DIAMAGNETISM OF SOME ORGANIC LIQUID MIXTURES

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1. Introduction

A large amount of work has been accomplished recently on the magnetic susceptibility of binary mixtures of organic and inorganic liquids. Unfortunately reports are not unanimous regarding the behaviour of such mixtures from the point of view of the additive law of magnetic susceptibilities. Certain general tendencies however are sufficiently clear, but the detailed results of different authors differ considerably.

Trew and Spencer undertook more recently a careful study of the changes in physical properties of binary mixtures when their composition was varied. They measured the density, refractive index, heat of mixing, specific heat, and magnetic mass susceptibility of a series of binary mixtures of the liquids: benzene, toluene, m-cresol, aniline and nitrobenzene. Nitrobenzene-m-cresol mixtures showed the least deviation from the additive law. None of the other pairs of liquid mixtures could be considered ideal. They could not obtain any general rule to govern the deviations, but they have observed that the magnetic mass susceptibility proves a more nearly additive property than any other property investigated.

A careful and thorough investigation on the magnetic susceptibilities of binary mixtures of some organic liquids has been carried out by Seely. Benzene-nitrobenzene mixtures followed the additivity law in the range of temperature 10°–50° C. For mixtures of carbon tetrachloride with either benzene or nitrobenzene, a systematic deviation from additivity was found. The deviations for both the groups showed a definite dependence upon concentration and temperature.

At the same time, solutions of salts in water have also been examined carefully and we have very reliable results on this subject. Ikenmeyer studied the solutions of alkali halides in water and calculated the ionic susceptibilities of the alkali and halogen ions. Farquharson and Scott and Blair found small deviations from linearity in the case of some alkali halides. Hocart examined a number of halides and obtained results for dissolved
salts at 30 to 60% concentration. He found that the susceptibility of the dissolved salts as calculated from an application of the additivity law to the solutions, was 2–3% higher than the susceptibility for the corresponding solid salts.

Hoare and Brindley have recently determined the susceptibility of salts composed of ions with inert gas configurations and found that in the halides of lithium and caesium the additivity law breaks down. Flordal and Frivold obtained large changes of susceptibility when some alkaline earth halides were dissolved in water. Similar results were also recorded by Subramaniam who discussed the magnetic effects accompanying ionic deformations in the solid salts studied. Varadachar had previously drawn attention to such effects in his study of sulphuric acid-water mixtures. He investigated also acetic acid-water mixtures and obtained no departure from the additive law.

Investigations by Rao and Sriraman have shown that when some salts are dissolved in water, departures from the additivity law may be observed. In these cases, the percentage changes appear to be independent of concentration and have been attributed to (1) interaction between the ions and water molecules, (2) depolymerisation of water, (3) release of constraints within the molecules due to their breakage into ions and (4) change of valency of any of the ions when the salt is dissolved. While the first two causes do not produce more than 1% change from the additive law, the other two causes give rise to much larger changes.

Stoner has presented a clear account of the possible theoretical support for such deviations. He has suggested that some of these deviations could be attributed to the hydration of ions. The enormous electric fields at molecular distances round an ion are sufficient to orientate water molecules. It would be expected that such a close association of the water molecules with ions will bring about a reduction in the diamagnetism of water.

A straight inference from this discussion leads one to expect that molecules having large electrical moments would give rise to a large interaction with other molecules also having large electric moments. The exact operation of such inter-molecular interactions is uncertain in the present state of our knowledge of the subject but the investigations of Trew and Spencer and Seely suggest small changes in diamagnetic susceptibility due to these causes.

It was believed, therefore, that a careful examination of the diamagnetism of some binary mixtures of organic liquids, whose molecules carry a large dipole moment, might be of interest. Thorough purification of the liquids