168. *The Effect of Acetaldehyde on the Conductivities of Electrolytes in Ethyl Alcohol.*

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Conductivity data for solutions of a number of uni-univalent electrolytes have been obtained in this laboratory in recent years. The ethyl alcohol employed was never completely free from acetaldehyde, and it is therefore important to find out what effect the presence of this impurity has upon the results. Potassium iodide and silver perchlorate were the salts chosen, because their conductivities have been measured by Barak (Diss., Oxford, 1929), and they are strong electrolytes that deviate only to a slight extent from theory in ethyl-alcoholic solution. The possibility of chemical action between the acetaldehyde and the solute has been investigated, and its effect is negligible.

Experimental.

Preparation of Materials, and Determination of Conductivity.—EtOH was purified by the method of Copley, Murray-Rust, and Hartley (J., 1930, 2492). Poulenc's Me·CHO was distilled twice and collected over the range 22—23°. Pure specimens of the salts were available and were in all cases dried to const. wt. before the solutions were made up. The electrical conductivities of the solutions were determined by the method of Frazer and Hartley (*Proc. Roy. Soc.*, 1925, *A*, **109**, 351).

Estimation of acetaldehyde in alcohol. The Me·CHO was estimated by means of the magenta test (cf. Paul, *Z. anal. Chem.*, 1896, **35**, 647). 50 C.c. of a filtered 0·1% aq. solution of magenta were treated with SO_2 aq. containing 0·5 g. of SO_2 and made up to 100 c.c. A standard Me·CHO solution was made up by wt.

The estimation was carried out in a standard colorimeter. 50 C.c. of the EtOH to be tested and 50 c.c. of standard Me·CHO solution were introduced into the two limbs, and the temp. was kept at about 16° by immersion in a water-bath. When the solutions had attained temp. equil., equal amounts of the decolorised magenta solution were added to each of them, and the colours compared as rapidly as possible, the standard solution being diluted as required with Me·CHO-free aq. EtOH and the total vol. kept const. The aq. EtOH used for dilution gave no coloration with the magenta solution.

The results with various samples are given below:

Alcohol	A	B		C		D		E		F
Me·CHO, g./l.	0·183	0·174	0·150	0·049	0·043	0·031	0·037	0·031	0·031	0·017
Mean	0·183	0·162		0·046		0·034		0·031		0·017

A. Laboratory absolute alcohol.
B. Distilled from CaO, which was part of the normal procedure of removing H_2O.
C. Dried over CaO for 5 days, filtered, and distilled.
D. Prepared by Copley's method, but of high conductivity.
E and F. Prepared by the same method, but of low conductivity.

This seems to indicate either that fired CaO adsorbs Me·CHO in the cold from an alc. solution and gives it up on heating, or that CaO acts as a catalyst in the atm. oxidation of EtOH at its b. p. It is evident that the subsequent treatment with Al–Hg and prolonged refluxing in pure dry air, which was applied to samples D, E, and F, eliminated Me·CHO more effectively than distillation after treatment with CaO in the cold. The distillation from CaO is essential for removal of water and was therefore employed as before in the preparation of conductivity EtOH.

Reducing properties of acetaldehyde in alcoholic solution. Amounts of Me·CHO varying from 0·5% to 10% were added to a series of solutions of $AgNO_3$ in conductivity EtOH. No reduction product could be detected in any of the solutions even after **3** days' standing at room temp. In presence of H_2O, the mechanism of the reduction is comparatively simple, and the absence of reduction in dry EtOH may be due to the much more complicated reaction that would be involved.

Conductivity Results.—Additions of Me·CHO were made to solutions of KI in EtOH, and the change in conductivity was measured. In all cases the rise in conductivity was proportional to the amount of Me·CHO added, having a mean of $2.6 \pm 2\%$ for an addition of 1%. These measurements were made directly after the addition of Me·CHO, but the conductivity subsequently fell to a figure close to its original value. It is shown below that the initial rise in conductivity is due to a rise in temp. produced by the mixing of Me·CHO and EtOH.

The fact that the change in conductivity was a function of the time made expts. in a mixed solvent even more essential for investigating the effect of Me·CHO than for similar investigations of H_2O additions (cf. Hughes and Hartley, *Phil. Mag.*, **1933**, **15**, **610**). Therefore a mixture of 0·5% Me·CHO in EtOH was prepared, and the conductivity of $AgClO_4$ was measured in this solvent. Sudden changes in the composition of the solvent, and consequent heat effects, were avoided in this way. The results are given below, κ being the sp. conductivity of the solvent in reciprocal megohms, c the concn. of the solution in g.-mols./l., Λ_c the equiv. conductivity at concn. c, Λ_0 the equiv. conductivity at infinite dilution, and x the slope of the $\Lambda_c/\sqrt{c}$ line.

Pure alcohol: $\kappa = 0.012$; $\Lambda_0 = 51.4$; $x = 203$.			Alcohol + 0·50% acetaldehyde: $\kappa = 0.039$; $\Lambda_0 = 51.0$; $x = 197$.		
$c \times 10^4$.	Λ_c.	Diff.	$c \times 10^4$.	Λ_c.	Diff.
0·827	49·53	−0·01	0·778	49·19	−0·07
1·707	48·67	−0·05	1·538	48·60	+0·04
3·022	47·86	+0·01	2·998	47·81	+0·21
5·152	46·79	+0·04	5·307	46·71	+0·26

The column headed "Diff." gives the differences between the observed values of Λ_c and those calculated from the equation $\Lambda_c = \Lambda_0 - x\sqrt{c}$. Evaporation of Me·CHO was taking place throughout the series of measurements, and the solution scarcely smelt of it at the end of the expt.

The increase in viscosity due to the addition of 0·5% Me·CHO is given as 0·5% by McKelvey (*Bull. Bur. Standards*, **1913**, **9**, **327**). The results quoted above show a 0·8% decrease in the conductivity, but this value is subject to a large error, as it depends upon the drawing of a straight line through points which cannot be expected to lie on that line because of the evaporation of the aldehyde. The decrease in conductivity, however, is of the same order as the increase in viscosity. For H_2O additions the depression is rather less than the viscosity increase, owing to the partial solvation of the ions by H_2O mols. Unfortunately, the extreme volatility of Me·CHO prevents measurements being made of an accuracy sufficient to determine the change in ionic size when it is present.

The amount of Me·CHO present in conductivity EtOH is of the order 0·03 g./l., or about 0·004% by wt. Conductivities measured in such EtOH are presumably in error to about 1 part in 15,000, which is well within the limits of exptl. error. There does not seem to be any need for modification of the method of purifying EtOH, for even although refluxing with CaO leaves a relatively large amount of Me·CHO in the EtOH, yet most of the Me·CHO is removed in subsequent stages of the purification.

Heat Changes on Mixing.—Owing to the extreme volatility of Me·CHO it was essential to make any measurements of the heat change on mixing very quickly. The apparatus employed for this purpose consisted of a Cu calorimeter which was placed inside a beaker and thoroughly lagged with cotton-wool. Me·CHO was admitted from a burette to a weighed quantity of EtOH contained in the calorimeter, and the temp. rise measured at once. The heat of dilution was neglected. Two series of expts. were made:

G. of Me·CHO per 100 g. of mixture	1·38	3·10	4·65	6·12	
Heat evolved when 1 g. Me·CHO is added to 100 g. mixture, cals.	123	128	112	105	
G. of Me·CHO per 100 g. of mixture	1·61	3·15	4·70	6·12	7·55
Heat evolved when 1 g. Me·CHO is added to 100 g. mixture, cals.	137	123	120	111	104

The quantity of heat evolved falls off with increasing additions of Me·CHO: this is due, at least in part, to the more rapid evaporation of Me·CHO as the temp. rises. In the more dil. mixtures the heat change observed is more likely to be the correct one. The addition of **1** g.

of Me·CHO to 100 g. of EtOH causes the evolution of 128 ± 12 cals., the average increase in temp. produced thereby being 2·0° ± 0·2°.

The addition of 1% of Me·CHO to EtOH produces a decrease of approx. 1·6% in the conductivity owing to the increased viscosity. It also brings about a rise in temp. of 2°. Now the temp. coeff. of conductivity is approx. 2% per degree (Ogston, private communication), so the net increase of conductivity upon direct addition of 1% Me·CHO is 4 − 1·6 = 2·4%. This agrees well with the directly observed value of 2·6%.

SUMMARY.

1. The amounts of acetaldehyde present in various specimens of ethyl alcohol have been estimated colorimetrically by the magenta test.

2. The effect of acetaldehyde on the electrical conductivities of two salts in ethyl alcohol has been measured.

3. It has been found that the amount of acetaldehyde likely to be present in conductivity alcohol would not have an appreciable effect upon the conductivity of electrolytes in that solvent.

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