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Determination of the water content of amphiphilic liquid crystals by coulometric Karl Fischer titration

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An apparatus is described, which allows the precise determination of the water content of amphiphilic liquid crystals by means of coulometric Karl Fischer titration. The scope and limitations of this method are described.

1. Introduction

The investigation of amphotropic liquid crystals is an important topic in contemporary liquid crystal research [1]. One reason is that these compounds bridge the gap between two classical types of liquid crystalline materials, the thermotropic liquid crystals with a rod-like, poly-catenar or disc-like molecular geometry which became technologically relevant, and the lyotropic liquid crystals consisting of detergent/water mixtures, which are of special interest as mimics of biological membranes.

The amphotropic properties can be realized by combining hydrophilic polar groups, such as ionic groups, polyether chains or polyhydroxyl groups, with a calamitic, a discotic or a taper-shaped molecular structure. Many of these compounds can readily take up moisture from air during their preparation, purification and storage. These small amounts of water significantly change the mesomorphic properties, and this water has to be removed before the investigation of the thermotropic behaviour of such compounds can be made. The investigation of their lyotropic behaviour in water does not necessarily require strict drying, but on the other hand the amount of adsorbed water must be exactly known. A highly sensitive and specific method for the determination of very small amounts of water is therefore required for these investigations.

2. Experimental set-up and measurements

Coulometric titration according to Karl Fischer is a sensitive standard method for water determination in

the microgram range [2], and modern computerized techniques allow the precise determination of water in liquids and solids [3]. If the sample is inert towards the reagent, it can be added directly into the titration vessel. Another mode of operation involves the liberation of the water from the sample at elevated temperatures by passing a stream of a carrier gas over the sample, sweeping the water vapour into the reagent solution. This method can be used for any compound, even those with functional groups interacting with the Karl Fischer reagent (e.g. double and triple bonds) [4]. This method should therefore enable the precise determination of water in amphotropic liquid crystals. A serious problem with this method arises from water contamination of the carrier gas which can give rise to errors. Therefore an apparatus was developed by Spohn *et al.* [5], in which the gaseous phase above the titration vessel is used as the carrier gas and is circulated in a closed system.

The heating chamber of this apparatus is displayed in figure 1. The sample (*c.* 5–10 mg) is placed between two pieces of ceramic wool (RAD, Meissen, Germany) which are located in a glass container dried in an oven at 200°C. This container is put into the heating chamber. A stream of the dry carrier gas is blown over the sample; it then passes through the coulometric cell which contains the Karl Fischer solution. The liberated water reacts immediately with the reagent by reduction of iodine to iodide ions, which are detected by a biamperometric electrode system. The iodine is electrochemically regenerated, the applied electric current being proportional to the amount of water consumed (Faraday's Law). After passing through the Karl Fischer solution,

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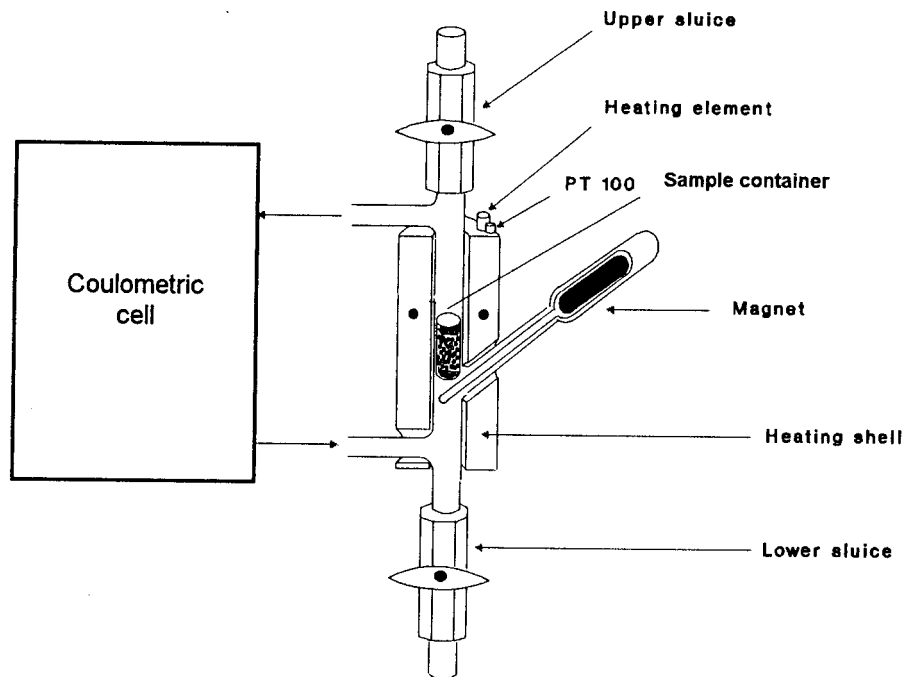
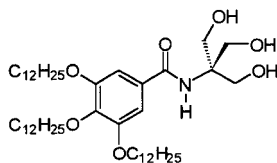


Figure 1. Heating chamber and sample positioning in the coulometric Karl Fischer titrator AQUA 20.00. The sample container is inserted through the upper sluice and removed, after measurement, through the lower sluice.

the water-free carrier gas again passes over the sample. The sample is heated at a rate of $2^{\circ}\text{C min}^{-1}$ up to 250°C and the amount of water desorbed from the sample is monitored as a function of the temperature.

3. Results

The desorption curves of compound **1** as obtained directly from synthesis (curve A) and of a freeze dried sample of compound **1** (curve B) are shown in figure 2.



This example was chosen because this compound represents an especially difficult case; it is extremely hard to obtain a water free sample. As can be seen from the desorption curves, the material obtained by the conventional work up procedure contains large amounts of water (*c.* 3 mol). The water bound to the surface is immediately removed, whereas the more tightly bound water is only liberated above 150°C . In fact it can be completely removed only by prolonged heating of the sample to 250°C . Even in the freeze-dried sample (B) a significant amount (*c.* 0.8 mol) of water can be found. Therefore we conclude, that the water cannot be completely removed from this material by a single freeze drying cycle. This has to be repeated several times until the absence of water is proved. The observed mesophase type and the transition temperatures strongly depend

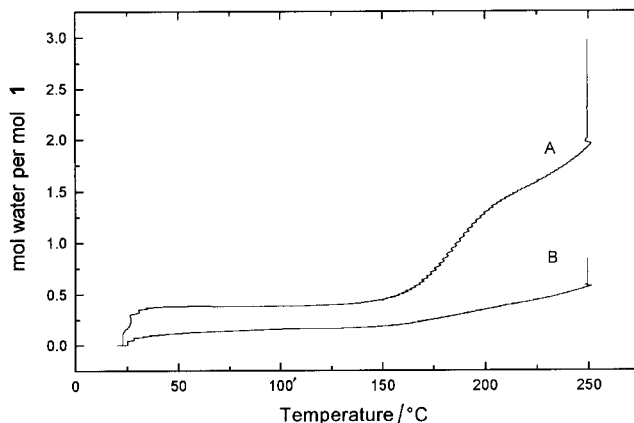


Figure 2. Thermodesorption curves (2K min^{-1}) of two different samples of compound **1** (curve A: as obtained from a conventional work up procedure, curve B: freeze dried sample). The steep straight lines at the ends of the curves result from continuing water desorption at the final temperature of 250°C . This temperature was held until water desorption was complete.

on contamination with small amounts of water. Only the completely dried sample displays a cubic mesophase (transition temperatures: Cr 48 Col_{H2} 65 Cub₁₂ 78 I, $^{\circ}\text{C}$; abbreviations Cr=crystalline solid, Col_{H2}=hexagonal columnar mesophase, Cub₁₂=inverted miscellar cubic mesophase, I=isotropic liquid) [6]. The compound obtained directly after the usual work up procedure has only a hexagonal columnar mesophase (Cr 62 Col_{H2} 75 I, $^{\circ}\text{C}$). The transition temperature from the columnar

to the cubic phase decreases with decreasing water content of the sample.

4. Discussion and conclusions

Investigation of several different amphiphilic liquid crystals has shown that the water absorption behaviour strongly depends on the molecular structure. There are several compounds which can take up moisture only in the liquid crystalline state, the crystalline solid being non-hygroscopic. Other compounds lose their water completely after heating to temperatures approximately 20–50 K above the clearing temperature, whereas some compounds cannot be dried in this way, and retain their water until temperatures are used such that serious decomposition occurs.

The method described here allows the rapid and selective determination of small amounts of water in many amphiphilic liquid crystals. The main advantage of this method consists in its high sensitivity (low microgram range, in comparison to the milligram range of thermogravimetry) and therefore only very small samples are necessary. Furthermore it allows the selective determination of water.

It is, however, not possible to follow the water desorption process as a function of its effect on the phase

transitions. This is due to the fact that the circulating carrier gas contains methanol vapour (the solvent of the Karl Fischer reagent). Because methanol can be adsorbed by the amphiphilic molecules, their phase behaviour may change under these conditions.

We use this method to monitor the success of different drying methods. Furthermore one can check whether the water can be removed simply by heating to a certain temperature which is below the decomposition temperature. The temperature and time required for complete removal of the water can also be roughly estimated.

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