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Conductometric determination of ethanol concentration

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ABSTRACT: Conductivity of the dyes, methylene blue, crystal violet and a mixture of both dyes in aqueous solutions increased with concentration giving a linear relationship in each case. The conductivity of various ethanol concentrations in aqueous solution with dyes and a combination of the dyes generally decreased with ethanol concentration. But the reciprocal of conductivity increased with ethanol concentration, and in a particular case where a mixture of crystal violet and methelene blue was used, the reciprocal of conductivity of the ethanol concentrations was linear.

Key Words: Conductivity measurements; Conductometric determination; Ethanol concentration.

Introduction

Ethanol concentration has been determined by methods such as distillation at 78°C (Hart and Fisher, 1971), use of gas-liquid chromatography (GLC) (Afschar and Schaugeri, 1986) and recently by refractometry (Owuama and Ododo, 1993). However, these methods require electricity, are generally expensive and usually unavailable in some laboratories in developing countries. The distillation process which is readily used to estimate ethanol concentrations from fermentation broths in these laboratories usually yield ethanol distillate of varying concentrations because electricity supply is usually erratic and unreliable for use in thermostatically controlled heating system necessary to obtain absolute ethanol. This work therefore reports on a simple, rapid and accurate method for determining the concentration of laboratory distilled ethanol using a battery operated conductivity meter.

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Materials and Methods

Absolute ethanol (James Borough Ltd., London), crystal violet (BDH Chemicals Ltd.), methylene blue (Ajax Chemicals) and the conductivity meter were used for this work. Preparation of 10, 20, 30, 40, 50, 60, 70, 80 and 90 percent ethanol were made by mixing appropriate volumes of absolute ethanol and MilliQ water. Methylene blue and crystal violet solutions, each at concentrations of 0.000625, 0.00125, 0.0025, 0.005, 0.00625, 0.0125, 0.025 and 0.05% (w/v) were prepared with MilliQ water. Equal volumes of crystal violet [0.05% (w/v)] and methylene blue [0.05% (w/v)] were mixed to produce dye-mixture solution [0.025% (w/v)]. From the 0.025% (w/v) dye-mixture solution, other lower concentrations as prepared for each of the dyes were made by mixing with appropriate volumes of MilliQ water. The conductivity of the dyes and dye-mixture solutions were then monitored at 20^{o}C. A portion (12.5 ml) of 0.0125% (w/v) of the dye-mixture was mixed thoroughly with equal volume of each of the ethanol preparations in a 50 ml Pyrex glass beaker. The conductivity of each of the ethanol/dye-mixture solution was determined at 20^{o}C with a conductivity meter standardised with sodium chloride solution as described by Gordon and Macrae (1987). A portion (12.5 ml) of 0.0125% (w/v) of each dye was also mixed with equal volume of the different ethanol concentrations and the conductivity of each ethanol/dye mixture was determined. The conductivity of the various concentrations of dyes and dye-mixture in aqueous solutions were also monitored.

Results and Discussion

The values of conductivity measurements were averages of three results. The conductivity of each of the dyes or dye-mixture in aqueous solutions increased with concentration. However, the conductivity for similar concentrations differed with the dyes and dye-mixture solutions (Table 1). This may be due to variations in the solubility of crystal violet and methylene blue in ethanol and water, and other inherent properties such as degree of hydration, charge, size and their interaction in the solution (Gordon and Macrae, 1987; Jones, 1907; Conn, 1946; Gurr and MacConaill, 1965).

Table 1: Conductivity of aqueous solutions of different concentrations of crystal violet, methylene blue and crystal violet + methylene blue mixture.

Dye concentration (%w/v)	Conductivity (μS/cm^{-1}) at 20°C		
	Methylene blue (MB)	Crystal violet (CV)	MB + CV
0.000625	6.7	3.8	6.3
0.00125	5.2	5.5	11.0
0.0025	7.9	8.2	12.8
0.005	15.5	14.8	25.0
0.00625	17.5	15.3	28
0.0125	35.3	28.0	57.3
0.025	62.5	59.2	115
0.05	122.5	117.0	225.1

Crystal violet, a hexa-methyl-pavarosanitin has solubility of 1.68% in water and 13.87% in absolute alcohol at 26°C but 9% and 8.75% respectively at 15°C while methylene blue, a basic dye of the thiazine group and theoretically tetra-methyl thionin, has a solubility of 3.55% in water and 1.48% in absolute alcohol at 26°C but 9.5% and 6% respectively at 15°C (Conn, 1946; Gurr and MacConaill, 1965). The variation in the solubility of the dyes in water apparently influences the number of ions in solution and consequently the conductivity. Linear regression analysis showed significant ($P<0.001$) relationship in each case and correlation coefficients of 1.000, 0.999 and 0.999 for dye-mixture, methylene blue and crystal violet in aqueous solutions respectively. The variation in conductivity observed with different concentrations of dye-mixture, crystal violet and methylene blue in aqueous solutions can be represented by equations 1,2 and 3 respectively.

$$y = a + bx$$
$$y = 2.735 + 4447.3x \qquad \text{- Equation 1}$$
$$y = 1.067 + 2289.1 \qquad \text{- Equation 2}$$
$$y = 3.406 + 2384x \qquad \text{- Equation 3}$$

where y = conductivity (μScm^{-1}), x = dye concentration, a = estimate constant and b = dye constant.

The conductivity of crystal violet, methylene blue or dye-mixture aqueous solutions containing different ethanol concentrations decreased with increase in ethanol concentration (Fig. 1). However, a plot of the reciprocal conductivity of the dyes and dye-mixture solutions against increasing ethanol concentration produced linear variations (Fig. 2). Linear regression analysis showed significant ($P<0.001$) relationship and correlation coefficients of 0.967, 0.993 and 0.999 for crystal violet, methylene blue or dye-mixture solutions, respectively. The differences in the solubility of the two dyes in the two solvents and their interaction invariably affects the number of ions in solution with changes in percentage alcohol in aqueous solution. Thus, variation in conductivity may be attributable to increase or decrease in number, type, degree of hydration, mobility and interaction of the ions in solutions, particularly in the case of dye-mixture solution, as the ethanol (a non-electrolyte) concentration increased and water molecule decreased (Gordon and Macrae, 1987; Jones, 1907; Conn, 1946; Jones, 1912).

Using the ethanol/dye mixture solutions which gave the highest correlation coefficient, the variations can be represented by equation – 4:

$$1/y = a + bx$$
$$1/y = 0.032273 + 0.0065091x$$
$$y = 1/(0.0323 + 0.0065x) \qquad \text{Equation 4.}$$

where y = conductivity (μScm^{-1}), x = percentage ethanol, a = estimate constant and b = ethanol constant.

Thus, concentration of laboratory distilled ethanol can be determined by monitoring the conductivity of a mixture of equal volumes of the alcohol and 0.0125% (w/v) dye-mixture solution and reading the concentration off a standard graph or by calculation using equation – 4. However, the conductivity of the test solution must be determined at the same temperature as that used in plotting the standard curve to ensure accuracy since the solubility of the dyes in water and alcohol varies with temperature (Conn, 1946). The conductometric method for determining ethanol concentration has the advantage that it is reliable, easy, quick, inexpensive and requires the use of battery operated conductivity meter.

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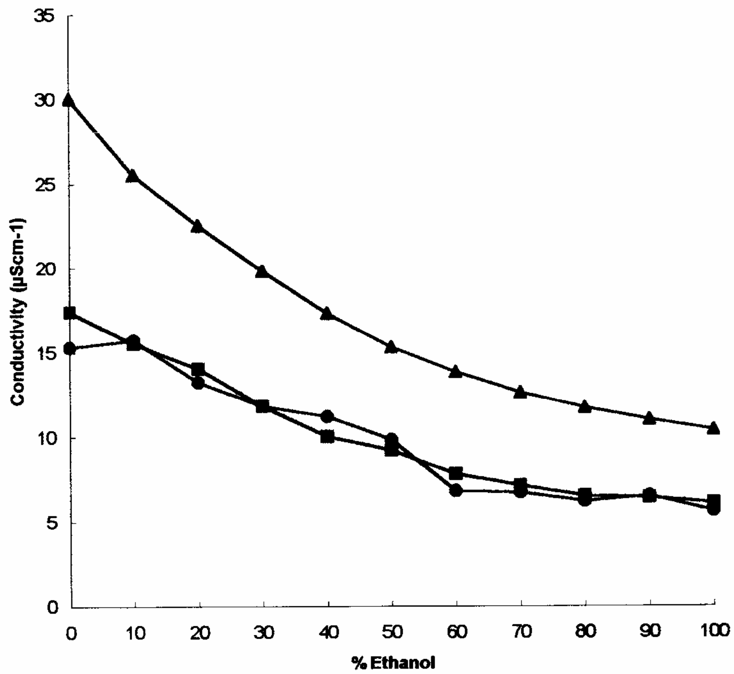

Fig. 1 Variation of conductivities (μScm^{-1}) of aqueous solutions of dyes and dye-mixture mixed with various concentrations of ethanol: (a) Crystal violet, -◆-; (b) Methylene blue, -■- and (c) Crystal violet/ methylene blue, -▲-.

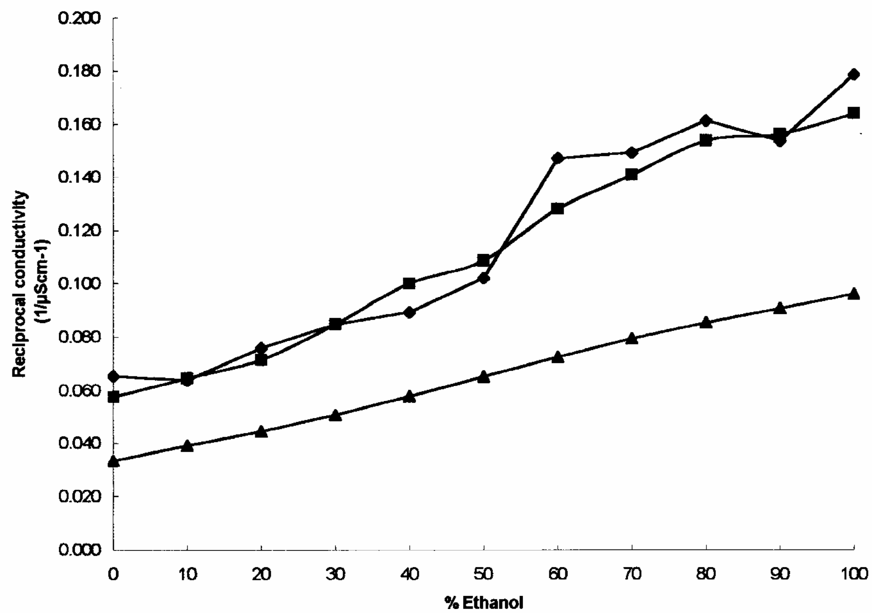

Fig.2 Reciprocal conductivities ($1/\mu Scm^{-1}$) of aqueous solutions dyes and dye-mixture mixed with various ethanol concentrations: (a) Crystal violet, -◆-; (b) Methylene blue, -■- and (c) Crystal violet/ methylene blue, -▲-.

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