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Ethylbis-2,4-Dinitrophenylacetate, a New pH Indicator Determination of Saponification Equivalents in Dark-Colored Oils

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A new acid-base indicator, ethylbis-2,4-dinitrophenylacetate, has been studied and its preparation described. The pH range over which the change from colorless to deep blue occurs is found to be from 7.5 to 9.1 (pK ca. 8.3), making the indicator suitable for most titrations which are ordinarily performed with phenolphthalein. The indicator gives an accurate end point in amber-colored solutions where the phenolphthalein end point is not visible, and it is therefore recommended for use in the determination of acid numbers and saponification equivalents of dark-colored oils.

N THE course of an investigation on the preparation and properties of substituted phenylmalonic esters, the compound identified by Richter (6) as ethylbis-2,4-dinitrophenylacetate was obtained, and the opportunity was taken to study



its indicator properties. Richter noted the color change of this compound from colorless in acid to intense blue in base and accordingly suggested its possible application as an acid-base indicator, but he reported no further studies along this line. The authors' results show not only that the compound may serve as a satisfactory substitute for phenolphthalein in the titration of most weak acids with strong bases, but also that it is specially

suited to the titration of orange- and red-colored solutions in which the phenolphthalein end point is not visible. Because of the frequency with which dark-colored oils are encountered in organic analysis and because of the inadequacy of present-day methods of performing titrations with these products (1-5). data were obtained to determine the applicability of this indicator for such work. It was found that satisfactory results are obtainable even with extremely dark-colored oils and that the accuracy of the method approaches that of ordinary phenolphthalein titrations.

PREPARATION AND PROPERTIES

The indicator is not difficult to prepare and, while the yield is not good, enough of the compound may be obtained from 0.5 mole of dinitrochlorobenzene to serve for thousands of titrations. The following procedure furnished 19.0 grams (18.1 per cent of theoretical) of recrystallized material sufficiently pure for use as an indicator.

One-half gram-atom (11.5 grams) of sodium was dissolved in 200 ml. of absolute alcohol in a 1-liter three-necked flask fitted with a reflux condenser, motor stirrer, and dropping funnel. The solution was cooled and 0.25 mole of diethyl malonate was added dropwise, with stirring, over a 30-minute period. Stirring was continued for another 10 minutes and a hot solution of 0.5 mole of 2,4-dinitrochlorobenzene in about 200 ml. of absolute alcohol was then added over a 30-minute period. The deep red reaction (A small amount of a second compound with indicator properties can be isolated from the alcohol washings; it appears to be the monophenylated ester, ethyl-2,4-dinitrophenylmalonate, which would be expected as an intermediate in the formation of the diphenylated ester. After recrystallization from alcohol this compound melted at 48° C. and dissolved in dilute base to give a deep red color. The change from colorless to red was found to occur over a pH range of ca. 7.2 to 9.0, but the compound is not recommended as a substitute for phenolphthalein because the change is less distinct.)



Figure 1. Indicator Ranges in Titration of Potassium Acid Phthalate with Sodium Hydroxide

The exact range over which the color change occurs was determined by titration of a buffered hydrochloric acid solution with sodium hydroxide, using the glass electrode to measure pH. About 5 drops of a saturated solution of the indicator in 50-50acetone-ethyl alcohol were added to each 100 ml. of solution to be titrated. At pH 7.5 the first blue tinge appeared in the solution, and at pH 9.1 the change to deep blue was complete. (The indicator has been successfully used in the authors' analytical laboratories by students who, by reason of deficiencies in color vision, do not easily recognize the phenolphthalein end point.)

The pK of the indicator is therefore about 8.3. Figure 1 shows the indicator range given by ethylbis-2,4-dinitrophenyl-acetate compared with that given by phenolphthalein in the titration of potassium acid phthalate with sodium hydroxide. The same reversible color change was observed to occur in anhydrous solvents such as absolute alcohol, dry ether, and dry benzene.

TITRATION OF DARK-COLORED OILS

Since the basic color of ethylbis-2,4-dinitrophenylacetate, instead of being masked in amber-colored solutions as is the case with phenolphthalein, becomes more pronounced as a result of the complementary spectral relations, the end point is easily visible even in titrations involving dark-colored oils. In order to check the accuracy of the end point determined under

 Table I.
 Saponification Equivalents Determined for Colored Oils

 (Using athylbis-2 Admitrophenylegetate as indicator)

(Using Chiyibis-2,7-amit	Saponification Equivalent Observed Calcu- Un-			Approxi- mate Color Density, ix
Oil	lated	colored	Colored	i_s
Propyl benzoate Propyl benzoate Propyl benzoate Ethyl-3-carbethoxy-2-furanacetate Ethyl-3-carbethoxy-2-furanacetate Oil A Oil A Oil A (electrometric) Oil B Oil B	164 164 164 113 113 	165 167 166 	$165 \\ 166 \\ 164 \\ 113 \\ 256 \\ 254 \\ 256 \\ 276 \\ 270 \\$	$1.85 \\ 1.85 \\ 1.85 \\ 1.85 \\ 1.55 \\ 1.55 \\ 1.55 \\ 1.55 \\ 1.55 \\ 0.3 \\ 60.3$

these conditions, saponification equivalents were determined for samples of pure propyl benzoate and ethyl-3-carbethoxy-2furanacetate both before and after the addition of an artificial coloring material. For this purpose the addition of a few milliliters of a highly colored neutral caramel solution prepared from pure cane sugar was found to be satisfactory.

About 0.3 gram of the carefully distilled ester was weighed into a 125-ml. Erlenmeyer flask and the mixture was saponified with 15.00 ml. of a standard alcoholic sodium hydroxide solution according to the procedure of Shriner and Fuson (7). The saponification mixture was titrated almost to neutrality with standard acid, 5 drops of the indicator solution were added, and the end point was determined by adding an excess of acid and backtitrating with standard alkali to the first blue tinge. Several milliliters of aqueous caramel were then added to the alkaline solution and the end point was redetermined in the dark green mixture by adding acid until the amber caramel color just returned. In the dark-colored solutions the end point was approached from the basic side, not from the acid side as in the case of the uncolored solutions.

In Table I the saponification equivalents thus determined for uncolored propyl benzoate and for artificially colored propyl benzoate and ethyl-3-carbethoxy-2-furanacetate are compared with the true values calculated from the molecular weights of the esters. The agreement between the calculated and the observed values is sufficiently good to prove the usefulness of the procedure as an analytical method.

Two heat-bodied linseed oils, one of which (oil B, Table I) was almost opaque when viewed by daylight in thicknesses greater than 5 cm., were studied in order to determine the reproducibility of the results under actual working conditions. Oil A was also subjected to electrometric titration, thus affording an additional check on the accuracy of the results. The following procedure is recommended as a working method.

A sample of 0.2 to 0.4 gram of the oil was saponified as before, and after reducing the alkalinity of the mixture by titrating almost to neutrality with 0.25N hydrochloric acid, 5 drops of saturated solution of the indicator were added. More acid was then run in until the dark green color of the indicator just disappeared. Two more determinations of the end point were then carried out on the same sample by adding a few milliliters of standard sodium hydroxide solution and back-titrating with acid. The results of the triplicate determination were then averaged and the saponification equivalent was calculated. The electrometric titration on a saponified sample of oil A was performed in the usual manner, using a Beckman pH meter and a glass electrode.

As can be seen by reference to Table I, the values for oil A obtained by means of the relatively simple indicator method agree with the value obtained from the more elaborate electrometric method, and even the very high color density of oil B does not seriously interfere with the precision of the determination.

The approximate density of the amber color of both the naturally and the artificially colored oils is recorded in the last column of Table I with reference to 0.017*M* potassium dichromate solution arbitrarily assigned a value of unity. The

or

was calculated from the equation

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Pycnometer for Volatile Liquids Control of Diffusion as an Aid in Precision Pycnometry

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This paper reports the design of a pycnometer which is especially well suited for the determination of density on 5 ml. of volatile liquid with an accuracy of ± 0.0001 gram per ml.

light absorption was measured by comparison of the various oils with the standard on a Klett-Summerson photoelectric colorimeter

without a filter. With the instrument adjusted to give a scale reading, R, of zero for the reference standard, the ratio of the

light absorbed by the oil, i_s , to that absorbed by the standard, i_s ,

 $\log \frac{i_x}{i_s} = 0.002R$

 $\frac{i_x}{i}$ = antilog 0.002R

Thus oil B has a light-absorbing power approximately 60

times that of 0.017M potassium dichromate solution.

URTHER publication in the field of density determinations might seem unnecessary in view of the large number of devices which have already been described. However, most of these instruments were designed for a special purpose and a simple pycnometer for general use in hydrocarbon analysis, and particularly for obtaining precise densities on materials as volatile as pentane, has not previously been described.

Many general references (1, 9, 15, 19, 20, 24, 29) are available on the determination of density, and Irving (16) gives a general discussion of the method of floating equilibrium. Unusual method ods include measuring the frequency of acoustic vibration (17) which is dependent on the density of the surrounding medium. Especially interesting are the balanced column methods (4, 7, 11, 13) which eliminate the use of an analytical balance, and which merit further investigation.

The more conventional pycnometers, such as the pipet types (8, 10, 33) and the Sprengel-Ostwald type with its modifications (6, 19, 20, 23, 27), often involve some kind of closure or cap to prevent rapid vaporization of volatile materials. These caps are in part successful, but are not entirely satisfactory with materials as volatile as pentane and ether.

as volatile as pentane and ether. In 1884 Perkin (22) recognized the advantage of having both menisci remote from the ends of the pycnometer arms, so that vaporization would be somewhat hindered. This principle is in-volved in the design of several flask-type pycnometers (2, 3, 30, 31) and many capillary-arm pycnometers (5, 12, 21, 22, 25, 26). However, the control of diffusion by the use of an unfilled capil-lary arm has not have reacond to capital experiment of the property of the pro lary arm has not been generally recognized and has never, as far as the authors are aware, been discussed on a quantitative basis.

PYCNOMETER

The pycnometer which has been developed (Figure 1) has been in use in these laboratories for about 4 years. It is of Pyrex and consists of a 0.3-, 1-, 3-, or 5-ml. bulb blown in one side arm of a capillary U-tube. About 2 cm. of the upper end of the other side arm are bent over to form a hook for filling the pycnometer by capillary action and for hanging the pycnometer in the balance

This hook is a self-filling device, previously described by Hennion (14). The liquid is first drawn into the pycnometer by capillary action and the pycnometer then fills by siphoning. Parker and Parker (21) also used the principle of siphoning to fill their pycnometer. Siphoning has the definite advantage over filling by a suction technique that it reduces the loss of the more

volatile components of gasoline. Both upper side arms of the U-tube are calibrated in scale divisions from 0 to 8.0 with ten intermediate scale divisions between each major scale division. Each major scale division equals 10 The capillary tube should have a 0.6- to 1.0-mm. bore mm. and should not be over 6 mm. in outside diameter. The pycnometer is similar to those of Shedlovsky and Brown (26) and Robertson (25), which feature two calibrated stems and 25-ml. capacity. The present pycnometer, however, is of much smaller capacity and is easily handled on an analytical balance. It is constructed with a bulb in only one side arm, which allows the pycnometer to be filled easily and avoids loss of volatile products by the slow rate of diffusion through unfilled capillary arms.



Figure 1. Pycnometer Capillary bore 0.6 to 1.0 mm., outside diameter 6 mm. maximum, material Pyrex, total weight not to exceed 30 grams

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