

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Some Studies in the System Zinc Acetate-Hydrogen Chloride-Acetic Acid

BY ARTHUR W. DAVIDSON AND WILBERT CHAPPELL

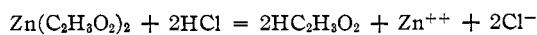
In previous papers from this Laboratory and elsewhere, numerous similarities have been pointed out between solutions of acids, bases and salts in anhydrous acetic acid on the one hand, and familiar aqueous systems on the other. As yet, however, few acetic acid systems containing analogs of so-called acid or basic salts have been described. It is obvious that the anhydrous ternary systems zinc chloride-zinc acetate-acetic acid and zinc chloride-hydrogen chloride-acetic acid might be regarded as analogous, respectively, to zinc chloride-zinc oxide-water and zinc chloride-hydrogen chloride-water; and that in the former case basic salts might be expected to occur, in the latter case, acid salts.

The study of equilibria between solid and liquid phases in binary solutions of zinc chloride in acetic acid presents extraordinary difficulties because of the extremely high viscosity of the concentrated solutions, which, as previously noted by Reddelien,¹ form thick sirups at ordinary temperatures. The same difficulty arises also in ternary solutions containing hydrogen chloride. Hence, except for a rough determination of the solubility of zinc chloride, the quantitative data obtained for these "neutral" and "acid" systems are limited to solutions from which acetic acid separates as solid phase. It was found possible, however, to investigate the "basic" system over a considerable concentration range at 30°, and to isolate two "basic" salts in the solid state.

Method

Preparation of Materials.—Pure anhydrous acetic acid and zinc acetate were prepared as described in previous papers of this series.²

Because of the difficulty of preparing and handling anhydrous zinc chloride, no attempt was made to use the solid salt, except in preliminary qualitative experiments. It was found, however, that a solution of zinc chloride in acetic acid might be obtained readily by the passage of dry hydrogen chloride over dry zinc acetate; a metathetic reaction takes place, which may be regarded as a neutralization



Gaseous hydrogen chloride, prepared in the usual manner, was dried by passage through two towers filled with glass

wool which had been moistened with anhydrous sulfuric acid. The gas was then passed into a flask containing zinc acetate (suitably protected from atmospheric moisture), and the mixture was warmed, with gentle agitation; gradual liquefaction resulted, in accordance with the above equation. After all the solid had disappeared, the solution, which contained at this stage a slight excess of hydrogen chloride, was analyzed both for chlorine and for zinc; the former was determined gravimetrically, the latter by titration against potassium ferrocyanide solution, with uranyl nitrate solution as an external indicator. From these data the amount of excess hydrogen chloride was calculated, and zinc acetate was added to the solution in quantity just sufficient to react with this excess. Thus a mixture containing 1 mole of zinc chloride to 2 of acetic acid was obtained; this was used as a stock solution, from which more dilute solutions were prepared by the addition of acetic acid.

Binary System $\text{ZnCl}_2\text{-HC}_2\text{H}_3\text{O}_2$.—Cryoscopic determinations were made, as described in previous papers, on samples of known composition prepared by dilution of the stock solution. The freezing points reported, except for concentrations of above 16 mole % of solute, are believed to be correct to within 0.1°. Up to a concentration of 22 mole %, only acetic acid was obtained as solid phase. Beyond this point the solutions became so viscous that they yielded no solid phase on cooling.

Reddelien¹ gave the solubility of zinc chloride in glacial acetic acid at 15° as 47.8 g. per 100 cc. of solution. While this figure, in the absence of density data, cannot be exactly interpreted, it appears to be much too low, for even our 33.33 mole % solution proved to be still unsaturated at 30°. Some of this solution was warmed with an excess of solid zinc chloride and then maintained in contact with the solid at 30°, with occasional agitation, for three months. Before the end of this period, additional crystals were observed to have separated out. Samples of the extremely viscous solution, upon analysis, showed 40.1 mole % of zinc chloride. Since the solid used may not have been absolutely anhydrous and since equilibrium was approached from supersaturation, this figure may be regarded only as a maximum value for the solubility of zinc chloride at 30°.

Ternary System $\text{ZnCl}_2\text{-HCl-HC}_2\text{H}_3\text{O}_2$.—Solutions containing zinc chloride in proportions up to 33.33 mole %, and saturated with hydrogen chloride, yielded, on cooling, no solid phase other than acetic acid. In many cases such solutions, even on being cooled to liquid air temperatures, showed no tendency to crystallize, but merely set to glassy solids. A few cryoscopic determinations were made, however, upon dilute solutions containing both zinc chloride and hydrogen chloride, in the following manner. Freezing point measurements were first made on solutions of hydrogen chloride, the composition of which had been determined by analysis. Then small weighed quantities of concentrated zinc chloride solution were added, and the freezing points were again determined. Because of the

(1) Reddelien, *Ann.*, **388**, 190 (1912).(2) Davidson and McAllister, *This Journal*, **52**, 512, 519 (1930).

relatively high vapor pressure of hydrogen chloride from dilute solutions in acetic acid,³ no great accuracy is claimed for these results.

Ternary System $\text{ZnCl}_2\text{-Zn}(\text{C}_2\text{H}_3\text{O}_2)_2\text{-HC}_2\text{H}_3\text{O}_2$.—Equilibrium in this system at 30° was studied by the analytical method; because of the high viscosity of many of the solutions, seeding was necessary in order that equilibrium might be attained in a reasonable time. Portions of the stock solution referred to above were diluted to the desired extent with acetic acid, and varying quantities of zinc acetate were added. The mixtures were placed in glass-stoppered bottles, heated until all of the solid had dissolved, cooled to about 40° and seeded with the appropriate solid phase, as determined from preliminary experiments. The bottles were then sealed, placed in a thermostat maintained at 30°, and agitated mechanically for about two weeks. (Preliminary experiments had shown this time to be sufficient for the attainment of equilibrium, even in the most viscous of the solutions.) The solutions were then allowed to stand for a day in order to allow complete settling of the solid phase, portions of the liquid were withdrawn, and their zinc and chlorine contents were determined as described above. The proportions of zinc chloride and of zinc acetate were calculated from these analyses, and that of acetic acid was determined by difference. It was found possible to investigate this system up to concentrations of almost 30 mole % (48% by weight) of zinc chloride, beyond which point the solutions were too viscous to permit reliable results to be obtained.

The composition of solid phases was determined both by direct analysis of crystals which had been freed from mother liquor by means of filtration and pressure between porous tiles, and by the Schreinemakers method of analysis of wet residues.

Results

1. Freezing Point Data.—In Table I, S denotes the mole percentage of zinc chloride in the binary solution, and T is the temperature at which the solution is in equilibrium with solid acetic acid.

TABLE I

ZINC CHLORIDE-ACETIC ACID			
S	T	S	T
0	16.60	12.88	8.55
1.77	15.75	14.14	7.30
3.46	14.95	16.16	4.80
4.31	14.45	17.80	2.8
7.31	12.85	18.45	2.0
9.67	11.45	22.07	-4.0
10.99	10.35		

In Table II, S_1 and S_2 denote the mole percentages of zinc chloride and of hydrogen chloride, respectively, in the mixed solution, and Δ_1 and Δ_2 are the freezing point depressions corresponding to these mole percentages of solute in the respective binary systems.⁴ R is the ratio of the num-

(3) Rodebush and Ewart, *THIS JOURNAL*, **54**, 419 (1932).

(4) The values for Δ_1 and Δ_2 were determined by interpolation, from plots which for space considerations are not reproduced here.

ber of moles of zinc chloride to the number of moles of hydrogen chloride, and Δ_3 is the observed freezing point depression in the mixed solution.

TABLE II

ZINC CHLORIDE-HYDROGEN CHLORIDE-ACETIC ACID							
S_1	Δ_1	S_2	Δ_2	R	$\Delta_1 + \Delta_2$	Δ	
2.53	1.22	0.74	0.44	3.42	1.66	1.05	
1.60	0.78	1.50	1.03	1.07	1.81	0.75	
0.57	.30	1.51	1.04	0.38	1.34	.95	

It will be noted that, in each case, Δ_3 is much less than the sum of Δ_1 and Δ_2 .

2. System $\text{ZnCl}_2\text{-Zn}(\text{C}_2\text{H}_3\text{O}_2)_2\text{-HC}_2\text{H}_3\text{O}_2$.—In Table III, S_1 and S_2 represent the mole percentages of zinc chloride and of zinc acetate, respectively, in the ternary solution which is in equilibrium, at 30°, with the solid phase indicated. These data are also represented graphically in Fig. 1.

TABLE III

ZINC CHLORIDE-ZINC ACETATE-ACETIC ACID			
S_1	S_2	S_1	S_2
Solid phase A, $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$		Solid phase B	
0	0.0025 ^a	7.45	1.68
0.334	.115	9.24	1.88
.431	.175	11.50	2.09
.611	.255	12.86	2.33
.834	.356	15.81	2.66
.931	.414	17.65	2.85
Solid phase B, $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)\text{Cl}$		Solid phase C	
		$\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)\text{Cl}\cdot\text{ZnCl}_2$	
1.24	0.365	21.20	2.78
1.88	.426	22.83	2.45
2.18	.582	25.01	1.93
3.12	.844	27.39	1.43
4.99	1.17	28.91	1.07
6.18	1.43	29.36	0.828

^a Ref. 2, p. 522.

The mean of four analyses on dried samples of the solid phase B, from solutions of different composition, gave Zn, 41.3%; Cl, 22.5% (calcd. for $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)\text{Cl}$: Zn, 40.9%; Cl, 22.2%). Because of the hygroscopic nature of this compound, and the difficulty of completely removing the very viscous mother liquor from it, it seemed desirable to supplement these analyses by determinations made by the Schreinemakers method. Accordingly, tie-lines through six pairs of corresponding compositions of solution and wet residue were plotted on a triangular diagram (not reproduced here), and were found to intersect the $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2\text{-ZnCl}_2$ axis at a point corresponding to 49.88 mole % $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$, 50.12 mole % ZnCl_2 . This result confirms the analysis of the dried salt, and

shows the solid phase to be a compound of the composition $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{ZnCl}_2$, or $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)\text{Cl}$, which may be regarded as a basic salt of the acetic acid system.

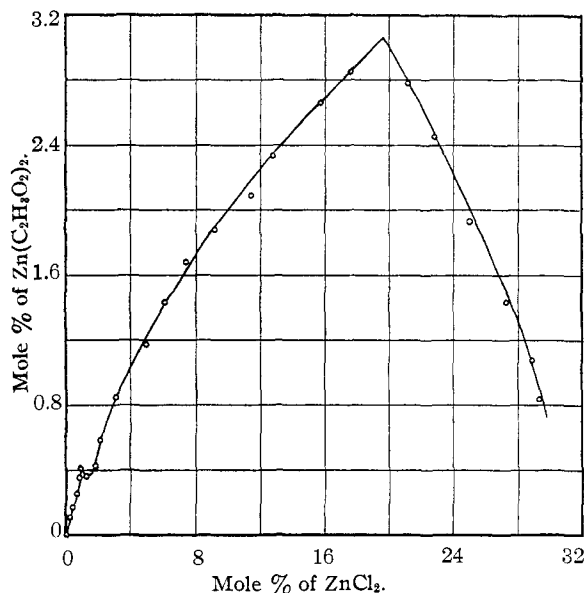


Fig. 1.—System ZnCl_2 - $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ - $\text{HC}_2\text{H}_3\text{O}_2$ at 30° .

The mean of two analyses of solid phase C (which was very sticky when moist and could be dried only with difficulty) gave Zn, 43.4%; Cl, 35.5% (calcd. for $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)\text{Cl} \cdot \text{ZnCl}_2$: Zn, 44.1%; Cl, 35.9%). Again these results were checked by the method of wet residues; tie-lines through four pairs of corresponding compositions of solution and wet solid intersected the $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ - ZnCl_2 axis of the triangular diagram at a point corresponding to 23.72 mole % $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$, 76.28 mole % ZnCl_2 . These results prove the compound to be a second basic salt of the composition $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{ZnCl}_2$, or $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)\text{Cl} \cdot \text{ZnCl}_2$.

The composition of solid phase A was determined by means of wet residues only. Wet residues from this portion of the system contain only very small amounts of chlorine, and hence the tie-lines lie very close to the $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ - $\text{HC}_2\text{H}_3\text{O}_2$ axis, and are almost parallel to it. Since it has been found in previous work^{2,5} that zinc acetate forms no solvates with acetic acid, it may be safely concluded that this solid phase consists of unsolvated zinc acetate.

It may be seen from Fig. 1 that at 30° the solubility of zinc acetate increases from 0.0025 mole % in pure acetic acid to a maximum of about 0.41

mole % in a solution containing about 0.93 mole % of zinc chloride. With the appearance of a new solid phase, the proportion of zinc acetate in the saturated solution at first falls off slightly with increasing concentration of zinc chloride, then rises to a maximum of about 3% at approximately 20% of zinc chloride. Here another new phase appears, and thereafter the proportion of zinc acetate again declines sharply with increasing concentration of chloride.

Discussion

Zinc chloride is found to be by far the most soluble in acetic acid of any salt so far studied, its saturated solution at 30° containing more than 11 moles per 1000 g. of solvent.

Freezing point data for this salt show that the value of j , the freezing point divergence function, remains practically constant at 0.74 for molalities from 0.3 to 1.3. Such constancy in the value of j , while quite contrary to the behavior of aqueous solutions, appears to be characteristic of most salt solutions in acetic acid.⁶

With regard to the system ZnCl_2 - HCl - $\text{HC}_2\text{H}_3\text{O}_2$, although it would be unwarranted to attempt to draw quantitative conclusions as to the molecular complexity of ionizable solutes from cryoscopic data, yet the relatively small freezing point depressions in solutions containing both zinc chloride and hydrogen chloride point strongly toward the formation of some sort of addition compound between the two solutes. Hildebrand and Bowers⁷ have presented evidence of the existence of a complex acid, of the composition HZnCl_3 , in dilute aqueous solution, and hydrates of this acid and of HZn_2Cl_5 have been obtained in the solid state⁸; no such complex has as yet been isolated from acetic acid solutions, however.

The system ZnCl_2 - $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ - $\text{HC}_2\text{H}_3\text{O}_2$, as has been stated previously, may be regarded as analogous to the system ZnCl_2 - ZnO - H_2O , which has been studied recently by Feitknecht⁹ and by Holland.¹⁰ It is of interest to note that both of these observers isolated the compound $\text{ZnCl}_2 \cdot \text{ZnO} \cdot \text{H}_2\text{O}$, or $\text{Zn}(\text{OH})\text{Cl}$, of which the exact analog, $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)\text{Cl}$, was found to be stable over a considerable range of concentrations in the present work. The other "basic" salt found here, Zn -

(6) Davidson and Chappell, *ibid.*, **60**, 2043 (1938).

(7) Hildebrand and Bowers, *ibid.*, **38**, 785 (1916).

(8) Engel, *Compt. rend.*, **102**, 1068 (1886); Kuznetsov and Kozhukhovskii, *J. Applied Chem.* (U. S. S. R.), **9**, 185 (1936).

(9) Feitknecht, *Helv. Chim. Acta*, **13**, 22 (1930).

(10) Holland, *J. Chem. Soc.*, 643 (1930).

(5) Davidson and Griswold, *THIS JOURNAL*, **57**, 423 (1935).

(C₂H₃O₂)Cl·ZnCl₂, is analogous to the compound Zn(OH)₂·3ZnCl₂, or Zn(OH)Cl·ZnCl₂, earlier described by Ephraim.¹¹ Neither of these aquobasic salts can be dissolved in water without decomposition, but, like their acetic acid analogs, they are stable in contact with solutions containing a large excess of zinc chloride.

Summary

1. A convenient method of preparing anhydrous zinc chloride-acetic acid solutions has been

(11) Ephraim, *Z. anorg. Chem.*, **59**, 67 (1908).

devised, and the freezing points of such solutions, over a wide concentration range, have been determined.

2. Evidence for the presence of an addition compound of zinc chloride and hydrogen chloride, even in dilute solution in acetic acid, has been obtained.

3. The system ZnCl₂-Zn(C₂H₃O₂)₂-HC₂H₃O₂ has been studied at 30°. Two new double salts, Zn(C₂H₃O₂)Cl and Zn(C₂H₃O₂)Cl·ZnCl₂, have been isolated and analyzed.

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Effect of Polar Groups upon Esterification Velocities of Substituted Benzoic Acids with Cyclohexanol

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The effect of substituents on the reaction velocity of various compounds has long been of interest. There have been attempts made to group the effect of substituents under a single theory. Williams² classifies reactions into three groups according to the effect of polar substituents on reaction rates as follows: (A) those favored by accession of electrons to the point of reaction; (B) those favored by recession of electrons from the point of reaction; and (C) those in which the data available are insufficient to classify in either group A or B. Of the three esterification studies cited by Williams, two, those by Goldschmidt³ and Kailan⁴ are in group C. The third, by Michael and Oeschlin⁵ is placed in group B, *i. e.*, the esterification reaction was accelerated by a substituent such as the nitro group. Hammett⁶ has expressed the effect of a substituent in the meta or para position on the benzene ring upon the rate of a side chain reaction by the equation

$$\log k = \log k_0 + \sigma\rho$$

where k is the velocity constant for the substituted reactant, k_0 the constant for the unsubstituted reactant, σ a constant depending upon the substituent, and ρ a constant depending on the reaction,

(1) This paper is constructed from a dissertation presented by Lee B. Storms to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

(2) Williams, *J. Chem. Soc.*, 37 (1930).

(3) Goldschmidt, *Ber.*, **28**, 3220 (1895).

(4) Kailan, *Ann.*, **351**, 186 (1907).

(5) Michael and Oeschlin, *Ber.*, **42**, 317 (1909).

(6) Hammett, *THIS JOURNAL*, **59**, 97 (1937).

medium, and temperature. Hammett found a probable error for $\log k$ of less than 0.1 in thirty-three of thirty-nine reactions, including equilibrium as well as velocity constants. The equation was applied to the esterification work of Goldschmidt.³ The probable error found was 0.118. Hartman and Borders⁷ applied the equation to the esterification of substituted benzoic acids with methanol. They found an average error of 0.058. The values of σ used in the work of Hartman and Borders as well as those used in this work were taken from Hammett⁶ and were determined by him from the data of Dippy⁸ for the dissociation constants in water of substituted benzoic acids.

The object of this investigation was to determine the velocity constants of hydron-catalyzed esterification of substituted benzoic acids with cyclohexanol. Using the data thus obtained, the energies of activation are determined in order to analyze the data from the point of view of the Arrhenius equation. Hammett's equation is tested for its applicability to the esterification of the cyclic alcohol, cyclohexanol.

Experimental

Materials.—Pure cyclohexanol was first dried by the method of Bjerrum and Lund⁹ and then by refluxing over calcium oxide. The acids were

(7) Hartman and Borders, *ibid.*, **59**, 2107 (1937).

(8) Dippy, *J. Chem. Soc.*, 644 (1936).

(9) Bjerrum and Lund, *Ber.*, **64B**, 210 (1931).