscript 1 refers to water, the subscript 2 refers to the electrolyte whose molality remains constant in a series of observations, and the subscript 3 refers to the electrolyte whose concentration is being varied (including the case where $m_2 = 0$).

[11] O. Redlich and J. Bigeleisen, THIS JOURNAL, **64**, 758 (1942).

[12] H. Kohner, *Z. physik. Chem.*, **B1**, 427 (1928).

0.36 N $HClO_4$
$\Phi_3 = 44.013 + 1.790X + 0.234X^3$, av. dev. ±0.023 ml.
0.66 N $HClO_4$
$\Phi_3 = 44.355 + 1.681X + 0.384X^2$, av. dev. ± 0.045 ml.
0.99 N $HClO_4$
$\Phi_3 = 44.616 + 1.820X + 0.350X^2$, av. dev. ± 0.042 ml.
2.24 N $HClO_4$
$\Phi_3 = 45.270 + 2.260X$, av. dev. ± 0.056 ml.

where $X = \mu_v^{1/2} - C_2^{0\,1/2}$, and μ_v is the volume ionic strength of the solution.

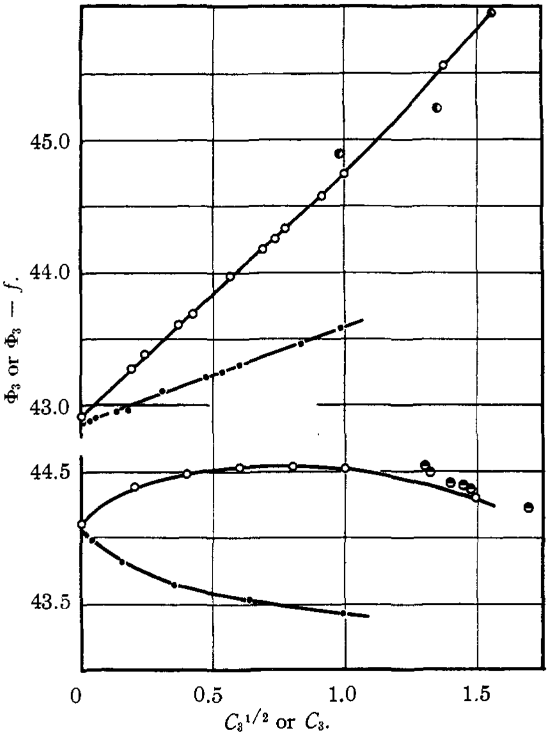

Fig. 1.—Apparent molal volumes of sodium perchlorate (upper curve) and of perchloric acid (lower curve) in aqueous solution *vs.* the square root of the volume concentration: data of Kohner[12] (◐), data of Kohner and Gressmann[3] (◓), this research (O). The function $\Phi - 2/3\ S_v\ \Omega_v\ C^{1/2}$ for sodium perchlorate (upper curve) and for perchloric acid (lower curve) *vs.* the volume concentration (●).

With the aid of the above equations the densities of solutions which were exactly 0.16, 0.36, 0.64, 1.0 and 2.25 molar in sodium perchlorate were calculated, and from these densities the apparent and partial molal volumes of perchloric acid in sodium perchlorate solutions were obtained (Table IV).[9] The equations representing the apparent molal volumes are

0.16 m $NaClO_4$
$\Phi_3 = 44.777 + 0.1830X - 0.435X^2$, av. dev. ± 0.004 ml.
0.36 m $NaClO_4$
$\Phi_3 = 45.014 - 0.0934X - 0.391X^2$, av. dev. ± 0.004 ml.
0.64 m $NaClO_4$
$\Phi_3 = 45.215 - 0.277X - 0.343X^2$, av. dev. ± 0.003 ml.
1.00 m $NaClO_4$
$\Phi_3 = 45.418 - 0.603X - 0.350X^2$, av. dev. ± 0.007 ml.
2.25 m $NaClO_4$
$\Phi_3 = 45.936 - 2.690X + 1.570X^2$, av. dev. ± 0.007 ml.

From a knowledge of the partial molal volumes of sodium perchlorate and of perchloric acid, the partial molal volumes of water in these solutions were obtained (Table IV).[9]

As was found for solutions of sodium chloride in hydrochloric acid,[8] the partial molal volumes of sodium perchlorate are less in solutions of perchloric acid than in water alone, and the decrease is the greater the higher the concentration of the perchloric acid (Fig. 2). The limiting values of the partial molal volume of sodium perchlorate ($\bar{V}_3^0$) in perchloric acid solutions of concentration C_2 may be represented by the equation

$$\bar{V}_3^0 = 42.926 + 1.973C_2^{1/2} - 0.270C_2$$

with an average deviation between observed and calculated values of ±0.010 ml. The decrease in the partial molal volume of sodium perchlorate due to a given concentration of perchloric acid is about twice that observed for the effect of hydrochloric acid on sodium chloride.

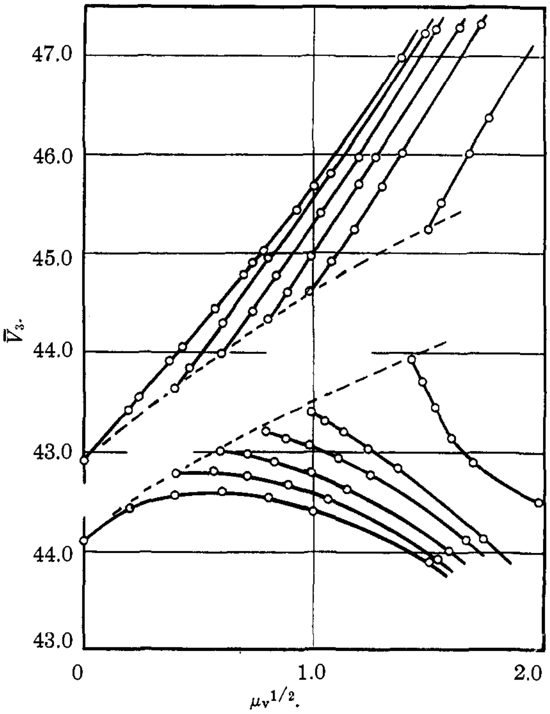

Fig. 2.—Partial molal volumes of sodium perchlorate in water, and in approximately 0.16, 0.36, 0.64, 1.0 and 2.25 N perchloric acid solutions (upper curves) and partial molal volumes of perchloric acid in water, and in approximately 0.16, 0.36, 0.64, 1.0 and 2.25 N sodium perchlorate solutions (lower curves) *vs.* the square root of the volume ionic strength.

In a similar manner, the partial molal volumes of perchloric acid are increased in solutions containing sodium perchlorate. The limiting values of the partial molal volumes of perchloric acid in sodium perchlorate solutions are given by the empirical equation

$$\bar{V}_3^0 = 44.118 + 1.547C_2^{1/2} - 0.194C_2$$

with an average deviation of ±0.031 ml., where C_2 is the concentration of the sodium perchlorate.

The maximum value of $\bar{V}_3$ in aqueous perchloric acid solution and for perchloric acid in 0.16 and 0.36 *m* sodium perchlorate appears at the same volume ionic strength in the three cases (Fig. 2). In higher concentrations of sodium perchlorate no maxima are observed.

The partial molal volumes of sodium perchlorate in perchloric acid solution, and the partial molal volumes of perchloric acid in sodium perchlorate solution, do not depend on the volume ionic strength alone but are influenced by the specific nature of the other electrolyte present.

Discussion of Results

Owen and Brinkley[5] have shown that the apparent molal volumes of electrolytes in solution can be represented by the equation[13]

$$\Phi_v - \Phi_v^0 = 2.303\nu RT\mathcal{S}_f\left(\frac{1}{1+\kappa a}\frac{\partial \ln D}{\partial P} - \frac{\beta}{3}\right)C^{1/2} + 2.303\nu RT\mathcal{S}_f A'\frac{\partial \ln \mathring{a}}{\partial P}\theta C + {}^1/_2 K_v C \quad (1)$$

This reduces to

$$\Phi_v - \Phi_v^0 = {}^2/_3\,\mathcal{S}_v\Omega_v C^{1/2} + {}^1/_2 K_v C \quad (2)$$

where $\Omega_v = 1.3513/(1 + \kappa a) - 0.3513\sigma$, if it is assumed that $\partial \ln \mathring{a}/\partial P$ is zero. Equation 2 was found by Owen and Brinkley to represent the apparent molal volumes of sodium chloride up to 0.75 *N*, of potassium chloride up to 1.0 *N* and of hydrochloric acid up to 0.2 *N*. Using the value of 4.8 Å. for $\mathring{a}$ obtained by Robinson and Baker[14] from vapor pressure measurements on perchloric acid at 25°, the function $\Phi - 2/3\,\mathcal{S}_v\Omega_v\cdot C^{1/2}$ was calculated using the revised values for the required physical constants given by Harned and Owen.[15] This function is plotted against the concentration in moles per liter in Fig. 1. A straight line is not obtained. It was found, however, that the data could be represented with an average deviation of ±0.016 ml. by the equation

$$\Phi_v - 44.039 = {}^2/_3\mathcal{S}_v\Omega_v C^{1/2} - 2.452\theta C - 0.1475\,C \quad (3)^{16}$$

from which $\partial \ln \mathring{a}/\partial P$ was calculated to be -2.68×10^{-5} per bar.

It was also found that the data of Wirth[7] on hydrochloric acid could be represented in the range 0–4 *N* by an equation similar to (3) if a value of $\partial \ln \mathring{a}/\partial P = -0.7 \times 10^{-5}$ per bar is assumed, and taking $\mathring{a} = 4.3$ Å.

For sodium perchlorate the function $\Phi_v - 2/3\,\mathcal{S}_v\Omega_v C^{1/2}$ is linearly related to the volume concentration up to concentrations of 1 *N* (Fig. 1) ($\mathring{a}$ was taken as 4.4).[17] Deviations were found at higher concentrations, but equation 1 was found to be valid for all concentrations studied if $\partial \ln \mathring{a}/\partial P$ was taken as -0.15×10^{-5} per bar. Since the apparent molal volumes of most other strong electrolytes depend on the concentration in much the same way as found here for sodium perchlorate, similar small values for $\partial \ln \mathring{a}/\partial P$ can be assumed to apply to such electrolytes.

According to this viewpoint the unique behavior of perchloric acid solutions is due to their high compressibility, since $\partial \ln \mathring{a}/\partial P$ should be directly related to the compressibility. There is no direct information on the compressibility behavior of perchloric acid solutions, but Gibson[18] has shown that the bulk compression of many salt solutions is linearly related to the "modified ionic strength" and that the bulk compressions of sulfuric acid solutions are greater than that of the salt solutions studied and do not fit the general rule. Lanman and Mair[19] have found that the compressibility of hydrochloric acid solutions is greater than that of solutions of alkali hydroxides and chlorides, and is not much less than that of water. Corey[20] found that the compressibility of ammonium chloride solutions is greater than that of other electrolytes studied. Ammonium chloride solutions also show the same type of deviation of partial molal quantities from ideal behavior exhibited by acid solutions. It would be predicted, on the basis of the results reported here, that the compressibility of perchloric acid solutions is greater than that of any other electrolyte solution and may even exceed the compressibility of water.

The equation of Owen and Brinkley leads to values for Φ^0 of 44.039 and 42.847 for perchloric acid and sodium perchlorate, respectively, which are somewhat less than those obtained by the empirical equations employed, but are self-consistent. The equation was not applied to the mixed solutions as values of $\mathring{a}$ are not available for the mixed solutes.

If the equation of Stokes and Robinson[5]

$$\log \gamma_{\pm} = \frac{-\mathcal{S}_f C^{1/2}}{1+\kappa a} - \frac{n}{\nu}\log a_w - \log\left(1 - 0.018\,(n-\nu)m\right) \quad (4)$$

where *n* is the number of moles of hydrate water per mole of solute, is differentiated with respect to pressure the relation is obtained

$$\bar{V}_2 - \bar{V}_2^0 = \frac{\mathcal{S}_v C^{1/2}}{1+\kappa a} + \frac{W_v C}{(1+\kappa a)^2} - n(\bar{V}_1 - \bar{V}_1^0) - RT\left(\ln a_w - \frac{0.018\nu m}{1 - 0.018\,(n-\nu)m}\right)\frac{\partial n}{\partial P} \quad (5)$$

W_v includes the term in $\partial \ln \mathring{a}/\partial P$, so the value given in Harned and Owen[15] was corrected, assuming $\partial \ln \mathring{a}/\partial P = -0.15$ and -2.68×10^{-5}

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(13) The symbols used are consistent with those of Harned and Owen, "Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1950.

(14) R. A. Robinson and O. J. Baker, *Trans. Roy. Soc. New Zealand*, **76**, 250 (1946–1947).

(15) Harned and Owen, ref. 13, p. 587. Values of σ were obtained by use of the table on p. 597.

(16) The function $\theta = 4/3(\tau - \sigma)/\kappa a$ was obtained by the use of tables of the τ function kindly supplied to the authors by Dr. Stuart R. Brinkley, Jr.

(17) J. H. Jones, *J. Phys. Chem.*, **51**, 516 (1947).

(18) R. E. Gibson, This Journal, **57**, 284 (1935).

(19) E. H. Lanman and B. J. Mair, *ibid.*, **56**, 390 (1934).

(20) V. B. Corey, *Phys. Rev.*, **64**, 350 (1943).

per bar for sodium perchlorate and perchloric acid, respectively.

Using values for the activity of water in sodium perchlorate solutions given by Jones,[17] and the self consistent values of $\mathring{a}$ and n (4.04 Å. and 2.1, respectively) given by Stokes and Robinson[6] values of $\bar{V}_3 - \bar{V}_3^0$ which fit the intermediate concentration ranges for sodium perchlorate solutions are obtained if $\partial n/\partial P$ is taken as 7.0×10^{-4} mole per bar. The calculated values deviate from the observed values by +0.1 ml. at low concentrations and by as much as +0.5 ml. in the 2.4 N solution.

If equation (5) is applied to the perchloric acid solutions, using $n = 7.4$ and $\mathring{a} = 5.09$ Å.,[5] and the values of the activity of water in perchloric acid solutions given by Robinson and Baker,[14] the deviations between observed and calculated values of the partial molal volumes vary from +0.15 ml. at 0.04 N to −0.5 ml. in 2.25 N solution when $\partial n/\partial P$ is taken as -3.2×10^{-4} mole per bar. A closer fit at the intermediate and higher concentrations may be obtained by taking $\partial \ln \mathring{a}/\partial P = -6.2 \times 10^{-5}$ per bar and $\partial n/\partial P = -0.92 \times 10^{-4}$ mole per bar.

In general this method does not appear to be as satisfactory as that of Owen and Brinkley as the equation is cumbersome and the fit with experimental values is not as good. The addition of an empirical constant in C would unquestionably improve the fit. The fact that the term $(\bar{V}_1 - \bar{V}_1^0)$ is taken from the data to be represented, and that values of the activity of water in the solutions must be known, detracts from the utility of this approach.

A third approach to the interpretation of the observed behavior of electrolytic solutions is to consider the effect of electrolytes on the structure of water. X-Ray diffraction measurements,[21] Raman spectrum studies[22] and infrared measurements[23] all indicate that the addition of electrolyte decreases the degree of coördination of water. Such a change in the water structure is reflected in a decrease in the partial molal volume of the water.

Fajans and Johnson[24] have shown that ammonium chloride fits into the structure of water and conclude that the molal volume of the ammonium ion is equal to that of the chloride ion. In Fig. 3 the partial molal volume of water in sodium perchlorate, ammonium chloride, hydrochloric acid, and perchloric acid solutions is plotted as a function of the concentration of the electrolyte. Ammonium chloride does have less effect on the partial molal volume of water than sodium perchlorate, which is a typical electrolyte.

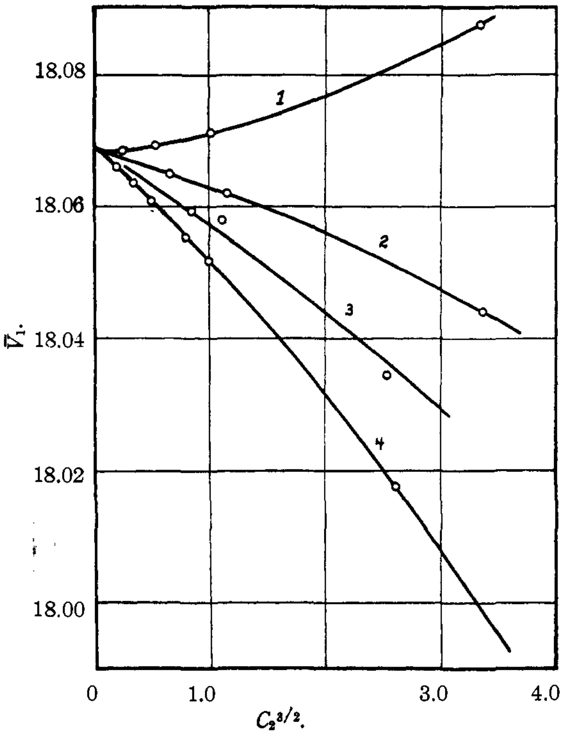

Fig. 3.—Partial molal volumes of water in perchloric acid solutions (1), in hydrochloric acid solutions (2), in ammonium chloride solutions (3) (from the data of J. N. Pearce and G. G. Pumplin, THIS JOURNAL, 59, 1221 (1937)), and in sodium perchlorate solutions (4) *vs.* the three-halves power of the volume concentration of the electrolyte.

If this means that ammonium chloride fits into the water structure, then hydrochloric acid fits even better, and perchloric acid actually increases the degree of coördination of water. Such an increase in the degree of coördination would also explain the compressibility behavior inferred above, as the more highly coördinated (ice-like ?) structure would be expected to be more compressible than the less highly coördinated water present in most electrolyte solutions.

The effect is dependent on the presence of both the hydrogen ion and the perchlorate ion in the solution. The sodium ion masks completely any specific effect of the perchlorate ion. The data of Mazzucchelli and co-workers[25] indicate that lithium and silver perchlorates show the same behavior as sodium perchlorate, while ammonium perchlorate is similar to ammonium chloride. The data are not of sufficient precision to show minor deviations of behavior.

The Raman spectra of sodium perchlorate and perchloric acid solutions at high concentrations (5–8 N) have been investigated by Kujumzelis[22] and by Rao.[22] Kujumzelis considers the possibility that the perchlorate ion fits into the structure of water, but does not distinguish between

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[21] J. A. Prins and R. Fonteyne, *Physica*, **2**, 1016 (1935); G. W. Stewart, *J. Chem. Phys.*, **7**, 869 (1939); *ibid.*, **11**, 72 (1943).

[22] C. S. Rao, *Indian J. Phys.*, **11**, 143 (1937); Th. G. Kujumzelis, *Z. Physik*, **110**, 742 (1938).

[23] E. Ganz, *Z. physik. Chem.*, **B35**, 1 (1937); A. M. Buswell, R. C. Gore and W. H. Rodebush, *J. Phys. Chem.*, **43**, 1181 (1939).

[24] K. Fajans and O. Johnson, THIS JOURNAL, **64**, 668 (1942).

[25] A. Mazzucchelli and S. Anselmi, *Gazz. chim. ital.*, **52**, 147 (1922); A. Mazzucchelli and D. Pro, *ibid.*, **56**, 99 (1926); A. Mazzucchelli and A. Rossi, *ibid.*, **57**, 383 (1927).

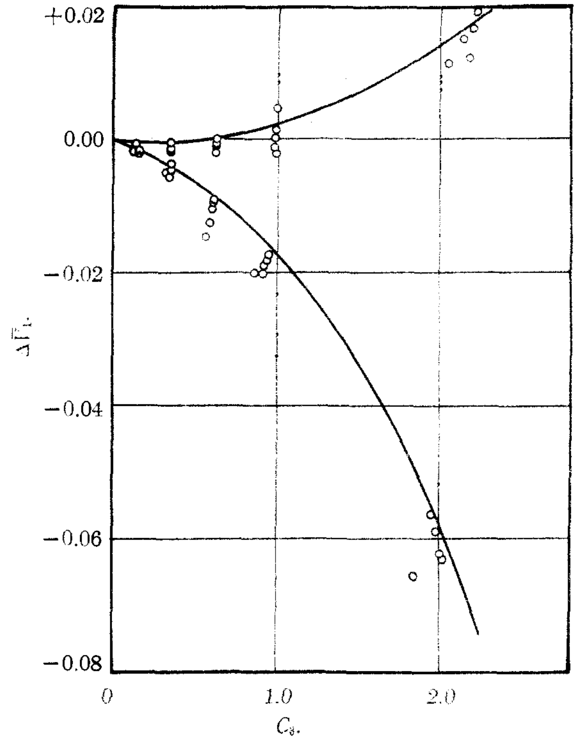

Fig. 4.—The change in the partial molal volumes of water in mixed solutions as a function of the volume concentration of perchloric acid (upper points), and as a function of the volume concentration of sodium perchlorate (lower points). $\Delta \bar{V}_1 = \bar{V}_1$ (in a solution containing C_2 moles of the first electrolyte and C_3 moles of the second electrolyte) $- \bar{V}_1$ (in a solution containing C_2 moles of the first electrolyte only). The solid curve represents the change in partial molal volume in solutions containing only perchloric acid ($C_2 = 0$) (upper curve) and in solutions containing only sodium perchlorate (lower curve).

the behavior of sodium perchlorate and perchloric acid. Rao found that the water band was shifted to higher frequency (to 3800 cm.$^{-1}$) and was very sharp in 8 N solutions of perchloric acid. In sodium perchlorate (8 N) the band was broader, although shifted to a higher frequency as compared to water. He interpreted this as a shift in water equilibrium toward the formation of single molecules. A similar shift to higher frequency and sharpening of the water band was reported by Landsberg and Malyshev[26] on diluting water with dioxane, so it is probable that in the concentrated solution the water is strongly diluted with $(H_3O^+)(ClO_4^-)$ and it would be impossible to observe any evidence of the highly coördinated water assumed to be present in the moderately concentrated solutions studied here.

In Fig. 4 the change in the partial molal volume of water in the mixed solutions of sodium perchlorate and perchloric acid is given as a function of the concentration of the added electrolyte. This shows clearly that the change in the volume of the water is a specific effect for the particular electrolyte added and is but slightly influenced by the electrolyte already present.

According to this view, the partial molal volume of an electrolyte will depend solely on the total volume ionic strength, as observed for potassium chloride, potassium bromide and sodium sulfate in sodium chloride solutions,[7] only when the two electrolytes individually have the same effect on the structure of water. The departure from the ionic strength rule, found in solutions of hydrochloric acid and sodium chloride[8] and in solutions of sodium perchlorate and perchloric acid, is the greater the greater the difference in the effect of the individual electrolytes on the water structure.

Summary

The apparent and partial molal volumes of sodium perchlorate and perchloric acid have been determined in water solution and in mixed solutions. The partial molal volume of the water in these solutions has been calculated.

The observed maximum in the apparent and partial molal volumes of perchloric acid has been explained on the basis of its compressibility behavior which is in turn due to the increase in the coördination of water in perchloric acid solutions.

The partial molal volumes in solutions of mixed solutes will depend solely on the volume ionic strength only if the individual electrolytes have the same effect on the structure of water.

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[26] G. S. Landsberg and V. S. Malyshev, *Compt. rend. acad. sci., U. R. S. S.*, **18**, 549 (1938).