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Titrimetric Determination of Water and Alcohols by their Acid Catalyzed Reactions with Acetic Anhydride in Organic Media

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The present work is an outgrowth of earlier observations on the acid catalyzed hydration of acetic anhydride in acetonitrile[1,2] and of a non-aqueous titration method[2] developed in this connection. For a review of the pertinent literature on the determination of water and alcohols reference is made to two papers by Smith and Bryant[3] which appeared while the present study was in progress. The method reported here is different in principle and scope from that of Smith and Bryant so that depending upon the nature of the analytical problem the one or the other will be preferable.

It was previously[2] shown that acetic anhydride can be titrated accurately in organic media by sodium methylate in methyl alcohol with thymol blue as an indicator according to

$$(CH_3CO)_2O + OCH_3^- \longrightarrow CH_3COOCH_3 + CH_3COO^- \quad (1)$$

while after hydration double the amount of methylate is consumed.

$$(CH_3CO)_2O + H_2O \longrightarrow 2CH_3COOH \quad (2)$$

$$2CH_3COOH + 2OCH_3^- \longrightarrow 2CH_3OH + 2CH_3COO^- \quad (3)$$

It was observed in this connection also that reaction (2) in dilute solution in acetonitrile is extremely slow, while in the presence of perchloric acid (0.1 *M* as cystine perchlorate) the reaction is complete in less than one hour. On account of certain disadvantages of perchloric acid (its liquid nature, uncertain degree of hydration and tendency to decompose with oxidation in the dehydrated state) in the present study 2,4-dinitrobenzenesulfonic acid was used as the acid catalyst. This acid was shown by Elgersma[4] to be comparable in acid strength with the strong mineral acids, it is easily obtained in a non-hygroscopic crystalline form with 2 molecules of water and it appears stable in a dehydrated solution. A concentration of this acid of the order of 10^{-3} *M* is sufficient catalytically to complete the above reaction (2) in organic media within from one hour to one day, depending on the nature of the medium. The reactions

$$(CH_3CO)_2O + ROH \longrightarrow CH_3COOR + CH_3COOH \quad (4)$$

($R = CH_3^-$, $C_2H_5^-$) were found to be accelerated to a similar degree, while the ester reaction

$$CH_3COOH + ROH \rightleftarrows CH_3COOR + H_2O \quad (5)$$

in both directions proved to be very slow under similar conditions compared with reactions (2) and (4). These circumstances permit determination of water by its acid catalyzed reaction with an excess of acetic anhydride according to equation (2), the molar amount of water present being equal to the increase in titration value compared with a blank, according to equations (1) and (2, 3). Alcohol can be determined by first letting reaction (4) go to completion in presence of excess anhydride and then decomposing the unused anhydride by excess water according to equation (2), while in a blank the same amount of anhydride is made to react directly with excess water. The difference between the two titrations is equal to the molar amount of alcohol present since each hydrolyzed molecule of anhydride consumes two equivalents of base while each alcoholized molecule consumes only one. Comparison of equations (1) and (4) will also show that in the water determination the presence of alcohol does not interfere since in the methylate titration acetic anhydride uses the same amount of base whether it has reacted with an alcohol previous to the titration or not.

The present investigation has been limited to establishing the principles and practicability and examining the accuracy and limits of sensitivity of the proposed method. The technique to be followed varies according to the problem at hand, and the examples given further on will enable the reader to adapt the method to his needs.

Experimental

Reagents.—2,4-Dinitrobenzenesulfonic acid was prepared according to Elgersma.[5] By dissolving 100 g. of the crude trihydrate in 440 cc. of acetonitrile and precipitating with 7.5 volumes of benzene the dihydrate was obtained in almost colorless crystals; equivalent weight by aqueous titration: found, 284.2, 283.8; calcd., 284.15,

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[1] G. Toennies and T. F. Lavine, *J. Biol. Chem.*, **100**, 474 (1933).

[2] T. F. Lavine and G. Toennies, *ibid.*, **101**, 727 (1933).

[3] D. M. Smith and W. M. D. Bryant, THIS JOURNAL, **57**, 61 and 841 (1935).

[4] J. N. Elgersma, *Rec. trav. chim.*, **48**, 770 (1929).

[5] J. N. Elgersma, *ibid.*, **48**, 752 (1929).

The yield is at least 50% in terms of initial chloro-2,4-dinitrobenzene. The dihydrate should not be stored in a closed container until acetonitrile has been very completely removed as the latter will react on standing with the crystal water with resulting odor of acetic acid.

$$\mathrm{CH_3CN + H_2O \longrightarrow CH_3COONH_4} \qquad (6)$$

$$\mathrm{CH_3COONH_4 + RSO_3H^{6} \longrightarrow RSO_3NH_4 + CH_3COOH} \qquad (7)$$

A 0.1 *M* solution of the acid in dry acetonitrile (Merck Reagent) undergoes a slow change according to equations (6) and (7) (*cf.* also Ref. 2), but if kept at 0° can be used for several weeks.

A 1 *M* solution of acetic anhydride (Merck Reagent, about 95% $(\mathrm{CH_3CO})_2\mathrm{O}$) in dry acetonitrile remains unchanged for months at room temperature.

A 1 *M* solution of water in acetonitrile is also stable for months.

A 0.1 *M* solution of sodium methylate in methyl alcohol (Merck Reagent) keeps a stable titer if it is set up in a closed titration system, protected against carbon dioxide and evaporation. Its absolute value is established by comparing it with standard sodium hydroxide in presence of an equal methanol concentration (about 15%) by titration against hydrochloric acid, using a (minor) correction for the effect of the methanol on the methyl red end-point. Regarding the standardization of sodium methylate *cf.* also Reference 2.

Thymol blue (Hynson, Westcott and Dunning) was used in a 0.125% methyl alcohol solution neutralized with 1 mole equivalent of sodium methylate solution. Approximately 10 drops per 20 cc. end-volume were used in the titrations.

General Technique.—The initial concentration of acetic anhydride preferably should be not higher than about 0.2 *M* in experiments extending over a few hours, or 0.04 *M* in experiments of one day or longer duration. After reaction with the water or alcohol present (including the crystal water of the catalyst and other water present in the blank) not less than 0.01 *M* acetic anhydride should be left. Also, in the alcohol determination the amount of water added to decompose the excess acetic anhydride is regulated so as to leave an unused excess of about 0.01–0.1 *M*. The sulfonic acid concentration of the test is made 0.002–0.004 *M*. Care must be taken to maintain a sufficiently high acetonitrile concentration to prevent crystallization of the sulfonic acid. In the case of ether 5% acetonitrile is sufficient with 0.004 *M* sulfonic acid, even though an opalescence may appear, on standing, while for benzene 10% acetonitrile is necessary.

Suitable amounts of acetic anhydride and sulfonic acid solution are combined immediately before the start of the experiment and equal amounts of the mixture are pipetted for tests and blanks. Glass-stoppered Erlenmeyer flasks, in case of the water determinations dried for several hours in high vacuum in the presence of calcium chloride, should be used. Suitable amounts of the liquid to be analyzed are added to the tests, and after sufficient time has elapsed both tests and blanks are titrated with the 0.1 *M* sodium methylate to a blue end-point. In the alcohol determination, after completion of the alcohol–acetic anhydride reaction excess water solution is added to tests and blanks and allowed to decompose the unused acetic anhydride before the titration is made. After adding to the solutions sufficient methylate to neutralize the sulfonic acid, thereby stopping the catalytic action, the solvent composition of all tests and the blanks is made the same by addition of the required amounts of the liquid used in the tests, and, after addition of indicator, the titration is finished. By this procedure perfect compensation[7] for medium effects on the end-point is obtained, and the absolute color of the end-point is immaterial as long as it is the same in blank and test.

Reaction Times.—No exact kinetic measurements were made in this study since it was realized that each analytical problem would present a different situation with regard to medium and concentration of reagents. It was established, however, that at ordinary temperatures a period of two hours is ample for the completion of the reactions of water, methyl and ethyl alcohol with acetic anhydride under the specified conditions in acetonitrile or a 4:1 mixture of benzene and acetonitrile, while in ether–acetonitrile (20:1 to 10:1) the reactions are approximately ten times slower. In presence of a catalyst concentration of the order of 10^{-2} *M* the water reaction in acetonitrile is complete in less than ten minutes, but as this concentration is, for reasons of solubility, too high for use in the presence of ether and similar solvents, catalyst concentrations about ten times lower were chosen throughout. Completeness of the reaction is made certain by running several tests with varying amounts of solution, varying excesses of acetic anhydride, or for different periods of time.

Practical Examples

Determination of Water. **(a) In Acetonitrile.**—Blanks: 0.045 millimol. $\mathrm{RSO_3H}$ + 1.25 mml. $(\mathrm{CH_3CO})_2\mathrm{O}$ in

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(6) $\mathrm{RSO_3H}$ is used throughout as a symbol for 2,4-dinitrobenzenesulfonic acid.

(7) For maximal compensation the methyl alcohol content of blank and test should also be made equal at the end-point.

4 cc. acetonitrile. Tests: the same as the blank, + 5 cc. acetonitrile. Titration after four hours. Difference between tests and blanks (2 of each): 0.1555 $\pm$ 0.003 (average deviation from mean) mml. methylate. The same amounts of RSO_3H and $(CH_3CO)_2O$, 5 cc. and 10 cc. of acetonitrile. 2 blanks. Titration after twenty hours. Difference from blanks: for 5 cc. 0.156 $\pm$ 0.002, for 10 cc. 0.311 $\pm$ 0.002 mml. Result: the water content of the acetonitrile is 0.0311 $\pm$ 0.0003 *M*. Similar determination on another batch of acetonitrile gave (4 blanks, 1 test with 5 cc., 2 with 10 cc., reagents as before, three hours): 0.0143 $\pm$ 0.0005 *M* H_2O. The water concentration of the former acetonitrile was increased by 0.0206 *M;* found (4 blanks, 1 test with 10 cc.; 2 with 5 cc., reagents as before, three hours) 0.053 $\pm$ 0.001 *M;* calculated 0.052 *M*.

(b) **In Ether.**—For the determination of the minute residual water content of ether treated exhaustively with sodium the following technique was used: 0.225 mml. RSO_3H + 1.4 mml. $(CH_3CO)_2O$ in 5 cc. of acetonitrile, +50 cc. (2 blanks) and +100 cc. (2 tests) ether. Titration after twenty-four hours (1 pair) and after forty-eight hours (1 pair). Difference after twenty-four hours 0.040 mml., after forty-eight hours 0.035 mml. Result: the water content of the dried ether is 0.00075 $\pm$ 0.00005 *M*. The water concentration of the ether was increased by 0.00060 *M;* found by the same technique 0.0011, 0.0012 *M;* calculated 0.0013 *M*. A solution of water and alcohol in ether was made: 0.5644 *M* in water and 0.5241 *M* alcohol (0.2332 *M* C_2H_5OH + 0.2909 *M* CH_3OH). 0.045 mml. RSO_3H + 2.25 mml. $(CH_3CO)_2O$ in 10 cc. of acetonitrile, +4 cc. acetonitrile (blanks), and +5 cc. acetonitrile containing 1 cc. of the ether solution (tests). Titration after three hours (2 blanks and 2 tests): difference 0.567 $\pm$ 0.005 mml., after four hours (2 blanks and 2 tests): 0.568 $\pm$ 0.005 mml.; calculated 0.5644 mml.

Determination of Alcohols. (a) **In Acetonitrile.**—0.11 mml. RSO_3H + 2.1 mml. $(CH_3CO)_2O$ in 10 cc. of acetonitrile, +2 cc. 1 *M* H_2O in acetonitrile (4 blanks), and +25 cc. of acetonitrile (4 tests). After twenty minutes 2 cc. 1 *M* H_2O in acetonitrile were added to 2 tests and after an additional eighty minutes they were titrated together with two of the blanks. Blanks minus tests = 0.002 $\pm$ 0.005 mml. 2 cc. 1 *M* H_2O in acetonitrile was added to the other two tests after one hour's standing and they were titrated, together with two blanks, after an additional two hours. Blanks minus tests = −0.004 $\pm$ 0.004 mml. Results: less than 0.005 mml. of alcohol is present in 25 cc. of acetonitrile, *i. e.*, the alcohol concentration is less than 0.0002 *M*. A 0.00142 *M* solution of C_2H_5OH in acetonitrile was made. Analysis as above gave 0.035 $\pm$ 0.001 and 0.033 $\pm$ 0.005 mml.; found 0.0014 $\pm$ 0.0002 *M* alcohol; calculated 0.0014 *M*.

(b) **In Ether.**—The same dried ether that was used in the water determination was tested for alcohol as follows: 0.225 mml. RSO_3H + 1.8 mml. $(CH_3CO)_2O$ in 5 cc. of acetonitrile, +50 cc. (5 blanks), and +100 cc. (5 tests) ether. 2 blanks and 2 tests to which 2 cc. 1 *M* H_2O in acetonitrile was added after one day were titrated after another day (I). Of 3 blanks and 3 tests to which water solution was added after two days, one pair was titrated after one additional day (II) and two pairs after two days (III). Blank minus test = −0.004, −0.007 mml. (I); −0.010 mml. (II); −0.022, −0.015 mml. (III). The reaction with acetic anhydride of any alcohol should produce a positive difference between blanks and tests. A faint yellow discoloration observed during these protracted periods suggests that the slight tendency toward a difference in the opposite direction is caused by a minor polymerization or decomposition of the acetic anhydride. Tentatively the conclusion is drawn that the alcohol content of the ether is at the most 0.0001 *M*. A solution of 0.00058 *M* C_2H_5OH in this ether is made and analyzed in the same manner. Found after one + one day: +0.023, +0.028 mml., after two + two days: +0.017, +0.013 mml. By using the negative differences obtained in the previous experiment as corrections (−0.006 $\pm$ 0.002 mml. for one + one day and −0.019 $\pm$ 0.004 mml. for two + two days) one obtains 0.00061 $\pm$ 0.00006 *M* and 0.00068 $\pm$ 0.00010 *M*, or an average result of 0.00065 $\pm$ 0.0001 *M* alcohol; calculated 0.00058 *M*. The synthetic solution of water, methyl and ethyl alcohol mentioned above (under Determination of Water (b)) was analyzed for alcohol. 0.045 mml. RSO_3H + 2.26 mml. $(CH_3CO)_2O$ in 10 cc. of acetonitrile, +4 cc. of acetonitrile (4 blanks), and +5 cc. of acetonitrile containing 1 cc. of the ether solution (4 tests). Two cc. of 1 *M* H_2O in acetonitrile was added to two blanks at once and to two tests after thirty minutes. All were titrated after a total of two hours. Blanks minus tests = 0.526 $\pm$ 0.002 mml. Another 2 blanks and 2 tests, after addition of water after two and a half hours, were titrated after a total of six hours. Blanks minus tests = 0.524 $\pm$ 0.002 mml. Found 0.525 $\pm$ 0.003 mml.; calculated 0.524 mml.

Scope and Limitations.—The method seems primarily suited for the determination of small and moderate concentrations of water and alcohol in solvents that are inert against acetic anhydride and low concentrations of a strong acid, and that have no pronounced acidic or basic properties. As two extreme examples acetonitrile and ether, the one with an exceptionally high dielectric constant and the other with a low one, have been studied in detail. By proper modifications benzene (found 0.014 $\pm$ 0.001 *M* H_2O and less than 0.001 *M* alcohol; added C_2H_5OH 0.0602 *M*, found 0.0595 *M*) and chloroform (found 0.049 $\pm$ 0.002 *M* H_2O and 0.20 *M* alcohol) were studied.

The experiments show a maximum practical error of 0.010 mml. for a tested volume of 50 cc. equal to 0.0004% H_2O (by volume) and similarly for the alcohol determination a maximum error of 0.005 mml. for 50 cc. equal to 0.0004% C_2H_5OH or 0.0003% CH_3OH, while for tested volumes of 1 cc. the respective maximum errors encountered were 0.006% H_2O and 0.005% C_2H_5OH.

Substances that under the influence of acid split off water, such as for instance formic acid or acetone (mesityl oxide, phorone and mesitylene formation) should be expected to cause errors in the water determination. While these reactions prevent application of the method to the determination of water in acetone, acetone concentrations of the order of 0.1% or less cause only minor errors when the reaction medium is chiefly acetonitrile. In the water determination of acetonitrile (5 cc. of RSO_3H – $(CH_3CO)_2O$ mixture and 10 cc. of acetonitrile, titrated after three hours) to which 0.1 and 0.01% of acetone had been added, less than 1 mole per cent. of the added acetone reacted as water. In the case of the more protracted reaction in ether the error is more serious so that the presence of acetone should be excluded by specific tests. The fractions of the added acetone reacting as water were, with ether as the medium

Vol. % acetone added		1	0.1	0.01
Mol. % acetone reacted after	1 day	4.7	31	—
	2 days	5.2	37	85

In the case of the 1 and 0.1% acetone concentrations a yellow deposit was formed in the solutions and a very rapid fading of the blue titration end-point took place. It seems probable that the precipitation phenomenon contains the explanation for the inverse variation of the extent of the pseudo water reaction with the acetone concentration.

The question as to how far the respective reaction kinetics make the alcohol method practicable for higher alcohols, phenols, thiol compounds, etc., has not been covered in the present work, as the method is primarily intended for determining the purity of inert solvents with respect to their more common contaminants water and lower alcohols. For the same reason application to the water determination in alcohols has been left in abeyance for the present.

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Summary

The vigorous catalytic acceleration by strong acids in non-aqueous media, of the hydrolysis and alcoholysis of acetic anhydride is shown to be useful as a basis for the separate determination of water and alcohols in inert solvents. The error in concentrations of the order of one per cent. is less than ±1%. The lower limit of response is less than 0.001%.

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Application of the Glass Electrode to Unbuffered Systems

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Introduction

In the realm of unbuffered or very weakly buffered systems the measurement of hydrogen-ion concentration or *p*H value becomes exceedingly difficult and involves considerable uncertainty. Most of the familiar methods of determining the *p*H value have been modified for use in such systems, but complete success can hardly be claimed for practical accurate measurement. For application of the hydrogen electrode to unbuffered systems reference may be made, among others, to the work of Beans and Hammett,[1] Kolthoff and Kameda,[2] and Hammett and Lorch.[3] Similar use of the quinhydrone electrode is described by Best.[4] Colorimetric methods have been discussed by numerous workers, among whom are Stern,[5] Acree and Fawcett,[6] and Kolthoff and Kameda.[2b]

The glass electrode with its obvious adaptability for use in unbuffered systems appears to have received definite attention only recently. Burton, Matheson and Acree,[7] who used a Thompson glass electrode, have given a brief account of some measurements on dilute buffers and distilled water. The development of glass electrode technique to its ultimate refinement has, however, been merely started and the field offers many possibilities for further research.

Accordingly, an extension of the use of the glass electrode and the development of methods whereby the accurate determination of the *p*H

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(1) Beans and Hammett, THIS JOURNAL, **47**, 1215 (1925).

(2) (a) Kolthoff and Kameda, *ibid.*, **51**, 2888 (1929); (b) **53**, 821 (1931).

(3) Hammett and Lorch, *ibid.*, **55**, 70 (1933).

(4) Best, *J. Phys. Chem.*, **34**, 1815 (1930).

(5) Stern, *J. Biol. Chem.*, **65**, 677 (1925).

(6) Acree and Fawcett, *Ind. Eng. Chem., Anal. Ed.*, **2**, 78 (1930).

(7) Burton, Matheson and Acree, *ibid.*, **6**, 79 (1934).