is less than tetragonal. In $\delta$-$Na_2UF_6$, by a similar argument, the symmetry of the electric field should be close to that found in $\gamma$-$Na_2UF_6$. Unfortunately the absorption bands at shorter wave lengths cannot be traced with the same degree of assurance from compound to compound, thus severely limiting the interpretation of the results.

It can be seen from Fig. 2 and Table I that the spectra of $KUF_5$ and $NaUF_5$ are identical. Since these two salts are isomorphous,[4] the result is not surprising but is merely an illustration of the fact that it is the fluoride ions which influence the electronic configuration of the $U^{+4}$ ions, the particular cation, whether $Na^+$ or $K^+$, having no observable effect.

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## The Acidity Function of Perchloric Acid in Aqueous Acetic Acid

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In the course of investigations of the kinetics of of the rearrangement of benzopinacol[2] and of the dehydration of 1,1,2-triphenylethanol[3] it became necessary to have available acidity function,[4] $H_0$, values for solutions of perchloric acid in acetic acid–water mixtures. $H_0$ values for perchloric acid in this solvent previously have been reported only for anhydrous acetic acid[5a] and for acetic acid containing 0.12 wt. % of water.[5b] Our measurements cover the water concentration range of 0 to 5 wt. % and perchloric acid concentration range of $10^{-2}$ to $10^{-5}$ *M*.

### Experimental

**Materials.**—Acetic acid (Mallinckrodt, A. R. Bichromate Test Grade) was distilled from chromic acid[6] and dried by azeotropic distillation with benzene and fractionation[7]; m.p. 16.60–16.64°. Titration with Karl Fischer reagent[8] indicated a water content of less than 0.004%. Acetic acid–water mixtures were prepared by the addition of water from a weight buret to a weighed portion of the anhydrous acetic acid. Stock solutions of perchloric acid were prepared by the addition of 1.00 ml. of the 70–72% reagent grade commercial product to approximately 250 ml. of anhydrous acetic acid which contained the stoichiometric amount of redistilled acetic anhydride required to react with the water of the aqueous perchloric acid. The solution was standardized by titration with a standard solution of sodium acetate in glacial acetic acid with brom phenol blue as indicator.[9] 4-Chloro-2-nitroaniline (I) (Eastman Kodak Company, practical grade) was crystallized twice from ethanol–water solution; m.p. 116.0–116.5° (cor.). *o*-Nitroaniline (II) was purified in a similar manner; m.p. 71.0–71.6°. 2,4-Dinitro-N,N-diethylaniline (III) was prepared by heating 2,4-dinitrochlorobenzene in a large excess of diethylamine at reflux temperature for 1 hour. The product was precipitated with water and crystallized twice from ethanol; m.p. 79.6–79.9°.

**Procedure.**—The molar extinction coefficient, $E_N$, of each of the indicator bases, B, was measured at the wave length of maximum absorption in anhydrous acetic acid with a Beckman DU spectrophotometer and 1.00-cm. cells. For indicator I, $E_N$ = 4730 l./mole-cm. at 4060 Å.; for II, $E_N$ = 4800 l./mole-cm. at 3950 Å.; for III, $E_N$ = 15,950 l./mole-cm. at 3720 Å. These values of $E_N$ were not changed by the addition of a small quantity of potassium acetate to the solution, and were the same for 95% acetic acid and for the anhydrous solvent. Values of $E_B$, the molar extinction coefficient of the conjugate acid of the indicator $BH^+$, measured at these wave lengths, were zero for I and II and 150 l./mole-cm. for III. The indicator ratio was calculated from the relationship[10]

$$(B)/(BH^+) = (E_A - E_B)/(E_N - E_A)$$

in which $E_A$ is the molar extinction coefficient of a given acid solution. The value of $H_0$ for each such solution was then calculated from the equation[9]

$$H_0 = \log \frac{(B)}{(BH^+)} + pK_a \qquad (1)$$

Values of $pK_a$ used in these calculations were −0.91[5] for I, −0.17[4] for II and 0.30[6] for III.

### Results

In the anhydrous solvent and in water–acetic acid mixtures containing up to 2% of water $H_0$ varies linearly with log $[HClO_4]$, as reported by Smith and Elliott[5b] for approximately anhydrous solutions in which the indicator concentration is small relative to that of the acid. The lines shown in Fig. 1 have slopes varying between −1.02 and −1.09 with an average value of −1.05. This establishes the relationship

$$\frac{H_0 - H_0'}{\log [HClO_4] - \log [HClO_4]'} = -1.05 \qquad (2)$$

which is valid if the solvent composition is constant. A linear variation of $H_0$ with log molarity of sulfuric acid in glacial acetic acid has been reported.[11]

Values of $H_0$ were measured for two concentrations of perchloric acid ($2.38 \times 10^{-3}$ and $4.76 \times 10^{-3}$ *M*) in a series of acetic acid–water mixtures. From these results and also from the data of Fig. 1 average $H_0$ values for $1.00 \times 10^{-3}$ *M* perchloric acid were calculated with the aid of equation 2. These values are summarized in Table I. From a graph of these data $H_0$ for other water concentrations up to 5 wt. % may be interpolated and for other perchloric acid concentrations within the range $10^{-2}$ to $10^{-5}$ *M* may be computed from equation 2. For the anhydrous solvent Smith and Elliott have reported an $H_0$ value of −1.58 for $5.0 \times 10^{-3}$ *M* perchloric acid. This corresponds to a value of −0.88 for $10^{-3}$ *M* acid, in complete agreement with our value. Their value for acetic acid containing 0.12% water (−0.44 for $1 \times 10^{-3}$ *M* $HClO_4$) lies slightly above our curve (Fig. 2). The data of Lemaire and Lucas[5a] for the anhydrous solvent also are in agreement with these results, the

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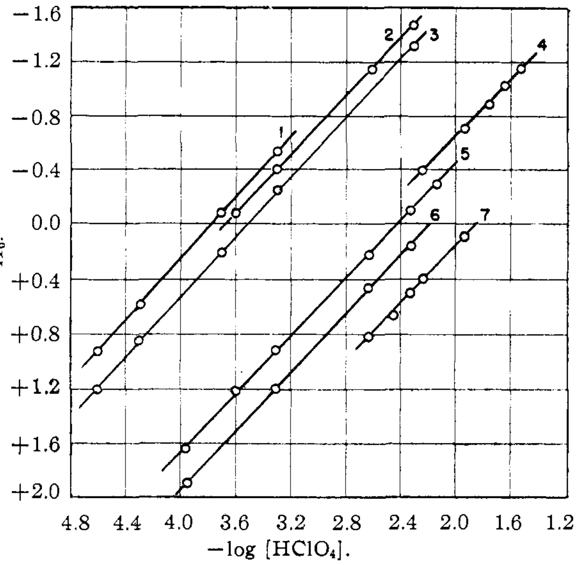

Fig. 1.—$H_0$ *vs.* log molarity of perchloric acid in seven water–acetic acid mixtures. Indicator used and wt. % of water: 1, indicator II, 0.00%; 2, indicator I, 0.01%; 3, indicator II, 0.03%; 4, indicator I, 0.51%; 5, indicator III, 0.98%; 6, indicator III, 1.40%; 7, indicator II, 1.95%.

average of their three values adjusted to $10^{-3}$ *M* perchloric acid being −0.86.

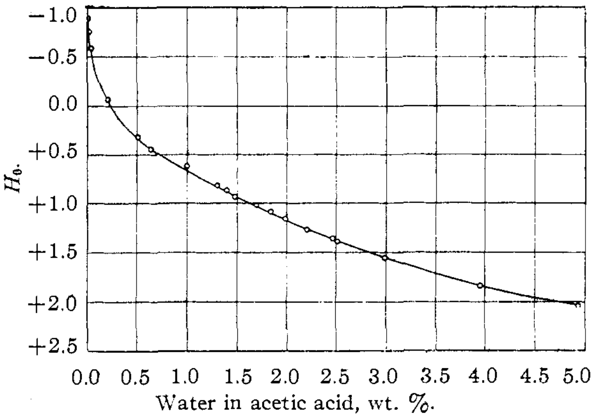

Fig. 2.—$H_0$ of 0.001 *M* perchloric acid in aqueous acetic acid.

The rapid decrease in acidity with increasing water content of the solvent and constant molarity of the acid (Fig. 2) previously has been observed for acetic acid solutions of sulfuric acid[7] and for ethyl alcohol, dioxane and acetone solutions of hydrochloric acid.[12] For low water concentrations the slope of the curve of Fig. 2 is approximately three times that of the corresponding curve for sulfuric acid. This fact may be of importance in the study of reaction rate – $H_0$ correlations because with perchloric acid it is possible, without changing the molarity of the acid, to obtain variations of as much as 3 units in $H_0$ apparently without changing other solvent characteristics, such as dielectric, to a troublesome degree.

Because of an apparent lack of constancy of the activity coefficient ratio $f_B/f_{BH^+}$ for bases of different structure in a solvent of low dielectric, the applicability of the acidity function concept to such solvents recently has been questioned.[13] Other difficulties may arise in mixed solvents of low dielectric where changes in $H_0$ are achieved, as in the present study, by changing either or both solvent composition and acid concentration. When the latter is in the range within which log (acid) is proportional to $H_0$ it is necessary to change the solvent composition in attempting to correlate $H_0$ with reaction rate. If the acid concentration alone is changed only a trivial correlation can be demonstrated, since under these conditions the rate is proportional to the stoichiometric acid concentration. Consequently, in an acid-catalyzed reaction of mechanism

TABLE I

$H_0$ FOR 1.00 × $10^{-3}$ *M* SOLUTIONS OF PERCHLORIC ACID IN ACETIC ACID–WATER MIXTURES

| Water content, Wt. % | Water content, *M*[a] | $H_0$ | Indicator |
|---|---|---|---|
| 0.00 | 0.00 | −0.88 | II |
| .01 | .006 | − .76 | II |
| .03 | .017 | − .58 | II |
| .25 | .145 | − .05 | I |
| .50 | .290 | + .33 | I |
| .63 | .366 | + .45 | I |
| .98 | .570 | + .62 | III |
| .99 | .576 | + .64 | II |
| 1.29 | .751 | + .83 | III |
| 1.40 | .815 | + .87 | III |
| 1.42 | .827 | + .88 | III |
| 1.48 | .862 | + .94 | II, III |
| 1.68 | .979 | +1.02 | III |
| 1.78 | 1.04 | +1.08 | III |
| 1.98 | 1.16 | +1.17 | II, III |
| 2.18 | 1.27 | +1.27 | III |
| 2.47 | 1.44 | +1.36 | II |
| 2.52 | 1.47 | +1.39 | II, III |
| 2.97 | 1.74 | +1.56 | III |
| 3.95 | 2.31 | +1.84 | III |
| 4.94 | 2.90 | +2.04 | III |

[a] Computed from aqueous acetic acid density values at 25°; "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 123.

$$B + H^+ \rightleftharpoons BH^+ \quad \text{(equilibrium)}$$

$$BH^+ \longrightarrow \text{products} \quad \text{(slow)}$$

in mixed solvents of low dielectric and varying composition differences in the rate of the slow step would be expected for solutions which are iso-acidic in terms of $H_0$, even if the latter provides an adequate measure of the equilibrium concentration of $BH^+$. These difficulties not withstanding, satisfactory correlation of reaction rate and acidity function was observed in the reactions[2,3] previously mentioned and has been reported for other reactions in mixed solvents of low dielectric.[14]

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