minute and the temperature to ±1°. The samples were calculated to a weight basis by means of their densities. Control experiments indicated that the errors introduced by failure to use equivalent quantities of the various esters were small. The results given in Table I should be correct to about ±0.5%, except the ten minute experiments, in which the error is probably greater.

Analytical Results

The following esters were saponified completely by the above procedure after thirty minutes at 60°: *t*-butyl, cyclohexyl and phenyl acetates; pentaerythritol tetraacetate; isopropyl and isobutyl propionates; methyl, *n*-propyl and isobutyl isobutyrates; diethylene glycol diisobutyrate; methyl 2-methylbutanoate, ethyl 3-methylbutanoate, methyl and *n*-propyl 2-methylpropenoates; ethyl malonate, tartrate and citrate; phenyl and benzyl benzoates; *n*-butyl and cyclohexyl phthalates, and the lactones phthalide and coumarin. The ester content, calculated from the average of at least two determinations each, was in no case outside the limits 98.9–100.5%, and only with coumarin did the precision fall below ±0.3%, in this case due to poor end-points with both phenolphthalein and thymol blue. Brom thymol blue indicator was employed in the experiments with phenyl acetate and benzoate, to minimize the acidic reaction of phenol. Esters requiring the more severe two-hour treatment at 100° were: 2,2-dimethylbutyl-3 and 2,4-dimethylpentyl-3 acetates; ethyl 2-methylbutanoate, ethyl trimethylacetate, methyl 2-methylpentanoate and ethyl tiglate. These analyzed 100.0–100.8%, with a precision of ±0.2%. 2,2-Dimethylbutyl-3 acetate appears in this category although results only 0.4% lower were obtained after thirty minutes at 60°. Ethyl ethylmalonate and ethyl diethylmalonate, methyl abietate, and 2,4-dimethylpentyl-3 phthalate gave quantitative conversions only after seventeen to eighteen hours at 100°. These approached theoretical within 99.0–101.1% with a maximum error of ±0.8%. 2,4-Dimethylpentyl-3 trimethylacetate was unique in that it required four hundred hours of heating at 100° for complete saponification. The process was only 84% complete after two hundred hours. Results of 101.6 ± 0.4% of the theoretical were obtained for the longer interval. These experiments were conducted in Pyrex bomb tubes, using 2 *N* sodium hydroxide in absolute methanol to ensure homogeneity. Results in 90% methanol solution were similar but erratic.

Interfering Substances

In thirty minutes at 60°, pure ketones did not affect appreciably the above procedure as shown by experiments with acetone, butanone-2, pentanone-3, heptanone-4, 2,4-dimethylpentanone-3 and mesityl oxide. Longer heating at 100° produces interference in some cases. Most aldehydes interfere with the method if present in excess of a few per cent.

Summary

1. A procedure has been developed for the quantitative saponification of esters of widely varying structure. Choice of experimental conditions is guided by relative rate experiments designed to show the effect of steric hindrance. The method has been applied to 34 esters, chiefly aliphatic.

2. The phthalate and trimethylacetate of 2,4-dimethylpentanol-3 have been synthesized.

3. *t*-Butyl acetate has been prepared from acetyl chloride and *t*-butanol in the presence of pyridine.

WILMINGTON, DELAWARE RECEIVED MARCH 5, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

Photoelectric Colorimetry. VIII. "The Starch–Iodine System"[1]

BY RALPH H. MÜLLER AND MARY HELEN MCKENNA

The starch–iodine system has been the object of many investigations and the contemporary status of the subject is well summarized in Gmelin.[2] The use of the reaction between starch and iodine for analytical purposes has been limited on account of the complexity of the system, *i. e.*, the dependence upon concentration of starch, iodine, iodide, total volume and the temperature. Despite this Turner[3] has used it for some time for the colorimetric determination of iodine and recently Woodard[4] has developed a procedure with appropriate corrections for apparent deviations from Beer's law.

We have made photoelectric titrations which throw some light on the true behavior of this system and yield an interpretation of the reaction which eliminates most of the need for empirical correction.

Apparatus

All titrations were made with a photoelectric photometer employing a barrier-layer cell. The circuit has been described.[5] The only modifica-

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(1) Read before the Microchemical Section, Kansas City, Mo., Meeting of the American Chemical Society, April, 1936.

(2) Gmelins "Handbuch der anorganischen Chemie," Vol. VIII, 1933, p. 200.

(3) R. G. Turner, THIS JOURNAL, **52**, 2768 (1930).

(4) H. Q. Woodard, *Ind. Eng. Chem., Anal. Ed.*, **6**, 331 (1934).

(5) R. H. Müller, *ibid.*, **7**, 223 (1935).

tion consisted in the substitution of a 400-cc. beaker for the usual absorption cells. Provision was made for a motor stirrer and reagent was added from a microburet. The total volume of solution was 320 cc. and addition of reagent caused a volume change which was negligible. The system was calibrated with solutions which had been shown to follow Beer's law.[5] The "extinction" shown in the curves represents the logarithm of incident light divided by the emergent light

$$E = \log (I_0/I)$$

where I_0 and I are given by the respective photoelectric currents. Approximately monochromatic light was supplied by means of a yellow glass filter (Corning No. 348 H.R. Red Shade Yellow 3.86 mm.).

This filter was chosen after the approximate nature of the absorption curve for starch–iodine had been measured (Fig. 1) with a Zeiss gradation photometer.

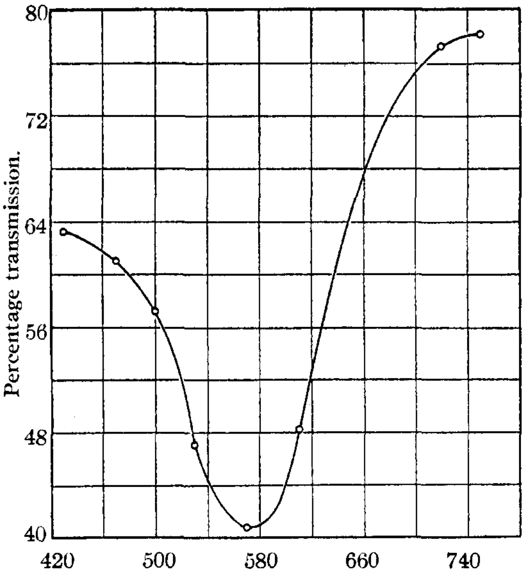

Fig. 1.

Titrations

A solution containing 0.25% Kahlbaum soluble starch prepared in the usual manner and 1 cc. of 1% potassium iodide, was titrated with dilute iodine solution. The latter contained potassium iodide of the same concentration as the iodine. Figure 2 shows the extinction values as a function of the iodine concentration. The curve rises gradually and then assumes a strictly linear course. In this region Beer's law is obeyed quite precisely. The curved portion represents the well-known dissociation phenomenon.[6]

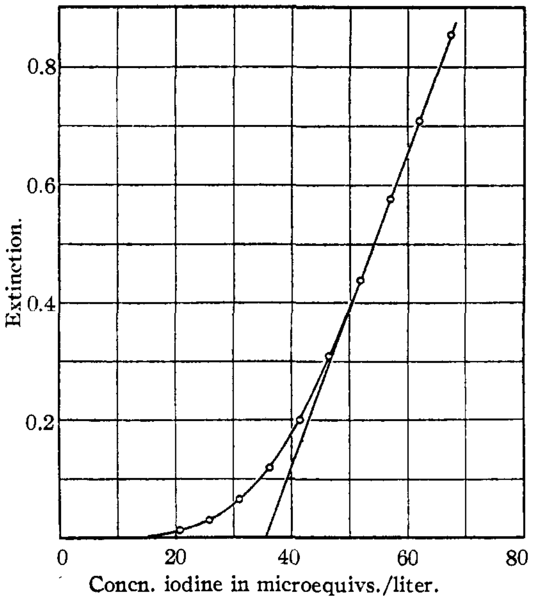

Fig. 2.

Extrapolation of the straight line portion to the concentration axis gives a value which we may call c_0. The linear part may then be represented by the equation

$$E = k(c - c_0)$$

where k is a constant, and c is the concentration of iodine. It should be emphasized that c_0 is also a function of the iodide-ion concentration and decreases as I^- increases (see below).

It will be apparent that for all concentrations of iodine within the linear range the extinction can be calculated directly. That this is not limited to any special optical method may be seen by applying the equation to the Duboscq type instrument. At balance in this instrument

$$E_1 = E_2$$

therefore

$$k(c_1 - c_0)d_1 = k(c_2 - c_0)d_2$$

or

$$d_1/d_2 = (c_2 - c_0)/(c_1 - c_0)$$

in which the c's represent concentrations and the d's the corresponding cup depths.

Figure 3 shows a typical case in which the cup depth ratio is plotted against the corresponding concentrations.

This equation permits the calculation of colorimeter readings directly and without the introduction of arbitrary factors. The constant c_0

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(6) Treadwell and Hall, "Analytical Chemistry," Vol. II, 1919, page 653.

has definite significance because it is possible to calculate an amount of iodine which can be added initially as a result of which the dissociation curve will be eliminated (intercept at the origin instead of at c_0).

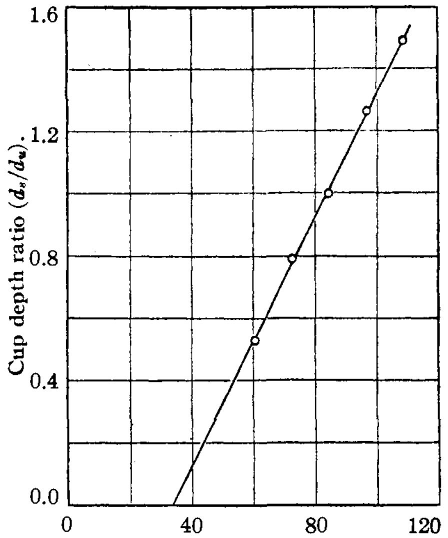

Fig. 3.

Table I gives the results of a typical determination. The numerical values have been substituted in the equation to simplify the calculation. In this equation c is in microequivalents per liter. The actual values in the table have been corrected to mg.

TABLE I

FOR DUBOSCQ COLORIMETER

$c = 50\, d_s/d_u + 33.7$

Mg. I, taken	Mg. I, found	Error, mg.	Error, %
0.192	0.191	0.001	0.52
.230	.232	.002	.86
.268	.268	.000	.00
.306	.308	.002	.65
.345	.344	.001	.29
		Av. =	.47

The addition of excess iodide has a profound effect. Small amounts increase the sensitivity enormously, large amounts produce a shift in the absorption band toward shorter wave lengths (violet or red color instead of blue). For small amounts, the increase in the extinction is a linear function of the iodide-ion concentration. If we prepare a starch solution in which sufficient iodine has been added to bring the extinction value within the Beer's law range and then titrate with iodide ion, the linear relationship is clearly shown. Figure 4 illustrates a typical titration.

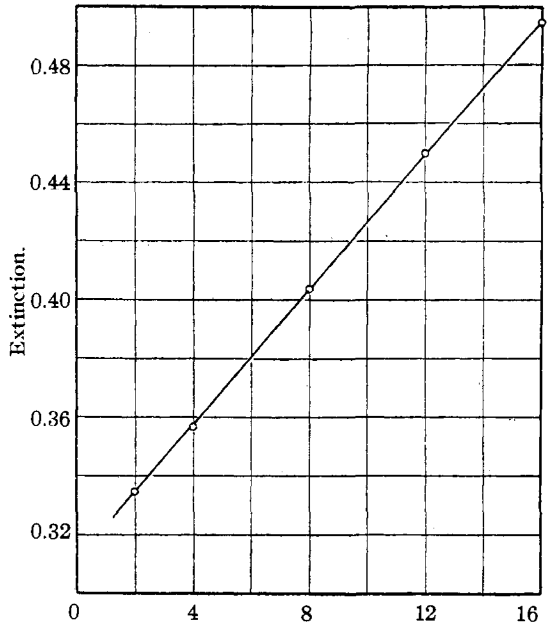

Fig. 4.

The titration with thiosulfate is also instructive. Solution consisted of 40 cc. of 0.5% starch, no excessive iodide, total volume 320 cc. (c_0 in this case is equal to 52.5). As shown in Fig. 5, the linear extrapolation of the thiosulfate curve intersects the concentration axis exactly at c_0. For the extremely small amounts of iodine with which we are dealing here, this value represents only about half of the total iodine present. However, if we add to c_0 the amount of thiosulfate corresponding to the intersection of the curved portion with the axis, then the true amount of iodine is given exactly. This illustrates perfectly the well-known fact that in any iodine-thiosulfate titration the total volume must be kept reasonably constant since the disappearance of the blue color occurs at a point at which there is still a small amount of free iodine present. Under ordinary conditions of a macro titration (0.1 or 0.01 N reagent) this source of error is entirely negligible.[6]

Discussion

In our opinion the foregoing experiments clarify the analytical aspects of this system. By this statement we do not imply that the analytical problem is reduced to its simplest form, but rather that all previous methods can be interpreted on a rational basis in terms of definite optical principle. There are many questions of theoretical interest which may be elucidated. For example, the initial course of the extinction curve enables one to calculate the "apparent" dissociation constant of the starch–iodine complex, or alternately to calculate the adsorption equilibria which may be involved. We are deferring such computations until measurements, which are now under way using pure beta amylose instead of starch, are completed.

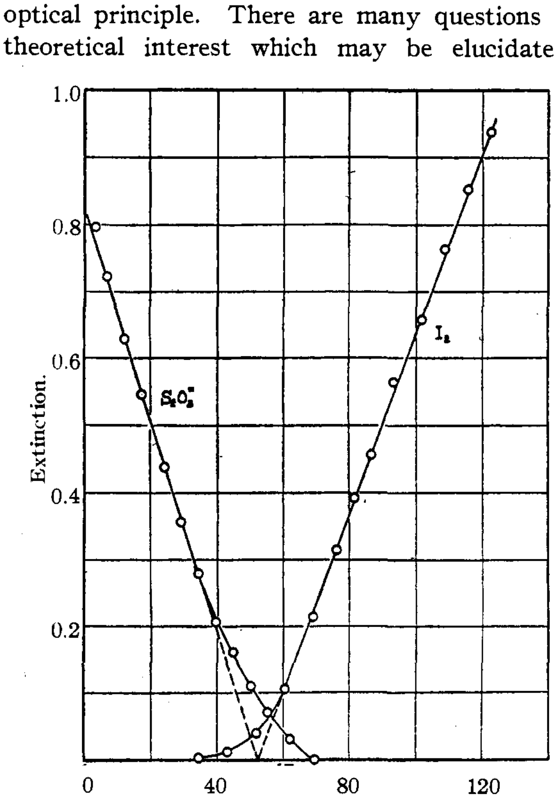

Fig. 5.

It should be pointed out that, in general form at least, our equation $E = k(c - c_0)$ has been used before, primarily to correct for deviations at various cup depths.[7,8] Our suggested c_0 is not purely empirical, however, but is definitely related to the dissociation equilibria.

Summary

Photoelectric titrations with approximately monochromatic light have been performed on the starch–iodine system. Beer's law is obeyed beyond a preliminary "dissociation stage." The equation $E = k(c - c_0)$ is satisfactory and may be applied to the Duboscq type instrument. Though admittedly complex, there is nothing about this system which requires the use of purely empirical correction.

(7) M. Winkler, *Chem.-Ztg.*, **56**, 86–87 (1932).

(8) H. Ginsberg, *Z. anorg. allgem. Chem.*, **209**, 105–112 (1932).

NEW YORK CITY, N. Y. RECEIVED APRIL 18, 1936

[CONTRIBUTION NO. 40 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Relation of Extract to Residue in a Bituminous Coal

BY BURNARD S. BIGGS

In an earlier contribution from this Laboratory[1] it was shown that the amorphous material which constitutes the bulk of the extract dissolved from a Pittsburgh seam coal by benzene at 260° is composed of hydrocarbon units containing an average of four or five rings interspersed with oxygen-containing heterocycles or other inert oxygen linkages. It was demonstrated that the average molecular weight of these fundamental units is about 300, but that they normally exist in associated aggregates with molecular weights ranging from 450 to about 1600. In this paper evidence is presented in support of the viewpoint that such a structure is typical of the whole coal substance, and that the difference between the residue of benzene pressure extraction and the extract itself lies more in the size of the aggregate than in the essential chemical structure. The residue, except for a small portion which is very resistant toward hydrogenation, appears to be composed of large groups of nuclei which are associated or polymerized in such a complex manner that the treatment with benzene cannot dissociate them sufficiently to effect their dissolution. This conception of the structure of coal has been suggested previously by a number of investigators in this field.[2] Fischer, Peters and Cremer,[3] to account for the practically complete conversion of coal to "pseudo-bitumens" on mild hydrogenation, have definitely suggested that the residue differs from the extract mainly in its

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(1) Biggs, THIS JOURNAL, **58**, 484 (1936).

(2) Schrauth, *Brennstoff-Chem.*, **4**, 161 (1923); Fuchs, *ibid.*, **12**, 266 (1931); Francis and Wheeler, *J. Chem. Soc.*, **127**, 2240 (1925).

(3) Fischer, Peters and Cremer, *Brennstoff-Chem.*, **14**, 181 (1933).