SOLID CLATHRATE SOLUTIONS

Yu.A.Dyadin, G.N.Chekhova, N.P.Sokolova
Institute of Inorganic Chemistry, Academy of Sciences of the
USSR, Siberian Branch, Novosibirsk 630090,
U.S.S.R.

ABSTRACT. The classification of solid clathrate solutions may be sub-
divided into three types: interstitial solutions, those with the sub-
stitution of one guest by another and those with the substitution of
the particles in a host framework is given. All these types of solu-
tions are illustrated by experimental (or computed) state diagrams of
binary and ternary systems of guest-host and host-guest1-guest2 kinds,
where host components are water, urea, thiourea and hydroquinone.

1. INTRODUCTION

Three types of solid solutions: 1) iskhoric solutions, i.e. interstitial
ones, formed by filling the host framework cavities with any appropria-
te particles to some degree, $y(0<y<1)$("iskhoric" is derived from Greek
$\varepsilon\iota\sigma\chi\omega\rho\tilde{\omega}$ – to intrude), 2) alloxenic solutions, i.e. those with the
substitution of one guest by another ("alloxenic" is derived from the
greek words $\alpha\lambda\lambda os$ – another, $\xi\varepsilon\mathcal{N}OS$ – guest), 3) allokiric solutions,
i.e. those with the substitution of particles in a host framework ("al-
lokiric" is also derived from the greek words $\alpha\lambda\lambda os$ – another, $cv\rho\iota os$ –
host) may be observed in the clathrate systems.
     The interstitial solutions are typical of clathrate compounds and
they have been considered [1]. Studying water [2,3], urea [4,5], thio-
urea [6] and hydroquinone [7-9] clathrates we have found that only the
latter (in the presence of the limited guest set [10-12]) forms the so-
lutions of this type.
     Allokiric solutions are formed in H_2O – Bu_4NA – Bu_4NB systems (whe-
re Bu_4N^+ is tetra-n-butylammonium cation, A and B are single charged
anions). These clathrate frameworks consist of water molecules and ani-
ons, the guest being organic cation.
     Alloxenic solutions are wide-spread in clathrate chemistry. These
are the natural gas hydrates, mixed hydroquinone clathrates and mixed
channel inclusion compounds. The conditions of their formation seem to
be sufficiently simple and are in fact the same as those of the forma-
tion of the individual clathrate compound.

2. EXPERIMENTAL

2.1. Reagents

Urea and thiourea were of especially pure grade. Tetra-n-butylammonium (TBA) hydroxide was prepared and purified as in [13]. All the operations with it were carried out in the free from carbon dioxide atmosphere and by using boiled water.

TBA fluoride was synthesized by neutralizing diluted TBA hydroxide solution with hydrofluoric acid, followed by recrystallization of TBA fluoride as the clathrate hydrate (all the operations were carried out by using polyethylene or teflon vessels).

TBA bromide was purified by means of thrice-repeated recrystallization of pure grade reagent out of ethyl acetate.

Hydroquinone was purified by thrice-repeated recrystallization out of aqueous solutions which were slightly acidified by sulfuric acid.

Benzene, cyclohexane and acetonitrile were of chromatography grade, n-paraffins were of chemical pure one.

Carbon tetrachloride and chloroform were purified by means of conventional methods.

The formic and acetic acids were purified from water and other contaminants in different ways: the former was recrystallized many times out of aqueous solution at $8,5^{o}C$, the latter was kept together with acetic anhydride for 24 hours followed by the distillation.

2.2. Analysis

The concentration of hydroxyl ions was determined by means of titration by 0,1N nitric acid solution with methylorange as an indicator, that of Br^- anions and thiourea – by 0,05N $Hg(NO_3)_2$ titration (in the presence of ethyl alcohol) with diphenylcarbazone as an indicator, that of F^- anions – by direct potentiometric method [14], that of hydroquinone – by 0,1N $Ce(SO_4)_2$ solution titration in the presence of sulfur acid with phenylanthranilic acid as an indicator, that of formic and acetic acids – by 0,07N NaOH solution titration with thymol blue as an indicator.

2.3. Methods

The DTA method has been used for binary systems study. Two versions of Schreinemakers's method have been utilized: the classical one [15]("wet residue" method has been applied to hydroquinone and water systems) and the modified one ("initial weighed portion" method [16] has been used for thiourea systems). In the latter the liquid phase composition has been determined by means of CCl_4-C_6H_6, CCl_4-C_6H_{12}, $CHCl_3$-C_6H_{12}, CCl_4-n-$C_{10}H_{22}$ solution density measurements (the thiourea concentration in these equilibrium solutions has been shown by means of analyses to be less than 0,1%). The Schreinemakers's ray has been drawn through the figurative points of the liquid and "initial weighed portion" compositions. The solid solution composition was obtained by combining the usage of Schreinemakers's and Cameron's [17] methods (acetic acid was used as an inert and easily analyzed admixture).

Particular attention was given to equilibrium data obtaining. So, for example, the samples for DTA placed into the sealed ampoules were being kept for 1-1,5 months, "initial weighed portions" samples in three-component thiourea systems being kept for 7-8 months (by agitation), in the water systems the phase equilibrium was set at the period ranging from 4 hours to some days, in hydroquinone systems - from 5 to 20 days.

3. RESULTS AND DISCUSSION

3.1. Interstitial solutions

In the foregoing it has been mentioned that the hydroquinone clathrates in the presence of the limited set of guests (such as inert gases or their analogs) form the solutions of this type. It should be noted that hydroquinone possesses the unique property: in its initial stable α-modification there are cavities of molecular dimensions, which may contain such kind of guests as the clathrate β-modification. Since α- and β-modification structures [18,19], $\Delta\mu^{\alpha\to\beta}$ [20] and the necessary thermodynamic data [21,22] are known for hydroquinone one can simulate these systems easily enough and estimate them quantitatively up to computing the total phase diagram of the binary hydroquinone - guest system [11,12]. The agreement of the computed and experimental data is illustrated in Fig. 1 for the hydroquinone - krypton and hydroquinone - xenon systems.
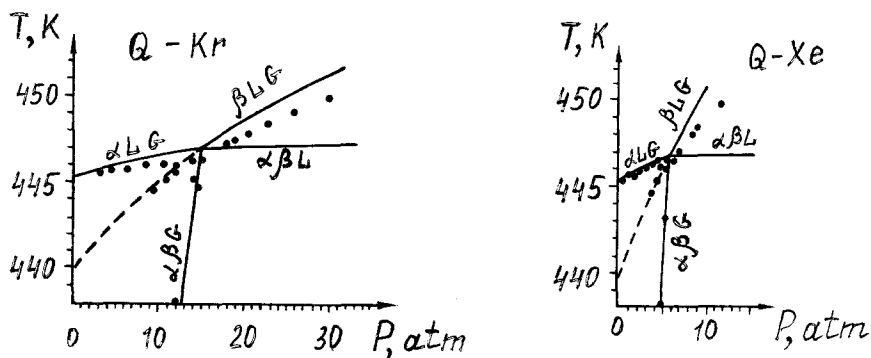

Figure 1. The phase P,T-diagrams of the hydroquinone - inert gas systems. The computed (── stable state and - - - unstable one) and experimental (●) data [23].

The comparison of the computed data with the experimental ones indicates that the former not only reflects qualitatively the phenomenon nature (namely the existence of clathrates in inert gas (except He and Ne)- hydroquinone systems and the dissolving of guests in the host α-modification) but describes the phase diagram quantitatively. Computed P,x- and T,x-sections of the hydroquinone - xenon system diagram (see Fig.2) confirm the berthollide nature of hydroquinone clathrates which helps to clarify the essence of Kurnakov's imaginary compounds [17].
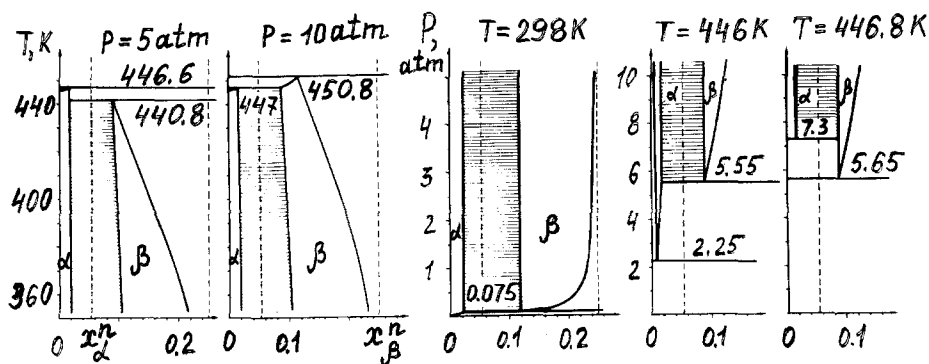
Figure 2. The isobaral and isothermal sections of P,T-diagrams of the hydroquinone - xenon system.

3.2. Allokiric solutions

The solutions with the substitution of particles in a host framework are rather rare in clathrate chemistry. The present data are not yet enough to draw the final conclusions concerning the regularities of the formation of the solutions of this kind. Nevertheless some features attract our attention.

    At 20°C in TBA hydroxide - TBA fluoride - H_2O system (see Fig.3) the continuous series of the solid solutions of the typeI (according to Roozeboom) on the basis of the cubic 1:28,6 (salt:water) hydrate is being crystallized out of the liquid solutions impoverished by water. When crystallized out of the liquid solutions enriched by water, the solid solutions with the break in continuity of the typeV on the basis of 1:28,6 TBA hydroxide hydrate and that of 1:32,8 TBA fluoride hydrate are formed.
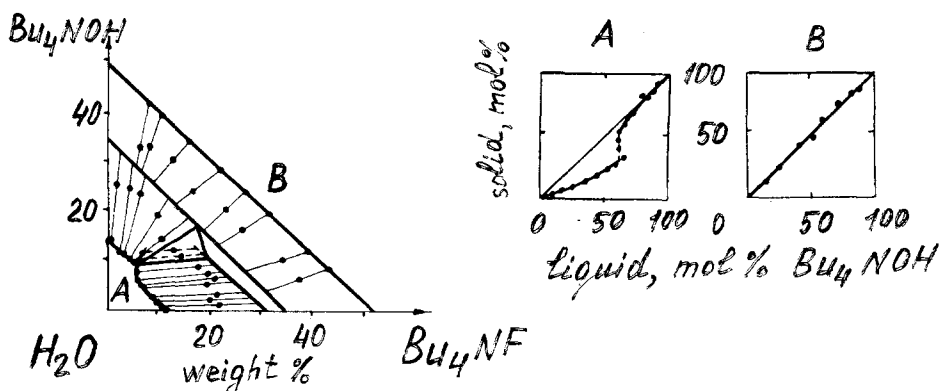

Figure 3. The solubility isotherm (20°C) in the $(C_4H_9)_4NF$ - $(C_4H_9)_4NOH$ - H_2O (a) and the diagram of the component distribution among the solid and liquid phases (without taking account of water) (b).

Figure 4. The solubility isotherm (8°C) in the $(C_4H_9)_4NOH$ - $(C_4H_9)_4NBr$ - H_2O (a) and the diagram of the component distribution among the solid and liquid phases (without taking account of water) (b).
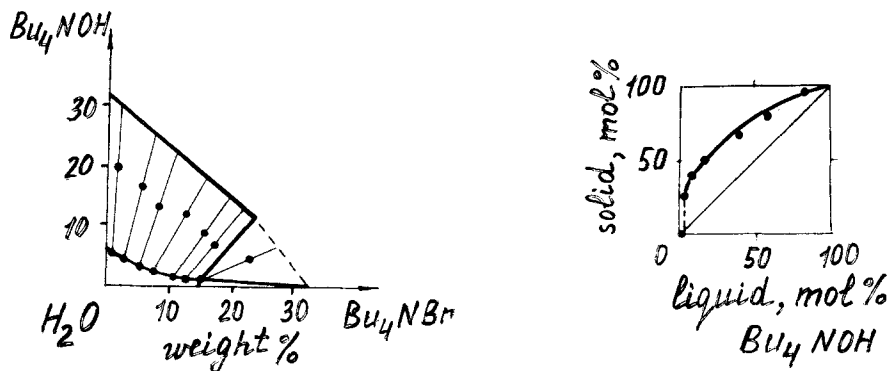
Such a behaviour may result from the stability of the individual hydrates [13,24]: the fluoride and hydroxyl anions stabilize the 28,6 hydrate framework to the same extent (which is verified by the equality of the congruent melting points (as high as 27,4°C) of the corresponding hydrates) and therefore hydrates form with each other the practically ideal solid solutions whatever crystallization region. The hydrate solid solutions having tetragonal cell are enriched with the fluoride component because of its greater stability. So, TBA fluoride hydrate has the congruent melting point as high as 27,2°C, whereas TBA hydroxide hydrate has the incongruent melting point as high as 19°C. For the same reason in the TBA hydroxide - TBA bromide - H_2O system the limited solid solutions of type IV (according to Roozeboom) are realized (see Fig.4).

3.3. Alloxenic solutions

The conditions of the formation of the solution of such kind for channel inclusion compounds are simplified substantially and seem to be reduced to those of the formation of the individual clathrates, i.e. to the conformity of the guest molecules dimensions to the cross-section of the clathrate framework channel (for urea 5,25Å, for thiourea 6,9-7,4Å). n-Paraffins ranging from pentane to eicosane form with one another the continuous series of the solid solutions of the typeI in the urea framework channels whatever the number of the carbon atoms, while the same paraffins without the urea framework form the solutions with the break of the continuity. As noted in [25] for the latter case the problem of the molecule packing may be subdivided into two   (namely that of the molecule packing in a layer and that of the layer packing - the difference of the latter resulting in the well-known variety of the n-paraffin structures). In the case of the clathrates these restrictions are eliminated substantially and the solid solutions are formed without any difficulties. In the same way CCl_4 with cyclohexane (C_6H_{12}) forms the solutions of the typeI
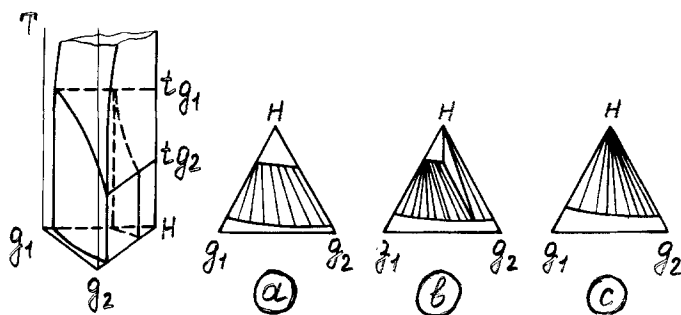
Figure 5. The scheme of the solubility polytherm of the host(H) – guest1 (g1) – guest2(g2) system: t_{g1} – the peritectic point of the clathrate with guest1, t_{g2} – the peritectic point of the clathrate with guest2. The isothermal sections at the temperatures: a) lower than t_{g2}; b) lower than t_{g1} and higher than t_{g2}; c) higher than t_{g1}.

in , thiourea channels, whereas the CCl_4–C_6H_{12} system is of eutonic type [28]. In the thiourea – guest1 – guest2 systems (where guests are: CCl_4, C_6H_{12}, $CHCl_3$, C_6H_6) the solutions of the type1 enriched with the guest component making the more stable clathrate (C_6H_{12}>CCl_4>$CHCl_3$>C_6H_6 [6]) are formed. At 20°C n-decane does not form the clathrate with thiourea [27], but together with CCl_4 it is cocrystallized being up to 50 mol% in solid (without taking account of the host). In all the studied systems the interstitial solutions are not formed: the guests in the channel form an extremely dense one-dimensional packing and the framework is stable only under this condition. Thereby as well as in the case of the urea clathrates a number of the rather "severe" restrictions (according to A.I.Kitaigorodsky for the molecular crystals) is eliminated because by the joint inclusion of the above mentioned guest pairs into the rhomboedric thiourea the one-dimensional packing takes place.

On the ground of the studied isotherms the generalized polythermal phase diagram of the thiourea – guest1 – guest2 system has been made in which one can observe "the transformation" of the spontaneous adduct (according to the earlier adopted terminology [28]) into the unspontaneous one (and vice versa) at the temperature change.

In Fig.5 the situation when the peritectic temperature of the clathrate with the guest1 is higher than that of the clathrate with the guest2 is given. When $t<t_{g2}$ in the whole concentration region the continuous series of the solid solutions enriched with the guest1 seems to be realized (see Fig.5, section a). This case was observed when the isotherms (20°C) of the thiourea systems (where the guest pairs were: CCl_4–C_6H_{12}, CCl_4 – C_6H_6, $CHCl_3$ – C_6H_{12}) were being studied. When $t_{g2}<t<t_{g1}$ there appears the region of the host crystallization (see Fig.5, section b); it is realized in the thiourea – CCl_4 –n-$C_{10}H_{22}$ system; when the temperature rises the region of the solid solutions is getting narrow and when t>
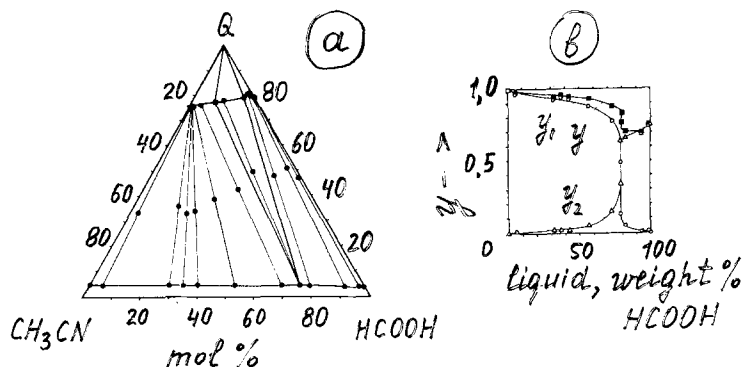
Figure 6. The solubility isotherm in the hydroquinone – HCOOH – CH₃CN system (a); b – the variation of the total (y) and the constituent degree of the clathrate framework filling (y_1 – for acetonitrile, y_2 – for formic acid).

$>t_{gl}$ the pure thiourea is crystallized (see Fig.5, section c). All this allowed us to establish, for instance, the fact of existing individual thiourea clathrate with benzene as a guest at the usual temperatures[29]. At 20°C in the hydroquinone – HCOOH – CH₃CN system the alloxenic solid solutions (see Fig.6,a) with the continuity break (the typeIV) are formed which is also confirmed by comparison of the behaviour of the external vibrations in Raman spectra of the individual and mixed clathrate samples [30].

The stoichiometry of the mixed clathrates is represented in Fig.6,b, from which one can deduce that the degree of filling the clathrate phase varies depending on the formation conditions of the latter, when HCOOH: :CH₃CN=3,4 in the liquid it undergoes the leap. It is seen especially clearly when examining the character of the change of the filling degree with each of the guests separately (see Fig.6,b). The break in the continuity of the solid solutions which seems to be due to the different symmetry of the unit cells of hydroquinone clathrates with acetonitrile and the formic acid as guests is a quite unexpected phenomenon. It may be explained by different distortions of ß–framework with each of the guests and the greater interaction among guest molecules of the same kind.

Thus, due to the nature of the clathrate compounds one can observe the rather distinct division into two subsystems: a guest and a host one. The former is more "mobile" as its properties are similar to those of liquid at least at usual temperatures. Therefore in this subsystem the solutions are formed with the same ease as in the liquid phase. The latter posesses all the properties of solid with the corresponding "strict" restrictions of the substitution of the particles.

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