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Apparatus For Dielectric Constant Measurements and Measurements For Water-Methanol Mixtures

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Abstract

A system for measuring dielectric constants has been constructed using a Sargent Oscillometer and an air bath for temperature control. The design and construction of the air bath as well as the temperature control achieved with it are described. The overall performance of the system including a computer program for forming the calculations is described. The system is one that requires calibration using two or more standard solvents and is good for both conducting and non-conducting liquids. Data are presented for water-methanol mixtures at 25 degrees with several points near pure methanol and also near pure water.

Introduction

Dielectric constants of pure and mixed solvents are frequently needed to treat kinetic data, electrolyte measurements, and other data in solutions. Values are tabulated for most pure solvents (1) at the more common temperatures, but this is not true for many mixed solvents except water-alcohols (2). With more and more work being done at high and low temperatures, even values for pure solvents frequently need to be measured.

Since the apparatus generally used for measurement of dielectric constants are large, delicate and relatively expensive (2-6), few laboratories are equipped to make these measurements. The major constraint is the space required and the fact that the apparatus cannot be set up and taken down conveniently.

Most systems that have been used are for direct measurement of dielectric constant, but there is a commercial device with which measurements can be made relative to two standards. This device is a Sargent Oscillometer. The Oscillometer is very compact but is not equipped for temperature controlled measurements.

This paper discusses the design of a temperature bath for the Sargent Oscillometer, a computer program for data analyses, and measurements of water-methanol mixtures with the system.

Temperature Bath

Dielectric constant depends on temperature according to the following relationship (7):

$$D = D_0 e^{-L/T} \quad (1)$$

where D is the dielectric constant, T is the absolute

temperature, and D_0 and L are constants for a given solvent. Values of D_0 and L for typical standard solvents are presented in Table I.

TABLE I

Constants for the Equation $D = D_0 e^{-L/T}$ for Standard Solvents (7)

Solvent	D_0	$L \times 10^3$
Benzene	2.95	0.876
Methanol	157.6	5.39
Nitrobenzene	164.7	5.21
Water	311.17	4.63

At any given temperature, close temperature regulation is only important for precise dielectric constant measurements. For nitrobenzene, D is only decreased 0.18 units for a temperature change from 298°C to 299°C. The same temperature change decreases D for water by 0.35 units. However, since many studies where dielectric constants are needed are over wide temperatures ranges, the dielectric constant must be measured over a wide range. For various mixed solvents, a range of at least -20 to 100°C is desirable since this is the most common range for kinetic and other studies in solutions.

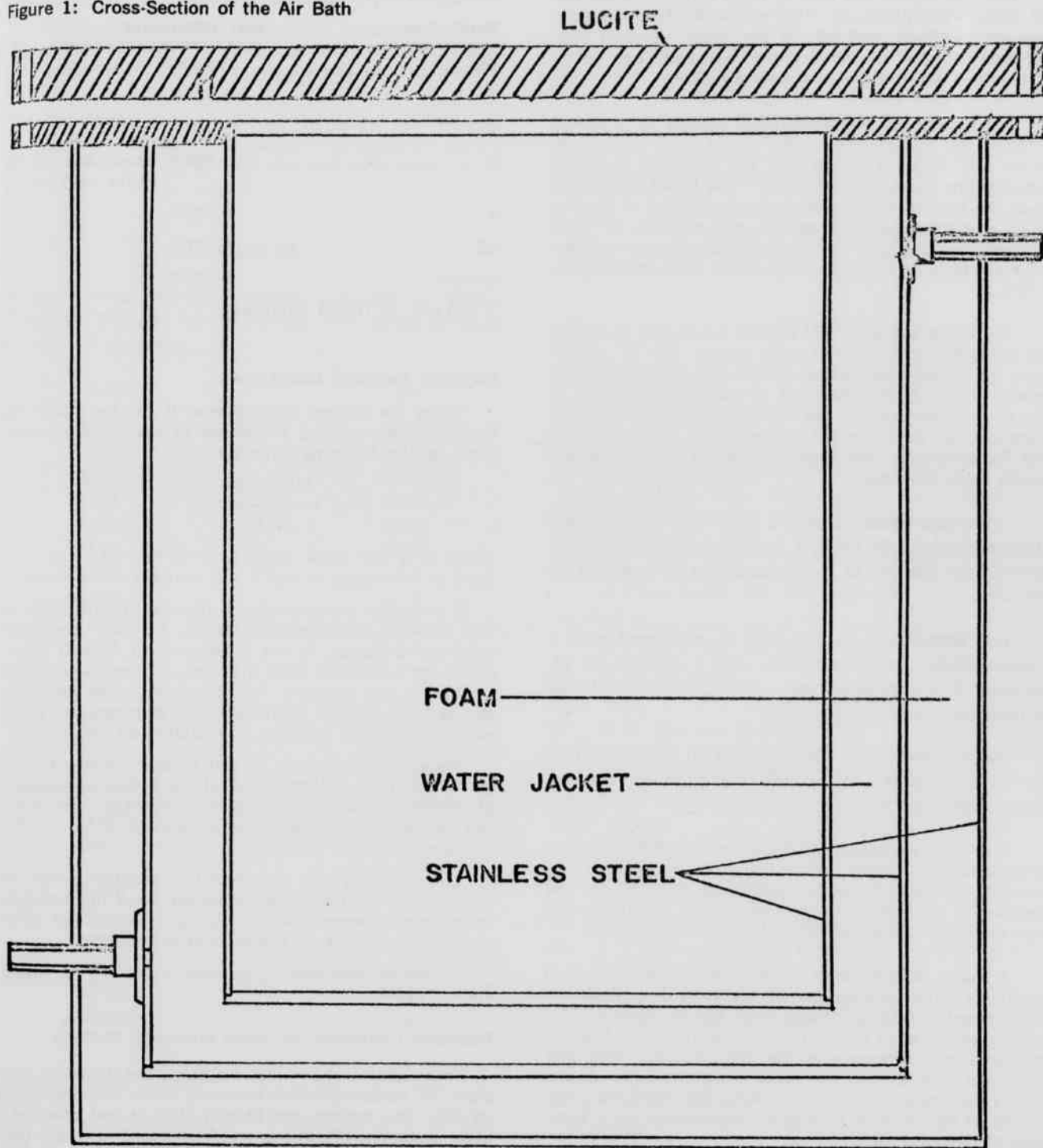
Because of the design of the oscillometer and its cells, the bath media has to be air or some other gas. The cell electrodes are externally applied metal coated areas which will cause fringe electrical loss in conduct-

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ing media such as water. This media requirement was the principal consideration for the bath design. A static system was chosen for easier temperature control since slow equilibration could be tolerated.

The design chosen for the bath is a large jacketed container where the cell could be placed in an air medium that would be maintained at a constant temperature. Figure 1 is a cross-sectional view of the bath.

Figure 1: Cross-Section of the Air Bath



SCALE: 1 inch = 1/2 inch

The bath is constructed of stainless steel so that the problems of corrosion from the circulating liquid are minimized.

The first wall of the bath is filled with Lockfoam No. BX-105-B6 for insulation. This one inch of foam insulation reduces heat exchange to the room. A room temperature variation of two degrees centigrade has no effect on the temperature of the air medium.

The liquid used for temperature control is circulated through the second wall. This liquid is a mixture of water and ethylene glycol and can be used over the temperature range -30° to 150°C. The liquid is pumped in at the bottom of the wall and pumped out at the top at a rate of about two gallons per minute. A short fluctuation of 0.2°C in the circulating liquid has no measurable effect on the cell temperature at thermal equilibrium.

The lid to the bath is made of Lucite and is bolted on to the lip of the bath at eight points. An "O" ring is used for a tight seal so that air movement to the atmosphere is minimized. There is a hole in the center of the lid to allow entry of the thermocouple and the cable from the cell holder to the oscillogram. The cable and the thermocouple pass through a No. 3 rubber stopper which seals the hole.

The cell holder is placed in a resin stand of low thermal conductivity so that basically no heat is transferred from the cell to the walls of the bath except by the air.

The temperature in the bath is monitored with a copper-constantan thermocouple with a melting ice reference. A K-3 potentiometer with a D-C null detector is used for measuring the EMF.

The described bath was operated at $25.00 \pm 0.05^\circ\text{C}$ for several weeks. In general, the deviation was approximately 0.01°C.

A sample previously thermostated at 25°C and then transferred to the cell in the bath requires about thirty minutes to reach thermal equilibrium at 25°C. If the sample is at room temperature (22°C), approximately one hour is required to attain thermal equilibrium.

A major concern with a static air bath is thermal gradients. The temperature of the bath was measured at different depths and these data are in Table II. The maximum variation of the EMF in the region of the cell amounts to a difference of less than 0.02°C. This data indicates that at thermal equilibrium the bath design meets the requirements for measuring dielectric constants of liquids with a Sargent Oscillometer as a function of temperature.

TABLE II

Temperature as a Function of Depth in the Air Bath. Temperature Given as EMF with a 0.0° Reference Using a Copper-Constantan Thermocouple

Depth (inches)	EMF (Millivolts)*
Top	0.9800
2	0.9845
4	0.9872
6	0.9901 (Maximum Height of the cell)
8	0.9894
10	0.9900
Bottom	0.9900

* ($25.0^\circ\text{C} = 0.990$ millivolts)

Dielectric Constant Calculations

Using the Sargent Oscillometer, it can be shown (8) that the scale reading is related to the dielectric constant by the following equation:

$$S = \frac{A(D - 1)}{1 + BD} \quad (2)$$

where S is the scale reading, D is the dielectric constant of the liquid, A and B are complex cell constants.

A computer program was written in FORTRAN IV so that several measurements taken for two standards could be averaged, A and B determined, and D determined for unknowns from averages of several measurements. In this manner, four place dielectric constants should be calculated statistically and standard deviations established. (This program is available on request.)

Equation 2 is limited in that organic standards cannot be used for determination of the dielectric constant of conducting solutions. However, methanol and water can be used as standards for conducting solutions if a precision of a few tenths of a percent is acceptable.

Using the system for dielectric constant measurements, the best results are obtained when the unknown values are between the two standard values. In other words, interpolation is better than extrapolation.

A similar procedure has been used for a water-ethanol system (9).

Dielectric Constants for Water-Methanol Mixtures

In order to test the entire system, the dielectric constant of water-methanol mixtures were determined at 25.0°C. This system was chosen since it had previously been measured (2) at ten weight percent intervals over

the entire range. There also was some interest in possible discontinuous changes in dielectric constant near pure methanol and pure water since some electrochemical measurements appeared to be discontinuous in these regions (10).

Triply, glass distilled water and redistilled spectrograde methanol were used as standards as well as solution preparation. The nitrobenzene was vacuum distilled (11).

Using methanol and water as standards, the dielectric constant for nitrobenzene was found to be 34.85 at 25°C which is in good agreement with the NBS value (1) of 34.82.

TABLE III

Measurements for the Dielectric Constant of Water-Methanol Mixtures at 25.0°C as a Function of Mole Fraction of Methanol

N _{MeOH}	D ₂₅
.9773	33.4 ₅
.9548	34.1 ₂
.9346	34.7 ₆
.9141	35.3 ₉
.8935	35.9 ₅
.8736	36.5 ₄
.8547	37.0 ₈
.8354	37.7 ₃
.8176	38.3 ₀
.7994	38.8 ₃
.6400	43.7 ₅
.5092	48.5 ₂
.3999	53.5 ₅
.3076	58.2 ₃
.2283	62.6 ₈
.1600	66.9 ₉
.09988	71.3 ₃
.04715	74.8 ₀
.04185	75.1 ₃
.03716	75.8 ₃
.03262	76.1 ₁
.02773	76.3 ₄
.02291	76.7 ₀
.01836	77.1 ₄
.009131	77.8 ₆

All water-methanol mixtures were prepared in 100 ml volumes by weight. Mole fractions of methanol were calculated from these weights which were corrected for air buoyancy.

The data for water-methanol mixtures at 25°C are presented in Table III. These data are in good agreement with the data of Akerlof (2) below a mole fraction methanol of 0.4, but are higher at higher mole fractions. However, Akerlof's data has a dielectric constant of 31.5 for pure methanol which is below the 32.63 value in the NBS Circular No. 514. The data in Table III extrapolate to a value of 32.7 for pure methanol which is in good agreement with the NBS value.

The water-methanol data product a smooth curve with no discontinuities at either extreme which means that the electrochemical results must be explained by something other than bulk dielectric constant changes.

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