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Closed System Electrical Conductance Apparatus for Non-Aqueous Systems

By ALEXANDER I. POPOV, WILLIAM A. DESKIN
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INTRODUCTION

Studies of electrical conductance in non-aqueous solvents is often hampered by the ability of the solvents to absorb moisture and/or carbon dioxide from the atmosphere. Even small traces of these impurities may alter considerably the conducting properties of the solution and render the measurements invalid. The errors become especially important when the solutes are highly hygroscopic themselves. The usual technique for cases where contact of solutions with the atmosphere is to be avoided is to prepare them in a conventional dry-box. This renders the operation tedious and time-consuming especially when a number of exact dilutions have to be made. These disadvantages could be eliminated by the use of a closed system in which the solvent is purified, the solution prepared, accurate dilutions made, and the electrical conductance measured in a completely inert atmosphere.

A closed system has been recently described (1) in which it is possible to prepare the solutions and to measure their conductances out of contact with atmospheric moisture. This apparatus is only applicable when the solute is in a liquid state and it is not convenient for carrying out precise successive dilutions.

A modification which seems to eliminate the difficulties of this apparatus has been constructed, and its performance has been found to be quite satisfactory in a study of the electrical conductance of interhalogen compounds in non-aqueous solvents (2).

DESCRIPTION OF THE APPARATUS

A schematic diagram of the apparatus is given in Figure 1. The system is constructed of Pyrex glass and the individual parts are connected by either standard taper or ball joints. In order to avoid contaminations by stop-cock grease, the latter were lubricated by a fine layer of platinum. The essential components are a standard distilling assembly, two receiving flasks, a solution flask, a thermostated dilution chamber, and a thermostated conductivity cell with two pair of electrodes. The volumes of the two receiving flasks, #1 and #2, are 500 and 2000 ml., respectively.

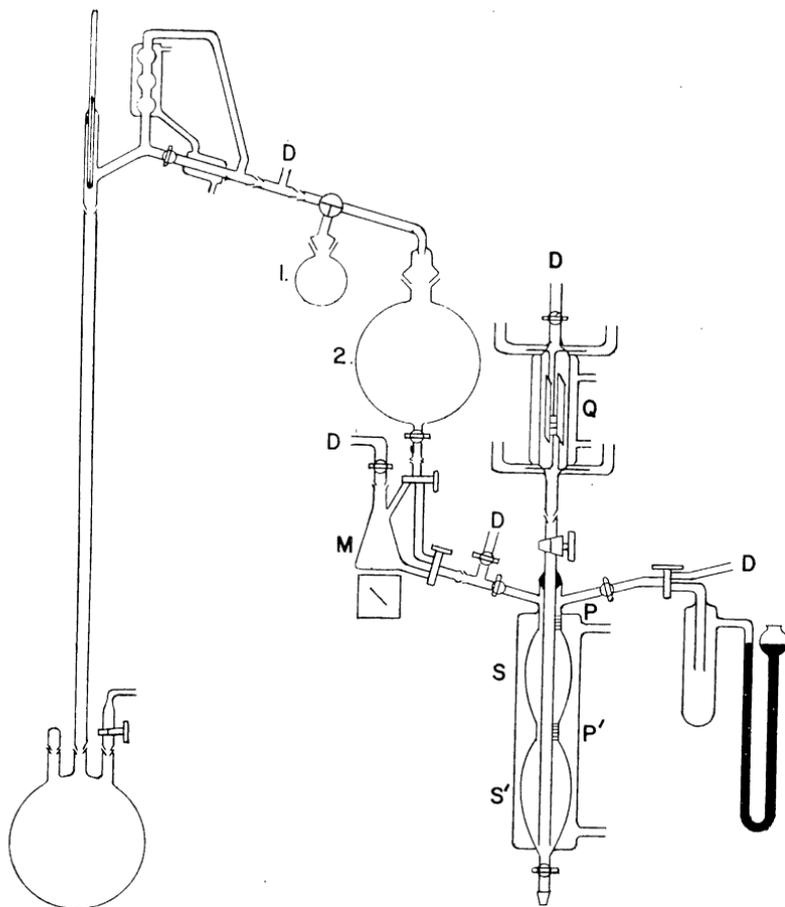


Fig. 1. Schematic diagram of the apparatus.

The solution flask M is made from a 125 ml. erlenmeyer flask and good mixing is ensured by use of a magnetic stirrer. The dilution chambers, S and S', have volumes of 49.89 and 46.45 milliliters, respectively. These chambers have calibrated necks, P and P'. The upper neck P has 0.087 ml. per division and the lower one, P', 0.089 ml. per division. Drying tubes were connected at points D to protect the system from atmospheric moisture.

The cell constants for the conductivity cells in chamber Q were determined by use of aqueous potassium chloride solutions of known concentrations at 25°. The potassium chloride was recrystallized twice from conductivity water and fused in a platinum crucible. The equivalent conductance values for the potassium chloride solutions were taken from the literature(3). Results are given in Table

\bar{i} and represent the average of two values which agreed to better than 0.3%. The results in each case were corrected for the conductance of the solvent. These cells are designed so that the leads are brought out at opposite ends of the cell in order to minimize the "Parker effect" (4).

The dilution chamber and the conductivity cell were jacketed and a constant temperature was maintained by circulating an ethylene glycol-water mixture from a constant temperature bath which was regulated at $25 \pm 0.02^\circ$.

Table 1
Cell Constants of Closed Apparatus as Determined from Aqueous Potassium Chloride Solutions at 25°

Conc. <i>M.</i>	Electrodes	
	Small	Large
0.00200	0.1739	—
0.00100	0.1737	—
0.00050	0.1735	0.0644
0.00020	0.1732	0.0640
0.00010	0.1728	0.0638
0.00005	—	0.0634

MANIPULATION OF APPARATUS

When it was necessary to prepare a solution and to measure its electrical conductance in the apparatus each component part of the apparatus was dried in an oven at 150° . The apparatus was then assembled and dry nitrogen was passed through it for at least six hours and often over night. The solution flask was then removed to the dry box, loaded with solute and returned to the apparatus. Dry nitrogen was again passed through the apparatus, by-passing the solution flask for an additional hour.

Two liters of previously purified solvent was added to the distillation assembly and refluxed for two hours with an appropriate purifying reagent. The head fraction of approximately 500 ml. was then collected in the small receiving flask and the middle fraction of approximately one liter was collected in the large receiving flask and was used in subsequent operations. With the proper manipulation of the stop cocks solvent was allowed to flow into the solution flask. Mixing was obtained by means of a magnetic stirrer. When the solute was completely dissolved, the solution was then allowed to flow into the dilution chamber. The solution flask was then rinsed with small portions of fresh solvent and the rinses were added to the dilution chamber so as to bring the meniscus to the graduated neck P. By means of the mercury leveling bulb the solution was mixed by pumping it in and out of the conductivity cell. After a period of time necessary for thermal equilibrium to be obtained the

solution was raised to the cell and the resistance was measured.

After the resistance had been measured the solution was drained back into the dilution chamber and the amount of solution retained by chamber Q was obtained from the difference in the level of the meniscus in the upper neck, P. The solution was then removed from the dilution chamber through the bottom stop-cock, until a reading could be made in the lower neck, P'. Solvent was added, by-passing the solution flask, until a reading could be made in the upper neck of the dilution chamber. Since the volumes of S and S' are accurately known, together with the amount of solution retained by S and Q, the concentration of the new solution could be calculated.

The concentrations of the original solutions were obtained in the following manner: if the solute was such that it could be weighed accurately, the concentration could be calculated by knowing the weight of the solute and the volume of the dilution chamber. If the solute could not be weighed accurately as in the case of halogen and interhalogen compounds, the concentrations were determined spectrophotometrically and by an iodometric titration on a portion of the solution which was removed from the apparatus.

RESULTS

After the cell constants were determined and the volume of the dilution chamber measured, the performance of the apparatus was checked. By placing conductivity water in the large receiving flask, #2, and loading the solution flask with a known weight of potassium chloride an aqueous solution of known concentration was prepared. The conductance of this solution as well as of those obtained by successive dilutions were measured. The data for these measurements are given in Table 2. Reasonable accuracy was obtained with an error of 0.5% or less.

Table 2
Equivalent Conductance of Aqueous Potassium Chloride Solutions Measured in Apparatus at 25°

Conc. x 10 ⁴	(obs.)	(lit.) (3)
5.15	148.5	147.8
2.53	148.7	148.4
1.25	149.4	148.8
0.61	149.8	149.1

The apparatus was also checked with solutions of tetrapropylammonium iodide in acetonitrile. The solutions were prepared using acetonitrile which had been distilled in the apparatus. The solution flask was loaded with a weighed amount of the solute in the dry box and the solution prepared as outlined above. The data in Table

3 were obtained on these solutions and the literature values are those reported by R. Rygg (5), which were obtained using the conventional technique.

Table 3
Equivalent Conductance of Tetrapropylammonium Iodide in Acetonitrile
Measured in Apparatus at 25°

Conc. x 10 ⁴	(obs.)	(lit.) (5)
2.66	167.9	167.1
1.30	169.6	169.5
0.64	169.4	171.2

The apparatus has been used quite satisfactory in the study of the electrical conductivity of iodine monochloride in acetonitrile and these results will be published at a later date.

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