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Clathrate Formation and Retrograde Miscibility of Liquids in the Bu_4NF–NH_4F–H_2O System

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A region corresponding to separation into liquid phases with retrograde miscibility has been observed on fusion of clathrate-substituted solid solutions (two water molecules are substituted by the NH_4F ion pair).

It was shown[1] that in the water–tetrabutylammonium fluoride binary system two polyhydrates are formed, namely $Bu_4NF{\cdot}32.3\ H_2O$ (h_T) with a tetragonal structure I (TS–I) and $Bu_4NF{\cdot}28.7\ H_2O$ (h_c) with a super cubic structure I (SCS–I) [Fig. 1(*a*)].† Based on both of these polyhydrates, allochiric solutions (substituted solid solutions of skeletal species within the clathrate host system) were discovered on adding NH_4F ranged over a ternary system up to 46.0 mass % of NH_4F at 0 °C [point B in Fig. 1(*b*)].[2] On solid solution melting we observed separation into two liquid phases over a certain concentration range although the polyhydrates melt congruently and separation is not observed in the liquid phase until at least 100 °C. The salting-out of the organic component from the aqueous solution by the inorganic salt is not in itself unexpected,[3] but the fact that the miscibility of the liquids increases with decrease in temperature is noteworthy. Although retrograde miscibility is in fact known to occur, it is nevertheless a fairly rare phenomenon which requires some kind of special explanation.

Tetrabutylammonium fluoride was synthesised and purified in a previous study.[1] The ammonium fluoride employed was of 'specially pure' grade and was not further purified. The total quantity of fluoride ions was determined by potentiometric titration using 0.03 M lanthanum(III) nitrate solution in an aqueous alcoholic (~50 mass %) medium.[4] A detailed method for the determination of tetrabutylammonium by potentiometric titration with sodium tetraphenylborate in the presence of a large excess of ammonium fluoride was described previously.[2] The region corresponding to separation into two liquid layers was determined by the method of Alekseev.[5] A mixture of known composition was placed in a glass bulb, sealed hermetically and heated until the appearance of the second phase (the onset of turbidity). The rate of heating was 0.5 K min^{-1} at continuous mixing.

Information about the surface corresponding to separation into two liquid layers in the Bu_4NF–NH_4F–H_2O system, represented by a truncated dome expanding with increase in temperature, is presented in Fig. 2. We believe that the sections through the three-component system along the h_TA, h_cB and CD (C = 64.93 mass % Bu_4NF, D = 32.21 mass % NH_4F) lines provide a clear illustration. Fig. 3 presents polythermal sections through the three-component system along the compositions of the solid solutions based on the hydrates h_c(*a*) and h_T(*b*). Since the allochiric solid solutions are formed as a result of the substitution of the water molecules by the NH_4F ion pair[6] [from which the structural formulae of the solid solutions $Bu_4NF{\cdot}[xNH_4F(32.3-2x)H_2O]$ for TS–I and $Bu_4NF{\cdot}[xNH_4F(28.7-2x)H_2O]$ for SCS–I follow, the molecular masses of which are similar], the Bu_4NF content, expressed in mass %, is virtually constant along the sections indicated. The solid solutions melt congruently,[2] at least over the concentration range indicated (up to approximately 17–18 mass % NH_4F) and then begin to melt with decomposition into two liquid phases. The locus of the intersection of the boundary layer formation surface in the ternary system with the plane of the cross-section is illustrated in Fig. 3 and the retrograde variation of the miscibility of the liquids is clearly seen. For example, the solid

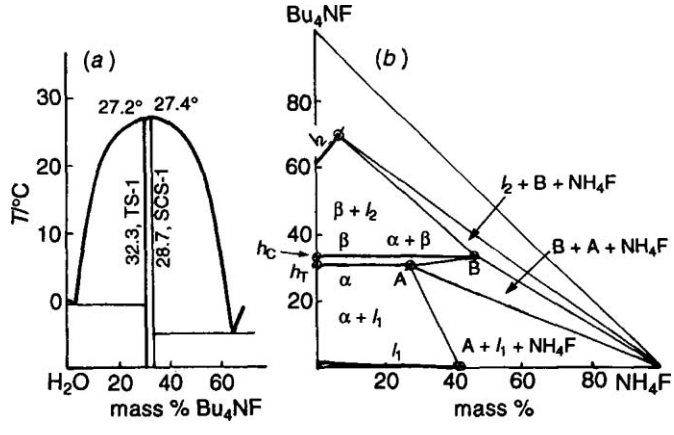

Fig. 1 (*a*) Phase diagram for the Bu_4NF–H_2O system[1]; (*b*) solubility isotherm (mass %) at 0 °C for the Bu_4NF–NH_4F–H_2O system.[2] Points h_TA and h_cB represent solid solution lines based on h_T (α) and h_c (β) hydrates, respectively; points A and B represent the limiting composition of the corresponding solid solutions; and l_1 and l_2 are the lines for those liquid phases in equilibrium with α and β, respectively.

† In general, regions of two-phase composition are to be expected within regions of three-phase composition. In the present case, the former are degenerate since isochoric solutions are not present, *i.e.*, solvation instead of occupation of the cavities by guest molecules.[9] As demonstrated earlier, peralkylammonium hydrates are stable only when the cavities are fully occupied.[10]

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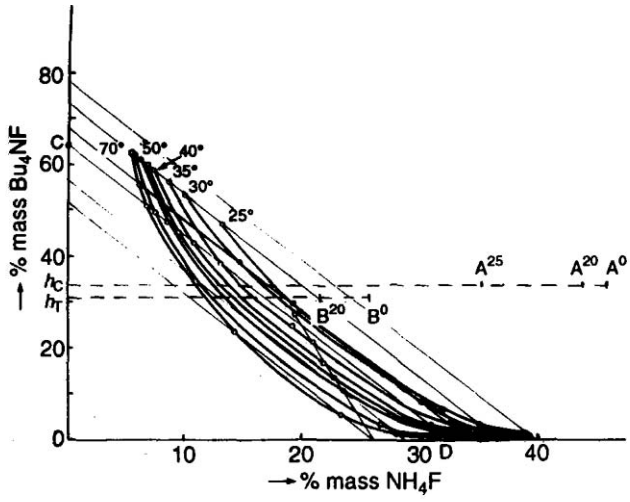

Fig. 2 Mutual solubility of liquids in the Bu_4NF–NH_4F–H_2O system at different temperatures. By means of thin lines are shown the sections on which are constructed the solubility polytherms. One of these, CD, which is constructed of separation temperatures on mixing solutions C and D, is shown in Fig. 4. By means of dotted lines are shown the solid solution lines based on hydrates TS–I and SCS–I, see also Fig. 1(*b*). Points A and B represent the limiting compositions of the solid solutions at the corresponding temperatures (upper scale).

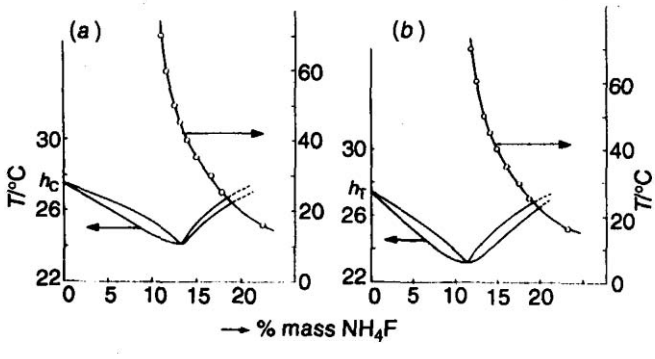

Fig. 3 Polythermic sections for the Bu_4NF–NH_4F–H_2O system over the composition range of the solid solutions obtained based on the h_c (*a*) and h_T (*b*) hydrates.

solution based on the super cubic structure I of composition $Bu_4NF·[23.47H_2O·2.61NH_4F]$ melts congruently at 25.7 °C and, on heating up to 50 °C the homogenous solution formed on fusion, separation into two liquids is observed. At higher NH_4F concentrations separation into two layers occurs at lower temperatures.

The boundary curve illustrated in Fig. 4 represents the locus of the intersection of the boundary layer formation surface in the three-component system with the plane of the section passing through CD and parallel to the T-axis. The curve along this section resembles the binodal curve in a binary system with a lower critical point (*i.e.* below 32 °C the liquids are infinitely miscible). However, following Francis,[3] we should like to draw attention to the difference between the binodal and boundary curves, *i.e.*, the fact that at the same temperature along the boundary curve the liquids are in general not involved in a conjugate relation.

One of the most likely reasons for the increase in miscibility with decrease in temperature may be clathrate formation in the liquid phase.[7] The increase in the miscibility of the liquids with decrease in temperature can be explained as follows. Two liquids which are immiscible under certain conditions interact on reduction of temperature in such a way that the content of clathrate-like structures (naturally, in the sense of short-range order) increases in the liquid phase. The clathrate-like components of the solution are structurally compatible with

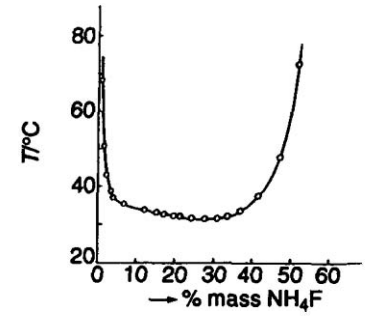

Fig. 4 Sections (64.93 mass % Bu_4NF, 32.21 mass % NH_4F) for the separation surfaces in the Bu_4NF–NH_4F–H_2O system.

the 'water-like' (we shall not consider this term in detail) and organic structures, *i.e.*, are homogenising components. It is logical to propose that the concentration of the clathrate-like component increases and attains a certain critical value sufficient to homogenise immiscible aqueous and organic phases. In relation to binary systems, this view is supported not only by the appearance of a lower critical temperature and the marked asymmetry in the position of the latter as a function of composition but also by the fact that the crystallisation region of the clathrate hydrates and the region of exfoliation into two liquids occur over approximately the same concentration range.[7]

In Atwood's recent studies,[8] there is convincing evidence in support of clathrate formation in the liquid phase for non-aqueous systems as well. In particular, one of the liquid phases in the $\{[N(C_5H_{11})_4][Al_2(C_3H_7)_6I]\}$ benzene system has a composition in which there are 42 benzene molecules per molecule of the organometallic component, whereas the second liquid is virtually pure benzene. The author explains the immiscibility of the organic phase containing such a large amount of benzene with benzene itself by the phenomenon of liquid clathrate formation. Unfortunately, polythermal studies were not performed, although in a personal communication to one of the authors Atwood stated that they sometimes observed an appearance of turbidity on raising the temperature.

Whereas clathrate formation in solution is a normal phenomenon for monomolecular clathrates, for example, the clathrates of cyclodextrins, for 'lattice' clathrates, to which the hydrates belong, this is by no means evident, but indirect inferences about this phenomenon may be drawn from the data presented above.

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