CRYSTALS OF MONOETHANOLAMINE TEREPHTHALATE

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In an attempt to find suitable separation methods for oxy amines we dissolved solid terephthalic acid in a c. 30% aqueous solutions of monoethanolamine. After the solution was filtered off and crystallization carried out either with slow cooling of the unstirred solution or from the stirred solution with rapid cooling, clear crystals with well-developed planes were obtained.

Since as far as we know no compound thus prepared has been described in the literature, we performed an X-ray diffraction analysis of the crystals on a Müller-Micro 111 apparatus (Table I) and determined the crystallographic system from goniometric measurements. The density was then determined pycnometrically; the immersion method was used to measure the refractive index of the crystals. The molecular formula of the compound under study was obtained by elementary analysis, and the structure was established by means of IR spectrometry of the normal and deuterated substances. The ionic character of the compound is demonstrated by its high water solubility and the electric conductivity of its solutions.

EXPERIMENTAL

Preparation of monoethanolamine terephthalate. On dissolving solid terephthalic acid (theoretical degree of acidity, obtained by hydrolysis of 99·9% dimethyl terephthalate) in c. 30% aqueous solution of technical monoethanolamine (commercial product of Chemické závody W. Piecka,

TABLE I

X-Ray Diffraction Analysis of Monoethanolamine Terephthalate (Müller-Micro 111, CuK_α radiation)

d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0
7·97	7	3·65	44	2·88	5	2·26	5
5·91	84	3·54	47	2·79	2·5	2·23	6
5·60	11	3·31	4	2·76	4	2·20	7
4·67	8	3·22	55	2·67	2·5	2·09	2·5
4·54	8	3·13	6	2·51	12	1·92	21
4·41	55	3·02	34	2·45	7·5	1·76	3
4·15	8	2·95	37	2·35	2·5	1·65	4
4·02	100			2·32	5	1·55	3
3·86	2·5			2·29	8		

Nováky), a solution was obtained, which after filtration yielded by both crystallization with slow cooling of the unstirred solution and from stirred solution with rapid cooling clear crystals with well-developed planes. For $C_{12}H_{20}N_2O_6$ (288·3), calculated: 50·00% C, 6·97% H, 9·70% N; found: 49·99% C, 7·28% H, 9·76% N.

Solubility in water was determined gravimetrically and found to be 22·94% by weight at 25°C. On the contrary, the solubility of terephthalic acid at 25°C is only $6 \cdot 10^{-4}$% by weight.

Conductivity of the aqueous solution was determined by means of a conductoscope (Laboratorní přístroje, Prague). Specific conductivity of a 0·40% solution of monoethanolamine terephthalate in redistilled water at 25°C was $\varkappa = 1{\cdot}95 \cdot 10^{-3}$ [Ω^{-1} cm^{-1}]; that of redistilled water at 25°C was $\varkappa = 5{\cdot}34 \cdot 10^{-5}$ [Ω^{-1} cm^{-1}].

Infrared spectra of both the normal and deuterated product were measured with a UR 10 apparatus, manufactured by Zeiss, Jena. The results obtained indicate that the compound has a ionic structure, and its composition is as follows:

$$HO\,CH_2\,CH_2\,NH_3^+ \,.\, {}^-OOC\,C_6H_4\,COO^- \,.\, NH_3^+\,CH_2\,CH_2\,OH\,.$$

Thermal analyses performed with a MOM OD 102 Derivatograph (Fig. 1) and a DSC-1 Perkin-Elmer apparatus indicate a strongly endothermic process starting at 220°C and connected with a weight loss of c. 25% (in dependence on the velocity and time of heating: 24·2%; 24·7%;

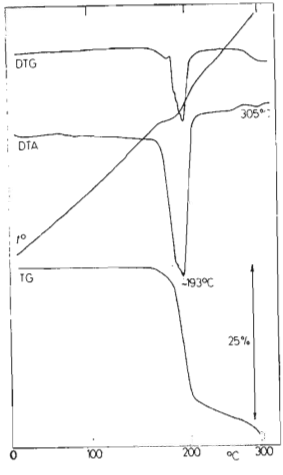

FIG. 1
DTA, DTG and TG Curves Recorded with Derivatograph

25%; 26·4%). Apparently, the reaction (theoretical weight loss 15·6%)

$$[HO\,CH_2\,CH_2\,NH_3^+\ {}^-OOC\,C_6H_4\,COO^-\,.\,NH_3^+\,CH_2CH_2OH]_x \rightarrow$$

$$\xrightarrow[-(2\,H_2O)_x]{} [HO\,CH_2CH_2NH\,OC\,C_6H_4\,CO\,NH\,CH_2\,CH_2\,OH]_x$$

occurs in this case, combined with the sublimation of the initial components of monoethanolamine and terephthalic acid; this is also corroborated by a white deposit in the surroundings of the heated sample. No ammonia was found in the reaction products; the content of nitrogen in the reaction did not decrease, but rose slightly to 10·15% and 10·23%.

Molecular weight of the reaction product determined in benzene by the osmometric method in vapour phase[1] varied from 400 to 700.

Density of crystals determined pycnometrically in xylene was 1·445 g/cm^3.

Refractive indexes measured by the immersion method on small fragments of crystals in sodium light:

$$n_\alpha = 1{\cdot}536\,; \quad n_\beta = 1{\cdot}586\,; \quad n_\gamma = 1{\cdot}655\,.$$

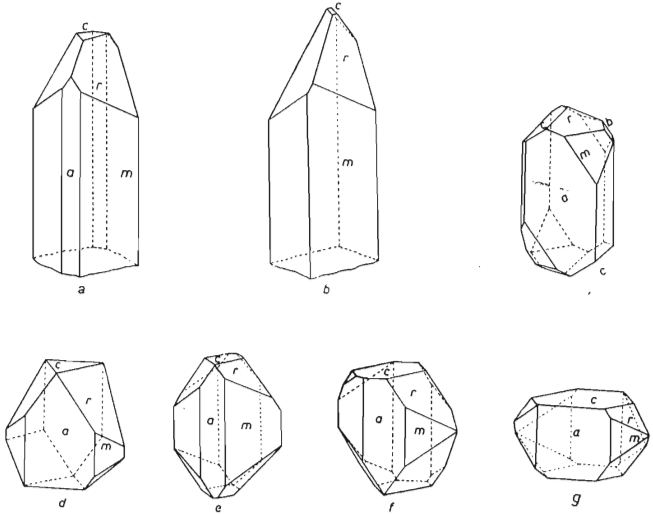

FIG. 2
Various Types of Monoethanolamine Terephthalate Crystals

RESULTS

Monoethanolamine terephthalate crystallizes in the monoclinic system, prismatic class. Crystals obtained from different media differ as to their habit. Crystallization in an agitated aqueous solution yields long column-like crystals; on the other hand, short column-like or even isometric crystals were obtained by continuous crystallization. The prevailing crystal type is mostly prismatic. With long column-like crystals, only simple shapes were observed:

$$a(100)\,,\quad c(001)\,,\quad m(110)\,,\quad r(122)\,,$$

represented in various combinations, as can be seen in Figs 2*a* and *b*. In the case of column-like crystals, the shape *b*(010) is found sporadically (Fig. 2*c*). Combination series of short column-like crystals are analogous to the long column-like types (Figs 2*d*, $-f$). Fig. 2*g* shows a crystal belonging to this group and having the basal-pinacoidal type. The shapes found with the crystals of monoethanolamine terephthalate are summarized in the gnomonic projection in Fig. 3. Most of the crystals show a strong monstrous development; the plane surfaces are smooth, glossy to mat in appearance.

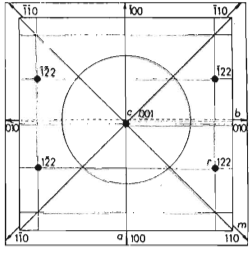

FIG. 3

Gnomonic Projection of the Shapes of Monoethanolamine Terephthalate Crystals

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