cera tuediae (Jan Olafsen) and *Actinostola callosa* (Grethe Kubberød).

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Fluoroalcohols

Part 13.[1] Solid-liquid Phase Equilibria of the System Hexafluoro-2-propanol—Water

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In Part 5 of this series, we reported[2] results of a study of the vapour-liquid equilibria in mixtures of 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) and water. These mixtures were found to behave exceptionally; the liquid curves had a plateau at low alcohol contents, and the plot of the logarithm of the activity coefficient of HFP against mole fraction had a minimum and that for water a maximum when x_{HFP} was about 0.4. Thus it was thought worthwhile to study also the cryoscopic behaviour of the mixtures.

HFP was purified as previously.[3] Each sample (about 10 ml) was frozen in a large test tube while being mixed with a propeller. The sample tube was in a larger test tube with an air space between the inner and the outer tube which was immersed in a cold bath consisting of alcohol and dry ice. The temperature was read from a calibrated mercury thermometer. The differences between the maximum and minimum temperatures on cooling curves for each HFP-water mixture were plotted against the maximum temperatures and the melting point was obtained by extrapolation to zero difference as proposed by Hoare.[4]

The results are plotted in Fig. 1. It is seen that addition of HFP to water decreases the melting point relatively rapidly until the content of HFP is about 3 mole %. In this region also the boiling point decreases rapidly[2] and the molar volume of HFP passes through a deep minimum.[3] Between 3 and 17 mole % of HFP, the decrease of the melting point is smaller; this region corresponds to the plateau in the isobaric vapour-liquid diagrams.[2] In this region the viscosity and energy of activation of viscous flow for the liquid are maxima.[3] The eutectic curve has an inflexion point in the region where the plateau in the vapour-liquid plot begins. A cooling curve of the same type has been

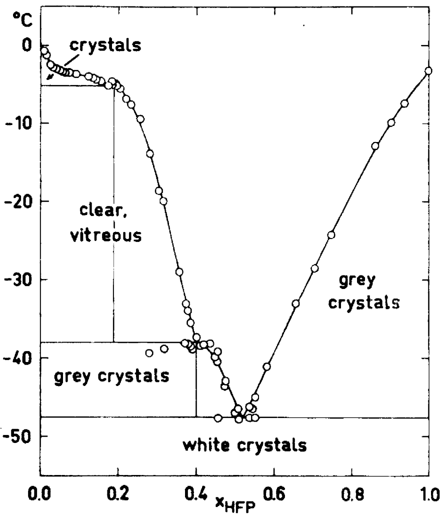

Fig. 1. Melting-point diagram for the system 1,1,1,3,3,3-hexafluoro-2-propanol — water.

obtained also for 2,2′-dichlorodiethyl ether — methanol mixtures.[5] The explanation given for it is that the components, although completely miscible, are not far from being partially miscible.[5] This may be the case also for HFP and water; these compounds (as well as 2-propanol and water) are completely miscible, whereas 1,1,1-trifluoro-2-propanol and water are not.

There is a weak melting point maximum at about −5° when $x_{HFP}=0.19$, and an indication of an eutectic point at −5.1°, where $x_{HFP}=0.17$ (because of supercooling, the eutectic temperature was not observed in the cooling curves). The maximum corresponds to a tetrahydrate (or pentahydrate). The heat of mixing of HFP and water is maximum at about $x_{HFP}=0.2$.[6]

Between −5° and −38° the solid was an amorphous, vitreous mass that appeared violet when white light passed through it. When the solid was heated, the violet colour disappeared at about −10°, and the solid crystallized slowly at about −5°.

Aqueous methanol [7] and ethanol [8] form vitreous states readily, whereas the tendency of pure methanol and ethanol to form vitreous states is much weaker. However, pure propanols form vitreous states readily.[9] Such states are formed only by HFP-water mixtures of low HFP content. This might be connected with the weaker tendency of HFP to undergo self-association than unsubstituted alkanols.[10]

At −38° there is an incongruent melting point, x_{HFP} being then 0.33. This indicates very clearly that a dihydrate is formed.

The eutectic point occurs at −47.7°C; the mole fraction of HFP is then 0.52 (93.9 wt % of HFP). Below this temperature, the solid exists in the form of white crystals.

There was no indication of the formation of new hydrates at high HFP contents. Pure HFP melted at −3.3°. The slope of the plot at $x_{HFP}=1$ gives for the molal freezing point constant of HFP the value $9.5\ \mathrm{K\ kg\ mol^{-1}}$.

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