

Fluoroalcohols

Part 14.¹ Densities, Refractive Indices, Viscosities, and Isothermal Vapour-Liquid Equilibria of Hexafluoroacetone-Water Mixtures

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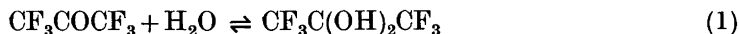
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Several methods were used in preparing aqueous hexafluoroacetone mixtures of accurately known composition. The densities, refractive indices, and viscosities of these mixtures were measured at 25°. Density seems to be the most suitable property for determining the compositions of the mixtures. A sharp viscosity maximum was found at the composition corresponding to the trihydrate. Vapour-liquid equilibria were measured at 35° with a Jones-Schoenborn-Colburn still. The vapour pressure was found to be a minimum (corresponding to an isobaric azeotrope maximum) for a composition corresponding to about 2.7 mol of water to 1 mol of hexafluoroacetone.

Hexafluoroacetone²⁻⁵ (HFA) is known to form several relatively stable hydrates.⁶⁻¹² The monohydrate is a solid that melts at 46°¹³ and deliquesces rapidly in air. The trihydrate is a liquid that can be distilled; it boils at 105°.^{8,10} The solid trihydrate melts at -11°.⁸ The hydrate that contains least water and is still a liquid is (approximately) the sesquihydrate.

The hydrates of HFA are excellent solvents for numerous synthetic and natural polymers.^{9,10,14} Their properties are due to a high polarity and hydrogen bonding ability. The hydrates of HFA are weak acids; the pK_a of aqueous HFA is 6.58.⁷ HFA is now relatively cheap, and thus it is to be expected that the use of HFA and its hydrates will increase in the future.

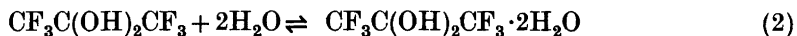
The hydrates are formed on leading gaseous HFA into water. If the molar ratio of the components in solution is 1 : 1, only the monohydrate is formed:



The monohydrate is thus a geminal diol and has some interesting properties (a spectrometric study of its structure is in progress; see also Part 3 in this

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series¹³). In the case of the liquid hydrates, also the equilibrium between the monohydrate and trihydrate must be considered:



Combining eqns. (1) and (2), we can write⁸



The existence of a relatively stable dihydrate seems not to have been mentioned in the literature (and also our own measurements do not indicate that such a hydrate exists).

There are some difficulties in the preparation of aqueous HFA mixtures of accurately known HFA content, because of the equilibria involved and because HFA is a gas at ordinary temperatures (it boils at -27.28° ⁵). Thus, with future work with these mixtures in mind, it was considered appropriate to collect first some data concerning the analysis of the mixtures.

EXPERIMENTAL

Chemicals. Gaseous HFA from Fluka AG was used as starting material in most experiments. It was liquefied in a cold trap, cooled with dry ice, and then allowed to boil slowly at ambient temperature. Only the middle fraction was taken. Commercial HFA monohydrate from Hynes Chemical Research Corp. was used in some experiments. The trihydrate prepared from this monohydrate showed considerable absorption in the UV, which disappeared when the hydrate was distilled once; this behaviour was observed also by Burkhardt and Wilcox.¹⁰

Preparation of the hydrates. To obtain aqueous HFA mixtures of known composition, we must start either from the gas or from the monohydrate. Various methods were tried (see also Refs. 8, 9, and 13):

1. HFA gas was led into a dropping funnel, cooled with dry ice. The liquid HFA was allowed to drop slowly into a weighed amount of water in a sealed, tared flask, which was then weighed again. The method was rapid and gave mixtures with relatively accurate compositions.

2. HFA gas was led into U tubes containing water.¹³ This method is suitable, only if small amounts of the monohydrate are needed.

3. HFA gas was led into water in a glass cylinder. The gas bubbles diminished very rapidly in size in water, and the loss of HFA was very small. The method is suitable for the preparation of the liquid hydrates, especially if the composition of the mixture need not be known with high accuracy. For accurate work, the composition must be determined by other means (*e.g.*, from the density).

4. Dilute aqueous solutions of HFA could be concentrated by leading more gaseous HFA into the mixture, or by distilling water from the mixture in a Vigreux column. The latter method gave a product whose composition was close to that of a trihydrate. The distillation could not be done in a Todd assembly, because solid monohydrate crystallized in the column. The trihydrate had a tendency to corrode the glass flask during the distillation.

5. The monohydrate (commercial product or products obtained by the methods 1 and 2 described above) was purified by sublimation. If a customary sublimation apparatus where the product condenses on a cooled surface was used, the product took up moisture when the system was opened. This was due either to a loss of gaseous HFA according to equilibrium (1) or (3), or/and to absorption of moisture according to equilibrium (2). The best results were obtained with a system which consisted of two 100-ml wide-necked erlenmeyer flasks, connected by a thick bent glass tube (ground joints). The flask containing the starting material was immersed in water at $30-40^\circ$, and the other flask was immersed in ice water. The product collected in the latter flask. It was not necessary to remove the hydrate from this flask when hydrate solutions of known

composition were prepared. The disadvantage of the method is its slowness, because voluminous needles of the monohydrate filled the flask and retarded the sublimation process. (Starting from 10 g of crude monohydrate, we obtained 0.5–0.6 g of pure monohydrate in 8 h.) Use of vacuum did not improve the yield markedly.

Measurements. The densities were measured with Ostwald-Sprengler pycnometers of 1–10 ml capacity. All weighings were corrected to vacuum. The refractive indices were measured with an Abbe refractometer (Model G, Carl Zeiss, Jena), employing a sodium lamp. The viscosities were determined with a Cannon-Ubbelohde viscometer;¹⁵ the amount of the liquid needed in one determination was about 4–5 ml. The equilibrium distillations were carried out in a modified¹⁶ Jones-Schoenborn-Colburn still, where the total holdup of liquid was about 20 ml. The barometric readings were measured with a cathetometer to the nearest hundredth of a millimetre, and were corrected to 0°. The samples were analysed with a refractometer.

The non-SI units used were: 1 centipoise (cP) = 10^{-2} dyn s cm⁻² = 10^{-3} N s m⁻²; 1 mmHg = 133.3 N m⁻².

RESULTS AND DISCUSSION

The results are given in Tables 1 and 2, and in Figs. 1–3. Because of the difficulties associated with the preparation of solutions of exactly known composition, the accuracy of the measurements is not comparable with that usually attained in such measurements.

It is seen that the refractive index and density change regularly (without maxima or minima) with composition. The refractive index changes relatively little with composition, but the change in density is large, as is usual in the

Table 1. Refractive indices, densities, and viscosities of hexafluoroacetone-water mixtures at 25°C. The values for pure water were taken from the literature. n_{H_2O} is the amount of water (in mol) present per mol of HFA.

wt.% HFA	n_{H_2O}/mol	x_{HFA}	n_D^{25}	$d_4^{25}/\text{g cm}^{-3}$	η/cP
0	∞	0.0000	1.3325	0.9970	0.890
15.14	51.65	0.0190	1.3320	1.0831	
16.37	47.02	0.0208	1.3320	1.0905	1.396
19.24	38.66	0.0252	1.3316	1.1053	1.494
32.29	12.67	0.0492	1.3304	1.2246	2.569
51.22	8.775	0.1023	1.3279	1.3552	
57.56	6.793	0.1283	1.3260	1.4143	
62.03	5.640	0.1506	1.3245	1.4533	6.14
65.97	4.753	0.1738	1.3230	1.4935	6.92
67.89	4.359	0.1866	1.3221	1.5126	7.29
69.16	4.110	0.1957	1.3214	1.5244	7.49
70.57	3.844	0.2065	1.3204	1.5455	
71.78	3.624	0.2163	1.3193		
75.44	3.000	0.2500	1.3172	1.5942	8.27
77.16	2.729	0.2682	1.3155	1.6133	
81.61	2.077	0.3250	1.3111	1.6577	
82.15	2.003	0.3330	1.3096	1.6643	7.10
85.58	1.553	0.3918	1.3053	1.6878	5.68
90.21	1.000	0.5000	^a	^a	^a

^a The compound is a solid.

Table 2. Vapour-liquid equilibria of hexafluoroacetone-water mixtures at 35.00°C. p is the total pressure, x'_{HFA} the mol fraction of HFA in the liquid, and x''_{HFA} the mol fraction in the vapour.

p/mmHg	$100 x'_{\text{HFA}}$	$100 x''_{\text{HFA}}$
42.2	0	0
38.9	3.8	0.7
36.2	7.1	0.7
33.7	12.4	2.4
30.9	15.7	4.0
27.5	18.7	6.0
27.4	18.6	7.6
26.3	20.1	9.4
25.2	21.3	11.4
23.9	22.2	14.5
23.8	22.4	14.2
22.5	24.7	21.3
22.5	24.7	20.2
22.4	24.6	19.9
22.2	24.5	21.8
22.0	25.8	23.5
21.6	26.1	25.7
21.3	28.2	28.9
21.7	29.4	31.8
21.9	29.3	32.8

case of fluoroalcohols.¹⁷ Measurement of the density seems to be the most suitable method for analysing aqueous HFA mixtures.

Also the viscosity changes rapidly with composition at low HFA contents, and thus the flow times in a viscometer can be used to analyse the mixtures.

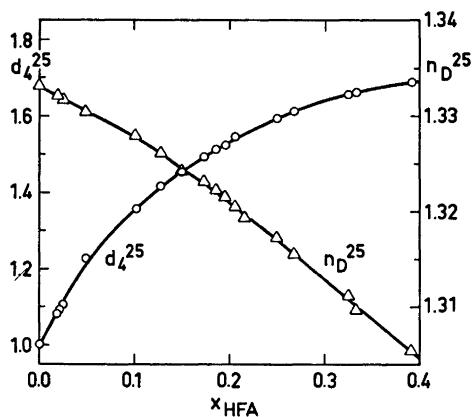


Fig. 1. Densities (circles) and refractive indices (triangles) of HFA-water mixtures at 25°.

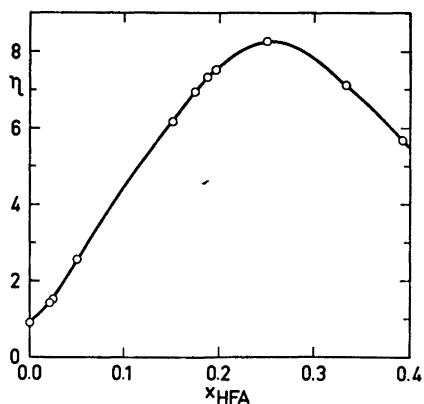


Fig. 2. Viscosities (in centipoise) of HFA-water mixtures at 25°.

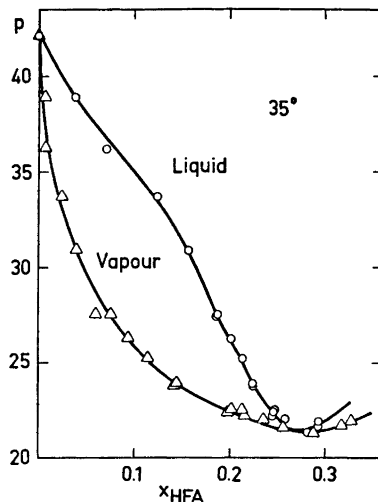


Fig. 3. Vapour-liquid equilibria of HFA-water mixtures at 35°. Pressures in mmHg.

However, the viscosity rises to a sharp maximum at $x_{\text{HFA}} = 0.25$; this indicates the formation of the trihydrate.

Equilibrium distillations were carried out at 35° to obtain somewhat larger pressure readings than would have been the case at 25°. There is a minimum (Fig. 3) at $x_{\text{HFA}} = 0.27$ (77 wt. % HFA), corresponding to the hydrate $\text{HFA} \cdot 2.7\text{H}_2\text{O}$ (it has been found previously⁸ that the "trihydrate" contains 2.73–2.92 mol of water per mol of HFA). In isobaric diagrams, there would be an azeotropic maximum. When water is distilled from a dilute aqueous solution of HFA, the remaining liquid concentrates. The fact that the composition at the minimum pressure (azeotropic maximum) does not correspond exactly to the trihydrate indicates that the trihydrate is not very stable. Also the fact that solid monohydrate deposited in the condenser (because of equilibrium (2)), when an attempt was made to distill the trihydrate in a Todd apparatus, points in the same direction. However, distillations of dilute aqueous mixtures in ordinary distillation columns of low plate number lead to products, whose compositions are approximately that of a trihydrate.

If aqueous solutions are prepared starting from the trihydrate, and if their concentrations must be known accurately, the latter must be determined separately.

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