In the determination of copper, zinc and manganese in the same solution there is intermetallic compound formation between copper and zinc in the mercury thin-film electrode; the stripping potential of Cu-Zn is almost coincident with that of copper. In order to overcome this we determine copper alone (deposition at -0.5V), and then deposit zinc and copper together (deposition at -1.25V): simple subtraction of the copper concentration from the copper plus zinc value gives the zinc concentration. In addition to regular stripping of the mercury film from the disc electrode, this was found to give reliable and accurate results.

An important advantage is that the same wall-jet sensor can be used for copper, zinc and manganese present in the same solution. We have applied it to the analysis of these trace elements in nutrient solutions for hydroponic cultures. No interferences from other species present in the nutrient solution were found.

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# DIELECTRIC PROPERTIES OF BINARY MIXTURES OF CYCLOHEXANOL AND NON-POLAR LIQUIDS

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## INTRODUCTION

Data on dielectric properties of cyclohexanol are scarce and those available quoted from rather old sources. As we need the values for the dielectric constant and electrical dipole moment for this compound some work has been done in order to determine these properties.

In this paper results for the static dielectric constant of cyclohexanol at temperatures between 12 and 35° C and of binary mixtures of this compound with cyclohexane and carbon tetrachloride at 25° C are presented. From these results it is possible to determine the electrical dipole moment of the polar component. The reason for using two non-polar solvents is to see to what extent the non-polar component plays any role in the value obtained for the dipole moment.

## EXPERIMENTAL

The dielectric properties have been measured with a Sargent oscillometer whose features have been described in another paper presented

at this Conference[1]. In the same paper are given the outlines of the technique used in measurements.

The instrument works at a resonance frequency of 5 MHz and the capacitance readings are expressed in arbitrary units. For converting instrumental readings into dielectric constants a working curve is needed, which was obtained using liquids of known dielectric constant, most of them recommended as dielectric standards.

The cell is a space between two concentric glass cylinders whose external surface walls are covered by fused metal.

All solutions were prepared by weight in humidity-free conditions and the liquids dried and distilled before use.

## RESULTS

The instrumental readings obtained for dielectric standard liquids in the range of dielectric constants 1.882 and 17.51, using a 4.9 µH inductance inserted in the electrical circuit in series with the cell, are represented in Fig. 1. The data fit the equation

$$S = \frac{2404(\varepsilon - 1)}{1 + 0.021\,\varepsilon}$$

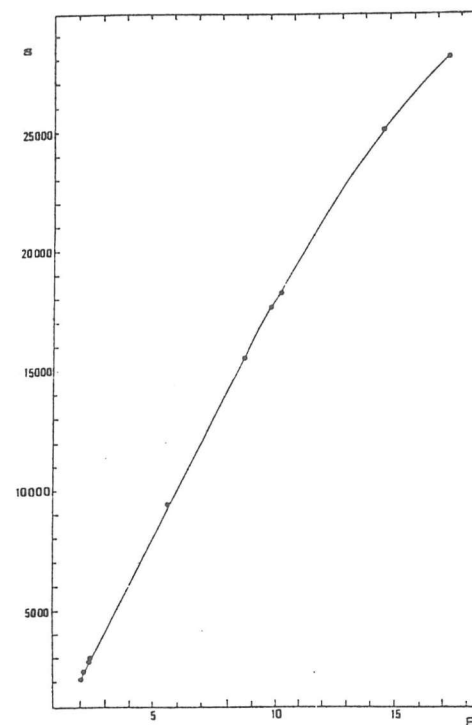S are the readings in the instrumental scale units and ε are the dielectric constants.

Fig. 1. Instrumental readings against dielectric constants for 4.9 uH series inductance

The values of ε for cyclohexanol as a function of the temperature are plotted in Fig. 2. It can be observed that at temperatures higher than 22.4° C cyclohexanol behaves as a liquid, since ε decreases regularly (0.125 per degree centigrade) as temperature increases. At temperatures below 18.6 the compound is in the solid state, as ε is constant with temperature (ε = 15.7). Just before melting a structural change occurs giving rise to a more favourable alignment of the dipoles and hence to an increase in ε.

The existence of polymorphism in the solid cyclohexanol has been well established since a long time however only one author has found a crystalline form transition just before melting [2,3].

The values quoted in literature for the melting point of the cyclohexanol are very different from each other[4,5]. From our results the value found is 22.4° C.
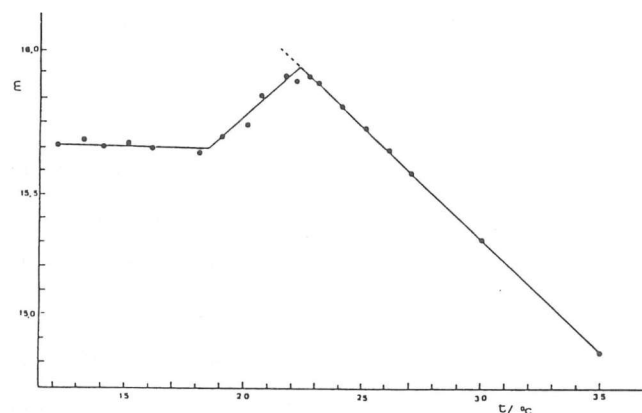
Fig. 2. Dielectric constant of cyclohexanol in the temperature range 12 - 35° C

The value obtained for $\varepsilon$ of the cyclohexanol at 25° C is 15.79, significantly different from that given by Williams[6].

In Fig. 3 the results obtained for $\varepsilon$ are plotted against the molar volume fraction of cyclohexanol. In the same figure a line corresponding to the Böttcher formula for cyclohexanol/cyclohexane is drawn. This is one of the various formulae derived for $\varepsilon$ of spherical particles of random orientation uniformly embedded in a continuous medium[7].

The curves obtained for both mixtures are identical and both seem to show that up to $\phi = 0.4$ the non-polar component produces a decrease in $\varepsilon$, whilst for $\phi > 0.4$ the structural ordering is dominated by molecular interactions between polar molecules, although apparently the non-polar component favours the dipole alignment.

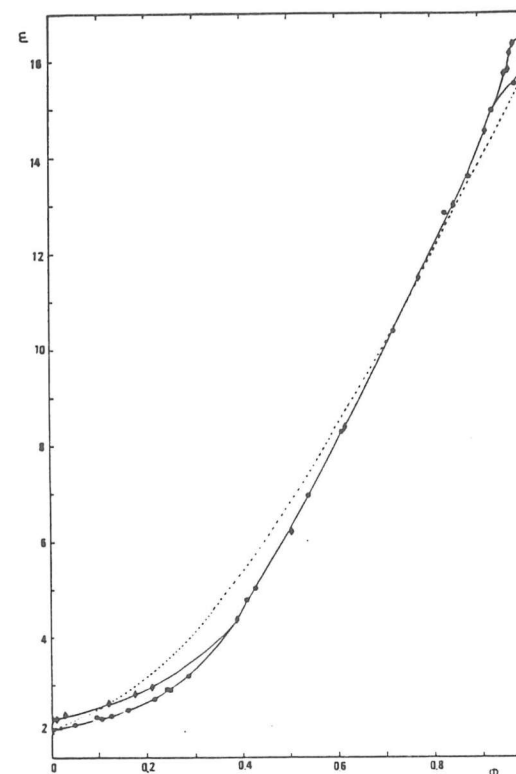For lower $\phi$ the molecular interactions between non-polar parts of

Fig. 3. Dielectric constant vs fraction molal volume of cyclohexanol/non-polar solvent mixtures.
● Cyclohexanol/cyclohexane. ◆ Cyclohexanol/carbon tetrachloride

both components are strong enough to make more difficult the dipole orientation of the polar molecules towards the electric field. For $\phi > 0.4$, interactions between polar molecules are important and the resulting structure favours a parallel orientation of the dipoles. However this ordering seems to be reinforced by the non-polar molecules since for mixtures richer in cyclohexanol $\varepsilon$ is higher than should be expected. This means that in the presence of the non-polar molecules the alignment of the dipoles is better than in pure cyclohexanol.

The effect of the non-polar molecule appears to remain up to $\phi = 0.93$ for cyclohexane and to $\phi = 0.98$ for carbon tetrachloride, where $\varepsilon$ reaches a maximum.

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# DETERMINAÇÕES POTENCIOMÉTRICAS POR ANÁLISE DE INJECÇÃO EM FLUXO. DESENVOLVIMENTO E UTILIZAÇÃO DE UMA CÉLULA DE FLUXO COM MÓDULOS DESCARTÁVEIS

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São muitas as situações que requerem a avaliação analítica de grande número de amostras num diminuto espaço de tempo. Para o efeito, torna-se imperiosa a utilização de técnicas analíticas adequadas.

Uma das possibilidades de conciliar tempo e qualidade de resposta reside na aplicação de análise por injecção em fluxo, FIA, que basicamente envolve a injecção duma amostra, directamente num transportador de fluxo, que pode ou não reagir com a amostra e que conduz a zona de amostra para um detector apropriado.

Recorrendo a

. condutores de pequeno diâmetro interno (ordem de 0,5 mm)

. detectores de passagem de fluxo de pequeno volume

. grandes velocidades de fluxo

. automatização

resulta um sistema que oferece

. rápida análise de grande número de amostras

. anulação de tempos mortos

. elevada precisão