POTENTIOMETRIC METHODS OF INVESTIGATING HIGH MOLECULAR WEIGHT COMPOUNDS OF PETROLEUM

I. POTENTIOMETRIC DETERMINATION OF ACIDITY

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Indicator methods of determining the content of acids, peroxides, and unsaturated compounds are widely used for characterizing the chemical nature of organic compounds. Nevertheless, indicator methods of titration, which are readily applied to low molecular weight compounds, in the majority of cases of uncolored organic compounds, are not applicable to a study of more complex, intensely colored organic products, of which petroleum, petroleum resins, shale and coal resins, asphalts, etc., are typical. In recent years therefore there has been an increasing tendency to switch over from indicator to potentiometric methods of titration, which give more objective and accurate results as compared with indicator methods. Work has started to appear on the application of potentiometric titration to both the study of light petroleum products, and the standardization of these methods, [1]. Hitherto, no reliable work has appeared on the application of potentiometric titration to a study of intensely colored complex organic compounds, of which resin solutions are examples.

Since we have to deal with intensely colored, high molecular weight compounds, of petroleum (resins, asphaltenes) which are insoluble in water and the lower alcohols, it was thought desirable to switch over to the use of potentiometric methods of titration, which seemed to use the most reliable and accurate method of characterizing chemically active groups of atoms entering into the composition of complex molecules. In this connection therefore, we made a preliminary survey of methods in order to work out potentiometric methods of determining unsaturatedness, acidity, and also peroxides, and saponifiable compounds in solutions of petroleum resins, petroleum, and heavy petroleum residues.

This article is the first of a series of studies which we have carried out on the application of potentiometric methods to the study of petroleum resins and other colored petroleum products.

Determination of the Acid Numbers of Resins

Before acidity can be determined the test material has to be dissolved in some solvent. Resins dissolve readily in benzene, dichloroethane, carbon tetrachloride, chloroform, and some of the mixtures of these solvents with alcohols. Solutions of resins in these media have a high internal resistance, so that if potentiometric determinations are to be carried out on them, tube amplifiers are necessary. We used the LP-5 and Moskip P-3 potentiometers in conjunction with a LU-2 amplifier.

The acid number, i.e. the number of milligrams of KOH used to neutralize the acid in 100 g of test sample is calculated according to the formula:

acid number = VT/g, where V – is the volume of KOH used to titrate the acids; T – the titer of KOH; g – the weight of resin.

It is very difficult to determine the end point of colored products such as petroleum and resins by means of an indicator. The potentiometric method of determining acid numbers in petroleum has not been checked on resins. Resins, which are essentially complex mixtures, can lead to complications.

According to the GOST* methods 1784–47, titration with an aqueous alkali solution is carried out until the E. M. F. is zero, i.e. when the potential of the indicator electrode is the same as that of the standard half element reference electrode. Determination of acidity is carried out in an alcohol-benzene mixture. Such measurements are not suitable, since titration to a potential determined beforehand is only possible if the same mixture is always

* GOST = All-Union State Standard.

used as the solvent. When the solvent is changed it is essential to change the standard electrode as well (the reference electrode).

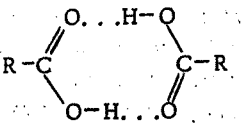
The use of aqueous alkali for titration of petroleum products leads to separation of the system into layers, which is always accompanied by a certain non-reproducibility of results. We have made various modifications to this method in order to eliminate this drawback.

In choosing a solvent we were guided by the following considerations: the solvent must dissolve petroleum products, including resins, and the solution thus obtained should have a sufficiently high electrical conductivity. The most suitable solvent would be one which would not necessitate the use of an amplifier. Examples of solvents which could fulfill this requirement are the basic solvents (pyridine, hydrazine, etc.): in such solvents however, it is impossible to use the most popular indicator electrodes. Moreover, it has been known for a long time that pyridine not only acts as a solvent, but as a chemical reagent for resins. A number of materials which themselves do not possess acid properties exhibit such properties in basic solvents.

The lower alcohols cannot be used as solvents, since they are poor solvents for petroleum and resins.

The best solvents for petroleum products are benzene, carbon tetrachloride, and dichloroethane (aprotonic solvents). Benzene has the added advantage that it is widely used in all laboratory and factory work. Even in dichloroethane, which has the highest dielectric constant, the electrical conductivity of acids is so small that the use of available amplifiers is insufficient for carrying out measurements. The use of various non-aqueous solvents modifies acid strength and titration conditions considerably [2].

An acid can only exhibit its acid properties when another material is present — a base, which can accept the protons liberated by the acid. This substance, in the case of hydroxyl-containing, and a number of other solvents, is the solvent itself. According to Brönsted's theory, the greater the capacity of the solvent-base to combine with a proton, the stronger the acid dissolved in it will be. In aprotonic solvents, however, proton transfer is excluded, so that acids exhibit acid properties by donating the proton either to an added base or to another molecule similar to itself. As spectrophotometric [3], and cryoscopic results [4], show, molecules of carboxylic acids are found in the form of dimers of the following type:



in aprotonic solvents.

Such a dimer can split up to form ions of the type $RCOO^-$ and $RCOOH_2^+$. It is completely obvious that the number of such ions will be insignificant, and that their number will be smaller the lower the dielectric constant, i.e acids will be weak in aprotonic solvents.

The weaker the acid, the less accurate the titration: this follows from Roller's formula [5],

$$\epsilon = \pm 200 \sqrt{K} \sin h\Delta,$$

where Δ is the error in determining the end point (equal to 0.158Δ mV during potentiometric titration and 0.58Δ pH for indicator titrations); sin h is the hyperbolic sine; K, a factor related to the dissociation constant of the acid and the ionic product of the medium as follows:

$$K = \frac{K_i}{K_a C_a}$$

(for titration of a weak acid with a strong base).

The ionic product of the solvent K_i is very small in this instance, which should mean that conditions are favorable for titration; the lower value of the dissociation constant of the acid K_a, however, more often than not, covers up this effect. It was essential, therefore, to choose an additive for an aprotonic solvent which increases the acid strength to a maximum. Alcohol is used as the additive in GOST methods. In an alcohol-benzene mixture, titration will improve because of the decrease in the ionic product of the alcohol (because benzene is present), and of an increase in acid strength compared to that in benzene alone (because of the addition of alcohol). An alcohol-benzene solution of acid will act as if conducting ions similar to alcohol were present, but with a modified ionic product and dielectric constant.

The higher the percentage of benzene in the mixture, the better the titration conditions. We titrated a strong acid, HCl, in alcohol-benzene mixtures, using various ratios of alcohol to benzene, and became convinced that this was the right choice.

On increasing the amount of benzene beyond the optimum, the mixture became gel-like and titration became difficult, and sometimes even impossible. Alcohol-benzene mixtures containing from 25-50% alcohol proved to be the best. We used mixtures of 2 : 5 and 1:1. The most suitable is a 2:5 mixture, since during titration with alcoholic potash, the amount of alcohol increases, and at the equivalence point reaches 50%.

For preparing the solvent mixture, as is evident from Table 1, alcohol and benzene of various degrees of purity were used (technical benzene, redistilled benzene, cryoscopic benzene, and alcohol, alcohol treated with alkali, rectified spirit, etc.). Other solvents, such as acetone, dichloroethane-alcohol, carbon tetrachloride-alcohol were also tried. The mixture of dichloroethane-alcohol (in a 2 : 5 ratio) can also be used as a solvent without using an amplifier. When this solvent was used saturated with LiCl, a Moskip P-3 potentiometer was used which had a sensitivity of 2-3 mV.

TABLE 1

Comparison of the acid numbers obtained for resins from Ilsky petroleum when solvents of varyious degrees of purity were used

Resin sample number	Purity of solvent	Weight taken, in g	Acid number
135	Cryoscopic benzene	0.1030	55.7
		0.1127	55.1
		0.0911	56.3
175	Alcohol, distilled over KOH	0.3112	16.6
		0.3378	16.7
135	Rectified spirit	0.0733	55.1
		0.0950	55.1
		0.0835	57.5
175	Technical benzene	0.2701	16.8
		0.4500	17.1
		0.3112	16.6
135	Cryoscopic benzene	0.0696	56.3
175	Redistilled alcohol	0.4373	16.8
		0.4381	16.4
		0.3599	16.7

Acetone and carbon tetrachloride were used because they are solvents for individual resin fractions.

We checked on the suitability of the most widely used electrodes, which are reversible with respect to hydrogen ions, for measurements in the media we used.

The hydrogen gas electrode, antimony, glass, and quinhydrone electrodes, etc., can be used as indicator electrodes for hydrogen ions. The suitability of these electrodes for determination of acids in alcohol-benzene mixtures was also checked. An antimony beaker was used as an antimony electrode; it proved unsuitable for determination of acidity in petroleum products; its potential changed with time, and depended on agitation, preliminary treatment of the surface, etc.

The hydrogen gas electrode is not suitable under ordinary laboratory conditions.

The potentials of the quinhydrone and smooth platinum electrodes, respectively, are stable enough and are easily reproducible. Preference was given to a smooth platinum electrode, since it does not necessitate the introduction of other additives into a titrant mixture, which is already complex enough.

The potential of the glass electrode is also reproducible and is rapidly established; the only snag with this electrode is its fragility, but if it is handled carefully, a glass electrode in conjunction with a tube potentiometer can be operated for a long time.

In preparing a new electrode, or using a new solvent, it is essential to check on the linearity of the relation between E.M.F and hydrogen ion concentration. A check on the behavior of a glass electrode in an alcohol-benzene mixture shows that in solutions with concentrations from 1 N acid to 1 N alkali, there is a linear relation between potential and pH, and that this line has the theoretical slope.

Thus, we finally decided on smooth platinum and glass electrodes, respectively, as indicator electrodes and a saturated calomel electrode as reference electrode, though a silver chloride or any other reference electrode can be used successfully. The important factor is that the potential of the reference electrode should be constant and reproducible.

The electrolytic circuit was made up of a siphon with a saturated aqueous solution of KCl. The whole set-up can be represented as follows:

$$\text{Pt} \;\Big|\; \begin{matrix}\text{Solution of resin} \\ \text{in alcohol-benzene}\end{matrix} \;\Big|\; \begin{matrix}\text{KCl} \\ \text{saturated}\end{matrix} \;\Big|\; \text{Hg}_2\text{Cl}_2 \cdot \text{Hg}$$

A 0.05 N alcoholic solution of alkali was used as titrant.

Analytical Procedure. 0.1 g of test material is dissolved in 10-15 ml of alcohol-benzene mixture. The solvent mixture is prepared beforehand by mixing alcohol and benzene in definite proportions; sometimes the test material dissolved very slowly. In these cases it is best to dissolve it in benzene alone and then add the alcohol. Beaker plus solution is covered with a ground glass cover, through which pass the indicator electrode, siphon, the tip of the buret containing titrant, and a stirrer (we used a bubbler instead of a stirrer). The calomel electrode is connected via siphon with the KCl. The general appearance of the test cell is shown in Fig. 1.

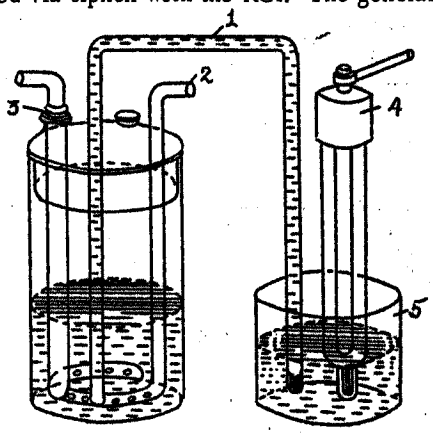


Fig. 1. General view of the cell used for titration. 1) Siphon with saturated KCl solution; 2) bubbler; 3) platinum electrode; 4) calomel electrode; 5) beaker plus saturated KCl solution.

Wires from the indicator and reference electrodes are, respectively, connected to the potentiometer, and other operations carried out as usual. When the initial potential has been determined, a small aliquot of the alkali solution is added and the potential measured again. The volume of alcoholic alkali is plotted (graphically) against E.M.F., (Fig. 2).

The equivalence point, which is given by the volume of alkali used for titrating free acids in the aliquot taken, is found from the curve. Since the amount

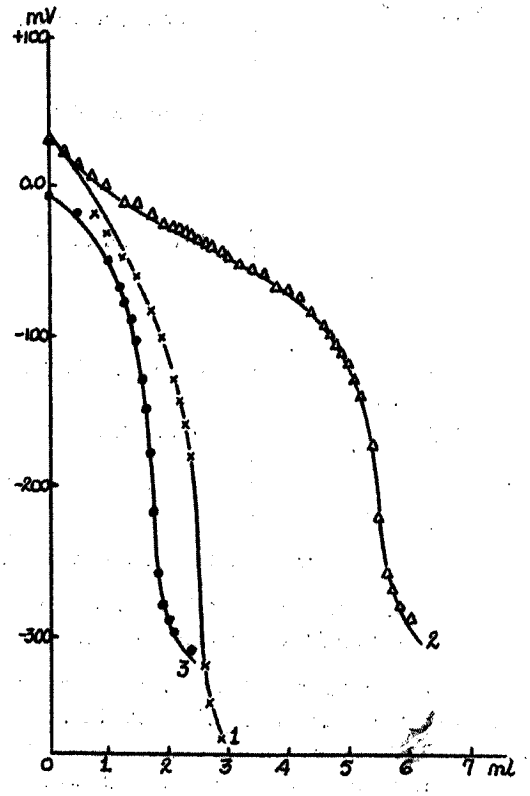


Fig. 2. Titration curves. 1) Benzoic acid; 2) 0.1111 g resin No. 135 to which benzoic acid has been added; 3) 0.0835 g resin No.135 without addition of benzoic acid.

of acids in the resins can be very small, the acidity of the resin and of the solvent itself may be of the same order so that errors in determinations can be very high. In such cases it is essential to determine the acidity of the solvent alone.

The acidity of the solvent itself is determined in the same way as that of the resin., the only difference being, of course, that no resin is added to the solvent. Alkali solution is added dropwise. Determination of the acidity of the solvent itself can often be very difficult. Since only a few drops of alkali is required for neutralization of the solvent, very steep curves are obtained, from which it is difficult to determine the maximum slope: it is best, therefore, to carry out titration to a definite potential (corresponding to the potential at the equivalence point during titration of the test sample).

One must remember that when carrying out such titrations there is a possibility of mistakes arising from the fact that the potential at the equivalence point differs with acids of various strength. The weaker the acid being titrated, the lower the potential at the equivalence point. This phenomenon is observed in any solvent; in aqueous solutions during titration of hydrochloric acid, the pH at the equivalence point coincides with the neutralization point and is equal to 7, but on titrating acetic acid the equivalence point lies at a pH of 9.

Only if the acids in the solvent and in the resin solution are similar in strength, does such titration give correct results. Much better results are obtained if the following technique is used: a small amount of some weak acid, e.g., benzoic acid, is added before titration. This solution is then potentiometrically titrated. The amount of alkali used for neutralization will include the alkali which has been spent in neutralizing the acids already present in the solvent. An aliquot of resin is then dissolved in a prepared solution of benzoic acid, and titration carried out as before.

As can be seen from the results given in Table 2, such a technique gives results which are in fairly good agreement with each other.

A graph is constructed relating the E.M.F. in millivolts to the volume of alkali added. The curves which are obtained are always similar to the curves in Fig. 2, and from them the amount of alkali used to titrate the resin can be determined.

By constructing a curve for the titration of the solvent it is possible to find the volume of alkali used for titrating the solvent on its own, and knowing this one can determine the amount of alkali used to titrate the aliquot of sample.

TABLE 2

Determination of acid numbers of Ilsk petroleum resin in the presence of standard additions of acid

Resin sample number	Weight of aliquot, in g	Acid number
135	0.0621	56.5
135	0.0696	56.3
135	0.1110	56.5
175	0.2427	16.9
175	0.4262	17.1
172	0.2510	9.0
172	0.2435	9.2

As can be seen from Table 3 the results obtained are good enough. Potentiometric methods always give more accurate results, so that it is better to use them not only for colored solutions, but also in uncolored solutions, where indicator methods could be used.

Table 4 contains results of determinations of the acid numbers of Turkmenian and Tuimazinsky petroleum, carried out potentiometrically and by indicator methods. The results obtained potentiometrically usually exhibit better reproducibility than those obtained by means of an indicator.

TABLE 3

Acid numbers of several samples of Ilsk petroleum resins

Resin sample number	Weight of aliquot, in g	Volume of alkali used for titration (ml) (N_{alkali} = 0.0382)	Acid number	Notes
	0.0911	2.40	56.3	
	0.1030	2.68	55.7	Smooth Pt-electrode
	0.1127	2.90	55.1	
	0.1149	2.98	55.5	Glass electrode
135	0.0835	2.25	57.3	Alcohol and benzene—unpurified
	0.0733	1.89	55.1	Smooth electrode
	0.0950	2.45	55.1	Smooth Pt electrode
	0.0709	1.82	54.9	Quinhydrone electrode
	0.0621	1.64	56.5	Titration carried out in the presence of
	0.0696	1.83	56.3	benzoic acid
	0.1110	2.93	56.5	
	0.4373	3.44	16.8	
	0.4481	3.36	16.4	
	0.3599	2.83	16.1	Alcohol and benzene—unpurified
	0.2707	2.13	16.8	
175	0.4500	3.60	17.1	
	0.3112	2.33	16.0	
	0.3378	2.64	16.7	Titration carried out in the presence of benzoic acid
	0.2427	1.92	16.9	
	0.4262	3.46	17.3	
	0.2033	0.93	9.8	Glass electrode
172	0.2510	1.055	9.0	In the presence of benzoic acid
	0.2435	1.05	9.2	Pt-electrode under the same conditions
	0.2251	1.01	9.6	
	0.2405	1.68	14.9	
139	0.2113	1.43	14.5	
	0.0860	0.44	10.9	
193	0.1455	0.70	10.3	

TABLE 4

Comparison of acid numbers of different fractions of resins from Turkmenian and Tuimazinsky petroleum obtained potentiometrically and by indicator methods

Resin sample	Indicator method	Potentiometric method	Resin sample	Indicator method	Potentiometric method
Tuimazinsky Petroleum			Turkmenian petroleum		
Total resinous materials	7.1; 7.4	8.4	Total resinous materials	22.7; 21.4	23.46; 23.98
Fractions, desorbed by CCl_4 *	1.3	1.43;1.32	Fraction, desorbed with CCl_4	3.4	3.6
Fraction, desorbed with C_6H_6	5.3;5.2	5.39; 5.38	Fraction, desorbed with C_6H_6		9.13; 8.58
Fraction, desorbed with CH_3COCH_3	10.4	10,03;9.95	Fraction, desorbed with CH_3COCH_3	65.8;62.6	68.5; 69.15

* The fractions of petroleum resins were obtained by adsorption of the resins on silica gel, from which they were subsequently removed with various solvents in the following order: CCl_4, C_6H_6, CH_3COCH_3, alcohol-benzene mixture in the ratio 1:1 [6].

SUMMARY

1. Optimum conditions have been found for the potentiometric determination of acidity in non-aqueous solutions of complex mixtures of organic compounds.

2. The applicability of the most common indicator electrodes for determination of acidity in alcohol-benzene solutions has been experimentally investigated, and it was shown that platinum and glass electrodes are most suitable for this purpose.

3. A method is proposed for potentiometric determination of acid numbers of petroleum resins.

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