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Correspondence of Change of Structure of Water with the Change of Apparent Volumes of Ions in Solution

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CORRESPONDENCE OF CHANGE OF STRUCTURE OF
WATER WITH THE CHANGE OF APPARENT
VOLUMES OF IONS IN SOLUTION

G. W. STEWART AND JAMES A. JACOBS

Careful measurements were made of the diffraction curves of dilute aqueous solutions of LiCl, NaCl, KCl, NH_4Cl , MgCl_2 , $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2$, CoCl_2 , KClO_3 , and AlCl_3 . In view of the inadequacy of the free ion theory to explain the nature of the change of apparent volume of ions in solutions, any evidence of any kind of correlation with that change is important. The x-ray diffraction of water was used to determine the magnitude of the alteration of water structure by the presence of ions. It is found that when the change of apparent molal ionic volume with concentration is more rapid, the alteration in the water structure is greater. The correlation is strong enough to make quite certain that the change of water structure is an important factor in the apparent volume change of the ions. With KClO_3 the apparent molal volume of the ions decreases with concentration, which is in the opposite sense. If the water structure is important, as claimed, then this structure must decrease in density with concentration of the ions. The x-ray diffraction of KClO_3 indicates that the alteration in water structure is certainly very different than in the cases of the other ions, and to this extent is confirmatory.

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