

HIGH FREQUENCY TITRATION

II. CHANGES IN THE ELECTRICAL CHARACTERISTICS OF SOLUTIONS DURING TITRATION

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On the basis of the analogy between the curves obtained during high frequency and ordinary conductometric titrations, respectively [1], we established, in our previous paper [2], that changes in total resistance ΔZ of a cell are determined, primarily, by changes in active (ohmic) resistance ΔR , and not in capacity resistance ΔX_{C_1} of the solution. This question is considered in somewhat greater detail in the present article.

On applying a high frequency (H.F.) voltage to the outer electrodes of a cell, a current will flow through any aqueous electrolyte solution, the density of which I_{total} will be equal to the sum of the densities of the conduction and displacement currents, respectively [3, 4].

$$I_{\text{total}} = \chi E + \frac{\epsilon}{4\pi \cdot 9 \cdot 10^{11}} \cdot \frac{\partial E}{\partial t} = \chi E_0 e^{i\omega t} + \frac{i\omega E_0}{4\pi \cdot 9 \cdot 10^{11}} e^{i\omega t},$$

where χ is the specific electrical conductivity of the solution in $\text{ohm}^{-1} \text{cm}^{-1}$; E , the field potential in volt cm^{-1} ; E_0 , the voltage amplitude; ω the frequency in angular units ($\omega = 2\pi f$, where f is the frequency in cycles); and ϵ is the dielectric permeability.

For aqueous solutions of electrolytes, I_{total} is basically determined by ionic conduction, and, to a much lesser extent by the displacement of permanent or induced dipoles [5].

The specific electrical conductivity of aqueous solutions of electrolytes χ depends to a large extent on electrolyte concentration; with increase in the latter, χ as a rule, attains a maximum and then drops [6]; its value is determined by the nature of the electrolyte within certain limits.

The dielectric permeability of aqueous solutions of electrolytes, ϵ differs very little from ϵ for pure water (81); changes in ϵ with concentration and nature of the electrolyte are insignificant.

Thus, according to Dmitriev's results [5], ϵ for a 0.38% aqueous solution of NaCl measured at a frequency of ~ 300 Mc, is equal to 78.5. Fradkina [7], investigating aqueous solutions of NaCl, KCl, MgSO_4 , CuSO_4 , $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$ in a concentration range up to 0.4 N, and in a frequency range of ~ 300 -3,000 Mc, found that ϵ for the solutions is greater than ϵ for water, nevertheless, the absolute increase in ϵ is not more than 15-20 units.

Thus, changes in concentration and nature of the electrolyte during H.F. titration affect the active resistance R , and consequently the total conduction current, and have little effect on displacement current, which is proportional, according to the formula adduced above, to the dielectric permeability, ϵ .

In order to make a quantitative evaluation of changes in dielectric permeability of electrolyte solutions during titration, we used a set-up built on the lines described by Hall [14].

A cell of the condenser type was connected in the anode circuit of a H.F. generator — a 6E5 tube, into the grid circuit of which was connected a quartz crystal operating at a frequency of 2 Mc to stabilize the vibrations. Capacity changes in the solution during titration are compensated by means of tuned condensers; by changing the capacity of these tuned condensers, oscillation starts; this is shown by closing of the magic eye, or by changes in the grid voltage measured by a cathode voltmeter. This set-up permits recording of differences in capacity by connecting the cell to the terminals of fixed condensers differing from each other by tenths of a picofarad.

Nevertheless, on connecting a cell with HCl solutions of various concentrations (0.1-0.001 N) and titrating with NaOH in this set up, we could get no observable changes in capacity; and we were unable to determine equivalence points; the capacity changes which occur with changes in solution composition were apparently very small (< 0.1 picofarad).

Using a 36 Mc generator described below, we took curves relating current strength to concentration for trichloroacetic acid CCl_3COOH in two solvents: 1) in benzene (Curve 1); and 2) in water (Curve 2), Fig. 1. In both

instances, 0.1, 0.2 ... 1, 2, 3 ml of acid was added to 20 ml of solvent; the direct component of the H.F. current flowing through the cell filled with these solutions, was measured by means of the set-up described below. For benzene, changes in current strength were extremely small; on addition of 4 ml of acid the change in current was only 10 μ A. For water on the other hand, addition of only 0.1 ml of acid led to a considerable change in current (>100 μ A), on further addition of acid, the current reached a limiting value of ~115 μ A.

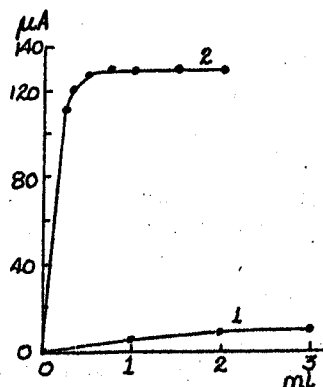


Fig. 1. Current changes through a H.F. cell. 1) Tri-chloroacetic acid added to 20 ml of benzene; 2) tri-chloroacetic acid added to 20 ml of water.

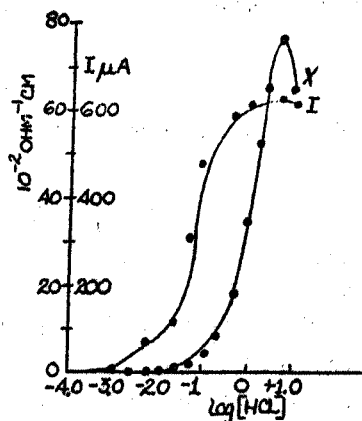


Fig. 2. Specific electrical conductivity (χ) and current strength (I) for various HCl concentrations.

In the first instance we were recording the displacement current, since in benzene ($\epsilon = 2.3$), trichloroacetic acid is undissociated and exists as molecules in solution; in the second case, we were dealing with a conduction current which was determined by ionization of acid in aqueous solution.

The conductivity of aqueous solutions of electrolytes increases at very high frequencies, as a result of relaxation effects [8, 9]; all the same for the frequencies used in H.F. titration, this increase is insignificant. At a frequency of ~300 Mc, the increase in conductivity for a solution of 0.001 M MgSO_4 is not more than 4% greater than its low frequency value [7]; for 0.001 N H_2SO_4 solution in the frequency range 300-3,000 Mc, this increase amounts to ~8%, etc.. We can, accordingly, use the low frequency value [11], instead of the high frequency conductivity of aqueous solutions of electrolytes, without introducing large errors.

Fig. 2 shows a curve illustrating changes in H.F. current (in μ A) with HCl concentration in aqueous solution, which we took with a set-up described previously [2]. The same figure also contains a curve for changes in χ , the low frequency specific electrical conductivity, for aqueous solutions of HCl at the same concentrations.*

Curve 1, current HCl concentration (c), to a certain extent is a repetition of the curve ($\chi - c$). In dilute HCl solutions, current changes are insignificant; they have maximum values at average concentrations, then fall a little, and finally show a tendency to increase in concentrated solutions.

Comparison of the curves in Figs. 1 and 2, confirms our conclusions regarding the relation between change in current during H.F. titration and the active resistance or electrical conductivity of the solution, which according to the results given above, does not differ from the low frequency electrical conductivity in practice.

It follows that for solutions of electrolytes, the physical basis of H.F. titration and of the ordinary conductometric method, respectively, is identical; viz., changes in active resistance of the solution as a result of changes in ionic concentration during the formation of slightly dissociated reaction products, complex compounds, etc..

It should be noted, however, that the mechanisms whereby the direct (or low frequency) and H.F. currents, respectively, pass through solutions, containing emulsions, colloids, or fine crystalline suspensions, are different.

When a low frequency current is used in conductometric analysis, the suspension of fine crystalline precipitate formed during a reaction screens the field between the electrodes, as result of which titration curves are distorted. These distortions can be considerable if the precipitate separating out should cover the electrodes with a non-conducting

* The specific electrical conductivity was calculated from tabulated results for the equivalent electrical conductivity λ_c by means of the formula $\chi = \frac{\lambda_c c}{1000}$, where concentration is expressed in gram equivalents per liter [10].

or badly conducting layer, since, in such a case, the so-called cell constant l/S (where l is the interelectrode distance, and S is their area) changes. When a H.F. A.C. current, however is applied to a cell containing a solution in which there is a fine crystalline suspension or a fatty emulsion, this screening should decrease, or disappear altogether.

Actually, the capacity resistance x_c , offered by each suspended, non-conducting particle to the H.F. current, will fall according to the formula $x_c = \frac{1}{\omega c}$; where ω is the frequency, and c is the capacity of a suspended particle.

Similarly, precipitates formed on the inner cell walls as a result of a reaction will not hinder the passage of a H.F. current through a solution, and changes in the latter will correspond to concentration changes which result when such a reaction is used for titration purposes.

This effect, in our opinion, makes it possible to carry out H.F. titration in solutions of colloids, in suspensions, and in emulsions.*

Approximate ideas of the optimum frequency, and the sensitivity limitations of H.F. set-ups for titration can be gained as a result of mathematical analysis of the total resistance of a cell, z , made up from the equivalent scheme [2].

It should be noted that the application, by certain authors, of this scheme to cells with outer electrodes of any shape is incorrect. Strictly speaking, the equivalent scheme, depicted in our previous article [2], related to a cell with plane-parallel electrodes; for any other arrangement of the electrodes, the electric field inside the cell is extremely complex and cannot be described by a simple scheme.

It was shown above, that the dielectric constant of aqueous solutions is practically constant during titration; consequently, in the expression for z , not only c_2 (the capacity of the cell walls) but c_1 (the capacity of the solution) is also constant. By assuming that c_2 and c_1 are constant, it is easy to derive the following conclusions.

1) For a strongly conducting solution, the total cell resistance $z = \frac{1}{\omega c_2}$ is a constant; the current is determined by the constant (for $\omega = \text{constant}$) resistance of the cell walls, and does not change (or changes by only an insignificant amount) for concentration changes during titration. Qualitatively, this conclusion is confirmed by the upper part of the current-HCl concentration curve, given in Fig. 2.

2) For dilute solution, (large values of R) the total cell resistance $z = \frac{1}{\omega} \cdot \frac{c_2 + c_1}{c_2 \cdot c_1}$ is a reactive resistance made up of two capacities in series, that of the cell walls and of the solution, respectively; the current changes to an insignificant extent during titration in dilute solutions; a H.F. set-up will have a low sensitivity (lower part of curve I-c, Fig. 2).

3) At low frequencies, ($\omega \rightarrow 0$), the capacity component of the total resistance, which is determined by the cell walls, has a high value, changes in the resistance of the solution are insignificant in comparison with the capacity component; the current hardly changes at all during titration.

4). At very high frequencies ($\omega \rightarrow \infty$), the capacity component of the solution becomes insignificant, and since it (because c_1 is practically constant) remains constant, the change in active resistance does not affect the current; consequently, even in this case a H.F. set-up is not sensitive to concentration changes.

From what has been said above, it follows that, in the first instance, in choosing the operating frequency, one should provide for a fairly large decrease in the reactive resistance of the cell walls so as to increase the relative changes in the actual resistance of the solution, and second, that the sensitivity of any H.F. set-up should be a maximum for certain mean concentrations of electrolyte.

EXPERIMENTAL

It was shown [2], that by increasing the frequency from 4 to 40 Mc one could use a beaker instead of a measuring tube for titration, i.e., the sensitivity of a set-up can be increased in accordance with the conclusions derived in the preceding section. A block scheme (Fig. 4), and a titration cell are described below, and results are given which are of interest to analytical chemists.

The cell, in contrast to the one described previously [2], is a glass beaker, the thickness of whose walls is 0.8 mm, while the internal diameter, and height are 21 and 73 mm, respectively (Fig. 3). The outer electrode rings

* Measurements of the concentrations of non-conducting solutions, e.g., in mixtures of organic polar and non-polar solvents, by means of changes in their dielectric permeability can be carried out with dielectric apparatus for precision measurements of small capacity changes [13].

of brass 2, 3 (width 20 mm) are arranged on the lower part of the beaker at a distance of 1 mm from each other.

To decrease inductive and capacity effects, the beaker is mounted in a metallic screen 4. The H.F. current from the generator is led to the cell via a coaxial cable 5 through a socket, 7, fixed in the cell casing. The inner conductor of the coaxial socket, 7, is connected with the upper ring, 2; a diode DG-Ts8, 9, is connected between the lower ring, 3, and the inner conductor, 8, to rectify the H.F. current. The lower ring, 3, is also connected through a H.F. choke, 10, to the casing, and, consequently through the outer sheath of socket 7, and the screen of the coaxial cable to the generator chassis. The choke holds back the H.F. current and passes the D.C. current along the circuit-diode-microammeter.

An attenuator is necessary to regulate the H.F. voltage amplitude applied to the cell; this is a variable condenser with a capacity of 8-10 μF .

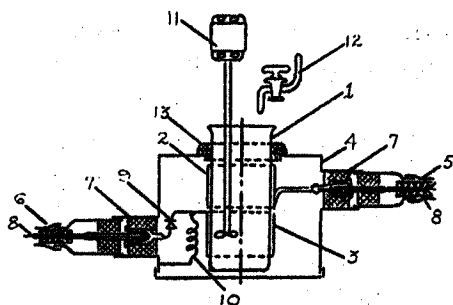


Fig. 3. Cell for H.F. titration. 1) Glass beaker; ϕ 21 mm, height 72 mm; 2,3) electrodes — sheaths of brass, width 20 mm; 4) metallic screen; 5,6) coaxial cables- 7) coaxial socket; 8) central conductor of the coaxial cable; 9) crystal diode DG-Ts8; 10) H.F. choke; 11) motor stirrer; 12) buret for titration; 13) supporting ring from plexiglass.

ductance L and a variable capacity C was introduced into the generator tube circuit, by means of which the generator and the cell and the microammeter connected to it are adjusted for maximum amplitude of the oscillations. Either a microammeter or a neon lamp can be used as an indicator in this set-up. Since current changes are very often small during titration, the sensitivity can be increased by means of the attenuator, by applying a greater voltage to the cell. In this case, the original current flowing through the cell is compensated by a reverse E.M.F., so that any original reading on the microammeter scale can be chosen, and subsequent readings during titration made up to a limit of 100 μA on the microammeter scale.

For this purpose a compensating battery with a constant voltage of 21.5 V is connected into the circuit; the voltage of the latter is regulated with a potentiometer, the crank of which is fixed on a panel. Titration is carried out at room temperature; the solution is stirred with a glass stirrer driven by a constant speed motor, 11.

In Fig. 5 curves are adduced which relate current flowing through the H.F. cell to concentration of HCl , NaOH , or NaCl . Both the arrangement of the curves, as well as their shape conform to the ideas developed above, regarding the mechanism whereby a H.F. current passes through an electrolyte solution.

1. Determination of Acid and Alkali in Aqueous-Alcohol Solutions of Synthetic Resins and Plasticizers, and Titration of Phenols*

Determination of the acidity of solutions of synthetic resins and plasticizers is of great importance for production control. A rapid determination of acidity in such solutions by means of colored indicators is not always possible, since the majority of these solutions have their own intrinsic dark colors.

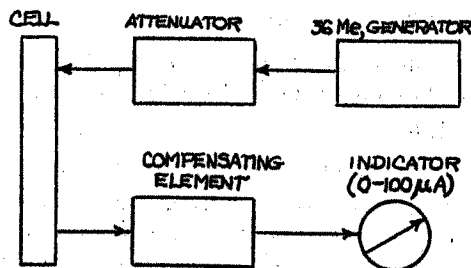


Fig. 4. Block scheme of set-up for H.F. titration using a 36 Mc generator.

On switching on the condenser its capacity increases and consequently the voltage applied to the cell increases, since the latter (together with the cable) acts purely as a capacitance load.

The 36 Mc generator was constructed as before [2], but with a few modifications. A loop consisting of an in-

* This investigation was carried out at the instigation of workers of the Scientific Research Institute of the Plastics Industry, and was carried out in conjunction with B. P. Ershov and V. L. Pokrovskaya. Work on the determination of free acid and alkali in solutions of plasticizer and synthetic resins, and on the determination of phenols, and other components, during production of synthetic resins will be continued with the cooperation of the above Institute.

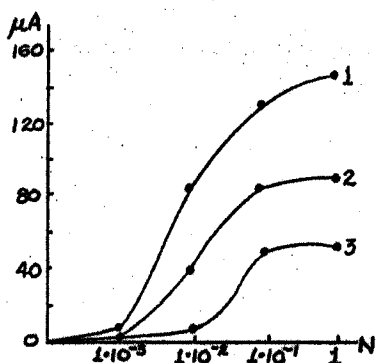


Fig. 5. Change of conductivity current with concentration: HCl (1); NaOH (2); and NaCl (3).

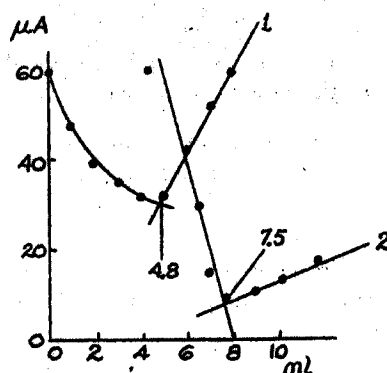
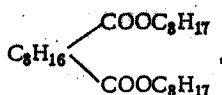


Fig. 6. H.F. titration of HCl with NaOH. 1) In a 10% alcoholic solution of phenol-formaldehyde resin; 2) in a 5% aqueous solution of "Epoxy" resin.

Potentiometric titration by means of platinum or glass electrodes, as well as conductometric analysis is also out of the question, since the electrodes are fouled during titration, and their normal operation interfered with.

We carried out experiments on titration of free HCl in an aqueous-alcohol medium of a 10% solution of phenol-formaldehyde resin - "Epoxy" (Fig. 6). In both cases, 10 ml of resin solution and 10 ml of water were poured into the titration beaker. In the first case (Curve 1), 4.0 ml of 0.1 N NaOH was used to neutralize the HCl, while in the second, the volume of NaOH was 7.5 ml; these values correspond to free HCl contents of 0.017 and 0.27 g, respectively. These amounts differ by only 0.2% from the theoretical amounts.

Fig. 7 represents the titration curve obtained for 10 ml of a saponified solution of the plasticizer dioctylsebacinate.



to which 10 ml of water was added. In this case, excess alkali remaining after saponification was titrated with 0.5 N HCl. The equivalence point corresponded to an expenditure of 3 ml of 0.5 N HCl, which was equivalent to 0.087 g NaOH.

To determine phenol, excess alkali was added to the solution, and the volume of acid used for the sodium

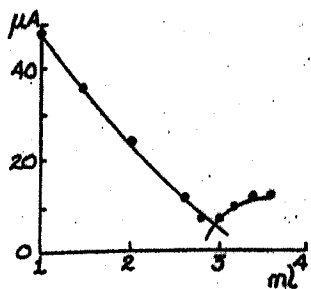


Fig. 7. H.F. titration of dioctylsebacinate

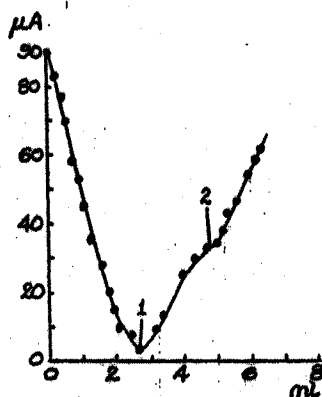


Fig. 8. H.F. titration curve of oxalic acid with 0.1 N NaOH.

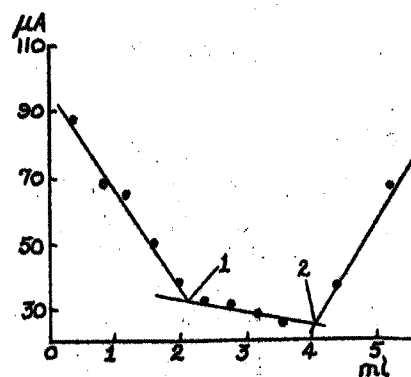


Fig. 9. H.F. titration of Na_2S with 0.1 N HCl.

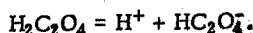
phenolate, found by difference between the volumes for the final end point (V_2), and the initial point (V_1) corresponding to titration of free alkali.

These results, on titration of acid in the presence of diphenylpropane resin, demonstrate the possibility of this method, for solutions containing non-conducting particles and emulsions.

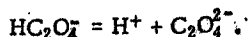
2. Titration of Dibasic Acids and Bases

The ratio of the two dissociation constants of oxalic acid $\text{H}_2\text{C}_2\text{O}_4$, $K_1:K_2 = 6.5 \cdot 10^{-2}:1.1 \cdot 10^{-5} \approx 6 \cdot 10^3$ is too small for titration of oxalic acid to its first equivalence point, potentiometrically or by means of colored indicators [12]. Fig. 8 contains the titration curve for 5 ml of 0.1 N $\text{H}_2\text{C}_2\text{O}_4$ 0.1 N with NaOH.

The first equivalence point, which is clearly defined, and was obtained after using 2.5 ml of 0.1 N NaOH, corresponds to the first dissociation stage.



The second equivalence point obtained after addition of 5 ml of 0.1 N NaOH, is poorly defined and corresponds to the second dissociation stage



The titration of Na_2S with 0.1 N HCl is illustrated in Fig. 9. In accordance with the two dissociation stages of H_2S ($K_1 = 3.31 \cdot 10^{-7}$, $K_2 = 2 \cdot 10^{-15}$), there are two equivalence points on the titration curve. The first corresponds to the formation of the hydrosulfide $\text{Na}_2\text{S} + \text{HCl} = \text{NaHS} + \text{NaCl}$, the second to the reaction $\text{NaHS} + \text{HCl} = \text{NaCl} + \text{H}_2\text{S}$. The amount of Na_2S in solution can be determined from the difference in the volumes corresponding to these two equivalence points; e.g., in this particular instance $2(4.08 - 2.10) = 3.96$ ml 0.1 N HCl, which corresponds to 0.015 g Na_2S .

Rough tests showed further that determination of Na_2S is possible, but to a lower degree of accuracy, when the solution also contains NaOH, the first equivalence point corresponding in this case to the total amount of HCl used to titrate NaOH, and to titrate Na_2S to the hydrosulfide.

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SUMMARY

1. Results on the dispersion of the dielectric permeability of aqueous electrolyte solutions at high frequency, and analysis of the results of H.F. titration lead to the conclusion that this method has much in common with normal conductometric methods. In both methods, the effects which are measured during titration, are determined by changes in the ohmic resistance of the solution, and not by capacity changes.

2. By means of an electrical equivalent scheme for cell + solution, the sensitivity of the H.F. titration method is considered for limiting values of the resistance of the solution, and of the frequencies used.

3. A set-up including a 36 Mc generator has been developed for H.F. titration, and examples are given of its use for acid-alkali titration in aqueous-alcoholic solutions of synthetic resins and plasticizers, determination of phenols, etc.,

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* See Consultants Bureau Translation, page 29.