THE DIFFERENTIATING EFFECTS OF SOLVENTS ON THE STRENGTH OF ACIDS

V. SEPARATE POTENTIOMETRIC TITRATION OF MIXTURES OF ACIDS IN ANHYDROUS ACETIC ACID

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In our previous investigations [1-5] we showed that organic solvents, especially ketones, had a large differentiating effect on the strength of acids of different natures. We showed, for example, that in 90% acetone, the pK of hydrogen chloride equalled 2.57, of benzoic acid 9.70 (in water 4.20), of acetic acid 10.27, etc. In mixtures of mineral acids with carboxylic acids, ketones increased the exponent of the ratio between their dissociation constants by 4 to 4.5 units. We made use of this circumstance to extend the possibilities of alkalimetric and acidimetric titration.

The use of acetone and acetone mixtures permits us to carry out a separate potentiometric titration of a mixture of acids which in water are so close to the same strength that their separate titration in aqueous solution is impossible. Both for purposes of titration and for an understanding of the acid-base relationship, anhydrous acetic acid was of interest.

Acetic acid is an acid solvent whose ionic product, according to Kolthoff's [6] measurements, equals $2.5 \cdot 10^{-13}$, according to Kilpi's [17] data equals $5.3 \cdot 10^{-11}$. The dielectric constant of acetic acid is very low (equal to 6). Acetic acid has chiefly donor properties, but with respect to perchloric acid, it becomes a proton acceptor [7]. As a solvent, anhydrous acetic acid has been used in a number of investigations to study the strengths of acids and bases [8-16]. It has been found that acetic acid has a differentiating action. For example, mineral acids, of uniform strength in water, are arranged in acetic acid in the following order:

$$HClO_4 > H_2SO_4 > HCl > HNO_3,$$

which indicates the great strength of perchloric acid, while nitric acid is revealed as very weak.

In acetic acid, aminobenzoic acid is titrated like a base [17]. Amino acids are also titrated, as the bases of perchloric and sulfuric acids [18], for under the influence of the acetic acid, not only is the dissociation of the basic groups in the amino acids increased, but the dissociation of the acid groups [19] is lowered. The basic groups of gelatin have a dissociation constant in water of the order of 10^{-12}, while in acetic acid these basic groups of gelatin can be titrated like strong bases,[20].

From the data of Hall and Werner [8], Hantzsche and Langbein [13] were able to suggest that the differentiating effect of anhydrous acetic acid was sufficiently great to permit separate titration of mixtures of mineral acids that are strong in water. The purpose of the present investigation was to throw light on this possibility and to make a quantitative determination of the differentiating effect of the acetic acid.

EXPERIMENTAL

Anhydrous acetic acid was prepared from commercial glacial acetic acid, which was carefully fractionated over potassium permanganate; the 117.5-118°

fraction was then frozen three times and again fractionated over potassium permanganate under conditions which prevented the moisture of the air from entering. The absence of water was confirmed by a determination of the melting point.

The acetic acid thus prepared was used as a solvent for the preparation of solutions of perchloric, hydrochloric, sulfuric, nitric, toluenesulfonic, and trichloracetic acids. A 0.01 N solution of each of these acids was prepared by the addition of the proper weight of chemically pure acid. Water, introduced with the acids, was combined with acetic anhydride. Within the limits of accuracy of analysis, there may have been a very small excess of acetic anhydride ($\pm$0.02%). 10 ml of the solution of acid or a mixture of acids was taken for titration.

As a base for the titration, we used pyridine and dimethyl aniline, which behave as strong bases in acetic acid. 0.05 N solutions in anhydrous acetic acid were prepared by adding the proper amounts of the freshly distilled bases.

The titration was carried out potentiometrically, by means of an Izmailov [21] lamp potentiometer. The electrochemical cell consisted of the following chain:

$$\mathrm{Pt}\ \underbrace{\left|\begin{matrix}\text{acid}\\ \text{quinhydrone}\end{matrix}\right|\ \begin{matrix}\mathrm{LiCl}\\ \text{sat.}\end{matrix}}_{\text{in } CH_3COOH}\ \Big|\ \underbrace{\begin{matrix}\mathrm{KCl}\\ \text{sat.}\end{matrix}\ \left|\begin{matrix}Hg_2Cl_2\\ KCl\ \text{sat.}\end{matrix}\right|}_{\text{in } H_2O}\ \mathrm{Hg}$$

In the case of the acetic acid titration, a chloranil electrode was used instead of the quinhydrone, in accordance with the proposal of Conant and Hall [8], as the quinhydrone is oxidized in an acetic acid solution of nitric acid. In all the other cases, the quinhydrone electrode served excellently; its potential was quickly determined, and after a lapse of 3 to 4 minutes the potential had changed only a tenth of a millivolt.

In Fig. 1 there is a sketch of the titration vessel. Isolation from the moisture of the air was maintained by enclosing the compound under a rubber stopper and using an electrode with a mercury seal. The platinum electrode also served as a stirrer. The surface of the electrode covered 3 cm^2. The left part of the siphon was filled with a saturated solution of LiCl in acetic acid, contact being made across a thin section. The right half of the siphon was filled with a saturated aqueous solution of KCl in agar-agar in order to diminish the resistance.

The titration was carried out at room temperature, which over a long period varied from 18 to 20°.

In studying the electrolytes in acetic acid, as the solvent had a low dielectric constant, it was necessary to consider the influence of the salt effect. In order to eliminate this, we introduced into the solution of acid being titrated a 0.01 N solution of lithium chloride.

In this way, solutions of $HClO_4$, HCl, H_2SO_4, HNO_3, CCl_3COOH and $CH_3C_6H_4 \cdot SO_3H$ were titrated. During the titrations we observed an interesting phenomenon, of which we shall speak below, in considering the results. Here we shall only indicate the fact that trichloracetic acid could not be titrated in anhydrous acetic acid. In the titration of perchloric acid, we sometimes found two points of inflection on the titration curve (Fig. 2).

The titration of mixtures of these acids is of great interest. The results given below are a solution to an extremely difficult analytical problem, and clearly confirm the fact that an evaluation of the strength of an electrolyte according to its behavior in water is misleading. The strength of an electrolyte is determined by the solvent.

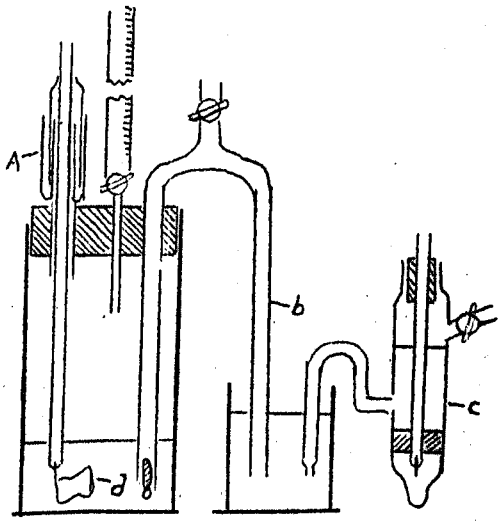

Fig. 1. Titration Vessel.

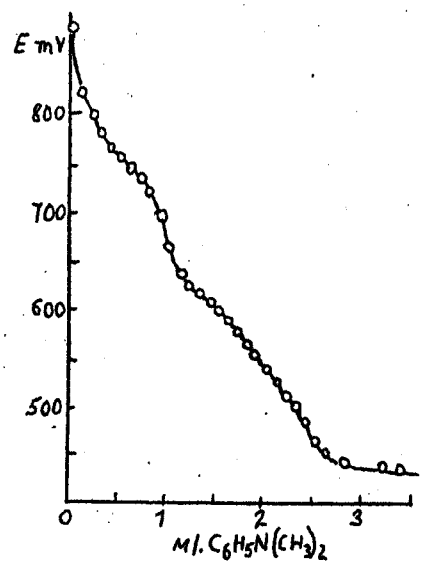

Fig. 2. Curve of titration of perchloric acid with dimethyl aniline. Chloranil electrode.

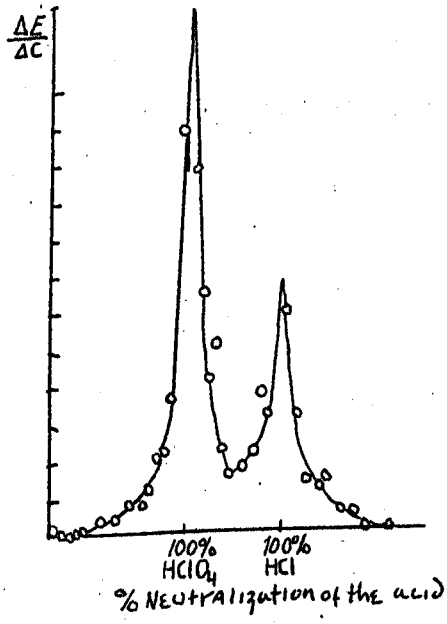

Fig. 3. Titration of mixtures of perchloric and hydrochloric acids with pyridine.

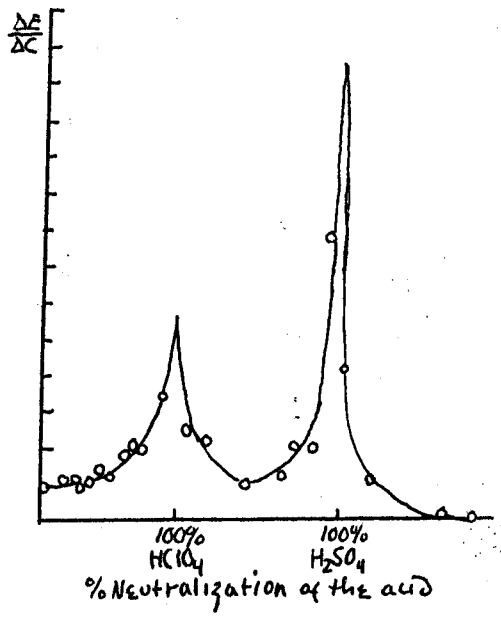

Fig. 4. Titration of mixtures of perchloric and sulfuric acids with pyridine.

For the titration of acid mixtures, 5 ml of a solution of each acid was taken, and the mixture was titrated in the manner described above. Mixtures of $HClO_4$ and H_2SO_4, $HClO_4$ and HCl, HCl and CCl_3COOH, and HNO_3 and $CH_3C_6H_4 \cdot SO_3H$ were titrated. The last pair was titrated with a chloranil electrode, all the others with a quinhydrone electrode. Results of the titration of mixtures are given in Figs. 3, 4, and 5. They completely confirm our belief that anhydrous acetic acid differentiates sufficiently between the strengths of acids to permit the separate titration of acids which in water, alcohol, and even in a differentiating solvent like acetone can not be titrated separately.

As was indicated above, trichloracetic acid could not be titrated in acetic acid. Neither could it be titrated in mixtures with mineral acids, but in this case, the separate amounts of both trichloracetic and mineral acid could be determined by a double titration: titration of the mixture in aqueous solution gives the total acidity, titration in acetic acid the amount of mineral acid.

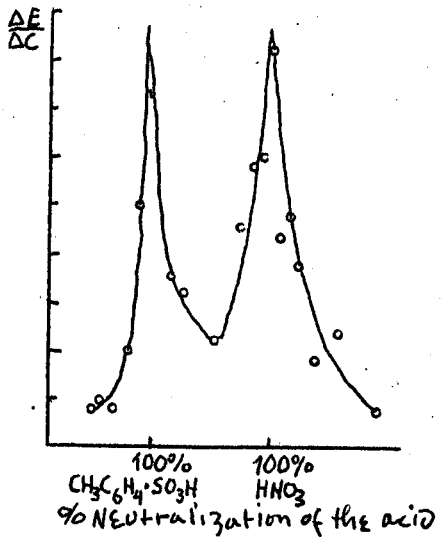

Fig. 5. Titration of mixtures of toluenesulfonic and nitric acids with dimethyl aniline.

Evaluation of Results

In the titration of sulfuric acid with pyridine, in the case where there was a possible excess of acetic anhydride, sulfuric acid behaved like a mono-monovalent electrolyte. The jump in potential on approaching the equivalent point was fairly great. This speaks for the great strength of this acid in anhydrous acetic acid.

This interesting phenomenon has been observed by other investigators. Russell and Cameron [16] showed that with aniline guanidine, and diethyl-o-toluidine, sulfuric acid is titrated as dibasic, while with sodium acetate it is incompletely titrated. The authors assume that in the presence of an excess of acetic anhydride, there is the formation of a product from it and the sulfuric acid — a mixed anhydride of sulfuric and acetic acids. This compound has ultra acid properties. Hutchison and Chandlee [22] consider sulfuric acid in acetic acid solution as a mono-monovalent electrolyte. Hall and Voge [23], from the results of measurements on the electrical conductivity of sulfuric acid, find that in acetic acid it behaves like a weak monobasic acid with pK = 8.2.

Similar anomalies have been observed with other acids than sulfuric. Russell and Cameron have suggested that in the case of an excess of acetic anhydride, there are two forms of perchloric acid present; their reason is that the titration curve of perchloric acid in their experiments has two points of inflection. It has been indicated above that in certain cases, this phenomenon was also observed in our experiments. In addition, in one case we observed two points of inflection for the hydrochloric acid titratinn curve as well.

According to Usanovich [24], acetic anhydride is an amphoteric compound; therefore it is very probable that it does have an influence. But the question cannot be decided on the basis of existing experimental data, as various invest-

igators have prepared solutions in different ways, and in almost all instances have not excluded the possibility of an excess (±) of acetic anhydride. To decide this question, we intend to undertake a special investigation; in addition, the nature of electrolytes in acetic acid will be determined under the influence of the solvent itself, of the anhydride, and possibly of the character of the base used for titration, and finally, we shall take account in all this of the salt effect.

It is of interest to estimate the strength of the differentiating effect of anhydrous acetic acid. The fact that it was possible, in acetic acid, to carry out separate titrations of mixtures of acids, testifies to the fact that $HClO_4$ behaves like a strong acid, H_2SO_4, HCl, and HNO_3 like weak acids. After perchloric acid comes toluenesulfonic acid, as this acid can be titrated separately in mixtures with nitric acid, but sulfuric and hydrochloric acids cannot be. On the other hand, nitric acid cannot be titrated in the presence of sulfuric and hydrochloric acids. On this basis, we can draw up the following series:

$$HClO_4 >> CH_3C_6H_4 \cdot SO_3H > H_2SO_4 > HCl > HNO_3,$$

agreeing with the series of Hantzsche and Langbein, which was obtained from data on electrical conductivity.

From the titration curves of the acid mixtures, we have made a quantitative estimate of the differentiating effect of acetic acid with regard to the quantity $\left(\frac{\Delta E}{\Delta C}\right)$ 1%, i.e., with regard to the jump in potential on approaching the equivalent point, which is characterized by the ratio of dissociation constants of the acids [2]. It has been shown that the ratio of the dissociation constants of perchloric and sulfuric acids amounts to 4.5 units in the exponent, and of perchloric and hydrochloric to 6.2, i.e., perchloric acid is more than 10,000 times stronger than sulfuric acid and more than 1,000,000 times stronger than hydrochloric acid. Consequently, the ratios of dissociation constants completely confirm the conditions for accurate separate titration [25].

One of us [27], on the basis of the data of Hantzche and Langbein, Kolthoff, and Willman on the electrical conductivity of acetic acid solutions of mineral acids, has calculated their dissociation constants. The values obtained are given in a table (Column 2). They confirm the series of acids given above. But the ratios of dissociation constants calculated from electrical conductivity data are less than the ratios of the constants from potentiometric titrations. The fact that in acetic acid it is possible to titrate mixtures of mineral acids separately testifies to a greater differentiating effect of acetic acid than does the ratio of the constants calculated from electrical conductivity data.

It is not without interest to consider several peculiarities of the differentiating effect of acetic acid as an acid solvent, and to compare it with the influence of liquid ammonia on acids and bases, for the latter is a solvent with clearly expressed basic properties [26]. The first peculiarity of acetic acid consists in the fact that the number of compounds exhibiting acid properties in it is much less than in water. Even nitric acid shows only weakly acid properties in anhydrous acetic acid solution: it can be titrated separately in mixtures with

Dissociation constants of acids in acetic acid in in liquid ammonia [27]

Acid	pK_{CH_3COOH}	pK_{NH_3}
$HClO_4$....	5.80	2.27
HBr.....	6.40	0.62
H_2SO_4....	8.20	—
HCl.....	8.85	0.87
HNO_3.....	9.38	0.37
CCl_3COOH.	11.46	—

toluene-sulfonic acid, and shows a trifling catalytic effect [13]; trichloracetic acid too, which is very strong in water, is so weak in acetic acid that it cannot be titrated as an acid. The dissociation of the acid groups in amino acids decreases to such an extent that amino acids in acetic acid can be titrated as bases, i.e., they do not exhibit acid properties. By analogy, the number of bases in liquid ammonia cannot be great [2s].

The second peculiarity consists in the fact that acetic acid sharply differentiates the strength of acids, weakening them considerably, while liquid ammonia has a leveling effect, increasing the strength of weak acids. Prussic acid, which is very weak in water, develops the properties of a strong acid in liquid ammonia.

The opposite phenomenon can be observed with regard to bases. The number of bases grows in acetic acid, and their strength increases. The number of bases in ammonia, as already indicated, is small.

Both acetic acid and liquid ammonia have low dielectric constants. Therefore the reciprocal electrostatic effects of ions in both solvents are greater than in water. But the protolytic properties of these solvents are of an opposite nature. Acetic acid is a proton donor, while liquid ammonia is a solvent with definite acceptor properties. Therefore, the difference in the influence of these two solvents on the strength of acids is related to the difference in protolytic properties.

SUMMARY

1. Anhydrous acetic acid has a differentiating effect on acids which are strong in water. This property of acetic acid is great enough to permit the separate titration of mixtures of the following acids: $HClO_4 + H_2SO_4$, $HClO_4 + HCl$, $CH_3C_6H_4 \cdot SO_3H + HNO_3$.

2. The strength of acids is decreased in anhydrous acetic acid. The titration curves show that perchloric acid is the strongest; it is more than 10,000 times stronger than sulfuric acid and more than 1,000,000 times stronger than hydrochloric. Dissociation constants of the mineral acids in acetic acid have been calculated from electrical conductivity data.

3. It is shown that a number of anomalies in the titration of anhydrous acetic acid are related to the possibility of the presence of acetic anhydride, and to the nature of the base used for titration. These anomalies are being investigated.

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Received April 18, 1948.