

temperature. In this case the solubility of sodium chloride was found to be 1.6 mg. in 100 cc. of solvent. The carbon occluded by a precipitate of about 0.5 g. of sodium chloride is approximately 1.5–1.0 mg. under these conditions. The weight of sodium chloride in the precipitate can be determined by dissolving it in water, drying the crucible with its carbon impurity, and weighing after filtration rather than before.

Summary

1. A method is described for the separation of sodium and lithium based upon the precipitation of sodium chloride from a solution of the perchlorates in anhydrous *n*-butyl alcohol by the addition of an alcoholic solution of hydrogen chloride.

2. Conditions affecting the accuracy of the process were studied and the accompanying errors eliminated.

3. The solubilities of the anhydrous perchlorates and chlorides of lithium and sodium in anhydrous *n*-butyl alcohol at 25° are given.

4. A table is given showing the density and composition of solutions of hydrogen chloride in butyl alcohol.

5. Test analyses show that one separation gives accurate results even in the presence of large amounts of lithium.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE DEGREE OF IONIZATION OF ETHYL ALCOHOL. I. FROM MEASUREMENTS OF CONDUCTIVITY¹

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Introduction

Ethyl alcohol may be assumed to ionize in either or both of the following ways $C_2H_5OH = C_2H_5^+ + OH^-$, and $C_2H_5OH = C_2H_5O^- + H^+$. The slow formation of ethyl chloride from alcohol and hydrochloric acid is an example of the reactions which indicate some ionization of the first type, while the rather rapid formation of alkali ethylates indicates the second type of ionization. That alcohol is in reality amphoteric, ionizing in both ways, is indicated by the formation of ether. The greater part of the evidence, however, points to the predominance of the second kind of ionization. The formation and decomposition of ethyl esters are slow, whereas there are a large number of smooth and rapid neutralization reactions between acids and alkali ethylates. In the present investiga-

¹ The material here given is taken from a thesis presented by the first-named author in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of California.

tion² the object has been to determine the extent of this ionization into hydrogen and ethylate ions, the amount of the other type of ionization being assumed to be negligibly small.

In a recent article dealing with solutions in ethyl alcohol, Bishop, Kittredge and Hildebrand³ have pointed out the need for a knowledge of the degree to which this important solvent is ionized. The only data to be found in the literature from which this might be calculated are values for the specific conductivity of the pure liquid, and since these values vary among themselves by more than a hundred fold such a calculation would be of little worth. The lowest value to be found is based on a single measurement by Carvalho⁴ of the conductance of alcohol at 17°, and is given as 9.0×10^{-9} "practical units." When this value is calculated as nearly as possible to reciprocal ohms at 25° and is then used to calculate the dissociation constant of alcohol, using the method which is described in detail in a later section, the figure obtained is 1.7×10^{-14} , a value which is nearly twice as great as the corresponding value for water,⁵ 1.006×10^{-14} . Due to the difference in molal volume of the two liquids these figures are, however, not truly comparable and when changed to the more fundamental units, the mole fraction dissociated, show alcohol to be about 5 times as highly ionized as is water. Since this is quite improbable, we may conclude that this lowest value which has been reported for the conductivity of ethyl alcohol is yet far above the true value. We, therefore, undertook to prepare a sample of alcohol of minimum conductivity, making the customary and doubtless quite justifiable assumption that this would be alcohol of maximum purity.

Preliminary Purification of Alcohol

Discussion of Methods.—Though a large number of rather elaborate methods for the purification of ethyl alcohol are to be found in the literature, no specific treatment for the removal of amines and other basic substances has been included. As commercial 95% alcohol may contain appreciable quantities of such substances, a preliminary distillation from a mixture with sulfuric acid⁶ has been adopted. The use of silver nitrate to remove aldehydes and other substances more easily oxidized than the alcohol itself has been quite general. Wildermann⁷ treated alcohol under a reflux condenser for several hours with silver nitrate acidified with nitric

² Preliminary work on this subject was reported in a thesis presented by Bruner M. Burchfiel and Philip S. Danner in partial fulfillment of the requirements for the degree of Master of Science at the University of California.

³ Bishop, Kittredge and Hildebrand, *THIS JOURNAL*, **44**, 135 (1922).

⁴ Carvalho, *Compt. rend.*, **156**, 1755 (1913).

⁵ Lewis, Brighton and Sebastian, *THIS JOURNAL*, **39**, 2245 (1917).

⁶ Borgstrom, unpublished *Thesis*, University of California, 1916.

⁷ Wildermann, *Z. physik. Chem.*, **14**, 232 (1894).

acid; Robertson and Acree⁸ used a neutral solution; and Winkler⁹ employed a suspension of silver oxide made slightly alkaline with potassium hydroxide. The last method has been adopted by us since it is found to be more rapid. A large number of methods have been employed for the removal of water from alcohol, many of which, though probably adequate, are not applicable where more than a few hundred cubic centimeters of liquid is to be dried. The general practice has been to make a preliminary drying with quicklime¹⁰ and then to resort to a more vigorous dehydrating agent to remove the last traces of water. Metallic calcium, which has been widely used for this purpose, was not suitable for our needs because of the danger of producing ammonia,¹¹ while the more vigorous dehydrating agents are undesirable because of the production of ether. Andrews¹² has shown that in so far as density, refractive index and critical solution temperature may be used to measure the water content of alcohol, freshly burned lime is as efficient as metallic calcium in removing water. Kailan¹³ has studied in considerable detail the rate of drying of ethyl alcohol, varying both the amount of lime and the time of treatment. His results show that when the ratio of lime in kilograms to alcohol in liters is approximately $\frac{6}{10}$, a product which is 99.5% pure is secured on boiling for $3\frac{1}{2}$ hours, and 99.9% in 6 hours. He also found that the latter degree of dehydration could be obtained in 575 hours at room temperature. This difference in the rate of drying is greater than would be expected from the difference in temperature alone and seems to point to the formation of a film of insoluble calcium hydroxide over the surface of the lime, which then almost completely stops any further reaction. If this film is kept from forming by constant, vigorous shaking, the rate of drying at room temperature should be considerably increased; and finally, if sufficient surface of pure calcium oxide can be provided, the drying should be practically complete and yet not give rise to appreciable quantities of ether. To this end we have prepared a special sample of lime by burning a mixture of calcium hydroxide and calcium carbonate which had resulted from allowing slaked lime to dry in the air and was thus in the form of an extremely fine powder. When the burning is carried out at a temperature sufficiently high to give complete conversion to the oxide and yet low enough to avoid any amount of sintering, a product is obtained which reacts very vigorously with water. Justification for the assumption that this lime gives a completely dry alcohol will be presented in the following paper.

⁸ Robertson and Acree, *J. Phys. Chem.*, 19, 381 (1915).

⁹ Winkler, *Ber.*, 38, 3612 (1905).

¹⁰ Attributed by Wildermann, Ref. 7, to Erlenmeyer.

¹¹ Moissan, *Compt. rend.*, 127, 497 (1898).

¹² Andrews, *THIS JOURNAL*, 30, 353 (1908).

¹³ Kailan, *Monatsh.*, 28, 927 (1907).

Procedure Adopted.—Commercial 95% alcohol was first distilled from a mixture with sulfuric acid, 5 cc. of conc. acid and 20 cc. of water per liter of alcohol. The distillate was then refluxed for several hours after the addition of about 10 g. of silver nitrate and 1 g. of potassium hydroxide per liter of alcohol. It was then distilled, placed over the best grade of commercial quicklime obtainable, 600–700 g. per liter, and treated under a reflux condenser for about 8 hours. The flask was then tightly corked and subjected to vigorous shaking at room temperature for 24 to 36 hours. The final drying was next effected by distilling onto the specially prepared lime, which was described in the last paragraph, 100–150 g. per liter, and again refluxing for 4 to 6 hours. The alcohol was then ready to be distilled into the vessel in which the final purification and the readings of conductivity were to be made.

Special Precautions.—Wherever it was impracticable to work in sealed glass apparatus, all cork and rubber connections were protected from the alcohol and its vapor by pure tin foil. In all distillations a very efficient still head was used to prevent any spray being carried over. In each distillation except the last the end fractions of the distillate were always rejected. After the first treatment the alcohol was protected from the atmosphere by calcium chloride and soda-lime tubes.

Apparatus

Vacuum Distillation Apparatus.—The vessel in which the final purification and the conductivity measurements were made is shown in Fig. 1. Bulbs A and B were of about

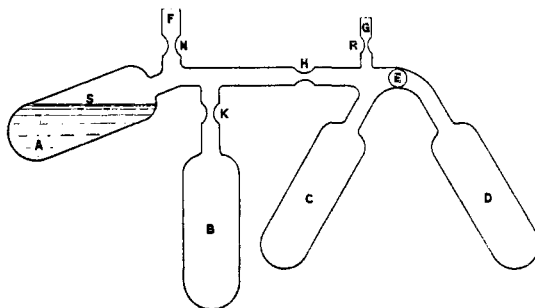


Fig. 1.

250 cc. capacity while C and D were somewhat smaller. Constrictions were made in the tubes at H, K, N and R for ease in sealing off when evacuated. The conductivity cell described in the following paragraph was sealed to this apparatus at E so that it formed a tripod with the bulbs C and D. The final apparatus was constructed of Pyrex glass because of its smaller solubility, its ability to withstand sudden temperature changes and the greater ease in working.

Conductivity Cell.—The cell shown in Fig. 2 was a slight modification of the concentric cylinder type designed by Pfeiffer¹⁴ and modified by Turner.¹⁵ The electrodes

¹⁴ Pfeiffer, *Ann. Physik*, [3] 25, 232 (1885).

¹⁵ Turner, *Am. Chem. J.*, 40, 558 (1908).

were made of heavy, bright platinum foil and were 70 mm. long and about 16 and 13 mm. in diameter, respectively. In previous cells of this type the cylinders have been held apart by glass beads stuck to their edges. With rapid changes in temperature, these beads often become loosened and fall off, allowing the cell constant to vary. To insure against this, the cylinders in the present cell were supported, as shown in the figure, by the lead wires welded at opposite sides of the cylinders and at opposite ends. Just opposite the lead from one electrode a short piece of wire was sealed to the other electrode

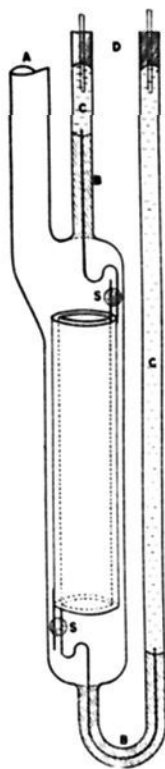


Fig. 2.

and a large bead of sealing glass made to surround both wires, as shown at S, Fig. 2, thus fixing their distance apart. The lead wires were made of stiff platinum wire which had been tempered and was sufficiently elastic to spring the electrodes back into position even when forcibly displaced. Proof of the efficacy of this method of suspension is afforded by the fact that the cell constant did not change by an amount equal to the error of measurement during the whole investigation. The long glass seals at B with the mercury seals at C rendered the platinum-to-Pyrex joint vacuum tight. Heavy copper lead wires were held in place in the mercury by the de Khotinsky cement shown at D. The tube A was sealed to the apparatus of Fig. 1 at E. The total volume of the cell was about 17 cc. and its cell constant was 0.00609, thus making it very satisfactory for use where small amounts of a very poorly conducting liquid are to be used.

Electrical Apparatus.—The Wheatstone bridge type of apparatus was used in making all measurements. The standard resistance was a commercial box with "Curtis" wound coils totaling 100,000 ohms. The bridge was a commercial drum-wound instrument of the Kohlrausch type with a wire 7.5 meters long and with end coils each $4\frac{1}{2}$ times as long. Adjustable air condensers were so arranged that they could be introduced in either half of the circuit as needed. The source of current was, in the earlier experiments, a Siemens-Schuckert high frequency generator and later an "Audio Oscillator." This instrument is simply an induction coil arranged through the use of a tuning fork to give a constant frequency of 1000. While it has the disadvantages attributed to any instrument which does not give a pure sine wave, it was found to be quite satisfactory in the present investigation. It was mounted in a double-walled sound-resisting box and placed in an adjoining room where the sound did not reach the observer. The remainder of the electrical apparatus was placed on a table and electrically shielded in the usual manner.

Thermostat.—The oil thermostat used was of the type which has previously been described in communications⁵ from this Laboratory and was constant to 0.01° .

Final Purification of Alcohol¹⁶

Alcohol from the final treatment with lime, already described, was distilled into the vessel shown in Fig. 1, by connecting the condenser to the tube F. When sufficient liquid had been introduced to fill Bulb A to the level S, F was sealed off at N and the apparatus evacuated through G. The pump was allowed to run for a sufficient length of time to insure the removal of most of the dissolved air, after which the apparatus was

¹⁶ It will be noticed that the method employed here is essentially that which was employed by Kohlrausch and Heydweiller, *Z. physik. Chem.*, **14**, 317 (1894), in their memorable investigation of the conductivity of pure water.

sealed at R. All of the bulbs were washed out a number of times with liquid from A which was then drained back as completely as possible into A. The bulb B was then immersed in a freezing mixture of ice and salt while the remainder of the apparatus was left exposed to the air. Bulb A was arranged at an angle, as shown, so that a thin layer of liquid with a large surface could be secured in as small an apparatus as possible. Convection currents in A due to cooling at the surface by evaporation afforded sufficient stirring so that an actual fractionation could be secured in this way. When about $\frac{1}{3}$ of the liquid in A had distilled, B was sealed off at K, and from $\frac{1}{2}$ to $\frac{2}{3}$ of the remaining liquid was distilled into C in the same manner. The tube was then sealed off at H. The 3 arms of the tripod, C, D and the cell sealed on at E, were so arranged that liquid could be poured from any one to any other without disturbing the contents of the third. Liquid could thus be distilled from C to D and successive portions of the distillate poured into the cell and then back into C. In this way the cell could be washed out several times with the liquid to be measured before each reading was taken, and the whole process could be repeated until no decrease in the conductivity was observed on successive washings. When the cell was first constructed a much larger number of washings were necessary in order to reach this condition than after it had been in use for some time.

Measurements

The cell constant was determined with 0.01 *M* potassium chloride solution, 3 samples of which were prepared at different times from an imported potassium chloride which had been thrice recrystallized from and finally dissolved in, conductivity water. The value given by Noyes and Falk¹⁷ for the equivalent conductance of this solution was used. The cell constant was repeatedly checked during the course of the investigation but at no time was it found to have changed appreciably. In making a reading several settings of the bridge were always made using different resistances in the box. Even in the case of the best samples of alcohol where the resistance was several million ohms, making it necessary to read near one end of the bridge, a setting could be made with an accuracy of 1 part in 20, which is well within the variation among the several samples.

Results

Values of Specific Conductivity.¹⁸—The values for the specific conductivity of alcohol obtained from a large number of measurements, fall quite definitely into groups which are determined by the method of purification. The approximate value for each group will serve to illustrate the importance of the several steps in the method of purification

¹⁷ Noyes and Falk, *THIS JOURNAL*, **34**, 454 (1912).

¹⁸ All values for conductance are given in reciprocal ohms at 25°.

which has been used. The preliminary purification which has been described gave an alcohol whose conductance was 1.0×10^{-7} , subsequent vacuum distillation in the sealed apparatus without the removal of the more volatile portion gave 2.2×10^{-8} while the final value, obtained by removing the more volatile portion and by distilling and washing back many times was 1.35×10^{-9} . The value of successive vacuum distillations and washings of the cell, after the volatile portion had been removed, is illustrated in Table I where results are given for the best 3 samples of alcohol that were obtained.

TABLE I

Number distillations Sample	VARIATION IN CONDUCTIVITY WITH SUCCESSIVE VACUUM DISTILLATIONS				
	0	3	5	10	15
	Specific conductivity $\times 10^9$				
17	90	10.0	4.2	2.20	2.10
18	79	7.7	1.6	1.35	1.35
22	80	8.1	3.6	2.00	2.00

The variation in the minimum obtainable value seemed to be due to the efficiency of the fractionation previous to sealing off the more volatile portion. Samples 19 to 22 were devoted to an attempt to improve this step in the procedure by using an apparatus in which a wide flat-bottomed flask had been substituted for the bulb A (Fig. 1) and a long fractionating column introduced between this flask and the remainder of the apparatus. By keeping the liquid in the flask at 20° , the column at 0° and the receiving bulb, B, at about -2° a considerable amount of refluxing was secured but, as is shown by the figures given above, without the desired result.

A number of attempts were made to secure a further purification by fractional crystallization, using liquid air as the freezing bath, but in every case the alcohol became so viscous before crystals began to form that a separation of the mother liquor from the crystals was impossible.

Calculation of Dissociation Constant.—The dissociation constant of a pure liquid, expressed in volume-concentration units, may be calculated from its specific conductivity according to the relation:

$$K = \left(\frac{\bar{L} \times 1000}{\Lambda_0} \right)^2$$

where \bar{L} is the specific conductance and Λ_0 is the sum of the equivalent conductances of the ions into which the substance dissociates. In the present case Λ_0 is given by the equation

$$\begin{aligned} \Lambda_0 &= \Lambda_{0\text{H}^+} + \Lambda_{0\text{C}_2\text{H}_5\text{O}^-} = \Lambda_{0\text{HCl}} + \Lambda_{0\text{NaOC}_2\text{H}_5} - \Lambda_{0\text{NaCl}} \\ \Lambda_0 &= 79.4 = 80.7 + 41.0 - 42.3 \end{aligned}$$

the equivalent conductances being of course for solutions in alcohol. The values used here were furnished to the authors by Professor W. C. Bray who had made the calculations by the method of Kraus and Bray¹⁹

¹⁹ Kraus and Bray, *THIS JOURNAL*, **35**, 1315 (1913).

from the data of Goldschmidt²⁰ for hydrochloric acid, of Goldschmidt and of Borgstrom⁶ for sodium chloride and of Robertson and Acree⁸ for sodium ethylate. The value of K calculated using the minimum value of \bar{L} from Table I is 2.89×10^{-16} , as compared with 1.006×10^{-14} for water. The value of the dissociation constant expressed in volume concentration units is related to the mole fraction dissociated, N_d , by the equation $N_d = \frac{M\sqrt{K}}{1000\rho}$ where M is the molecular weight and ρ the density. The value of N_d thus calculated for ethyl alcohol is 1.0×10^{-9} and the corresponding value for water is 1.8×10^{-9} . This comparison shows alcohol to be only about $\frac{5}{9}$ as strongly ionized as is water while the best value previously obtainable indicated this ratio to be about 5 to 1.

Discussion of Results

The two very important assumptions upon which this calculation of the degree of ionization of ethyl alcohol is based are, first that all of the conducting bodies are the ions of alcohol and that none are dissolved impurities, and second that all of the ions present are H^+ and $C_2H_5O^-$ with no $C_2H_5^+$ and OH^- ions. Since neither of these assumptions can be strictly true and both may be considerably in error, it is obvious that the degree of ionization thus calculated may still be far too large.

Summary

Methods of purifying ethyl alcohol are discussed.

Improvements in the construction of conductivity cells are suggested.

The conductivity method used by Kohlrausch and Heydweiller to determine the degree of ionization of water has been applied to ethyl alcohol.

A sample of alcohol having a specific conductivity of 1.35×10^{-9} reciprocal ohms has been prepared.

The dissociation constant for alcohol as calculated from the above value is 2.89×10^{-16} . The more fundamental figure, the mole fraction dissociated, is 1.0×10^{-9} as compared to 1.8×10^{-9} for water.

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²⁰ Goldschmidt, *Z. physik. Chem.*, **89**, 129 (1915).