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Phase Diagram of the Ternary System NaCl/CsCl/H_2O Elucidated by Mechanochemical Equilibration

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Mechanochemical equilibration of the ternary system NaCl/CsCl/H_2O was investigated using two types of grinders: (I) a ball mill (a closed system) and (II) a mortar grinder (an open system). Products obtained by grinding mixtures with different molar ratios of NaCl, CsCl, and H_2O were determined by X-ray diffraction, IR, NMR, and thermal analysis. These are either solid solutions of hydrated NaCl in CsCl, $Cs_{1-x}[Na(H_2O)]_xCl$, or a hydrated double salt, $Cs[Na(H_2O)]_2Cl_3$. By applying the ball mill grinder, it was possible to construct a phase diagram of the NaCl/CsCl/H_2O system in the area in which only solids exist in the equilibrium state. In the mortar grinder the ground material was in contact with the atmosphere and water was exchanged between the solids and the atmosphere (adsorption or desorption). Solid solutions were obtained by both techniques whereas the double salt was obtained only by ball mill grinding. The differences in the results of the two grinding technqiues were explained on the basis of the phase diagram.

Introduction

Solubility relations at 1 atm in the ternary system NaCl/CsCl/HOH have been investigated by Chou et al. (*1-3*). In that study, a monoclinic hydrated double salt having the composition $Cs[Na(H_2O)]_2Cl_3$ (*4*) and a solid solution series of hydrated NaCl in CsCl (*5*) with the general formula $Cs_{1-x}[Na(H_2O)]_xCl$, with x ranging from 0 to 0.427 (at 298 K) were precipitated from saturated aqueous solutions. On the basis of solubility data, a phase diagram was constructed for the ternary system NaCl/CsCl/H_2O, showing different fields in which solid phases (solid solution, $Cs[Na(H_2O)]_2Cl_3$, NaCl, or CsCl) are stable in equilibrium with aqueous solutions (*2*, *4*).

The technique employed by these researchers requires the presence of excess water for rapid equilibration, and as they stated in their paper (*2*), the area in the diagram with molar ratio NaCl:HOH $\geq$ 1, in which all components are in the solid state, was not investigated. Consequently, their phase diagram is incomplete.

We recently showed that by grinding NaCl and CsCl in an open mortar, water is adsorbed from the atmosphere and the solid solution is obtained (*6*). We also showed that by grinding in a closed ball mill NaCl and CsCl in the presence of water, with an NaCl:CsCl:H_2O molar ratio of 2:1:2, the double salt is obtained (*7*). The mechanochemical reaction is fast and needs only a few hours to reach equilibrium. In the present paper we shall demonstrate that stability fields of the NaCl/CsCl/H_2O system, with molar ratios NaCl:HOH $\geq$ 1, in the area where only solid phases exist, can be successfully determined by a mechanochemical investigation.

Two types of grinders were used in the present study: (I) a ball mill, a closed system in which the ground material is isolated from the atmosphere, and (II) a mortar grinder, an open system in which the ground material is in contact with the atmosphere. Mixtures with different molar ratios of NaCl and CsCl were ground, and the effect of water on the reaction products was investigated. In addition, the products obtained from certain mixtures after grinding for several hours were compared to those obtained by aging similar mixtures for 1 year under static conditions.

The double salt can be identified by X-ray diffraction. However, it is impossible from the X-ray data to differentiate between pure CsCl and the solid solution, since parameters for both phases are nearly the same. The IR spectra, on the other hand, show five characteristic sharp absorption bands and the differential thermal analysis (DTA) shows a characteristic endothermic peak (*6*, *8*, *9*). For this reason we employed IR spectroscopy and DTA to identify the solid solution. In addition, NMR and density measurements were employed in the present study, proving that these methods are also applicable to identify the solid solution. The NMR spectrum and the density of the double salt have not previously been investigated.

Experimental Section

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

Grinding. Ball Mill Grinding. The ball mill (Retsch Model S1) was equipped with a 50-mL agate cell and seven agate balls. Mixtures of NaCl and CsCl (total amount 500-8500 mg) in different ratios and containing different amounts of H_2O were ground in the ball mill (640-720 rpm) for up to 48 h. After the first 60 min, the grinding was stopped for a short time and the mixture was thoroughly homogenized.

Mortar Grinding. The mechanical mortar grinder (Fisher) was equipped with an agate pestle and mortar.

(*I*) ***Air Grinding.*** Mixtures of NaCl and CsCl (total amount 200-8500 mg) in different ratios were ground in air atmosphere

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Table I. Products Obtained by Grinding Mixtures of NaCl, CsCl, and H_2O at Different Molar Ratios in a Ball Mill for 24 h, Their Water Content (wt %), and Lattice Constants of Solid Solutions (pm)[a]

mixture no.	M_{NaCl}/g	M_{CsCl}/g	M_{HOH}/g	NaCl:CsCl:HOH molar ratio	products identified by X-ray diffraction[b]	lattice constant of solid solution/pm	water content/wt %	
							calcd	found
1	0.1461	1.6836	0.0450	0.25:1.0:0.25	S(+++++)	412.0	2.400	nd
2	0.2922	1.6836	0.0450	0.5:1.0:0.25	S(+++++), N(+)	412.2	2.227	2.58
3	0.1461	0.8418	0.0340	0.5:1.0:0.38	S(+++++), N(tr)	412.0	3.346	3.34
4	0.2922	1.6836	0.0900	0.5:1.0:0.5	S(+++++)	412.0	4.357	4.31
5	0.2922	0.8418	0.0270	1.0:1.0:0.3	S(++++), N(++)	412.1	2.326	2.38
6	0.2922	0.8418	0.0450	1.0:1.0:0.5	S(++++), N(++)	412.1	3.818	3.69
7	0.5844	1.6836	0.1800	1.0:1.0:1.0	D(++), S(+++++)	411.9	7.353	7.25
8	0.5844	0.8418	0.0225	2.0:1.0:0.25	S(++++), N(+++)	411.9	1.553	nd
9	1.1688	1.6836	0.0900	2.0:1.0:0.5	S(+++++), N(++)	411.9	3.059	3.16
10	1.1688	1.6836	0.1800	2.0:1.0:1.0	D(+), S(+++), N(+)	411.8	5.936	5.86
11	1.1688	1.6836	0.3600	2.0:1.0:2.0	D(+++++)		11.207	11.26
12	0.8766	0.8418	0.045	3.0:1.0:0.5	S(++), N(+++)	nd	2.552	2.43
13	0.8766	0.8418	0.090	3.0:1.0:1.0	D(+), S(++), N(++)	nd	4.977	4.89
14	0.8766	0.8418	0.045	3.0:1.0:2.0	D(+++), N(+++)		9.481	9.30

[a] nd, not determined. [b] N, NaCl; S, CsCl and/or solid solution; D, double salt. Plus sign indicates the relative amount of the product; tr means trace amounts.

for periods from a few minutes to 24 h.

(II) Wet Grinding. A few mortar grinding experiments were carried out under wet conditions. In this grinding process a drop of water was added to the mixture every 10 min.

The laboratory temperature was 25 °C, and the relative humidity of the laboratory atmosphere was about 40%.

Evaporation from Aqueous Solutions (Evaporites). Mixtures (200 mg) containing NaCl and CsCl in molar ratios of 0.3:1, 1:1, 2:1, and 26:1 were dissolved in 5 mL of H_2O, and the solutions were left for several days uncovered, at room temperature, until they were completely dry.

Aging of Mixtures Containing NaCl, CsCl, and H_2O under Static Conditions (Static Equilibration). Mixtures containing NaCl, CsCl, and H_2O in molar ratios of 0.5:1:0.5, 1:1:1, and 2:1:2 were left unground for periods up to 1 year in closed bottles.

Characterization of Reaction Products. During the grinding or aging, small amounts were taken for X-ray and IR examinations. Representative samples were examined by DTA and NMR. The water content of ground samples was determined by heating the samples overnight at 350 °C.

Instruments and Techniques. X-ray diffraction patterns were obtained on a Philips diffractometer using monochromatic Cu Kα radiation. A recording rate of 1 deg(2θ)$\cdot$min^{-1} was employed. Cell dimensions were calculated with the least-squares program of Warczewski and de Wolff (*10*) using NaCl as an internal standard.

Infrared absorption spectra were recorded on a Perkin-Elmer IR spectrophotometer, model 595, and on a Nicolet ZDX FTIR. Alkali-metal halide disks were prepared by using 1 mg of NaCl in 150 mg of CsCl, or 3–5 mg of the ground mixtures (the solid solution or the double salt) in 150 mg of KCl.

Simultaneous DTA–TG (thermogravimetry) runs were obtained on a Stanton Redcroft apparatus, model STA 780, using 10 mg of the ground mixtures and a heating rate of 10 K$\cdot$min^{-1}. DTA runs were also recorded on a home-made instrument at the University of Kassel, using 300 mg of the ground mixtures for each run and a heating rate of 2 K$\cdot$min^{-1} (*11*).

Proton magnetic resonance measurements were performed on 1 g of various mixtures of NaCl and CsCl with a Bruker PC-20 Multispec, operating at 20 MHz at 37 ± 1 °C. Spin–lattice relaxation times, T_1, were measured by the 180°–τ–90 pulse sequence. Spin–spin relaxation times, T_2, were measured using the Carr–Purcel–Meiboom–Gill (CPMG) multiecho pulse sequence. T_2 was determined by a linear fit of the logarithmic value of 20 echo amplitudes separated by 0.08 ms as a function of the decay time (τ). All signals were recorded using phase-sensitive detection. The samples were measured 16 times to increase the signal-to-noise ratio, and each experiment point was measured at least twice.

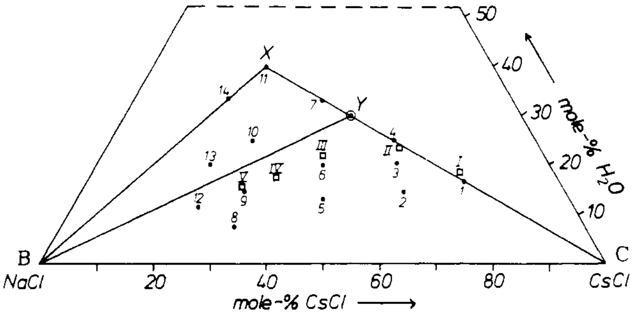

Figure 1. Phase diagram of the system NaCl/CsCl/H_2O for that part where only the solid phases are stable. Samples 1–14, obtained by ball mill grinding, are described in Table I. Samples I–V, obtained by mortar grinding in air, are described in Table II.

Results

1. The Ternary System NaCl/CsCl/H_2O. 1.a. Ball Mill Grinding (Closed System). Mechanochemical Equilibration in the System NaCl/CsCl/H_2O. Phases obtained by grinding mixtures of NaCl, CsCl, and H_2O in different molar ratios for 24 h are given in Table I. A phase diagram based on these results is shown in Figure 1. From the table it is obvious that NaCl can be found only as long as the molar ratio between H_2O and NaCl is smaller than 1. When this ratio is 1, but that between NaCl and CsCl is not greater than 2, all the NaCl employed takes part in the formation of the solid solution and/or the double salt.

In most cases the phases which are mentioned in Table I were already detected after 1 or 2 h of grinding and were the only existing phases. In the case of mixtures 9 and 12, very small amounts of the double salt were identified after 2 h of grinding, but disappeared after an additional 24 h of grinding.

At 350 °C the samples lost their water (Table I). Peaks of NaCl appeared in the X-ray diffractograms together with the CsCl peaks, due to the destruction of the double salt or the solid solution. The NaCl was obtained in very small crystals and consequently the x-ray diffraction (XRD) peaks were very small.

Reaction between the Double Salt and CsCl. A mixture containing the double salt (2 mmol) and CsCl (6 mmol) was ground in the ball mill. After 24 h the X-ray diffractogram showed that the reaction product was the solid solution. The reaction can be formulated as follows:

$$Cs[Na(H_2O)]_2Cl_3 + 3CsCl \rightarrow 2Cs_2[Na(H_2O)]Cl_3$$

Table II. Data on X-ray Study and Thermal Weight Loss for Mixtures Which Contained 5.0508 g of CsCl and Increasing Amounts of NaCl and Were Ground for 8 h[a]

	NaCl:CsCl molar ratio	NaCl [2,0,0]:CsCl [0,1,1] intensity ratio	lattice constant/pm	water content/wt %	calcd composition of mixtures
I	0.25	0.0	412.0	2.67	$0.08H_2O + Cs_{2.4}[Na(H_2O)]_{0.6}Cl_3$
II	0.5	0.0	412.1	4.09	$Cs_{2.04}[Na(H_2O)]_{0.96}Cl_3 + 0.07NaCl$
III	1.0	0.141	412.2	4.23	$Cs_{1.93}[Na(H_2O)]_{1.07}Cl_3 + 0.85NaCl$
IV	1.5	0.215	411.8	3.67	$Cs_{1.95}[Na(H_2O)]_{1.05}Cl_3 + 1.87NaCl$
V	2.0	0.287	412.1	3.29	$Cs_{1.95}[Na(H_2O)]_{1.05}Cl_3 + 2.86NaCl$

[a] Data include intensity ratios for the NaCl [2,0,0] and CsCl [0,1,1] peaks, lattice constants (pm) of the solid solution, water content (wt %), and the chemical composition of the different mixtures, calculated from the water content.

This result is in agreement with that obtained by grinding a mixture containing $NaCl:CsCl:H_2O$ in a molar ratio of 1:2:1.

Reaction between the Solid Solution and NaCl in the Presence and Absence of Water. A mixture containing the solid solution $Cs_2[Na(H_2O)]Cl_3$ (2 mmol), NaCl (6 mmol), and H_2O (6 mmol) was ground in the ball mill. The only solid phase present after 24 h was the hydrated double salt. The mechanochemical reaction can be formulated as follows:

$$Cs_2[Na(H_2O)]Cl_3 + 3NaCl + 3H_2O \rightarrow 2Cs[Na(H_2O)]_2Cl_3$$

This result is in agreement with that obtained by grinding a mixture containing $NaCl:CsCl:H_2O$ in a molar ratio of 2:1:2.

Another mixture containing the solid solution (2 mmol) and NaCl (6 mmol) was ground in the ball mill. The X-ray diffractogram after 24 h of grinding showed that no reaction occurred. This is in agreement with the result obtained by grinding a mixture containing $NaCl:CsCl:H_2O$ in a molar ratio of 2:1:0.5 (Table I).

1.b. Mortar Grinding in Atmospheric Ambient (Open System). Equilibration by Air Grinding. The results obtained after grinding mixtures with different NaCl:CsCl ratios can be summarized as follows.

1. XRD peaks which characterize NaCl gradually became very weak (Figure 2).
2. Intensity ratios for the NaCl [2,0,0] peak relative to the CsCl [0,1,1] peak for mixtures containing different molar ratios of salts, recorded after 8 h of grinding, are given in Table II. IR, NMR, and thermal analysis showed that the ground mixtures contained the hydrated solid solution of NaCl in CsCl.
3. There was no evidence of the formation of the double salt.
4. Compositions of the solid solutions formed in the various mixtures were calculated from the water content (thermal weight loss), assuming that the mixtures contained only NaCl and solid solution (Table II and Figure 1).

Equilibration by Wet Grinding. The mechanochemical behavior of NaCl/CsCl mixtures subjected to the wet grinding was similar to that of mixtures ground in air.

Mortar Grinding of the Double Salt in Atmospheric Ambient. A 0.200 g portion of the double salt was ground for 45 min. The X-ray diffractogram showed that the double salt was decomposed by air grinding into NaCl, CsCl, and/or solid solution.

1.c. Evaporites from Aqueous Solutions (Open System). These samples yielded diffractograms similar to those of the equivalent mortar ground mixtures. Only the solid solution was identified among the evaporites.

1.d. Static Equilibration (Closed System). XRD peaks of CsCl (or of the solid solution) persisted after 1 year. The peaks of NaCl became very weak but persisted even after 1 year. In the diffractograms of samples with $NaCl:CsCl:H_2O$ molar ratios of 1:1:1 and 2:1:2, new peaks which characterize the double salt appeared, but they were relatively small. In conclusion, the reactions occurring in the static equilibration were similar to those occurring during grinding, but they were incomplete even after 1 year.

2. Identification and Characterization of the Solid Solution. The following analyses were used to identify and characterize the solid solution and to differentiate it from CsCl.

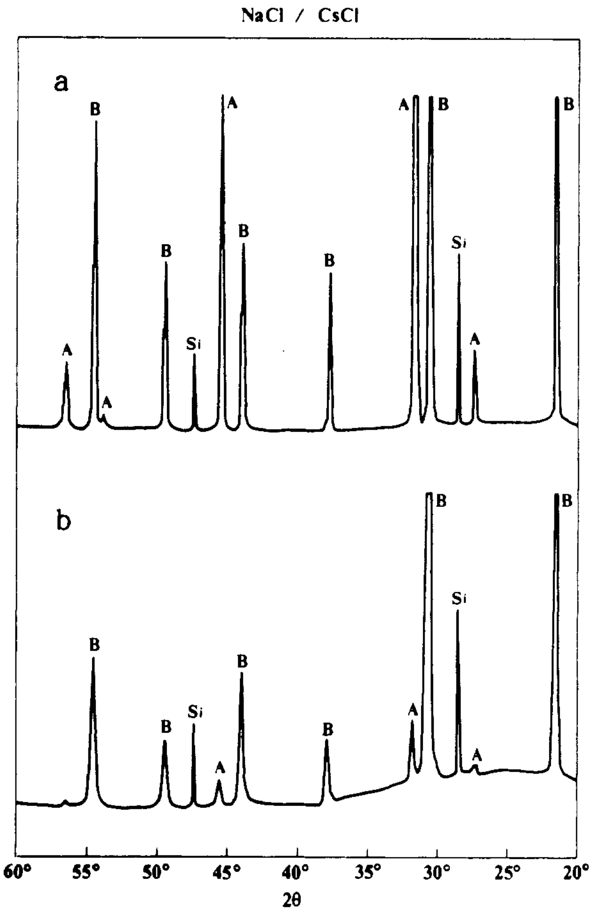

Figure 2. X-ray patterns of a mixture containing NaCl and CsCl in a molar ratio of 1:1 (total amount of 200 mg), before grinding (curve a) and after 1 h of air grinding (curve b): A, NaCl; B, CsCl; Si, silicon (for calibration).

X-ray Diffraction. Peaks of CsCl persisted, but the lattice constant decreased very slightly from 412.35 ± 0.05 to 412.0 ± 0.2 pm. Intensities of several of the CsCl peaks relative to that of the [0,1,1] plane were changed; those of the [1,1,1], [2,1,0], and [2,1,1] planes considerably decreased from 17%, 20%, and 30% to 5%, 8%, and 20%, respectively, whereas that of the [2,0,0] plane slightly increased from 11% to 15%.

Infrared Spectroscopy Study. The IR spectrum of the solid solution recorded at room temperature is very similar to that recorded after drying the disk at 110 °C (*6*, *8*) and is characteristic for H_2O occupying definite lattice sites in the CsCl crystal. The water bands became weak at 180 °C and disappeared at 250 °C, indicating the evolution of water in this temperature range (Figure 3).

The spectrum of a KCl disk of the double salt was similar to that of NaCl in a CsCl disk, probably due to the decomposition of the double salt during the preparation of the disk.

Thermal Analysis. The DTA, TG, and DTG (differential thermogravimetry) curves of the solid solution were described

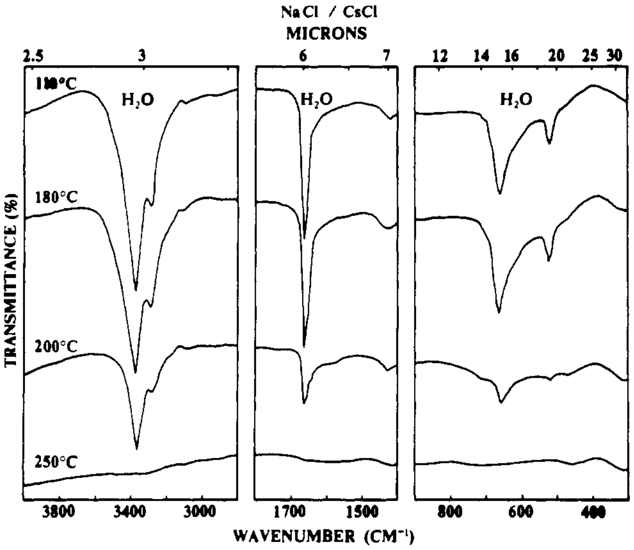

Figure 3. IR spectra of NaCl (1%) in a CsCl disk (NaCl:CsCl molar ratio = 0.03), ground for 5 min and left for 24 h in air atmosphere, recorded after heating the disk for 24 h at various temperatures as stated in the figure.

by Arkipov et al. (*8*, *9*), and those of the double salt were described by Severin et al. (*7*). The DTA curve of the double salt shows the first endothermic peak at 40 °C due to the loss of water whereas the solid solutions do not lose weight below 150 °C. The exact location of the DTA endothermic peaks depends on the NaCl:CsCl molar ratio. With ratios of 0.5:1, 1:1, 1.5:1, and 2:1 (samples II–V, Table II), it appears at 196, 188, 183, and 181 °C, respectively, indicating that thermal stability of hydrated solid solutions decreases with increasing degree of substitution. This peak is accompanied by two small endothermic shoulders at 168 and 246 °C. The TG curves show a weight loss of ca. 4%, due to the evolution of water.

NMR Study. NMR spectroscopy can probe a molecular environment on the time scale between 10^{-3} and 10^{-10} s. Relaxation times of mixtures containing NaCl and CsCl in molar ratios of 0.3, 1.0, and 26, after they had been ground for 1 h, were recorded. For comparison, relaxation times of evaporites obtained from solutions containing both salts in the same molar ratios as the ground mixtures and of various hydrated salts were also recorded. Relaxation times, T_1 and T_2, are given in Table III. Relaxation times, T_1, obtained for the ground mixtures, are extremely long, close to 10 s, increasing with the concentration of NaCl in the mixture. A long relaxation time is an indication of the "solidity" of the water molecules in the crystal structure. That is, a long relaxation time is an indication of water molecules occupying a definite lattice site, and thus behaving like solid and not like liquid. On the other hand, relaxation times of the examined hydrous sodium salts are much shorter, about half a second.

Relaxation times, T_2, of the ground mixtures are too short to be determined. A very short relaxation time is an indication of the association between the water molecules and of the absence of any kind of mutual interactions or proton exchange between the adsorbed water molecules. On the other hand, the relaxation times of the examined hydrous sodium salts were much longer, about half a second, indicating that there are some interactions, such as hydrogen bondings or proton exchange between the water molecules.

Relatively long relaxation times, T_1, were also obtained from the evaporites, but they were much shorter than those obtained from the ground mixtures.

Density Measurements. Densities of a solid solution with the composition $Cs_2[Na(H_2O)]Cl_3$ and of CsCl were measured. They were 3.17 and 4.00 g·cm^{-3}, respectively. Densities of this solid solution and of CsCl, calculated from the unit cell data, D_{cal} = $(Z(MW)/VN_A)$, where $V = a^3$, V and a are volume of the unit cell and lattice constant, Z is the chemical composition of the unit cell, MW is the formula weight, and N_A is Avogadro's number, are 3.27 and 4.00 g·cm^{-3}, respectively.

Table III. NMR Relaxation Times T_1 and T_2 (s) of Mixtures Containing NaCl and CsCl in Different Ratios (Total Weight 200 mg) after Being Ground for 60 min or Obtained as Evaporites from Dilute Aqueous Solutions and Relaxation Times of Several Hydrous Sodium Salts[a]

sample		relaxation time	
		T_1/s	T_2/s
ground mixtures	NaCl:CsCl molar ratio		
	0.3	7.44 ± 0.68	vs
	1.0	8.20 ± 0.90	vs
	26.0	9.30 ± 1.20	vs
evaporites	NaCl:CsCl molar ratio		
	0.3	5.27 ± 1.70	vs
	1.0	5.30 ± 0.88	vs
	26.0	5.62 ± 0.72	vs
hydrous sodium salts	$Na_2HPO_4 \cdot 12H_2O$	0.518 ± 0.020	0.45 ± 0.015
	$NaH_2PO_4 \cdot 2H_2O$	0.364 ± 0.016	
	$NaH_2PO_4 \cdot H_2O$	0.520 ± 0.092	
	$Na_2SO_3 \cdot ZH_2O$	0.402 ± 0.015	0.301 ± 0.03
	$Na_2Cr_2O_7 \cdot 2H_2O$	0.625 ± 0.020	0.146 ± 0.047

[a] vs, very short, cannot be determined.

Discussion

Use of Ball Mill Grinding for Constructing Phase Diagrams in the Area in Which the Components Are in the Solid State. A double salt or a solid solution was obtained by aging mixtures containing NaCl, CsCl, and water in the molar ratios of 2:1:2 or 1:2:1, respectively, but the process was incomplete even after 1 year. Grinding speeds up these processes and brings about their completion within a few hours. A mechanochemical equilibrium is achieved whether the reacting materials are binary compounds, NaCl, CsCl, and H_2O, or ternary compounds, i.e., the double salt or the solid solution. It is therefore obvious that mechanochemical equilibration can be used for constructing phase diagrams of solid mixtures.

Phase Diagram of the System NaCl/CsCl/H$_2$O. Our data obtained from ball mill grinding, for that part of the phase diagram in which all components were in the solid state, are complementary to those of Chou et al. (*2*, *4*) obtained for that part of the phase diagram in which solid phases were in equilibrium with aqueous solutions. Point X in the phase diagram represents the monoclinic double salt (mixture 11 in Table I) whereas point Y represents the cubic solid solution with maximum substitution according to Chou et al. (42.7 mol %). The line CY represents the solid solution series (mixtures 1 and 4, Table I). Along the line XY the solid solution coexists with the double salt (mixture 7), whereas along the line BX the double salt coexists with NaCl (mixture 14). Along the line BC (in the absence of water), no solid solution is formed and NaCl coexists with CsCl. In the area BCY the solid solution coexists with NaCl (mixtures 2, 3, 5, 6, 8, 9, and 12). In the area BXY three phases exist together, namely, the double salt, the solid solution, and NaCl (mixtures 10 and 13).

Comparison between Products Obtained in Ball Mill Grinding with Those Obtained in Mechanical Mortar Grinding. When NaCl and CsCl mixtures were ground in a mortar grinder, hydrated solid solutions of NaCl in CsCl crystals were obtained (Table II). In wet grinding, water was adsorbed from the liquid water phase which was added dropwise to the system. In air grinding, water can be adsorbed only from the atmosphere because all salts had been dried prior to grinding. The double salt was not obtained even after long grinding periods. On the other hand, the grinding of the double salt in the mechanical mortar resulted in desorption of water and the decomposition of this ternary compound into NaCl and solid solution. This indicates that the mechanochemical equilibrium in the open mortar grinder is determined by water exchange between the solids and the atmosphere.

The differences in the products of the two grinding techniques can be explained from the phase diagram. The ball mill is a closed system, and the adequate water partial pressure is maintained. In the open mortar grinder the adsorbed water comes from the atmosphere and its content is considered as the equilibrium water content. During grinding, H_2O partial pressure in the laboratory atmosphere was about 12 mbar. According to water determination and halide content of the mixtures, points II–V are located in the area BCY, where only two phases coexist, the solid solution and NaCl. It appears from the phase diagram that in open systems, due to the low water content of the atmosphere, the double salt is not stable. The solid solution, on the other hand, is stable.

The evaporites were also obtained in an open system, where the solid phase was in an equilibrium with the atmosphere and where water exchange between the solid and the atmosphere took place. Consequently, the double salt which was obtainable when the solid phase was in equilibrium with a saturated aqueous solution (*2*) was not detected among the evaporites.

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Registry No. NaCl, 7647-14-5; CsCl, 7647-17-8.

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Excess Volumes for the Systems Mesitylene + Dimethylformamide and Mesitylene + Hexamethylphosphortriamide at 298.15 K

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Excess volumes were measured for the systems mesitylene (1) + dimethylformamide (2) and mesitylene (1) + hexamethylphosphortriamide (3) at 298.15 K and atmospheric pressure. The excess volumes were negative for the mesitylene (1) + dimethylformamide (2) system with an excess volume minima at $x_1 = 0.332$. The excess volumes were positive for the mesitylene (1) + hexamethylphosphortriamide (3) system with an excess volume maxima at $x_1 = 0.248$. Data from both systems have been correlated by generalized equations.

This article reports the excess volume measurements for the systems mesitylene + dimethylformamide and mesitylene + hexamethylphosphortriamide at 298.15 K. The correlating equations relating excess volumes as a function of the mesitylene mole fraction are also reported for each system.

The systems were chosen in response to the unusual shape of the mesitylene + acetonitrile excess volume function as determined by Absood (*1*). The solvents, dimethylformamide and hexamethylphosphortriamide, are similar to acetonitrile in that all three are polar nonhydroxylic solvents.

Table I. Comparison of Component Densities at 298.15 K

compound	$\rho/(\mathrm{g\ cm^{-3}})$ lit. (*4*)	 this work
dimethylformamide	0.9439	0.9420
hexamethylphosphortriamide	1.0202	1.0179
mesitylene	0.8611	0.8587

Experimental Method

The excess volumes were measured directly by a continuous dilution dilatometer, as described by Kumaran and McGlashan (*2*). A back-pressure device was used to compensate for pressure differentials within the dilatometer during the dilution run. The temperature of the water bath used to contain the dilatometer was maintained to ±0.01 K with a Tamson TCV 70 bath and a Neslab Model PBC-2II bath cooler. The bath temperatures were measured with an NBS calibrated thermometer to within 0.05 K. A more detailed discussion of the experimental method has been described elsewhere (*3*).

The molar volume of each component was calculated via density values measured with a pycnometer. The measured values, along with values reported in the literature (*4*), are shown in Table I.

The test system benzene + cyclohexane at 298.15 K was studied in an effort to evaluate the accuracy of the experimental

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