

# CLATHRATE HYDRATES OF TETRABUTYLAMMONIUM CARBOXYLATES AND DICARBOXYLATES

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ABSTRACT. Phase diagrams of the binary aqueous systems with tetra-*n*-butylammonium (TBA) carboxylates  $((C_4H_9)_4NC_nH_{2n+1}CO_2$ , where  $n = 0\div 5$ ) and dicarboxylates  $([(C_4H_9)_4N]_2(CH_2)_nCO_4$ , where  $n = 1\div 3$ ) including some branched carboxylate anions, have been studied in the field of crystallization of clathrate hydrates. Monocrystals of many hydrates have been prepared and their composition, densities, melting points and X-ray data have been determined. In the set of TBA carboxylate hydrates the stability increases towards TBA propionate or butyrate hydrates (for different structures) and then it decreases as sizes of anions grow. This is explained by additional stabilization of the framework caused by small cavities being occupied until the hydrophobic part of the anion is able to go in the cavity. In the set of hydrates of TBA dicarboxylates the change of the stability is easily accounted for by the modelling of the inclusion of dicarboxylate ions in the cavities, within known structures, different ways of hydrophilic inclusion being taken into account.

## 1. INTRODUCTION

In the structures of polyhydrates of TBA salts with simple anions the big T- and P-cages (D-, T-, P-, H-cages are 12-, 14-, 15-, and 16-hedra, respectively [1]) are occupied by cation butyl radicals, the small D-cages are vacant [1]. The salts, discussed in the present communication, are of interest because when they interact with water, it is possible to study the dependence of clathrate formation upon regular increase of the anion dimensions, to follow the hydrates stability during the filling of the vacant D-cages and then also the big cages by the hydrophobic part of anion, it competing with the butyl radicals of the cation in the latter case. To solve these problems we have investigated the salt - water diagrams, have obtained hydrates and have carried out their X-ray analysis.

## 2. MATERIALS AND METHODS

The TBA carboxylates synthesis has been carried out by neutralization of

an appropriate acid by TBA hydroxide followed by the recrystallization of the salt as a clathrate hydrate. The analysis of the salt content has been carried out using the technique of potentiometric titration by tetraphenylborate sodium solution with a TBA-selective electrode [2]. The water content has been determined by means of Fisher's method.

Binary systems have been studied by the DTA technique (heating curves) in the range  $-40 \pm 30^\circ\text{C}$ . The reproducibility near the liquidus curve maximum is  $\pm 0.02^\circ$ . The density of the crystals has been determined by the flotation technique. X-ray investigations have been carried out by means of Laue and oscillation technique on  $\text{CuK}\alpha$ -radiation ( $-10^\circ\text{C}$ ).

### 3. RESULTS

The binary aqueous systems phase diagrams in the range of the crystallization of TBA carboxylate and isocarboxylate polyhydrates are given in Figures 1 and 2 respectively, and some properties of the hydrates are shown in Table I. Two hydrates with stable crystallization branches form in the TBA acetate - water system. One stable and several metastable hydrates have been discovered in each of the rest of the systems (from 1 (TBA formate) to 8 (TBA n-butyrate)).

To see whether the abundance of phases of similar stabilities is due to the influence of air on clathrate formation or not, the investigation of the systems has been undertaken in helium atmosphere. The results, obtained in helium and air atmosphere, are in agreement (Fig. 1).

Phase diagrams of the TBA dicarboxylate - water systems are presented in Figure 3, the characteristics of the discovered hydrates are given in Table II. Both TBA malonate and succinate form 3 hydrates (2 metastable and 1 stable), melting congruently. TBA glutarate forms 2 hydrates, having stable crystallization branches.

On the basis of phase diagrams the conditions have been chosen for growing monocrystals of the forming polyhydrates. In all the cases we have managed to obtain (stable and metastable) hydrates with tetragonal structure I, that is, perhaps, the most widely distributed among TBA salts polyhydrates. Hydrates with cubic structure III (acetate and glutarate hydrates being stable) are often found too. The structure of TBA propionate hexagonal hydrate seems to be a superstructure of the ideal framework [1] with threefold increase of the period  $c$ .

### 4. DISCUSSION

#### 4.1. STABLE AND METASTABLE PHASES

The presence of several polyhydrates (stable and metastable) is typical of the systems concerned and seems to be due to several causes.

**4.1.1. Clathrate frameworks.** The principal clathrate frameworks have a comparatively small set of polyhedra (cages D, T, P, H) in various combinations and with various degrees of distortion. A certain guest stabilizes the framework, whose cage geometry and their arrangement correspond to

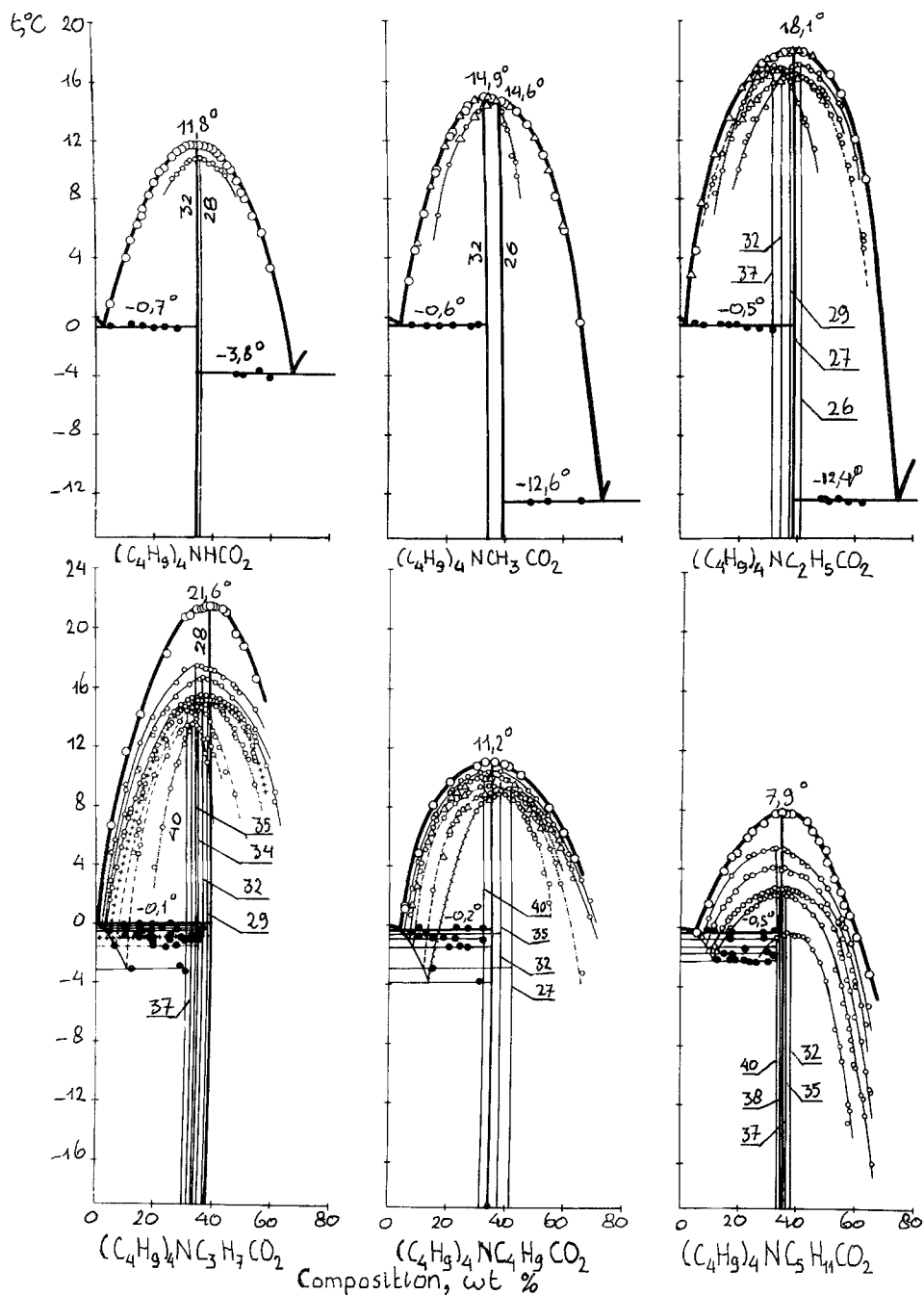


Figure 1. Phase diagrams of the TBA n-carboxylate - water systems. The thick line describes stable equilibrium, the thin line (solid or dotted) describes metastable equilibrium. The points obtained in helium atmosphere, are marked by triangles. To avoid overloading of the figure, we do not cite all the metastable equilibria. See the full data in Table I.

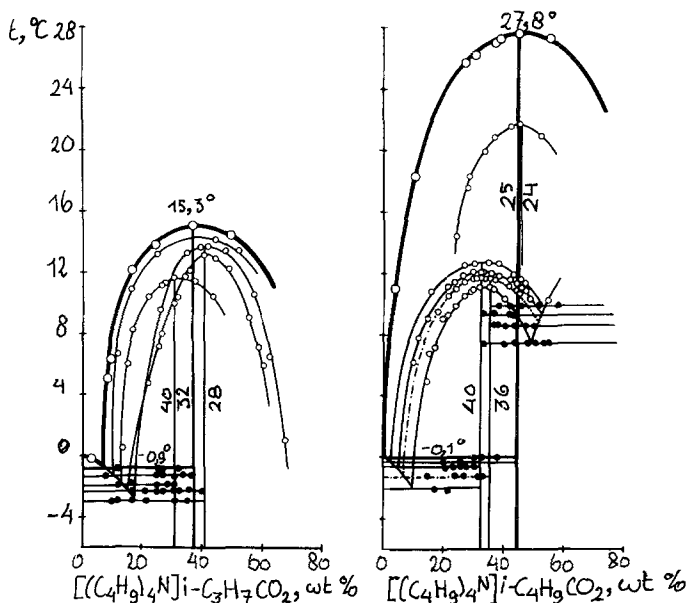


Figure 2. Phase diagrams of the TBA isocarboxylate - water systems. The designations are the same as in Figure 1.

the dimensions and configuration of the guest molecule. However, the cages, mentioned above, do not differ much from each other in this respect. Therefore, one and the same guest can stabilize different frameworks when conditions are changed [8].

**4.1.2. Kinetic factors.** Though many hydrates are not stable thermodynamically, they are not far from this state and exist as metastable hydrates. It is interesting that even the presence of the stable phase as seed did not always cause the crystallization of this very phase from the solution. The equilibrium in the solution does not seem to establish instantly. This is confirmed by the fact, that the repeated crystallization proceeds more readily after melting.

**4.1.3. Hydrophobic inclusion variants.** The diversity of polyhydrate forms (both differing in composition and having the same composition) may be related not only to different framework structures. Within the same framework structural type hydrates with different compositions can exist, this depending on the way of the guest inclusion.

The hydrophobic part of *n*-butyrate and *n*-valerate anions is, e.g., such, that it can still be arranged in D-cages, but it also stabilizes rather well, a T-cage. We have discovered [3,4] 3 variants of the filling of the cages in these systems: 1) the small cages are occupied (the composition for cubic structure III is 1:27.7 (salt:water), for tetragonal structure I it is 1:31.4), 2) the big cages are occupied (1:35.3, 1:40 respectively), 3) anion is distributed equally between the large and the small cages (1:31.5 and 1:35.7 respectively). *n*-Butyrate and *n*-valerate of TBA hydrates with cubic structure I are discussed in [5] (the composition is not given). The parameters obtained by us, are in

TABLE I. Some properties of polyhydrates of TBA carboxylates.

Anion of TBA salt	Hydrate number	M.p., °C	Density, g/cm <sup>3</sup>		Type of unit cell, dif.class	Parameters, <sup>R</sup>		Number of form. units, <sup>Z</sup>
			exper.	calc.		a	c	
HCO <sub>2</sub> <sup>-</sup>	31.6	11.8*	1.030	1.040	P4/m	23.5	12.4	5
	27.5	10.9	1.038	1.048	Im3m	24.6	-	12
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	31.4	14.9*	1.037	1.059	P4/m	23.6	12.2	5
	25.9	14.6*	1.046	1.040	Im3m	24.5	-	12
C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> <sup>-</sup>	36.8***	17.2	1.021	1.059	P6/mmm	12.1	36.7	3
	31.6	16.8	1.046	1.051	P4/mmm	23.7	12.5	5
	29**	16.3						
	27**	18.1*						
	26.0	17.2	1.066	1.040	Im3m	24.7	-	12
C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> <sup>-</sup>	40.4	14.7	1.035	1.011	P4/mmm	23.7	12.4	4
	35**	13.7						
	35.0	14.9		1.022	P4/mmm	23.6	12.5	4.44
	34**	17.6						
	32.6	15.5		1.118	P4/mmm	23.5	12.4	5
	31.7	16.8	1.060	1.072	Pm3m	12.3	-	1.33
	29**	15.1						
	27.5	15.3						
27.4***	21.6*							
C <sub>4</sub> H <sub>9</sub> CO <sub>2</sub> <sup>-</sup>	39.7	10.2	1.032	1.033	P4/mmm	23.5	12.3	4
	35**	11.2*						
	35**	8.9						
	35**	9.6						
	31.6	10.5	1.061	1.062	Pm3m	12.4	-	1.33
26.9***	9.4							
C <sub>5</sub> H <sub>11</sub> CO <sub>2</sub> <sup>-</sup>	40**	5.5						
	40.4	4.3	1.026	1.031	P4/mmm	23.7	12.5	4
	38**	2.3						
	37**	7.9*						
	35**	2.7						
	32**	-0.4						
i-C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> <sup>-</sup>	40**	11.8						
	32**	14.3						
	31.8	15.3*	1.051	1.072	P4/mmm	23.8	12.4	5
	28**	13.8						
	27.8	13.4	1.070					
i-C <sub>4</sub> H <sub>9</sub> CO <sub>2</sub> <sup>-</sup>	40**	12.9						
	39.4	12.2	1.035	0.982	P4/mmm	23.8	12.7	4
	36.2	11.8	1.025					
	24.8	27.8*	1.053	1.033	Im3m	26.8	-	15
	24.2	21.9	1.042					

\* the most stable hydrate,  
 \*\* data on the maximum of the liquidus curve only,  
 \*\*\* the single definition.

Error for the definitions averaged in the measuring of the hydrate number  $\sim 1\%$ , of the density  $\sim 0.1\%$ , in the determination of the parameters  $\sim 1\%$ .

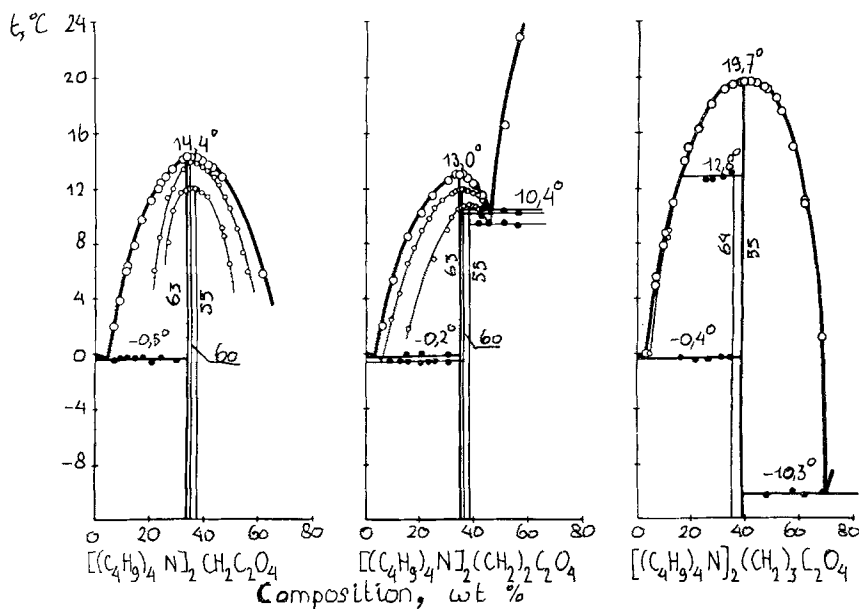


Figure 3. Phase diagrams of the TBA dicarboxylate - water systems. In TBA glutarate - water system data, obtained by means of the solubility technique, are designated by small points.

agreement with Jeffrey's ones (12.28 Å and 12.31 Å respectively). Attention should be paid to the fact, that the composition of these hydrates does not differ from the composition of the hydrates with tetragonal structure I within the determination accuracy (for variant I).

**4.1.4. The hydrophilic inclusion variants.** The composition of the hydrates of branched and normal TBA carboxylates show that anions are included into the host framework with two oxygen atoms of a carboxyl group, forming polyhedron edge. Judging by the TBA glutarate tetragonal hydrate composition (1:64.5) we can suppose, that the anion carboxyl groups displace two water molecules from the host framework and in the dicarboxylate hydrates with compositions 1:55 and 1:63 each anion seems to displace 4 water molecules. All the dicarboxyl-anions studied by us are likely to be arranged in the D-cavity.

#### 4.2. THE SIZES OF THE ANIONS AND THE STABILITY OF THE HYDRATES

As expected, the hydrate melting points increase from formate to propionate or n-butyrate of TBA (for different structures) and then it

TABLE II. Some properties of polyhydrates of TBA dicarboxylates.

Anion of TBA salt	Hydrate number	M.p., °C	Density, g/cm <sup>3</sup>		Type of unit cell diff.class	Parameters, Å		Number of form. units, Z
			exper.	calc.		a	c	
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	64.0	13.7i	1.047	1.019	P4/m	23.8	12.4	2.5
	57.3	16.2*	1.065	1.076	Im3m	24.6	-	6
	40**	8.0i						
CH <sub>2</sub> C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	63.3	14.4*	1.044	1.034	P4/mmm	23.6	12.5	2.5
	60.3	14.0	1.039	1.035	P4/mmm	23.5	12.2	2.5
	55**	12.0						
(CH <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	62.6	13.0*	1.048	1.026	P4/mmm	23.6	12.6	2.5
	60.2	11.9	1.043	1.034	P4/mmm	23.4	12.4	2.5
	55**	10.8						
(CH <sub>2</sub> ) <sub>3</sub> C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	64.5	12.8i	1.048	1.055	P4/mmm	23.5	25.3	5
	55.2	19.7*	1.069	1.091	Pm3m	24.5	-	6

i - melting incongruently, the rest of the designations see Table I.

decreases (Fig. 4a), which can be explained by the stabilization at the expense of filling of the small cages, whose dimensions agree best with the hydrophobic part dimensions of the anions mentioned. The D-cage volume is used still more effectively by isovalerate. The further increase of the anion dimensions results in its being able to be arranged only in a large cage, which causes a change of the composition (within the same framework) and lower melting points (D-cages are vacant).

The dependence of the melting points of the dicarboxylates hydrates with cubic and tetragonal structure upon the carbon atoms is shown in Figure 4b (some data are taken from [6]). If we do not take into account results for n=3,4 and partially 5, we can observe a "natural" picture, describing weakening of the interaction between dicarboxylic acid salt and water with increase of the anion hydrophobic part dimensions, which is conventionally depicted by a hatched line. If n=3,4, the interaction between the carbon chain and the water molecules of a framework due to the correspondence between the chain dimensions and the framework cages (glutarate is perfectly arranged in the D-cage, with the carboxyl groups forming diametrically opposite edges) causes not only lessening of destabilization, but also an appreciable stabilization of the structure in comparison with oxalate hydrates [7].

## APPENDIX

We have just come across and read the article by H. Nakayama and Sh. Torogata (*Bull. Chem. Soc. Jpn.*, 57, 171 (1984)), whose results do not contradict ours. The authors have studied 19 TBA carboxylate - water systems and have discovered one hydrate in each system. The melting points and

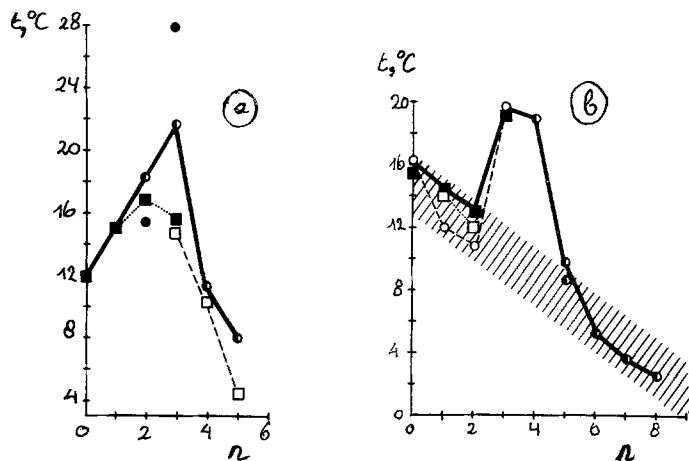


Figure 4. The dependence of the melting points of the hydrates on the anion length: a) TBA carboxylates, b) TBA dicarboxylates.  $n$  - the number of carbon atoms in the main alkyl chain, — - the most stable hydrate, ■ - tetragonal hydrate 1:31.4 (a) and 1:63 (b), □ - tetragonal hydrate 1:40 (a) and 1:63 (b), ○ - cubic hydrate 1:55 (a), ● - unknown structure.

hydrate numbers of these hydrates (formate  $12.2^{\circ}$ , 30; acetate  $14.8^{\circ}$ , 30;  $n$ -butyrate  $17.0^{\circ}$ , 31;  $n$ -valerate  $10.6^{\circ}$ , 40, isovalerate  $11.3^{\circ}$ , 39;  $n$ -caproate  $3.4^{\circ}$ , 40) agree rather well with those obtained by us either for the stable (formate, acetate, propionate) or for the metastable hydrates ( $n$ -butyrate,  $n$ -valerate,  $n$ -caproate, isovalerate) with the exception of TBA isobutyrate hydrate (m.p. =  $9.8^{\circ}\text{C}$ ) for which we have no analogue (Table I).

#### REFERENCES

1. G.A. Jeffrey and R.K. McMullan: Progr. Inorg. Chem., **8**, 43 (1967).
2. B.S. Smolyakov and N.I. Yakovleva: Izv. Sib. Otd. Acad. Nauk SSSR, **2**, 116 (1980).
3. Yu.A. Dyadin, L.S. Aladko and L.A. Gaponenko: Proceedings International Microsymposium of Clathrate Compounds and Molecular Inclusion Phenomena /Ed. A. Sopkova, P. Kralik, Czechoslovakia, Vysoke Tatry, 7-11 Sept., 146 (1981).
4. L.S. Aladko, L.A. Gaponenko and Yu.A. Dyadin: Izv. Sib. Otd. Akad. Nauk SSSR, **12**, 67 (1982); C.A., **98**, 53120u (1983).
5. G. Beurskens, G.A. Jeffrey and R.K. McMullan: J. Chem. Phys., **39**, 3311 (1963).
6. H. Nakayama and K. Watanabe: Bull. Chem. Soc. Jpn., **51**, 2518 (1978).
7. I.S. Terekhova and Yu.A. Dyadin: Izv. Sib. Otd. Akad. Nauk SSSR, **9**, 73 (1979); C.A., **91**, 163772w (1979).
8. Yu.A. Dyadin and K.A. Udachin: This issue, p. 61.