

Rabinowitch and Wood^{6,17} have pointed out that at sufficiently high viscosities the rate of diffusion will become too slow to maintain the "equilibrium" number of pairs of reactants adjacent to each other in the liquid (*i. e.*, within colliding distance of each other). Diffusion, rather than the passage of molecules through the activated state, becomes the rate controlling step when such viscosities are reached, and the rate will no longer be independent of molecular size and viscosity. For most reactions (those with very low values of E_0 excepted) extremely high viscosities would be required to effect a perceptible decrease in rate.

Some time ago the author published equations¹⁸ for calculating the numbers of molecules of various sizes in a linear condensation polymer. The validity of these equations rested entirely on the postulate, presented at that time without experimental proof, that the functional groups of all molecules, regardless of size, are equally reactive. Dostal¹⁹ objected to the size distribution equations on the grounds that this postulate could not possibly be valid. The present investigation furnishes proof that this postulate is correct. The quantities of molecules of various sizes in a linear condensation polymer can be determined reliably,

(17) See also E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 1225 (1937).

(18) P. J. Flory, *This Journal*, **58**, 1877 (1936).

(19) H. Dostal, *Monaish.*, **70**, 324 (1937).

therefore, by simple calculation using the distribution equations referred to above.

Summary

1. The kinetics of two polyesterifications, diethylene glycol-adipic acid, and decamethylene glycol-adipic acid, have been compared with several non-polymer forming esterifications, diethylene glycol-caproic acid, lauryl alcohol-adipic acid, and lauryl alcohol-lauric acid. Preliminary experimental data on the reaction of diethylene glycol with adipic acid catalyzed by *p*-toluenesulfonic acid have been presented also.

2. As the reactions proceed (in the absence of catalyst) the course followed corresponds to a continuous increase in kinetic order, becoming approximately third order at large extents of reaction.

3. Polyesterification and esterification follow similar courses, from which it has been concluded that reaction rate is not affected by either increase in molecular weight or the concurrent increase in viscosity.

4. This conclusion has been shown to be in agreement with theory, contrary to previous theoretical deductions.

5. The slow rate of polyesterification when the average molecular weight is large is due to the third order character of esterification.

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Acetometallates. II. Acetozincate

BY ALEXANDER LEHRMAN AND PHILIP SKELL

It has been shown^{2a} that the solubility of metal hydroxides in aqueous solutions of alkali metal hydroxides can best be explained as the formation of hydroxyl complex ions. $M(OH)_2$, for example, may dissolve to give $M(OH)_4^-$. In the case of zinc, Goudriaan¹ isolated as a solid phase the compound $Na_2O \cdot ZnO \cdot 4H_2O$ which was formerly thought to be $Na_2ZnO_2 \cdot 4H_2O$, but which according to the complex ion hypothesis could also be written as $Na_2Zn(OH)_4 \cdot 2H_2O$. More recently, Scholder and co-workers² have isolated a mono-

and a disodium zincate in both the anhydrous and hydrated condition. On the basis of the ease of removal of water from these compounds it was concluded by Scholder that they were $NaZn(OH)_3$ and $Na_2Zn(OH)_4$, respectively, and their hydrates, rather than the various hydrates of $NaHZnO_2$ and Na_2ZnO_2 . Subsequently Brintzinger and Wallach³ showed from the rate of diffusion of zincate ions through a cellophane membrane that their ionic weight is consistent with the formula $Zn_2(OH)_8^{4-}$. More light could be thrown on the question if the system $NaOH-Zn(OH)_2$ could be shown to be a simple binary system with com-

(1) Goudriaan, *Rec. trav. chim.*, **39**, 505 (1920).

(2) (a) R. Scholder, *Z. angew. Chem.*, **46**, 509 (1933); (b) R. Scholder and H. Weber, *Z. anorg. allgem. Chem.*, **215**, 355 (1933);

(c) R. Scholder and G. Hendrich, *ibid.*, **241**, 76 (1939).

(3) H. Brintzinger and J. Wallach, *Z. angew. Chem.*, **47**, 61 (1934).

pound formation. Such an investigation has not been carried out because zinc hydroxide readily decomposes to the oxide on heating.

For further elucidation it was necessary to resort to the results obtained in analogous systems where the possibility of a phenomenon similar to dehydration is not present. Davidson and co-workers⁴ have demonstrated a very close similarity between the water and the acetic acid systems. Davidson and McAllister^{4c,d} have carried this analogy into the field of amphoterism. Whereas Goudriaan and Scholder have shown the existence of two solvated compounds of zinc hydroxide and sodium hydroxide in which the ratios of $Zn(OH)_2$ to NaOH were 1:1 and 1:2, Davidson and McAllister were able to obtain from glacial acetic acid solution a solvated compound in which the ratio of zinc acetate to sodium acetate was 1:2, namely, $Na_2Zn(C_2H_3O_2)_4 \cdot 4HC_2H_3O_2$ which has been named sodium aceto zincate solvate. Unlike zinc hydroxide the analogous zinc acetate cannot undergo "dehydration" reaction but instead undergoes pyrolytic decompositions on continued heating of the melt. It was thus found feasible to determine the liquidus curve of the unsolvated system zinc acetate-sodium acetate and in this way cast some light on the analogous zinc hydroxide-sodium hydroxide system.

Experimental

Materials.—Zinc acetate and sodium acetate were recrystallized from dilute acetic acid and then dehydrated by the methods of Davidson and McAllister.^{4c}

Apparatus.—The temperature measuring device was a single copper-constantan thermocouple and potentiometer. A description of the wire, apparatus, and standardization appear in the literature.⁵

The bath was about 300 ml. of the eutectic mixture of lithium, potassium and calcium nitrates contained in a wide-mouthed Pyrex Erlenmeyer flask.⁶

Method.—The salts were weighed (to the nearest centigram) into 2.5×20 cm. Pyrex tubes, the zinc acetate being placed below the sodium acetate. The total weight of each sample was 12 g. The tube was placed in the bath whose temperature was controlled by inserting a thermometer enclosed in a Pyrex shield. The salts were stirred with the thin Pyrex tube containing the thermocouple.

To prevent pyrolytic decomposition of the zinc acetate, five drops of glacial acetic acid were added when the salts were partially melted. All except very small quantities of

the acid distilled out of the mixtures since the temperatures of the mixtures were usually raised to about 250°. This small amount of acetic acid enabled us to obtain and maintain a clear melt for a time sufficient to determine the melting point. If this aid is omitted it is almost impossible to get clear melts and maintain them so during the determination of the melting point.

After the mixtures had been melted the temperature of the bath was lowered and the mixtures stirred constantly. Considerable supercooling usually preceded initial crystallization. It was necessary to determine the temperature of disappearance of the last crystal as the mixture was heated. The bath was heated slowly until a large part of the crystals had dissolved and then very slowly to obtain the melting point. The disappearance of the last crystal was observed easily by placing the source of a sharp beam of light behind the bath so that the beam passed through the melt before reaching the eye. The temperature was noted when a clear sharp image of the light source could be seen through the melt. This obviated the possibility of too low a reading because of the presence of very fine crystals. This method was found to be very convenient and to give consistent and reproducible values.

All melting points recorded are the result of at least three determinations coming within a range of one degree.

Results and Discussion

Temperatures of the disappearance of the last crystal are given in the table and plotted in Fig. 1.

Compn., mole fraction of zinc acetate	M. p., °C.	Eutectic temp., °C.
0.000	328.3	
.101	313.4	
.200	277.5	
.226	261.4	
.265	233.2	218.0
.280	223.3	220.0
.300	225.7	
.333	227.2	
.333	227.1	
.333	227.1	
.350	226.4	
.400	220.2	
.460	203.9	
.480	198.0	
.490	194.6	
.500	192.5	
.510	189.1	
.520	183.0	178.6
.550	180.9	175.3
.600	197.8	
.667	212.5	
.700	221.8	
.800	236.5	
1.000	242.4	

(4) (a) A. W. Davidson, *THIS JOURNAL*, **50**, 1890 (1928); (b) A. W. Davidson and W. McAllister, *ibid.*, **52**, 507 (1930); (c) A. W. Davidson and W. McAllister, *ibid.*, **52**, 519 (1930); (d) A. W. Davidson and E. Griswold, *ibid.*, **57**, 423 (1935).

(5) (a) Lehrman, Selditch and Skell, *THIS JOURNAL*, **58**, 1612 (1936); (b) Lehrman and Leifer, *ibid.*, **60**, 142 (1938).

(6) Lehrman, *et al.*, *ibid.*, **59**, 179 (1937).

The eutectic between the sodium acetate and compound regions was found by means of time-temperature cooling curves on mixtures up to

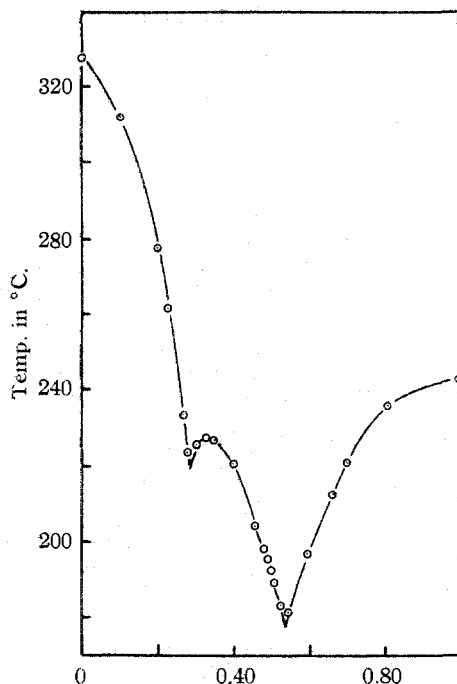


Fig. 1.—Mole fraction of $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$.

0.26 mole fraction zinc acetate to lie between 218 and 220°.

At temperatures below 210° the melts were extremely viscous so that great difficulty was experienced in obtaining crystallization and reproducible melting points. If cooling was rapid stable glasses resulted.

An attempt was made to obtain evidence for the existence of the compound 1 sodium acetate: 1 zinc acetate (0.5 mole fraction of zinc acetate).

A number of melting point determinations were made in this region. These freezing points alone, however, did not disprove the existence of this compound, for a slight rise in the curve to a maximum at 50 mole per cent. would not have been detected. However, the point of incipient melting seen on a mixture of 0.49 mole fraction of zinc acetate was 183°. This is wholly inconsistent with the supposition that a maximum in the curve exists at 0.5 mole fraction of zinc acetate. Further, the mixture of mole fraction 0.500 did not behave like a pure compound in that it did not solidify at anything that might reasonably be considered a constant temperature. We found no evidence for the existence of a one to one compound. An attempt was made to check this conclusion by optical and X-ray examination of the mixtures. Neither proved feasible.

The curve definitely points to the existence of the compound $2\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{ZnC}_2\text{H}_3\text{O}_2$ or $\text{Na}_2\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_4$ —sodium aceto zincate in the unsolvated system. This suggests the existence of the analogous sodium zincate as $\text{Na}_2\text{Zn}(\text{OH})_4$.

Summary

1. The liquidus curve of the binary system zinc acetate–sodium acetate has been determined.
2. The compound $2\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ or $\text{Na}_2\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_4$ was shown to exist.
3. The analogy between this compound and the hydroxyl zincates was discussed.

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Hydrolysis of Stannous Ion in Stannous Perchlorate Solutions

BY MEL GORMAN

The hydrolysis of stannous ion in stannous perchlorate solutions containing free perchloric acid has been investigated by adding sodium hydroxide solution and measuring the pH during the titration with a hydrogen electrode.¹ The purpose of the present investigation is to determine the extent of hydrolysis of stannous ion by a method involving the potentiometric measurement of the mean ion activity of total free perchloric acid and an analysis of total stannous ion concentration.

(1) Prytz, *Z. anorg. allgem. Chem.*, **174**, 355 (1928).

Method and Apparatus

The stannous perchlorate solutions containing free perchloric acid were prepared by the method of Noyes and Toabe,² and the concentration of free acid was determined by their method. A fresh stannous perchlorate solution was prepared for each experiment and stored in contact with metallic tin under nitrogen for at least one day before being used. The concentration of total stannous ion was obtained by titration in an atmosphere of nitrogen with 0.1 *N* iodine using starch indicator.

The mean activity of the hydrogen and perchlorate ions in the solutions of stannous perchlorate and perchloric acid was obtained with the aid of a hydrogen electrode and a

(2) Noyes and Toabe, *THIS JOURNAL*, **39**, 1539 (1917).