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The Insufficiency of the Electrostatic Explanation of Change of the Apparent Ionic Molal Volume with Concentration in an Aqueous Solution

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THE INSUFFICIENCY OF THE ELECTROSTATIC EX-
PLANATION OF CHANGE OF THE APPARENT IONIC
MOLAL VOLUME WITH CONCENTRATION IN AN
AQUEOUS SOLUTION

G. W. STEWART

If in an aqueous ionic solution the structure of the water remained constant or at least did not change its energy with concentration, then the change in partial molal free energy of the ions can be determined by the Debye-Hückel theory, and also finally the change in partial mol volume produced by a change in concentration. This may be called the free ion electrostatic explanation, involving the change of energy of the ionic charges with concentration, the change in dielectric constant with pressure and the compressibility. As a conclusion of this theory with increase in apparent ionic molal volume should be proportional to the increase in the square root of the mol concentration. This proves to agree fairly well with experiments in about one-half of the strong electrolytes, but the proportionality constant even with these varies widely, though it should not except for the change in amount of charge carried by the ion. The reason for the inadequacy of the Debye-Hückel theory probably rests chiefly in its omission of the change in the dielectric constant, or its equivalent, in the neighborhood of the ions, and the neglect of the change in energy of the water structure.

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