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Phase Diagram of the Ternary System NaBr/CsBr/H$_2$O Elucidated by Mechanochemical Equilibration

Shmuel Yariv*

Department of Inorganic and Analytical Chemistry, The Hebrew University, Jerusalem 91904, Israel

Hans J. Seifert and Jochen Uebach

Inorganic Chemistry, University Gh Kassel, D-3500 Kassel, Germany

Shlomo Shoval

The Open University of Israel, 16 Klausner Street, Tel-Aviv 61392, Israel

Mechanochemical equilibration of the ternary system NaBr/CsBr/H$_2$O was investigated using a ball mill which is a closed system. Products obtained by grinding mixtures with different molar ratios of NaBr, CsBr, and H$_2$O were identified by X-ray diffraction, IR spectroscopy, and thermal analysis. The water content of the different species in the mixture was determined by thermogravimetry. The products of grinding are solid solutions of hydrated NaBr in CsBr, Cs$_{1-x}$[Na(H$_2$O)]$_x$Br ($x \leq 0.48$), the hydrated double salt Cs[Na(H$_2$O)]$_2$Br$_3$, and NaBr·2H$_2$O. The phase diagram of the NaBr/CsBr/H$_2$O system was constructed for that part in which only solids exist in the equilibrium state. From the phase diagram it is obvious that the double salt cannot be crystallized from aqueous solutions.

Introduction

It has been previously shown that by ball mill grinding of NaBr and CsBr in the presence of water, with the molar ratio 2:1:2, a hydrated double salt Cs[Na(H$_2$O)]$_2$Br$_3$ is obtained (1). If the amount of NaBr is not sufficient for the formation of the double salt, or if NaBr and CsBr are ground in a mortar, which is an open system in which the salts are in contact with the atmosphere, a solid solution of H$_2$O and NaBr in CsBr crystals is obtained (2). In analogy with the ternary system NaCl/CsCl/H$_2$O (3–7), it has been suggested that the hydrated solid so-

lution of NaBr in CsBr has the general formula Cs$_{1-x}$[Na(H$_2$O)]$_x$Br (2).

We recently found that mechanochemical equilibration can be used as a method for the construction of a phase diagram of the ternary system NaCl/CsCl/H$_2$O, for that part of the diagram in which all components were in the solid state (8). In the present paper we report on the construction of a phase diagram of the ternary system NaBr/CsBr/H$_2$O for that region of the diagram where all components were in the solid state. In this system, in addition to NaBr, CsBr, Cs[Na(H$_2$O)]$_2$Br$_3$, and Cs$_{1-x}$[Na(H$_2$O)]$_x$Br, also sodium bromide dihydrate, NaBr·2H$_2$O, must be taken into consideration. In addition, the IR spectrum of the double salt which has not yet been described in the literature is described in this paper.

Experimental Section

Chemicals. The alkali-metal halides were of Suprapur grade, supplied by Merck.

Ball Mill Grinding. The ball mill (Retsch Model S1) was equipped with an agate cell of 50 mL and six agate balls. Mixtures of NaBr and CsBr (total amount 0.500–8.500 g) in different ratios were ground in the ball mill (640–720 rpm) for 24 h, in the presence of different amounts of water. After the first 60 min, the grinding was stopped for a short time and the mixture was thoroughly homogenized. The ground mixtures were allowed to stand in closed bottles at room temperature for 7 days before they were analyzed.

The laboratory temperature was 25 °C.

Aging of Mixtures Containing NaBr, CsBr, and H$_2$O (Static Equilibration). Mixtures containing 1.7025 g of CsBr, 0.4116,

Table I. Products Obtained by Ball Mill Grinding of Mixtures Containing NaBr and CsBr in Different Molar Ratios but H₂O in the Same Number of Moles as NaBr and DTG Peak Maxima (°C) of the Last Stage of the Dehydration[a]

mixture no.	M_{NaBr}/g	M_{CsBr}/g	M_{HOH}/g	NaBr:CsBr:HOH molar ratios	products identified by X-ray and thermal analysis[b]	chemical composition of solids determined by thermogravimetry	DTG peak temp/°C
1	0.1544	1.2769	0.0270	0.25:1.0:0.25	S	$Cs_{0.80}(Na\cdot HOH)_{0.20}Br$	204
2	1.0290	4.2562	0.1800	0.5:1.0:0.5	S	$Cs_{0.67}(Na\cdot HOH)_{0.33}Br$	204
3	0.5145	1.7025	0.0900	0.625:1.0:0.625	S	$Cs_{0.62}(Na\cdot HOH)_{0.38}Br$	176
4	0.4322	1.2343	0.0756	0.73:1.0:0.73	S	$Cs_{0.58}(Na\cdot HOH)_{0.42}Br$	174
5	0.4528	1.1917	0.0792	0.785:1.0:0.785	S	$Cs_{0.56}(Na\cdot HOH)_{0.44}Br$	148
6	0.4579	1.1811	0.0801	0.80:1.0:0.80	S, D	$Cs_{0.57}(Na\cdot HOH)_{0.43}Br + 0.03Cs(Na\cdot HOH)_2Br_3$	160
7	0.4631	1.1705	0.0810	0.82:1.0:0.82	S, D	$Cs_{0.56}(Na\cdot HOH)_{0.44}Br + 0.02Cs(Na\cdot HOH)_2Br_3$	150
8	0.4733	1.1492	0.0828	0.85:1.0:0.85	S, D	$Cs_{0.55}(Na\cdot HOH)_{0.45}Br + 0.01Cs(Na\cdot HOH)_2Br_3$	163
9	0.4939	1.1066	0.0864	0.92:1.0:0.92	S, D	$Cs_{0.54}(Na\cdot HOH)_{0.46}Br + 0.04Cs(Na\cdot HOH)_2Br_3$	150
10	1.1688	1.6836	0.1800	1.0:1.0:1.0	S, D	$Cs_{0.58}(Na\cdot HOH)_{0.42}Br + 0.16Cs(Na\cdot HOH)_2Br_3$	175
11	0.8747	1.7025	0.1530	1.063:1.0:1.063	S, D	$Cs_{0.56}(Na\cdot HOH)_{0.44}Br + 0.17Cs(Na\cdot HOH)_2Br_3$	184
12	0.4631	0.8512	0.081	1.125:1.0:1.125	S, D	nc	nd
13	0.5145	0.8512	0.090	1.25:1.0:1.25	S, D	$Cs_{0.52}(Na\cdot HOH)_{0.48}Br + 0.23Cs(Na\cdot HOH)_2Br_3$	160
14	0.6174	0.8512	0.108	1.5:1.0:1.5	S, D	$Cs_{0.61}(Na\cdot HOH)_{0.39}Br + 1.03Cs(Na\cdot HOH)_2Br_3$	172
15	0.6174	0.6384	0.108	2.0:1.0:2.0	D	$Cs(Na\cdot HOH)_2Br_3$	173

[a] nc, not calculated; nd, not determined. [b] S, CsBr and/or solid solution; D, double salt.

Table II. Products Obtained by Ball Mill Grinding of Mixtures Containing NaBr and CsBr in Different Molar Ratios and DTG Peak Maxima (°C) of the Last Stage of the Dehydration[a]

mixture no.	M_{NaBr}/g	M_{CsBr}/g	M_{HOH}/g	NaBr:CsBr:HOH molar ratios	products identified by X-ray and thermal analysis[b]	chemical composition of solids determined by thermogravimetry	DTG peak temp/°C
16	1.8522		0.6480	1.0:0.00:2.0	H	$NaBr\cdot 2HOH$	
17	0.9261	0.6384	0.3240	1.0:0.33:2.0	S, H	$Cs_{0.56}(Na\cdot HOH)_{0.44}Br + 1.22NaBr\cdot 2HOH$	180
18	0.3087	0.6384	0.1080	1.0:1.00:2.0	S, H	$Cs_{0.60}(Na\cdot HOH)_{0.40}Br + 0.20NaBr\cdot 2HOH$	186
19	0.2058	0.8512	0.0720	1.0:2.00:2.0	S	$Cs_{0.67}(Na\cdot HOH)_{0.33}Br$	206
20	0.2058	1.2769	0.0720	1.0:3.00:2.0	S	$Cs_{0.75}(Na\cdot HOH)_{0.25}Br$	225
21	0.0515	1.8089	0.0180	1.0:17.00:2.0	S	$Cs_{0.94}(Na\cdot HOH)_{0.06}Br$	230

[a] Number of moles of H₂O is twice that of NaBr. [b] S, solid solution; H, sodium bromide dihydrate.

0.8232, or 1.6464 g of NaBr, and 0.072, 0.144, and 0.288 mL of H₂O, respectively, were left unground in closed bottles for 6 months.

Equilibration in an Aqueous Saturated Solution. A mixture containing 0.4305 g of NaBr, 0.4453 g of CsBr, and 0.5374 g of H₂O was allowed to stand in a closed bottle. After 6 days the solid was separated from the solution and examined by X-ray diffraction.

Characterization of Reaction Products. During the grinding or aging, small amounts were taken for X-ray examinations. Characterization of ground or unground mixtures after aging was carried out by X-ray diffraction. The different hydrated products were determined by thermogravimetry (TG). Representative samples were examined by differential thermal analysis (DTA) and IR. Total water content of ground samples was determined by heating the samples overnight at 350 °C.

Instruments. X-ray diffraction patterns were obtained on a Philips diffractometer using monochromatic Cu Kα radiation. A recording rate of 1 deg(2θ)·min⁻¹ was employed. IR absorption spectra were recorded on a Nicolet ZDX FTIR. Alkali-metal halide disks were prepared by careful mixing of 10 mg of the ground NaBr/CsBr/HOH mixtures (the solid solution or the double salt) with 100 mg of KBr and pressing at 10 atm. TG and DTG runs were obtained on a Stanton Redcroft apparatus, model TG-750. Portions of 5–10 mg of aged ball mill ground mixtures were used for this purpose. The heating rate was 10 K·min⁻¹. DTA runs were recorded on a home-made device using 0.3 g for each run and a heating rate of 2 K·min⁻¹ (*9*).

Results

1. Construction of a Phase Diagram by Ball Mill Grinding. Composition of the Hydrated Solid Solution. In order to determine the maxmium substitution of NaBr and H₂O in CsBr,

mixtures containing NaBr and CsBr in different molar ratios, with the same number of moles of H₂O as that of NaBr, were ground in the ball mill for 24 h. The compositions of the mixtures were determined by X-ray diffraction and TG (Table I).

A single phase (solid solution) was obtained with NaBr:CsBr molar ratios smaller than 0.8 and two phases (solid solution and double salt) with molar ratios ≥0.8. Maximum substitution (48 mol %) was obtained with a molar ratio of 1.25.

The solid solution required 24 h of grinding for the completion of its formation. The double salt, on the other hand, in addition to the 24 h of grinding required an aging period of 7 days for its formation. However, small characteristic X-ray peaks were already detected after the 24 h of grinding.

Stability in the System NaBr·2H₂O/CsBr. In order to determine stability fields in the NaBr·2H₂O/CsBr system, NaBr/CsBr mixtures with different molar ratios but with a NaBr:H₂O molar ratio of 1:2 were ground in the ball mill for 24 h. The compositions of the solids were determined by X-ray diffraction and TG after an aging period of 7 days (Table II). In the absence of CsBr, sodium bromide dihydrate was obtained after 3 h of grinding, but in the presence of CsBr it was not stable and converted to the solid solution. It exists only with a Na-Br:CsBr molar ratio ≥0.8.

In addition to H₂O in the solid solution and in the dihydrate, which was determined by TG, the ground samples contained free water (0.5–3%), determined by heating at 350 °C.

Equilibrium in the System NaBr/CsBr/H₂O. Mixtures containing NaBr, CsBr, and H₂O in different ratios were ground in the ball mill for 24 h, and their compositions were identified by X-ray diffraction and differential thermogravimetry (DTG) (Table III). For a NaBr:CsBr molar ratio of ≤2, NaBr can be found only as long as the molar ratio between H₂O and NaBr is smaller than 1. When this ratio is 1, and so long as the ratio between NaBr and CsBr is not greater than 2, all the NaBr
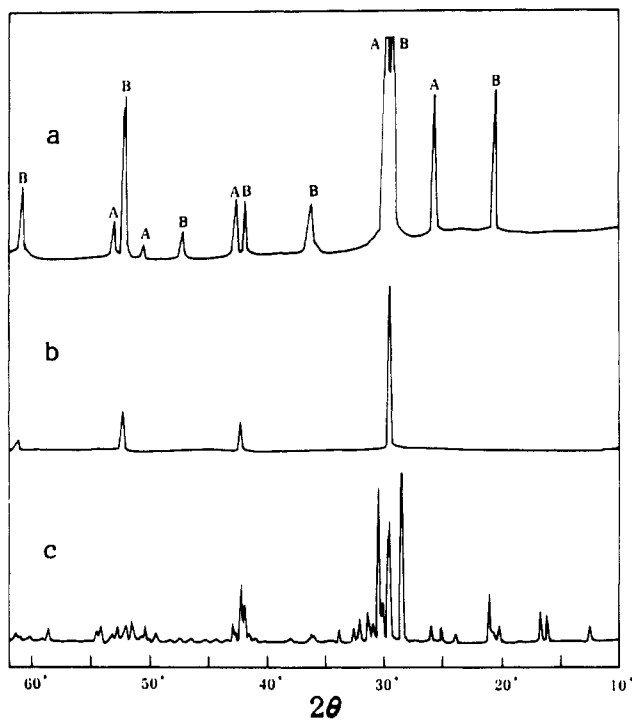
Table III. Products Obtained by Ball Mill Grinding of Mixtures Containing NaBr, CsBr, and H_2O in Different Molar Ratios and DTG Peak Maxima (°C) of the Last Stage of the Dehydration

mixture no.	M_{NaBr}/g	M_{CsBr}/g	M_{HOH}/g	NaBr:CsBr:HOH molar ratios	products identified by X-ray and thermal analysis[a]	chemical composition of solids determined by thermogravimetry	DTG peak temp/°C
22	0.2058	0.8512	0.0180	0.5:1.0:0.25	S, N	$Cs_{0.80}(Na·HOH)_{0.20}Br + 0.20NaBr$	206
23	0.4116	0.8512	0.0360	1.0:1.0:0.5	S, N	$Cs_{0.67}(Na·HOH)_{0.33}Br + 0.33NaBr$	168
24	0.3087	0.6384	0.0670	1.0:1.0:1.23	S, H	$Cs_{0.56}(Na·HOH)_{0.44}Br + 0.13NaBr·2HOH$	186
25	0.8226	0.8512	0.0180	2.0:1.0:0.25	S, N	$Cs_{0.80}(Na·HOH)_{0.20}Br + 1.40NaBr$	145–228
26	0.6174	0.6384	0.0270	2.0:1.0:0.5	S, N	$Cs_{0.67}(Na·HOH)_{0.33}Br + 1.00NaBr$	170
27	0.6174	0.6384	0.0540	2.0:1.0:1.0	S, D, N	$Cs_{0.73}(Na·HOH)_{0.27}Br + 0.46Cs(Na·HOH)_2Br_3 + 1.19NaBr$	153–210
28	0.7203	0.6384	0.1980	2.35:1.0:3.65	S, D, H	$Cs_{0.75}(Na·HOH)_{0.25}Br + 0.51Cs(Na·HOH)_2Br_3 + 1.66NaBr·2HOH$	185
29	0.9261	0.6384	0.0270	3.0:1.0:0.5	S, N	$Cs_{0.67}(Na·HOH)_{0.33}Br + 1.67NaBr$	175
30	0.9261	0.6384	0.0540	3.0:1.0:1.0	S, D, N	$Cs_{0.60}(Na·HOH)_{0.40}Br + 0.20Cs(Na·HOH)_2Br_3 + 1.19NaBr$	153–210
31	0.9261	0.6384	0.1080	3.0:1.0:2.0	D, N	$Cs(Na·HOH)_2Br_3 + NaBr$	170
32	0.9261	0.6384	0.1620	3.0:1.0:3.0	D, H, N	$2Cs(Na·HOH)_2Br_3 + NaBr·2HOH + NaBr$	157–167
33	0.9261	0.6384	0.2160	3.0:1.0:4.0	D, H	$Cs(Na·HOH)_2Br_3 + NaBr·2HOH$	150
34	0.9261	0.6384	0.2750	3.0:1.0:5.1	S, H	$Cs_{0.56}(Na·HOH)_{0.44}Br + 1.22NaBr·2HOH$	180

[a] S, CsBr and/or solid solution; D, double salt; H, sodium bromide dihydrate; N, sodium bromide.

Figure 1. Phase diagram of the system $NaBr/CsBr/H_2O$ for that part in which only solid phases are stable. Samples 1–34, obtained from ball mill grinding, are described in Tables I–III. Sample 35 was precipitated from a saturated solution of NaBr and CsBr in H_2O with a molar ratio of 2:1:14.27. The area in the diagram with molar ratio $NaBr:H_2O > 2$ (in the presence of excess water) was not investigated.

employed takes part in the formation of the solid solution and/or the double salt. When the $H_2O:NaBr$ molar ratio is >1 and the NaBr:CsBr molar ratio is greater than 0.8, $NaBr·2H_2O$ is also formed.

A phase diagram based on these results and those of Tables I and II is shown in Figure 1. Point X in the phase diagram represents the monoclinic double salt (mixture 15 in Table I) whereas point Y represents the single-phase cubic solid solution (one-component system) with maximum substitution (44 mol %, mixture 5 in Table I). The line CY represents the solid solution series (mixtures 1–5, Table I). Along the line XY, the solid solution coexists with the double salt (mixtures 6–14). Table I shows a variable composition of the solid solution with maximum substitution at 48 mol % $Na·H_2O$ (mixture 13). This is an indication that the crystallization of the double salt begins before the saturation of the solid solution. After the maximum substitution, the solubility of $Na·H_2O$ in CsBr slightly decreases with increasing concentration of NaBr.

Along the line BX the double salt coexists with NaBr (mixture 31). Point Z represents the dihydrate. Along the line XZ the

dihydrate coexists with the double salt (mixture 33 in Table III) whereas along the line YZ the dihydrate coexists with the solid solution (mixtures 24 and 34, Table III). Along the line BC (in the absence of water), no solid solution is formed and NaBr coexists with CsBr. In the area BCY the solid solution coexists with NaBr (mixtures 22, 23, 25, 26, and 29). In the area BXY three phases coexist, namely, the double salt, the solid solution, and NaBr (mixtures 27 and 30). In the area BXZ the three coexisting phases are the double salt, NaBr, and the dihydrate (mixture 32) whereas in XYZ the three coexisting phases are the double salt, the solid solution, and the dihydrate (mixture 28).

2. Static Equilibration. Three mixtures containing NaBr, CsBr, and H_2O in molar ratios of 0.5:1:0.5, 1:1:1, and 2:1:2 were left unground in closed bottles for 6 months. The X-ray diffractograms of these unground wet mixtures showed that CsBr (or the solid solution) persisted. The peaks of NaBr became very weak but persisted even after 6 months. Dihydrate appeared in all three samples. In the diffractograms of samples with molar ratios of 1:1:1 and 2:1:2, new peaks which characterize the double salt also appeared.

3. Equilibration in an Aqueous Saturated Solution. The solid separated from a solution of NaBr and CsBr in H_2O (molar ratio 2:1:14.27, sample 35 in Figure 1) showed by X-ray diffraction the presence of the dihydrate and the solid solution.

4. Characteristic Features of the Solid Solution. The following analyses were employed in order to characterize the solid solution and to differentiate it from CsBr.

X-ray Diffraction. 1. The peaks of CsBr persisted (Figure 2), but the lattice constant decreased very slightly from 430.13 ± 0.05 pm, that of our pure CsBr, to 429.93 ± 0.05 pm.

2. The intensities of several of the CsBr peaks relative to that of the [0, 1, 1] plane were changed; those of the [1, 0, 0], [1, 1, 1], [2, 1, 0], and [2, 1, 1] planes considerably decreased from 8%, 4%, 6%, and 43% to 2%, 2%, 0%, and 30%, respectively.

Infrared Spectroscopy Study. IR spectra of $Cs_{0.67}(Na·HOH)_{0.33}Br$, $Cs(Na·HOH)_2Br_3$ and $NaBr·2HOH$ in KBr disks are shown in Figure 3. Characteristic absorption maxima together with the assignments of the different bands are given in Table IV. The spectrum of the solid solution shows two H_2O stretching vibrations, one deformation vibration, and two librational vibrations. The fact that the stretching and deformation bands are sharp, and especially the presence of the two librational modes, indicates that the adsorbed water molecules are packed in a high degree of order, occupying definite lattice sites in the CsBr crystal. After heating the disks the water bands became weak (200 °C) and disappeared (250 °C), in-

Figure 2. X-ray diffractograms of mixtures containing NaBr (A) and CsBr (B) in a molar ratio of 1:1 before grinding (curve a), NaBr, CsBr and H₂O in a molar ratio of 1:2:1 after a ball mill grinding of 24 h (curve b), and NaBr, CsBr, and H₂O in a molar ratio of 2:1:2 after a ball mill grinding of 24 h and an aging period of 7 days (curve c). Curves b and c are diffractograms of the solid solution $Cs_{0.67}(Na \cdot HOH)_{0.33}Br$ and the double salt $Cs(Na \cdot HOH)_2Br_3$, respectively.
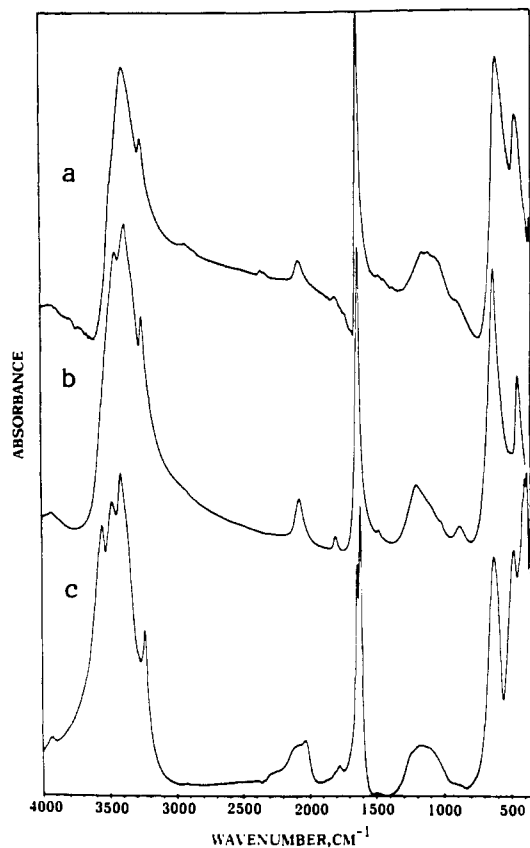

Figure 3. IR spectra of $Cs_{0.67}(Na \cdot HOH)_{0.33}Br$ (curve a), $Cs(Na \cdot HOH)_2Br_3$ (curve b), and NaBr·2HOH (curve c) in KBr disks.

dicating the evolution of water in this temperature range. No OH absorption bands were detected in the spectra of the thermal-treated disk, indicating that the evolution of water was

Table IV. Characteristic Absorption Maxima (cm⁻¹) of HOH Bands in the IR Spectra of $Cs_{0.667}(Na \cdot HOH)_{0.333}Br$, $Cs(Na \cdot HOH)_2Br_3$, and NaBr·2HOH, Recorded in KBr Disks[a]

assignment	$Cs_{0.67}(Na \cdot HOH)_{0.33}Br$	$Cs(Na \cdot HOH)_2Br_3$	NaBr·2HOH
stretching			3550
		3457	3479
	3392	3388	3414
	3257	3258	3236
bending	1641	1639	1639
			1617
librational mode	600	628	620
	460	441	473

[a] The assignments are according to Nakamoto (10).
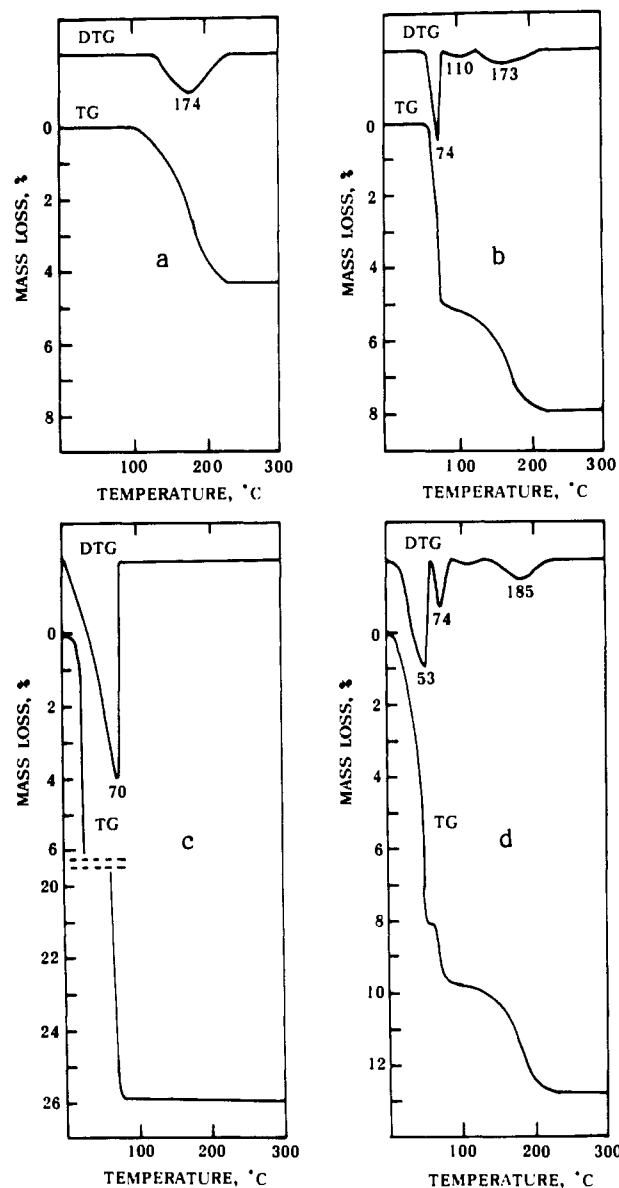
Figure 4. TG and DTG curves of $Cs_{0.58}(Na \cdot HOH)_{0.42}Br$ (sample 4, curves a), of $Cs(Na \cdot HOH)_2Br_3$ (sample 15, curves b), of NaBr·2HOH, (sample 16, curves c), and of a mixture containing the three phases $Cs_{0.75}(Na \cdot HOH)_{0.25}Br$ + $0.51Cs(Na \cdot HOH)_2Br_3$ + 1.66NaBr·2HOH (sample 28, curves d).

not accompanied by thermal hydrolysis.

The IR spectrum of the double salt shows an additional stretching absorption band, and the two librational modes shift to a higher and a lower frequency, respectively. When the disk

is heated at 110 °C its spectrum becomes similar to that of the solid solution.

The IR spectrum of the dihydrate has four stretching and two deformation vibrations. No water bands were detected after the disk was heated at 110 °C.

Thermal Analysis. Curves a, b, and c of Figure 4 are the TG and DTG curves of $Cs_{0.58}(Na \cdot HOH)_{0.42}Br$, $Cs(Na \cdot HOH)_2Br_3$, and $NaBr \cdot 2HOH$, respectively. The dihydrate gives a single DTG peak, the temperature of which depends on the amount of the sample which is used for the thermal analysis. It appeared at 72 and 65 °C with 9.2 and 7.8 mg of sample, respectively, shifting to lower temperatures (up to 40 °C) with smaller amounts of the salt. The double salt shows three DTG peaks. The first peak at 74 °C is very sharp. It is followed by a very broad and small peak at 110 °C (not always detected) and a third peak at 173 °C. Weight loss starts at 65 °C, and the first inclined slope is due to the loss of 59.7% from the total water of the double salt. The solid solution loses weight above 140 °C. The DTG curve shows a single peak, the location of which (148–204 °C) depends on the degree of substitution (Table I). With higher substitution the solid solution becomes less stable and the thermal decomposition takes place at a lower temperature. The DTA curves (below 400 °C) of these samples are very similar to the DTG curves, showing endothermic peaks due to the evolution of water.

Figure 4d shows the TG and DTG curves of a mixture containing these three compounds. Such a diagram can be used to determine the amount of each of the components. The first slope in the TG curve describes weight loss due to evolution of H_2O from the dihydrate. The second slope is due to the first stage in the dehydration of the double salt. In order to determine the total amount of water which forms the double salt, the weight loss at this stage is multiplied by the factor 1.675. Water belonging to the solid solution is determined by subtracting weight loss associated with the double salt from total weight loss in the third and fourth stages.

Density Measurements. Densities of the solid solution $Cs_2[Na(H_2O)]Br_3$ and of CsBr were measured. They were 3.73 and 4.44 $g \cdot dm^{-1}$, respectively. The calculated density of this solid solution, determined from its unit cell and from atomic masses, is 3.80 $g \cdot dm^{-1}$.

Discussion

When mixtures of NaBr, CsBr, and H_2O were ground in a ball mill, $NaBr \cdot 2H_2O$, the solid solution $Cs_{1-x}[Na(H_2O)]_xBr$, and/or $Cs[Na(H_2O)]_2Br_3$ were formed during the grinding process. The reaction products depended on the molar ratios (Tables I–III). The same products were obtained by aging mixtures containing NaBr, CsBr, and water, but the reactions were incomplete even after 6 months. Grinding speeds up these processes and brings about their completion within a few days.

A phase diagram was constructed from data obtained by grinding various mixtures (Figure 1). In the present study, we did not try to determine the phase diagram for the system in the presence of excess water (area ACYZ) and the broken line AY is not necessarily accurate. There is no doubt that in the area ACY two phases coexist, an aqueous solution together with a solid solution, whereas in the area AYZ three phases coexist, an aqueous solution and the solid solution together with the solid dihydrate. From the phase diagram it is obvious that the double salt cannot be crystallized from an aqueous solution. The only way to synthesize this salt is by mechanochemical techniques.

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