esters or anhydrides of weak acids, in this respect acting just the opposite from salts. Hydrolysis of esters and anhydrides (especially those of weak acids) is generally a rather slow reaction, while the hydrolysis of salts takes place instantaneously. (2) Esterification resembles in some respects the formation of acid anhydrides from acids, as both types of reactions are slow and therefore are not ionic in the ordinary sense, and both take place under dehydrating conditions. (3) Esters and anhydrides are alike in being poor conductors of electricity. (4) They are alike in the less fundamental but rather striking respect, that both are generally volatile, while salts are characteristically non-volatile, especially if they are not decomposed by heat. This classification of esters and like substances with acid anhydrides makes possible a better correlation of certain parts of organic with inorganic chemistry.[5]

We wish to thank our colleagues especially for the valuable criticisms and suggestions they have made.

Summary

1. Results were obtained which appear roughly to confirm those of Danner and Hildebrand on the ionization of alcohol into hydrogen and ethylate ions.

2. Assuming that esterification is a neutralization reaction, the degree of ionization of alcohol into ethyl and hydroxyl ions is shown by calculation to be nil.

3. Experimental chemical evidence is presented indicating that alcohols ionize in only one way, namely, as weak acids.

4. The advantages to be gained in the study of organic chemistry from emphasis on the acidic character of the alcohols are briefly pointed out.

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COMPLEXES IN SOLUTIONS OF COPPER AND COBALT SALTS

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In a recent paper by Watkins and Denham,[1] further evidence has been put forward concerning the presence of auto-complexes in solutions of copper halides. The evidence is mainly derived from migration experiments and is held to support the theory of complexes suggested by Donnan and Bassett[2] to explain the color changes exhibited by solutions of the

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[5] An elaboration and extension of this point of view by one of us, entitled "The Classification of Carbon Compounds and Their Correlation with Compounds of Other Elements" will appear shortly as a University of Oregon Publication.

[1] Watkins and Denham, *J. Chem. Soc.*, **115**, 1269 (1919).

[2] Donnan and Bassett, *ibid.*, **81**, 939 (1902).

halides of copper and cobalt when the temperature or concentration is changed, or when other haloid salts are added.

The action of aluminum chloride upon solutions of copper and cobalt halides is distinctly different from that of zinc chloride. The addition of the former salt to a fairly strong, pink solution of cobalt chloride causes the color to turn blue, while zinc chloride, when added to a very strong blue solution of cobalt chloride, turns the color pink. So far, no quantitative experiments have been published which support the view expressed by Jones[3] and his co-workers that this differential action of aluminum and zinc chloride is due to hydration. Abegg and Labendzinski[4] and Foerster and Yamasaki[5] have shown by e.m.f. methods that the addition of an alkali salt to a solution of a copper, cobalt or stannous salt of the same anion, increases the concentration of the complex anion. Donnan and Bassett have suggested that, in accordance with the general principles laid down by Abegg and Bodländer concerning complex formation, aluminum, the element of stronger electro-affinity, should exert a greater effect in forcing the copper salt into the complex anion and thus in intensifying the color change from green to brown, than does zinc with its weaker electro-affinity. On the other hand the action of zinc chloride in turning a concentrated blue solution of cobalt chloride pink, is held by Donnan and Bassett[2] to be due to the cobalt forcing zinc into the complex. Thus, in a strong solution of cobalt chloride the equilibrium is represented by the equation

$$\underset{\text{Pink}}{\mathrm{Co^{++}}} + 2\,\mathrm{Cl^{-}} + x\,\mathrm{CoCl_2} \longrightarrow \underset{\text{Pink}}{\mathrm{Co^{++}}} + \begin{bmatrix}\mathrm{Cl_2}\\ \mathrm{CoCl_2}\end{bmatrix}^{--}$$

and the predominating color is blue; but on the addition of zinc chloride the reaction

$$\underset{\text{Blue}}{\begin{bmatrix}\mathrm{Cl_2}\\ (\mathrm{CoCl_2})_x\end{bmatrix}^{--}} + x\,\mathrm{Zn^{++}} \longrightarrow \underset{\text{Colorless}}{\begin{bmatrix}\mathrm{Cl_2}\\ (\mathrm{ZnCl_2})_x\end{bmatrix}^{--}} + \underset{\text{Pink}}{\mathrm{Co^{++}}}$$

sets in, the blue solution turning pink. But while it is clear that aluminum with an electrode potential greater than zinc should exert a more marked effect in producing complex formation, the reason why cobalt (potential, +0.043) should force zinc (—0.493) so readily into the complex is less easy to explain. Experiments were undertaken in an endeavor to throw light upon this differential behavior of salts of aluminum and zinc when added to solutions of copper and cobalt salts.

Measurements of the e.m.f. of the cells, $\mathrm{Co} \mid \mathrm{CoCl_2} + x\mathrm{MCl}_y \parallel \mathrm{NH_4NO_3}$ sat. $\parallel \mathrm{HgCl_2}$, 0.1 N $\mathrm{KCl} \mid \mathrm{Hg}$, ($\mathrm{MCl}_y$ denotes the halide added) were made, and hence the ionic concentration ("activity") of the cobalt determined in accordance with the Nernst formula. Assuming the value of

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[3] Jones, *Am. Chem. J.*, **37**, 126 (1907); **34**, 291 (1905); *J. phys. chim.*, **3**, 455 (1905).

[4] Abegg and Labendzinski, *Z. Elektrochem.*, **10**, 77 (1904).

[5] Foerster and Yamasaki, *ibid.*, **17**, 361 (1911).

the 0.1 N calomel half-element at 25° to be 0.620 and the electrode potential of cobalt to be 0.043, it follows that π cell $= 0.577 - \frac{RT}{2F} \log [Co^{++}]$, whence, $\log [Co^{++}] = \frac{0.577 - \pi \text{ cell}}{0.029}$.

In carrying out the experiments, 20 cc. of a solution of cobalt chloride was put into each of a series of 100cc. flasks, and 10 cc., 20 cc., 30 cc., etc., of a solution containing a known quantity of halide (aluminum, potassium, magnesium, zinc) added. The volume was then brought up to 100 cc. In this way the concentration of the cobalt salt was kept constant throughout the series of experiments. The measurements were made by the Poggendorff compensation method, with accumulator, galvanometer, standard cadmium cell and rotary potentiometer.

Considerable difficulty was experienced in obtaining satisfactory and reproducible cobalt electrodes. Best results were obtained by depositing cobalt on a platinum wire from a solution of cobalt chloride containing 2 cc. of a 5% solution of orthophosphoric acid, 20 cc. of a 10% solution of monosodium orthophosphate and 2 cc. of a saturated solution of monosodium phosphite (NaH_2PO_2). With a current density of 0.008 amp., bright deposits of cobalt were obtained during the course of 24 hours. Table I gives the average results obtained from duplicate experiments carried out in the above manner. The potentials were steady, except in the presence of high concentration of aluminum chloride, where possibly the formation of basic salts complicated the equilibrium. The column headed Co^{++} denotes the concentration of cobalt ions calculated from the e.m.f. measurement.

TABLE I

CONCENTRATION OF $CoCl_2$, 0.27 N

Added salt	KCl		$MgCl_2$		$AlCl_3$		$ZnCl_2$	
N	E.m.f.	Co^{++}	E.m.f.	Co^{++}	E.m.f.	Co^{++}	E.m.f.	Co^{++}
..	0.6144	0.0514	0.6142	0.0521	0.6144	0.0514	0.6144	0.0514
0.57	.6218	.0286	.6195	.0341	.6159	.0457	.6175	.0402
0.86	.6250	.0222	.6213	.0298	.6169	.0420	.6191	.0353
1.14	.6291	.0160	.6224	.0271	.6176	.0397	.6201	.0327
1.71	.6329	.0118	.6246	.0228	(.6174)	(.0403)	.6217	.0287
2.28	.6362	.0091	.6257	.0209	(.6168)	(.0423)	.6230	.0259

Experiments with Copper Salts

Satisfactory results with the copper electrode were obtained only when it was prepared according to the method described by Getman,[6] when it gave results reproducible within 0.1 millivolt.

Owing to the tendency of cuprous chloride to separate on the electrode it was impossible to employ solutions comparable in strength with those described in the preceding section dealing with cobalt chloride.

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[6] Getman, *Trans. Am. Electrochem. Soc.*, **26**, 67 (1914).