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Solubility Relations in the Ternary System NaCl–CsCl–H_2O at 1 atm. 2. Solubility Relations at 25 °C

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Solubility relations in the CsCl-rich region of the ternary system NaCl–CsCl–H_2O have been determined at 25 °C by using the isothermal method. These data together with the halite solubility data reported in part 1 of this series complete the solubility relations for the entire ternary system at 25 °C. A new compound, $CsCl\cdot 2NaCl\cdot 2H_2O$, and a new solid-solution series, $[Cs_{1-x}(Na\cdot H_2O)_x]Cl$ with x ranging from 0 to 0.427, were found in this study. The new compound is monoclinic, belongs to space group $I2/c$, and has a = 13.620 (2), b = 5.831 (1), c = 10.709 (2) Å, β = 91.27 (1)°, Z = 4, V = 850.3 (1) Å^3; refractive indices are $n_\alpha = 1.520$, $n_\beta = 1.540$, $n_\gamma = 1.552$; density D_x = 2.509 g/cm^3. The solid solution is cubic with the cell edge slightly larger than that of CsCl and the refractive index $n^{25}{}_D = -0.14638x + 1.6405$.

Introduction

Solubilities of halite in the ternary system NaCl–CsCl–H_2O between 20 and 100 °C, measured by means of the visual polythermal method, have been reported in part 1 of this series (*1*). That experimental technique, however, is not applicable in the Cs-rich region of the ternary system, because more complicated phase relations are involved.

The solubility relations at 25 °C as determined by Plyushchev et al. (*2*) are summarized in Figure 1. In their experiment, Na^+ and Cl^- concentrations in the equilibrated solutions were determined gravimetrically with the concentration of Cs^+ being calculated by difference. The composition of solid phases was determined by using the Schreinemaker residue method along with the data on bulk composition and final solution composition. The existence of solid solutions between NaCl and CsCl was suggested and refractive indices were reported for three solid-solution samples. However, their compositions and crystal structure were not determined.

This paper presents the results of solubility measurements in the Cs-rich region of the ternary system at 25 °C. This report also includes chemical compositions, crystal structures, and optical properties of a new compound and a new solid-solution series found in this study. Solubility relations at 50 and 75 °C will be reported in the subsequent paper in this series. The preliminary results of this study have been presented earlier (*3*, *4*).

Experimental Section

The isothermal method was used in this study. Samples (12–15 g) of known composition were loaded into Pyrex tubes containing a Teflon-coated magnetic stirring bar. A layer of silicone oil (~1 cm) was added to seal the tube. The assembly was mounted in a constant-temperature glycol bath regulated at 25 ± 0.1 °C. The assemblage was well agitated and allowed to equilibrate for at least 2 weeks. The detailed experimental setup has been reported previously (ref *1*, Figure 3). It was found experimentally that equilibrium in the system could be reached within 12 days at 25 °C (*2*). At the end of a run, solids were separated from the solution, washed with alcohol in a vacuum-filtration system, and then dried in air for less than 30 min. Extreme care was taken to preserve the solids as prolonged drying may dehydrate the solids. The solids and the solution were then analyzed according to the following procedures:

(a) H_2O content for both the solution and the coexisting solid were determined by the weight loss of the sample dried to constant weight at 400 °C.

(b) A weighed amount of dried solid (W_{total} g) from the residue in step a was dissolved in distilled water to form a 25-mL solution, in which

$$M_{NA^+} + M_{Cs^+} = M_{Cl^-(total)} \quad (1)$$

$$(M_{Na^+})(W_{NaCl}) + (M_{Cs^+})(W_{CsCl}) = W_{total}(1000/25) \quad (2)$$

where M_i and W_i are molar (mol/L) concentration and molecular weight of i, respectively. $M_{Cl^-(total)}$ was measured coulometrically with a Buchler digital chloridometer, and the two unknowns, M_{Na^+} and M_{Cs^+}, were calculated from the two equations given above.

(c) The sample composition (in wt %) was calculated from M_{Na^+}, M_{Cs^+}, and H_2O content data according to the following relations:

$$x = \text{wt \% of } H_2O \text{ as determined in step a} \quad (3)$$

$$y = \text{wt \% of NaCl} = (100 - x)(M_{Na^+}W_{NaCl})/[(M_{Na^+}W_{NaCl}) + (M_{Cs^+}W_{CsCl})] \quad (4)$$

$$z = \text{wt \% of CsCl} = 100 - x - y \quad (5)$$

Results and Discussion

Solubility Data. Solubility relations determined at 25 °C in the CsCl-rich region of the ternary system are summarized in Table I and shown in Figure 2. These data and the previous halite solubility data (*1*) are used in Figure 3 to show the solubility relations for the entire ternary system.

The bulk compositions given in Table I are accurate to within ±0.03 wt %. The final solution compositions given in Table I are the average values of analyses of three aliquots. For each aliquot, one determination was made for H_2O content, and at least four were made for chloride. The precision of the H_2O content measurements (in wt %) ranges from ±0.02 to ±0.18 with an average of ±0.07. The accuracies are within ±0.38

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Table I. Solubility Data (in wt %) in the CsCl-Rich Region of the System NaCl-CsCl-H_2O at 25 °C

run no.	bulk composition			final composition						final solid phase[c]
				soln[a]			solid[b]			
	NaCl	CsCl	H_2O	NaCl	CsCl	H_2O	NaCl	CsCl	H_2O	
J	1.40	66.07	32.53	1.48	63.68	34.84	2.89	96.56	0.55	s
F	3.00	62.96	34.04	3.18	60.85	35.97	6.34	91.84	1.82	s
E	4.57	61.94	33.49	4.45	58.24	37.31	8.42	89.07	2.51	s
L	6.52	56.11	37.37	6.38	54.19	39.43	12.11	84.22	3.67	s
K	7.06	52.93	40.01	7.24	52.48	40.28	13.00[d]	82.99[d]	4.01[d]	s
H	8.95	51.19	39.86	8.18	49.85	41.97	15.01	80.59	4.40	s
N	9.84	47.79	42.37	10.21	46.80	42.99	15.90	78.44	5.66	s
I	10.97	47.21	41.82	10.29	46.01	43.70	16.94	78.00	5.06	s
M	11.97	44.20	43.83	10.71	44.61	44.68	30.63[e]	58.11[e]	11.26[e]	n + s
P	11.52	44.23	44.25	10.98	44.57	44.45	30.27[e]	60.93[e]	8.80[e]	n + s
G	12.47	43.93	43.60	11.11	44.09	44.80	33.98[e]	54.74[e]	11.28[e]	n
T	13.03	42.95	44.02	11.64	43.38	44.97	83.04	14.46	2.50	h + n
Q	12.92	41.86	45.22	11.91	42.30	45.79	f	f	f	h + (n)
R	12.90	40.92	46.18	12.40	41.04	46.56	f	f	f	h + (n)

[a] Average values from analyses of three aliquots. [b] Average values from analyses of one to three aliquots. [c] Final solid phases: s = solid solution, $[Cs_{1-x}(Na\cdot H_2O)_x]Cl$; n = new compound, $CsCl\cdot 2NaCl\cdot 2H_2O$; h = halite; the phase given in parentheses is less than 1% (estimated under the microscope). [d] Composition estimated from the refractive index (see Figure 6). Not enough solids were available for a reliable chemical analysis. [e] Analytical uncertainty greater than for other analyses; only a limited amount of solid was available for analysis. [f] Not determined.

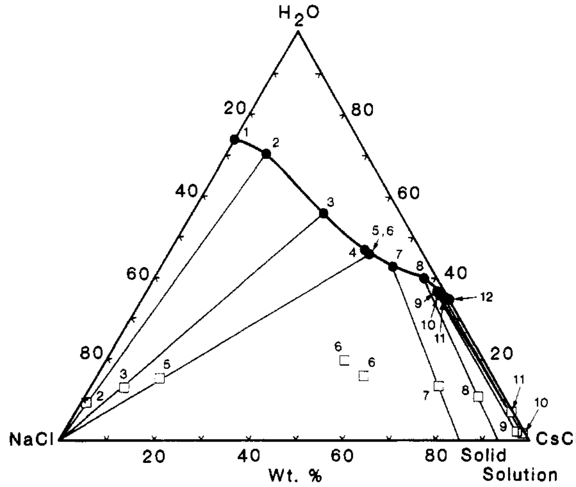

Figure 1. Solubility relations in the system NaCl-CsCl-H_2O at 25 °C, based on the data of Plyushchev et al. (2). Circles are solution compositions; squares are bulk composition. The compositions for solids were not determined. The numbers by the symbols denote run numbers.

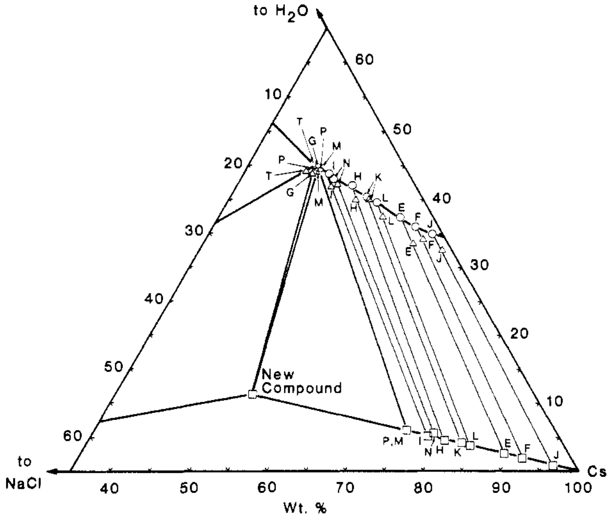

Figure 2. Experimental results in the CsCl-rich region of the system NaCl-CsCl-H_2O at 25 °C. Triangles are bulk compositions; circles and squares represent the final compositions of liquids and solids, respectively. Letters designate run numbers. The bulk solid compositions for those runs containing two solid phases are not shown. Data for runs Q and R are omitted for clarity.

wt %. In order to estimate the precision as well as the accuracy of the method used in this study to analyze the dried solid residues, three samples of known composition were prepared. These samples contained between 90.27 and 96.59 wt % CsCl. The precision of the measurements ranges from ±0.28 to ±0.65 wt % and gives an average of ±0.49. The accuracies in wt % range from ±0.11 to ±0.97 and give an average of ±0.67. As a result, the wt % of NaCl and CsCl reported in Table I for the final solution composition should be accurate to within ±0.63 wt %.

The quantity of the final solid available for chemical analysis varied and usually was not enough for a duplicate analysis. The accuracies of these analyses will be given later. The internal consistency of the data is demonstrated in Figure 2 by the collinear relation among the initial bulk composition and the final liquid and solid compositions for each experiment.

Solid Phases. A new compound (NC), $CsCl\cdot 2NaCl\cdot 2H_2O$ (point X in Figure 3), and a new solid-solution series, $[Cs_{1-x}(Na\cdot H_2O)_x]Cl$ with x = 0–0.427 (line CY in Figure 3), were found in this study. When exposed to air at room temperature, both the NC and the solid solutions are not stable and tend to dehydrate. The NC synthesized is prismatic and may reach the size of 1 mm × 1 mm × 10 mm. It is very easy to identify

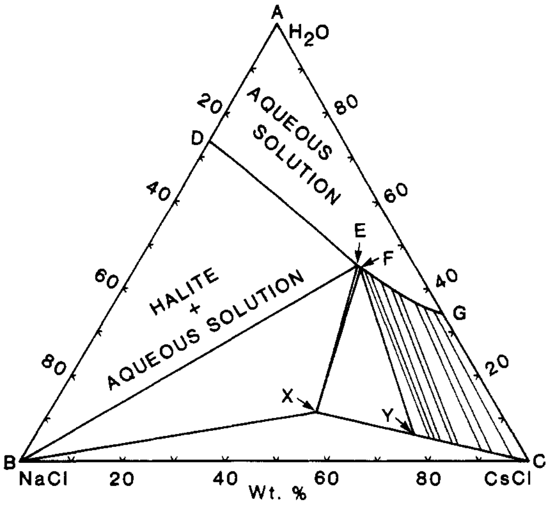

Figure 3. Solubility relations in the system NaCl-CsCl-H_2O at 25 °C. For details, see text. The area BCX was not investigated in this study.

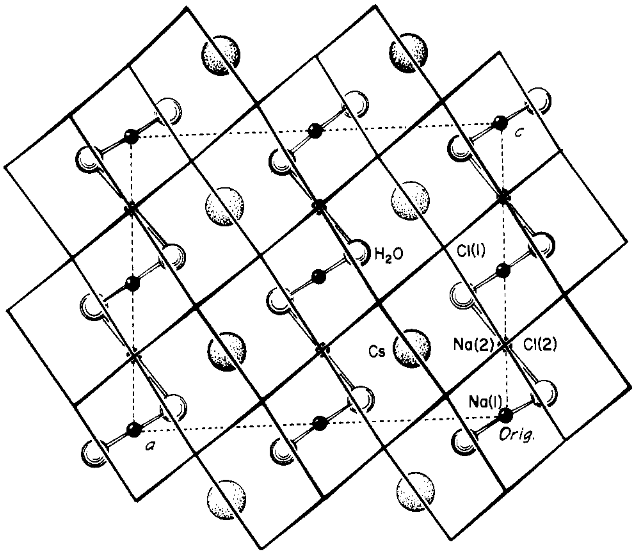

Figure 4. View along the monoclinic *b* axis of the new compound $CsCl\cdot 2NaCl\cdot 2H_2O$. The simple cubic Cl framework is seen viewed along a cube-face diagonal; large stipled circles are Cs, line-shaded circles are H_2O, and black circles are Na.

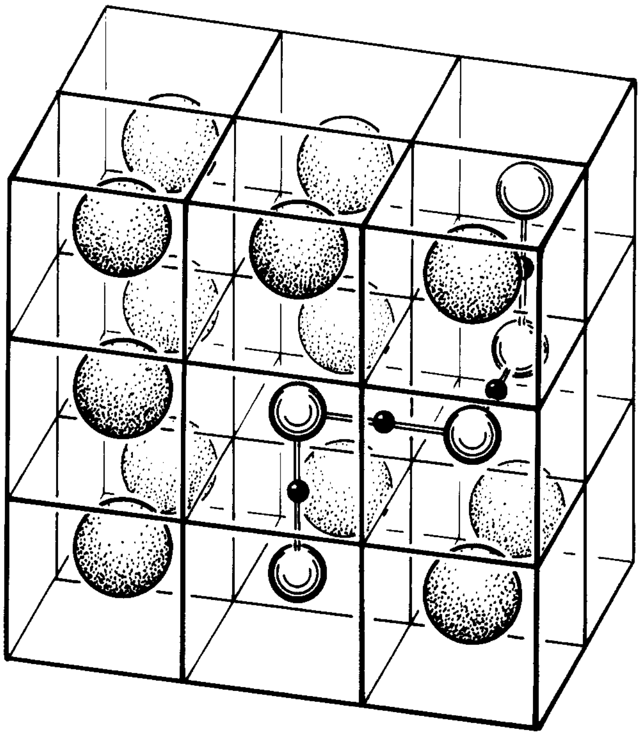

Figure 5. View of 18 unit cells of the CsCl structure in the solid solution $[Cs_{1-x}(Na\cdot H_2O)_x]Cl$. The Cl framework is shown as a simple cubic lattice as in Figure 4, and Cs, H_2O, and Na are similarly represented. The random formation of $\cdots H_2O\text{-}Na\text{-}H_2O\text{-}Na\text{-}H_2O\cdots$ is shown, replacing Cs.

Table II. Values of x and Refractive Indices of the Solid Solution Represented by the Chemical Formula $[Cs_{1-x}(Na\cdot H_2O)_x]Cl$

run no.	x values *a*	x values *b*	x values *c*	n^{25}_D (±0.001)
J	0.065	0.051-0.079	0.050	1.631
F	0.160	0.155-0.165	0.156	1.620
E	0.211	0.208-0.214	0.208	1.607
L	0.291	0.290-0.293	0.289	1.598
K				1.595
H	0.343	0.338-0.349	0.336	1.590
N	0.386	0.403-0.369	0.410	1.585
I	0.382	0.379-0.384	0.376	1.584
M, P				1.578

[a] Average values obtained from chloride titrations. [b] Ranges of x values derived from uncertainties in chloride titrations. [c] Values obtained from H_2O content analyses.

under the microscope, as it is the only nonisotropic solid phase present in this system. The NC is monoclinic, belongs to space group $I2/c$, and has a = 13.620 (2), b = 5.831 (1), c = 10.709 (2) Å, β = 91.27 (1)°, Z = 4, V = 850.3 (1) Å^3; refractive indices are n_α = 1.520, n_β = 1.540, n_γ = 1.552; density D_x = 2.509 g/cm^3. The chemical formula of the NC was established by chemical analysis as well as by a crystal structure determination, which refined to R = 0.036 using 1206 independent nonzero reflections within $2\theta < 60°$ (Mo Kα) (*4*). The structure consists of a CsCl-type framework in which layers of Cs atoms normal to a cube diagonal are replaced by H_2O molecules, with Na atoms inserted into cube-face centers, coordinated to four Cl and two H_2O (see Figure 4).

Plyushchev et al. (*2*) first reported the existence of solid solutions between NaCl and CsCl, but neither the chemical composition nor the crystal structure was determined. The direct chemical analysis of these solid solutions in this study (Table I) indicates that they contain water. The presence of water in the crystal structure of these solids is also supported by the unit cell and refractive index measurements (*4*). The solid solutions remain cubic. The cell parameters of these solids are slightly larger than those of CsCl. Because the crystal molar volume of NaCl is smaller than that of CsCl, the cell parameter of an anhydrous NaCl-CsCl solid solution should be smaller than that of CsCl.

The structural principle which accounts for the solid-solution mechanism is similar to that of the NC, except that Na and H_2O are arranged in a random fashion, probably in chains and loops (Figure 5). On the basis of this structural principle, the chemical formula for these solid solutions can be represented by $[Cs_{1-x}(Na\cdot H_2O)_x]Cl$. The values of x for each sample are calculated from the solid composition data given in Table I and are listed in Table II. The uncertainties associated with x, also given in Table II, vary considerably depending on the quantities of the samples available for analysis. Values derived from chloride titrations as well as those derived from the H_2O content data are given. The agreement between these two sets of data is generally good. The refractive indices of these solid solutions were measured at 25 °C by using the oil immersion method with a constant-temperature stage and a sodium light source. The refractive indices of the oils were calibrated by an Abbe refractometer. The n^{25}_D values reported in Table II are accurate to ±0.001. These n^{25}_D values are plotted against compositions in Figure 6. Compositions derived from chloride titrations are used because they are more accurate than those derived from H_2O content data. The least-squares regression of the data gives

$$n^{25}_D = -0.14638x + 1.6405 \qquad (6)$$

which is shown as a solid line in Figure 6. The composition of the final solid for run K given in Table I was obtained from the refractive index of that sample and the regression line shown in Figure 6. The refractive index of the isotropic phase in runs P and M and the regression line shown in Figure 6 define the maximum value of x in the $[Cs_{1-x}(Na\cdot H_2O)_x]Cl$ solid solution series at 25 °C. The maximum value of x is 0.427, which corresponds to point Y in Figure 3. For the bulk compositions that lie on line XY of Figure 3, the solid-solution Y, at 25 °C, is in equilibrium with the NC instead of a conjugate solid solution. Therefore, the solid solution described above belongs to the sixth type of solid solution in the Roozeboom classification (*5*).

Solubility Relations. In Figure 3, point E is defined by the final liquid composition of run T, in which the solution coexists with halite and the NC (point X). Line DE is defined by the halite

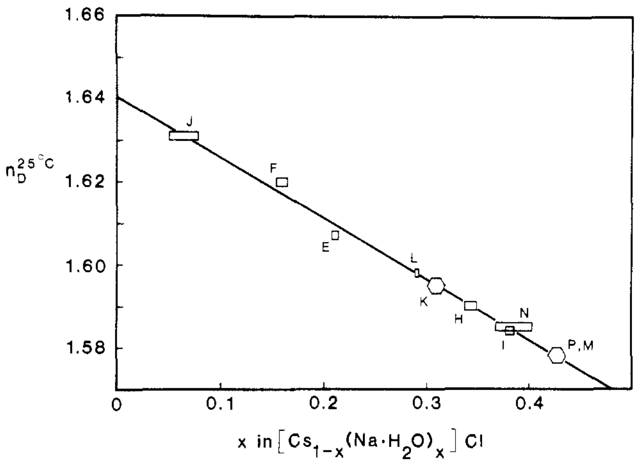

Figure 6. Refractive indices of the crystals in the solid-solution series $[Cs_{1-x}(Na\cdot H_2O)_x]Cl$ (Table II). Letters designate run numbers. Uncertainties are indicated by the size of the rectangles. The solid line represents the least-squares regression of the data. The compositions for K, P, and M (hexagons) were determined from the regression line and from the refractive indices.

solubility data (*1*) and the final solution compositions for runs T, Q, and R. The location of point F is defined by the final solution compositions of runs P and M, in which the solutions coexist with the NC (point X) and the solid solution (point Y). Inside the area EFX, the solution coexists with the incongruently saturated NC as demonstrated by run G.

In the area FGCY, the final solutions, with their compositions along the line FG, coexist with solid solutions along the line CY. The tie lines shown in Figure 3 were experimentally determined as shown in Figure 2. Point G is derived from CsCl solubility data (*6*). The solution-absent area BCX was not investigated in this study.

Conclusion

The solubility relations in the ternary system $NaCl-CsCl-H_2O$ are determined at 25 °C in this study. In addition, a new compound and a new solid-solution series are characterized in terms of chemical composition, crystal structure, and optical properties. Chou and Lee (*1*) have shown that halite solubilities in this system are slightly higher than those reported by Plyushchev et al. (*2*). In the CsCl-rich region, the present solubility data agree with the literature values (*2*) to within 0.5 wt % except that two data points reported by Plyushchev et al. (*2*) for saturated solutions contain 1.4 and 3.6 wt % more H_2O than the present data indicate. Furthermore, the solubility relationships given by Plyushchev et al. (*2*) are considerably revised by introducing a new compound and a new solid solution in the system.

Acknowledgment

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Registry No. $CsCl\cdot 2NaCl\cdot 2H_2O$, 86471-84-3; CsCl, 7647-17-8; NaCl, 7647-14-5.

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Solubility Relations in the Ternary System $NaCl-CsCl-H_2O$ at 1 atm. 3. Solubility Relations at 50 and 75 °C

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Solubility relations in the CsCl-rich region of the ternary system $NaCl-CsCl-H_2O$ were determined at 50 and 75 °C by the isothermal method. The new compound, $CsCl\cdot 2NaCl\cdot 2H_2O$, found at 25 °C in this system is not stable at 50 and 75 °C. However, the solid solutions, $[Cs_{1-x}(Na\cdot H_2O)_x]Cl$, remain stable with x values ranging from 0 to 0.352 at 50 °C and from 0 to 0.325 at 75 °C. By combining the present results with the halite solubility data reported earlier in this series, we have established the solubility relations of the entire system at 50 and 75 °C.

Introduction

Halite solubilities in the system $NaCl-CsCl-H_2O$ from 20 to 100 °C were reported in part 1 of this series (*1*). Solubility relations in this system at 25 °C were given in part 2 (*2*). This paper presents the solubility relations at 50 and 75 °C.

Experimental Section

The isothermal method (*2*) was used in this study. Samples were reacted at 50 and 75 °C for at least 14 and 7 days, respectively, to ensure equilibration (*3*). After each run, solids and solution were separated and analyzed.

Results and Discussion

The solubility data are given in Table I. The bulk compositions reported are accurate to ±0.03 wt %. The final solid

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