714. *The Chemical and Physical Properties of Ethanol–Water Mixtures.*

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Ethanol–water mixtures fall into three zones, low, medium, and high, with respect to ethanol content. Many physical and chemical processes taking place in the mixed solvents are quite different in the three zones, and possible reasons for this fact are advanced.

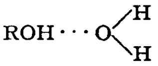
The results now presented, together with other experimental work (see, *e.g.*, preceding paper), show that in alcohol–water mixtures there exist three distinct zones with regard to the content of alcohol, *viz.*, low, medium, and high, and that in each of these zones chemical reactions proceed in a well-defined way characteristic for the particular zone. In the oxidation of ethanol by chromium trioxide, in the presence of fixed amounts of various mixed acids (see Bobtelsky and Cohn, *Z. anorg. Chem.*, 1933, **210**, 225), there is a " low " zone (below 25—30% of ethanol) in which the velocity of oxidation is proportional to the concentration of the alcohol; in the middle zone, 30—60% of ethanol (8—3 mols. of water per mol. of ethanol), the velocity falls very slightly with increasing concentration of the alcohol; in the high zone, above 60% ethanol ($\leqslant$ 3 mols. of water per mol. of ethanol), the velocity increases very steeply. The temperature coefficients, too, differ greatly in the low and the high zone, whilst in the medium zone they are not constant. The influence of the various acids on the reaction rate is linear in the case of the high zone and, when these rates are plotted against the concentration of acid, the curves show a typical angle of inclination for each acid. On the other hand, in the low zone the influence of acid is very similar to that observed in water solutions. The influence of catalysts also differs for the two zones: *e.g.*, aluminium nitrate is a good catalyst in the high zone, but does not affect the reaction rate in the low zone.

On investigating the catalytic decomposition of hydrogen peroxide, we found that this was greatly retarded by small amounts of ethyl alcohol (up to 5%) in the presence of specific catalysts, but that further addition of ethyl alcohol up to 30% increases the velocity of the decomposition very greatly. Between $\sim$30% and $\sim$60% the catalyzed reaction shows a steady maximum; above 60% it is stopped (Bobtelsky, Glasner, and Bobtelsky-Chaikin, *J. Amer. Chem. Soc.*, 1945, **67**, 966.) Also, the sensitivity of colloidal particles to coagulation is different in the three zones mentioned above (Jirgenson, *Z. physikal. Chem.*, 1931, *A*, **158**, 56). Further, the thermal effect of solution (see preceding paper) is distinctly different in the three zones of ethanol–water solvents.

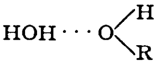
For methyl alcohol, similar zones of the action of the mixed solvent were observed by us. In other instances we were convinced by experiment that changes which can be brought about in the rate of chemical reactions by adding certain neutral salts in high concentration to the solution may be reproduced by using as solvent an alcohol–water mixture of appropriate composition.

From all the experimental evidence we consider that solutions prepared in the various ethanol–water mixtures are convenient for solvation studies, and it is to be expected that phenomena which are sensitive to changes in water or alcohol content should show breaks on passing from one zone to the other. Some time ago we wrote that " the rate at which electrons change their position in aqueous solutions depends greatly on the kind of the influence of the water molecules " (Bobtelsky and Radovenski-Cholatnikow, *Z. anorg. Chem.*, 1931, **199**, 241).

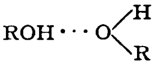
These extensive observations may be explained by the strong hydrogen bond between alcohol and between water molecules. Pauling (" The Nature of the Chemical Bond," 1945) considers that this bond in alcohol is even stronger than in water. The arrangement of the molecules in the mixed solvent depends on their relative amounts in the mixture. It is justifiable to assume that in various mixtures the following four simple combinations may exist:



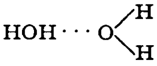
(*a*.)



(*b*.)



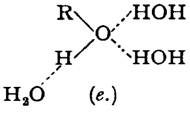
(*c*.)



(*d*.)

In the low zone seemingly only " polymers " of type (*d*) exist and the solvent acts as a pure water medium; (*a*) and (*b*) should be the types predominating in the middle zone (30—60% of alcohol) producing a mixed effect, and in the high zone type (*c*) exerts itself as in pure alcoholic solutions. Thus the oxidation of ethanol by chromium trioxide in the presence of acids proceeds in the high zone ($\geqslant$60%) through the intermediate $[ROH_2]^+$ and the rate of the reaction increases linearly with the concentration of the acid (the effect of sulphuric–perchloric acid in equimolar ratio is as 2 : 1). On the other hand, in the low zone the solvent is made up of " polymers " of type (*d*) and the various acids dissociate just as in pure water. The three different zones are thus the result of the existence of a small number of definite structures, the formation of which is not dictated by a principle of smallest volume. There are two other factors which fix the structure and the composition of the mixed solvent: (1) the energy of the hydrogen bond, which differs for the two pure solvents; (2) the ultimate form of the " polymers " which result from the various types of binding mentioned above.

For example, it is known that ethanol–water mixtures show a maximum contraction at the ratio $1C_2H_5{\cdot}OH : 3H_2O$. In this case the elementary structure may be represented as in (*e*). It is noteworthy that the discontinuity in ethanol–water mixtures and the abrupt passage from the middle to the high zone has been observed at the same concentration. We suggest that the maximum contraction is connected with the existence of an open structure. In this zone of concentration of the alcohol (60—70%) the water aggregates are completely depolymerized, and at higher concentrations the mixed solvent has properties similar to those of pure ethyl alcohol. Our experiments prove that in the high zone ethanol–water mixtures do in fact show



(*e*.)

the properties ascribed to pure alcohol. On the other hand, in mixtures containing more than 8 molecules of water for 1 molecule of alcohol (*i.e.*, below 30% alcohol) the natural structure of the water molecules is not disrupted, therefore such a solvent acts as pure water.

It seems to us that a study of the various structures in ethanol–water mixtures ought to afford an explanation of the perplexing properties of the three observed zones of concentration. Again, these zones may be exploited for a study of problems in the solvation of ions and molecules, a problem which has not yet been approached successfully by other methods.

The object of the present discussion is to emphasise the problem but not to offer a final solution.

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