Solubility of Water in Diethyl Ether at 25°

By H. H. Rowley and Wm. R. Reed[1]

During the course of another research problem it became necessary to know the correct solubility relationships of diethyl ether and water at 25°. Numerous values were found in the literature, but the agreement was poor and many of the methods of doubtful accuracy. The volumetric method of Hill[2] and Kablukov and Malischeva[3] appears to be the most reliable but, even using the same method, their results are not in good agreement. It was, therefore, decided to determine the value for the solubility of water in diethyl ether at 25° using the Karl Fischer reagent for the determination of water.

Experimental

The Karl Fischer reagent was prepared by accepted methods,[4-7] standardized against weighed samples of water and used to standardize a methanol-water solution. The dead-stop end-point method[8,9] was used with mechanical stirring for all standardizations and analysis of samples. When analyzing a sample for water, it was found that more precise results were obtained if the sample was added to a measured excess volume of Karl Fischer reagent. The excess Karl Fischer reagent was titrated with the methanol-water standard solution.

All systems of purified diethyl ether and water were brought to equilibrium in a water-bath at 25 ± 0.05° by means of a motor-driven stirrer with two agitators at different levels to ensure true equilibrium conditions. It was found that equilibrium was established within four hours under the conditions of the experiment. The system was allowed to stand unstirred for an additional hour to allow for complete separation of the two layers before analysis.

A desired volume of sample was drawn into a cooled, weighed pipet of suitable design and removed from the system. After sealing, to prevent loss of sample, the pipet and contents were weighed. The sample was then transferred quantitatively into excess Karl Fischer reagent and analyzed.

A number of diethyl ether-water systems were prepared and at least two independent samples were analyzed for each system. The average weight per cent. of water in diethyl ether was found to be 1.468%. The standard deviation of the mean for twelve determinations was 0.003. The average weight per cent. of diethyl ether is 98.532% by difference.

Discussion.—Many workers[2,3,10-14] have investigated the solubility of water in diethyl ether. The methods used were different and the values obtained for the system at 25° range from 1.19 to 2.66%. The reliability of the present work is based on the specific and quantitative reaction of the Karl Fischer reagent with water in the presence of many organic and inorganic reagents.[6] The fairly good precision for the per cent. water in the diethyl ether layer shows that the sampling method was good enough to give uniform samples of the system. Since the method used would keep the diethyl ether from evaporating from the sample before it is weighed or transferred, the precision also indicates that the average value obtained is more nearly correct than previously reported values.

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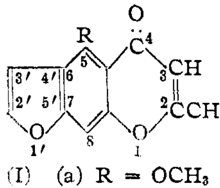
Khellin from Visnagin

By Alexander Schönberg and Nasry Badran

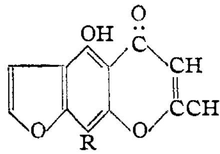
Khellin (IVb) occurs together with visnagin (Ia) in the fruits of *Ammi visnaga* (L). Visnagin is a by-product in the manufacture of khellin. Because of the attention which khellin has attracted in the medical profession, it becomes more than a matter of academic interest to find a method by which visnagin can be converted into khellin. The following scheme shows how this can be done. Attention is drawn to the change Ia → Ib by dilute hydrochloric acid.

$$\text{Ia} \xrightarrow[\text{dilute}]{\text{HCl}} \text{Ib} \xrightarrow{\text{HNO}_3} \text{IIa} \xrightarrow[\text{HCl}]{\text{Sn}} \text{IIb} \xrightarrow{\text{chromic acid}}$$

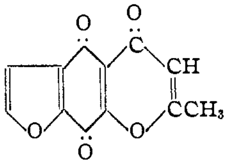
$$\text{III} \xrightarrow[\text{water}]{\text{SO}_2} \text{IVa} \xrightarrow{\text{CH}_3\text{I}} \text{IVb}$$



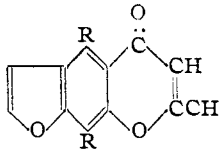
(I) (a) R = OCH_3
(b) R = OH



(II) (a) R = NO_2
(b) R = NH_2



(III)



(IV) (a) R = OH
(b) R = OCH_3

Experimental

2-Methyl-5-hydroxyfuro-4',5'-6,7-chromone (Ib).—A mixture of visnagin (Ia), 1.0 g., 15 ml. of hydrochloric acid (sp. gr. 1.16) and 15 ml. of distilled water was refluxed for one hour. The chromone dissolved and after about 20 minutes a precipitate began to form, increasing gradually in amount. The mixture was left to cool to room temperature and then filtered. The crystalline product weighed 0.8 g. and was recrystallized from glacial acetic acid giving yellowish crystals which melted at 156–158°.

The ferric chloride reaction was green; this was carried out by adding aqueous ferric chloride to an alcoholic solution of the substance. (Ib) when treated with methyl iodide in acetone, in the presence of potassium carbonate as described in the case of (IVa) (see below), yielded visnagin (Ia) (m.p. and mixed m.p.).

Anal. Calcd. for $C_{12}H_8O_4$: C, 66.7; H, 3.7. Found: C, 66.3; H, 3.8.

2-Methyl-5-hydroxy-8-nitrofuro-4',5'-6,7-chromone (IIa).—(Ib), 1.0 g., was dissolved in 20 ml. of acetone and to the solution 10 ml. of nitric acid (obtained by adding 35 ml. of water to 50 g. of nitric acid sp. gr. 1.42) was added and the mixture was allowed to stand for 30 minutes; the reaction proceeded with evolution of heat. Yellow crys-