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Solid−Liquid Phase Diagram for the System $MgCl_2-NH_3-CH_3OH$ at 298 K

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The ammoniated magnesium chloride compounds $MgCl_2\cdot nNH_3$, where n is 2, 4, or 6, are potentially usable as materials for producing anhydrous magnesium chloride. The $MgCl_2-NH_3-CH_3OH$ system was investigated at 298 K to determine phase stability regions for hexammoniate (HEX), tetrammoniate (TET), and diammoniate (DI). Five phase regions were determined. These were: HEX+Liq, HEX+T+T_{Liq}, T+T_{Liq}, $MgCl_2\cdot 6CH_3OH$+T+T_{Liq}, and a ternary liquid phase, T_{Liq}. The phase represented by the symbol T is a previously unknown ternary compound of composition $MgCl_2\cdot 4NH_3\cdot 2CH_3OH$, and Liq refers to the liquid phase with a composition along, or very close to, the NH_3-CH_3OH binary. An additional five phase regions were also predicted based on the existence of known crystalline phases. These were: HEX+$Liq_{(17.45\ \%NH3/MeOH)}$+$NH_3$, HEX+TET+T, TET+DI+T, DI+T+$MgCl_2$, and $MgCl_2\cdot 6CH_3OH$+T+$MgCl_2$. The ternary phase was unstable, breaking down to produce ammonium chloride, ammonia, and magnesium methoxide ($Mg(CH_3O)_2$). These were all partially soluble in the methanol-rich ternary liquid. The $MgCl_2-NH_3-CH_3OH$ system could potentially be used to produce magnesium chloride hexammoniate as feedstock for anhydrous magnesium chloride production, providing the ammonia concentration remains high enough to suppress formation of the ternary compound.

1. Introduction

Current molten salt electrolytic methods used for the production of magnesium all require the use of anhydrous $MgCl_2$ as the feedstock. This results in significant technical challenges to magnesium producers since magnesium chloride is extremely hydroscopic, forming a series of hydrated salts, $MgCl_2\cdot nH_2O$ (where $n = 1, 2, 4, 6$, or 12). The magnesium chloride must be dehydrated before electrolysis, otherwise the water of hydration will cause sludge formation, increased anode consumption, low current efficiency, and corrosion problems in the electrolytic cell.

At room temperature and ambient pressure, the stable form of magnesium chloride is the fully hydrated hexahydrate, $MgCl_2\cdot 6H_2O$. Dehydration by the removal of four of the six molecules of water occurs by the following reaction

$$MgCl_2\cdot 6H_2O_{(s)} \leftrightarrow MgCl_2\cdot 2H_2O_{(s)} + 4H_2O_{(g)} \qquad (1)$$

over the temperature range (298 to 390) K. Continued dehydration of the dihydrate $MgCl_2\cdot 2H_2O$ occurs via the monohydrate, $MgCl_2\cdot H_2O$, by the reaction

$$MgCl_2\cdot 2H_2O_{(s)} \leftrightarrow MgCl_2\cdot H_2O_{(s)} + H_2O_{(g)} \qquad (2)$$

although dehydration of the dihydrate can also proceed by hydrolysis. This results in the production of magnesium hydroxychloride according to

$$MgCl_2\cdot 2H_2O_{(s)} \leftrightarrow MgOHCl_{(s)} + H_2O_{(g)} + HCl_{(g)} \qquad (3)$$

The formation of the hydroxychloride can be suppressed by the use of HCl, provided that the partial pressure of HCl exceeds the equilibrium value for reaction 3. The vapor pressure of HCl and H_2O over the various hydrates of magnesium chloride, however, is strongly temperature dependent, so the dehydration conditions need to be carefully controlled.[1]

The final stage in dehydrating magnesium chloride is to remove the last water of crystallization from the solid monohydrate by the reaction

$$MgCl_2\cdot H_2O_{(s)} \leftrightarrow MgCl_{2(s)} + H_2O_{(g)} \qquad (4)$$

This stage of the dehydration also needs to be performed under a blanket of HCl and under controlled temperature to prevent hydrolysis to MgOHCl.

It is apparent from reactions 1 to 4 that the production of anhydrous magnesium chloride is not trivial. Substantial concentrations of HCl in the dehydrating gas are required to suppress hydrolysis, and the handling of gases rich in HCl and H_2O on the industrial scale is difficult, particularly when the dehydration must be performed at elevated temperatures, usually (500 to 600) K or higher.[1] Accordingly, many alternative methods have been proposed for the production of anhydrous magnesium chloride.[2–9] Most involve formation of a solution of hydrated magnesium chloride in a solvent, removal of water from the solution, formation of a magnesium chloride complex by reaction with a precipitating agent, and then calcination of the magnesium chloride complex to produce anhydrous magnesium chloride. A number of variations of this general approach have been proposed with a common feature being the use of ammonia as the precipitating agent. Differences in the processes lie in the use of different solvents to form the solution of hydrated magnesium chloride. For example, Vyas and Gavini[2] give information on the dehydration of magnesium chloride using water immiscible solvents such as benzene (C_6H_6) and toluene (C_7H_8). Other solvents proposed include: very low boiling point alcohols such as methanol (CH_3OH, Sivilotti et al.[3]) or ethanol (C_2H_5OH, Sivilotti et al.[3]), ethylene glycol ($C_2H_4(OH)_2$, Braithwaite and Allain,[4] Braithwaite,[5] Sheehan et al.[6]), *n*-butanol (C_4H_9OH, Zhang et al.[7]), and monohydroxy saturated aliphatic alcohols such as isoamyl alcohol ($C_5H_{11}OH$, Belchetz[8]). At present, no ammoniation process has commercially produced anhydrous magnesium chloride, although the Australian Magnesium Corporation built a 1500 tpa dem-

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onstration plant in Queensland, Australia, which used ethylene glycol as the solvent (Jenkins et al.[9]).

As part of a broader laboratory study on the methods of production of anhydrous $MgCl_2$ feedstocks, CSIRO has investigated a number of these systems. The current study describes results using methanol as the solvent, where the aim was to determine solid−liquid phase relations in the $MgCl_2-NH_3-CH_3OH$ system at 298 K and one atmosphere pressure. The study was undertaken to understand the conditions under which crystalline ammoniated magnesium chloride phases such as $MgCl_2 \cdot nNH_3$ (where $n = 2$, 4, or 6) are stable, with a view to potentially use these materials as feedstocks for the production of anhydrous magnesium chloride.

2. Experimental Section

2.1. Reagents. The anhydrous magnesium chloride contained > 99.7 % $MgCl_2$ (BDH Laboratory Reagent grade). All transfers of the $MgCl_2$ to produce bulk starting solutions or solid crystalline phases were carried out in an inert atmosphere using a nitrogen-filled drybox. The ammonia (type 179R supplied by BOC gases) contained < 10 ppm moisture. The methanol was Mallinckrodt AR grade Methyl Alcohol Anhydrous (absolute). Measured water contents in the methanol were < 0.01 %.

Magnesium chloride hexammoniate crystals ($MgCl_2 \cdot 6NH_3$ or HEX) were prepared by ammoniating at 323 K for 80 min a (10 to 15) % $MgCl_2$/glycol solution containing less than 1000 ppm H_2O. The resulting crystals were removed from solution via filtration, washed with ammoniated saturated anhydrous methanol (~17 % by weight NH_3), and dried at 333 K overnight. X-ray diffraction (XRD) analysis confirmed the presence of only HEX crystals, and chemical assay results indicated a $MgCl_2$:NH_3 ratio of ~1:6 (actual ratios varied between 1:5.8 and 5.9 for three determinations). Magnesium chloride diammoniate ($MgCl_2 \cdot 2NH_3$ or DI) was prepared by calcining magnesium chloride hexammoniate crystals at 473 K for 120 min. Subsequent XRD and assay analysis indicated complete conversion to DI with an $MgCl_2$:NH_3 ratio of ~1:2 (ratios varied between 1:1.9 and 1:2.0 for three determinations). The washed HEX and DI crystals typically contained < 0.3 % (by weight) adhering glycol and methanol.

2.2. Analytical Procedures. Ammonia. Ammonia analyses were carried out using a Tecator 1035 Automatic Kjeltec Analyzer. During calibration, recoveries of between 99.5 % and 100.2 % were obtained when using AR grade dried NH_4Cl.

Methanol. The methanol content of solutions and solids was determined at the AMC Demonstration Plant analytical laboratory (Gladstone, Queensland) using a Waters High Performance Liquid Chromatograph (HPLC) system equipped with a refractive index detector and running Millennium software. The column used was a BioRad Aminex HPX-87H 300 × 7.8 mm fast acid column running at 323 K. Phosphoric acid (0.01 % by weight) was used as the eluent, at a flow rate of $0.8\ mL \cdot min^{-1}$.

Water. Determination of moisture in the solid phases and liquors was carried out using a Metrohm 701 Karl Fischer (KF) Titrino apparatus using a stable hydranal hydrazine solution of iodine, sulfur dioxide, and imidazole dissolved in alcohol. For the determination of water contents in the solids, 3 g of benzoic acid was added to the KF cell as a buffer for the high pH caused by the ammonia content of the crystals. All titrations were carried out in duplicate and gave a consistent relative standard deviation (2σ) of ± 2 %.

Magnesium and Chloride. At the completion of all experiments, the recovered liquid and solid phases were dissolved in 10 mL of 10 % nitric acid and made up to 100 mL total volume with distilled water. Magnesium was determined by titration with a standard 0.1 M EDTA solution, while chloride was measured potentiometrically using a Metrohm 672 Titroprocessor.

Solid Phases. Characterization of all solid phases was by X-ray diffraction (XRD). For experiments in which the amount of solid material available was very small, the wet solid was scraped from the bottom of the reaction vessel and smeared onto a quartz zero-background plate. In experiments where a larger amount of solid material was able to be collected via centrifuging or filtering of the sample, the recovered solid was loaded in an aluminum sample holder. Samples were covered with a clear plastic film of low density polyethylene to avoid reaction with water vapor in the atmosphere and/or loss of ammonia.

XRD patterns were collected using a Phillips PW1710 powder diffractometer fitted with a diffracted beam graphite monochromator and employing Cu Kα radiation. The diffractometer was operated at 40 keV and 40 mA, and samples were analyzed over the range 5° to 65° 2θ using a step size of 0.04° 2θ and counting times of 0.25 s per step. Total scan times were of the order of 10 min per sample.

2.3. Methods. The solubility of NH_3 in methanol was determined by placing 100 mL of methanol into an open 250 mL glass Schott bottle and sparging continuously with ammonia. To avoid potential problems arising from the volatility of methanol and NH_3, the maximum solubility was approached by initially sparging the methanol at low temperature (278 K) and then gradually increasing the temperature over 120 min to the final temperature of 298 K. The solution was then kept at 298 K and sparged with ammonia for a further 120 min, or until a constant NH_3 solubility was reached. The flow rate of the ammonia was kept constant at $1.9\ L \cdot min^{-1}$, and the temperature was controlled by partially immersing the Schott bottle in a glycol shaker bath. The accuracy of the reported temperatures was estimated to be ± 0.5 K.

Solid−liquid equilibration experiments were performed along the $MgCl_2-CH_3OH$ binary: (a) to determine the maximum solubility of $MgCl_2$ in methanol and (b) to determine the composition of any solid binary compounds. Magnesium chloride was incrementally added to the anhydrous methanol in 250 mL glass Schott bottles until $MgCl_2$ saturation was reached (at ~15 % by weight $MgCl_2$). The temperature of reaction was then kept constant at 298 K by partially immersing the reaction vessel in a glycol shaker bath. Reaction times varied between (24 and 48) h, with an additional settling time of 24 h (to effect separation between solid and liquid phases). Results indicated that equilibrium was reached after 48 h (plus the 24 h settling time for solids).

Phase relations within the expanded $MgCl_2-NH_3-CH_3OH$ ternary were investigated using two different experimental approaches. The first method used accurately weighed amounts of $MgCl_2$ added to NH_3-saturated methanol solutions. A series of eight bulk compositions varying by ~1 % (by weight) $MgCl_2$ intervals from NH_3 saturated methanol to $MgCl_2$ saturated methanol were prepared. In the second method, excess HEX, DI, or a HEX/DI mixture was directly added to methanol. The HEX/DI mixture was used to simulate the tetrammoniate composition $MgCl_2 \cdot 4NH_3$ (TET) as there is some doubt as to whether $MgCl_2 \cdot 4NH_3$ exists as a stable phase.[10] Starting compositions for both series of experiments are listed in Table 1.

The solid and liquid reactants were mixed in 250 mL glass Schott bottles and agitated in a glycol bath that was kept at a constant temperature of (298 ± 0.5) K. To determine the

Table 1. Starting Compositions and Results from Solid/Liquid Equilibration Experiments within the $MgCl_2-NH_3-CH_3OH$ Ternary at (298 ± 0.5) K[a]

	bulk composition % (by weight)			final assemblage			
					liquid % (by weight)		
sample no.	$MgCl_2$	NH_3	CH_3OH	solid	$MgCl_2$	NH_3	CH_3OH
256H	2.74	14.26	83.00	HEX	0.02	11.79	88.19
256H2				HEX	0.02	11.48	88.50
256G	4.10	12.48	83.42	HEX	0.06	8.73	91.21
256G2				HEX	0.04	8.82	91.14
256F	5.47	10.70	83.83	HEX	0.18	6.23	93.59
256F2				HEX	0.18	6.14	93.68
256E	6.84	8.91	84.25	HEX	1.24	4.25	94.51
256E2				HEX	1.83	4.04	94.13
256D	8.21	7.05	84.74	HEX+T[b]	3.44	4.13	92.53
256D2				HEX+T[b]	3.24	4.16	92.60
256C	9.58	5.29	85.13	HEX+T[b]	5.85	4.09	90.06
256C2				HEX+T[b]	6.00	4.08	89.92
256B3	10.95	3.56	85.49	T[b]	9.56	3.20	87.24
256B4				T[b]	9.50	3.29	87.21
256A3	12.31	1.78	85.91	T[b]	11.40	1.63	86.97
252F (HEX)	13.13	13.96	72.91	HEX	3.61	3.67	93.00
253G (DI)	17.02	5.92	77.06	T[b]	15.76	4.43	80.10
253B (HEX+DI)	18.48	12.46	69.06	HEX+T[b]	15.05	4.39	80.76

[a] In all liquids, H_2O levels were < 1900 ppm. [b] These experiments also contained small amounts of NH_4Cl.

Table 2. Solubility of NH_3 and $MgCl_2$ in Methanol at 298 K

	solubility in methanol	
reference	NH_3 (%)	$MgCl_2$ (%)
this work	17.4	14.85
Frank et al. (1996)[11]	17.15	-
Lobry deBruyn (1892)[12]	16.5	-
Hatem (1949)[13]	16.36	-
Kudo and Toriumi (1959)[14a]	18.55	-
Emons et al. (1985)[15]	-	15
Zhang et al. (1992)[7]	-	~15

[a] Measured at 118.72 kPa (~1.2 atm).

minimum time required for the reacting system to reach equilibrium, preliminary experiments were conducted where excess HEX was added to anhydrous methanol at 298 K. Reaction times varied between (24 and 96) h plus an additional settling time of 24 h. Assay results indicated no further change in solid or liquid composition after 48 h reaction time (plus 24 h for solids settling). In all subsequent solid−liquid experiments, these conditions were employed.

3. Results and Discussion

3.1. Binary Systems NH_3-CH_3OH and $MgCl_2-CH_3OH$. The average NH_3 solubility in methanol at 298 K was 17.4 ± 0.3 % (by weight) NH_3 (average of three determinations), in good agreement with the most recent determination by Frank et al.[11] Earlier determinations report considerably lower NH_3 solubilities (Table 2). The cause of the apparent discrepancy is not clear.

Duplicate experiments to determine the solubility of $MgCl_2$ in methanol yielded values of (14.7 and 15.0) % (by weight), in very good agreement with previous measurements (Table 2). The solid phase coexisting with $MgCl_2$-saturated methanol was $MgCl_2 \cdot 6CH_3OH$.

3.2. $MgCl_2-NH_3-CH_3OH$ System. Final solid and liquid compositions (including duplicates) are listed in Table 1, and experimental results have been plotted on a ternary $MgCl_2-NH_3-CH_3OH$ diagram in Figure 1. The composition of the liquid coexisting with a solid phase (or phases) defines the position of the liquid−solid phase boundary within the ternary. XRD patterns for selected compositions are shown in Figure 2.

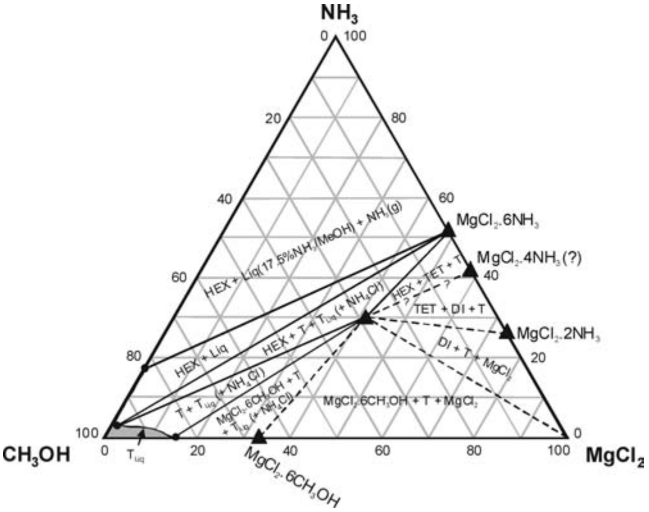

Figure 1. Phase relations within the $MgCl_2-NH_3-CH_3OH$ system at (298 ± 0.5) K. Phase region boundaries represented as solid lines were directly determined in the current study, while dashed boundaries are inferred. In phase fields where the ternary compound is stable, NH_4Cl is also present as part of the crystallizing assemblage. These phase regions lie off the plane of the ternary system indicating the system is pseudoternary.

Results show that starting initially from the NH_3-CH_3OH binary, as the bulk composition of the system becomes richer in $MgCl_2$ (i.e., compositions 256H through 256A), the following phase stability regions are encountered:

(1) HEX+Liq: a two-phase field where solid hexammoniate coexists with a liquid phase;

(2) HEX+T+T_{Liq}: a three-phase field comprising hexammoniate, a ternary compound (denoted "T"), and a ternary liquid phase, T_{Liq}; and

(3) T+T_{Liq}: a two-phase field containing the ternary compound plus T_{Liq}.

On the basis of assays of solid residues, the ternary compound has the formula $MgCl_2 \cdot 4NH_3 \cdot 2CH_3OH$ and was present in all bulk compositions containing greater than about 6 % (by weight) $MgCl_2$ and > 84.5 % (by weight) MeOH. It was also identified by the appearance of small, broad peaks at ~11° 2θ and ~59° 2θ in X-ray patterns of the solid residues (Figure 2). The existence of the T compound within the $MgCl_2-NH_3-$

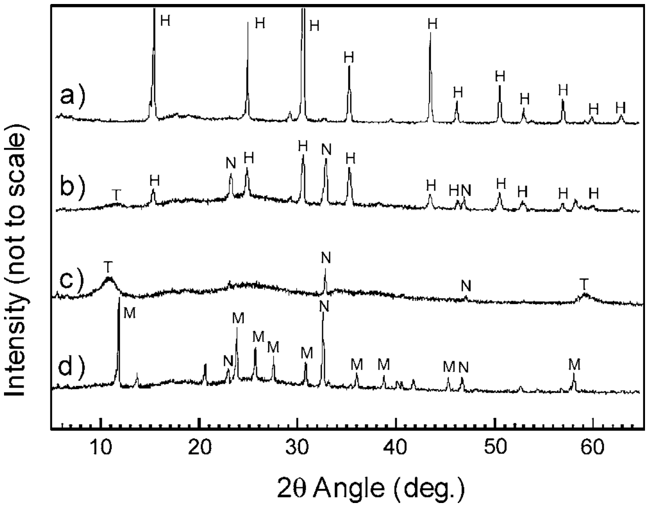

Figure 2. X-ray diffraction patterns for solid phases obtained from experiments within the $MgCl_2-NH_3-CH_3OH$ ternary: (a) HEX+Liq (Run 256H); (b) HEX+T+T_{Liq} (Run 256D); (c) T+T_{Liq} (Run 256A3); and (d) $MgCl_2 \cdot 6CH_3OH$+T+T_{Liq} (Run 258A). Key to peak labels: H = HEX; T = Ternary compound; N = NH_4Cl; M = $MgCl_2 \cdot 6CH_3OH$.

CH_3OH system was, however, not entirely unexpected based upon the known stability of a similar ternary compound $MgCl_2 \cdot 4H_2O \cdot 2CH_3OH$ in the $MgCl_2-H_2O-CH_3OH$ system.[15]

Examination of Figure 1 shows that for bulk compositions within the HEX+Liq field the composition of the liquid coexisting with the hexammoniate appears to lie along, or at least very close to, the NH_3-CH_3OH binary. It is not clear from the current results whether the liquid phase contains any significant magnesium chloride in solution—small amounts of $MgCl_2$ were detected, but this may represent contamination by fine-grained hexammoniate being collected in the filtrate. We therefore believe the HEX+Liq stability region represents a binary phase field with the liquid phase essentially a methanol-rich liquid with partial solubility of ammonia, i.e., a binary NH_3-CH_3OH liquid.

Once bulk compositions contain sufficient magnesium chloride to produce the ternary compound as part of the crystallizing assemblage, the liquid composition moves off the NH_3-CH_3OH binary join, resulting in the development of a ternary liquid phase region. We believe this expansion of the liquid phase field into the ternary indicates the ternary compound is partially soluble in the methanol-rich ternary liquid according to

$$MgCl_2 \cdot 4NH_3 \cdot 2CH_3OH \leftrightarrow 2NH_4Cl_{(s)} + 2NH_3 + Mg(OCH_3)_2 \qquad (5)$$

where the products of the solubility reaction include ammonium chloride, ammonia, and magnesium methoxide ($Mg(CH_3O)_2$).

Evidence for the solubility of the ternary compound comes from the analysis of solid residues. X-ray diffraction patterns obtained from solid residues where the ternary compound was part of the equilibrium assemblage always contained a small amount of NH_4Cl (Figure 2). This is consistent with reaction 5 where NH_4Cl is expected to precipitate as a solid phase as the ternary compound dissolves. The precipitation of NH_4Cl is particularly evident in experiments for which the bulk compositions equilibrated entirely within the T+T_{Liq} phase field. In these experiments, the only sharply crystalline phase identifiable was that of NH_4Cl (T compound was also present, but this was represented as two broad peaks; see Figure 2). The dissolution of the ternary compound as reaction 5 proceeds results in higher Mg, Cl, and NH_3 contents in the liquid phase and causes the expansion of the T_{Liq} phase region. Ammonia will be present as dissolved gas through partial dissolution of NH_4Cl in the methanol-rich ternary liquid (at 298 K, the solubility of NH_4Cl in methanol is ~3.4 %.[16,17] The dissolution of NH_4Cl would also result in higher chloride levels in the liquid. In addition, magnesium methoxide is known to be partially soluble in methanol-rich liquids, resulting in higher Mg levels in the T_{Liq}.[18]

On the basis of the observation that the ternary compound is unstable in the presence of a methanol-rich ternary liquid, the $MgCl_2-NH_3-CH_3OH$ system as shown in Figure 1 cannot be considered as strictly ternary. The presence of NH_4Cl as a separate phase within the system implies the system is at least quaternary with the phase regions HEX+T+T_{Liq} and T+T_{Liq} lying off the ternary plane and extending in the third dimension toward an NH_4Cl component. There was no evidence for precipitation of magnesium methoxide as a stable solid phase which would indicate a five-component system, but this may be due to the fact that for the particular bulk compositions prepared only a small amount of ternary compound was generated. Magnesium methoxide is known to be soluble in methanol to the extent of ~13 % at 298 K,[18] and the quantity of $Mg(OCH_3)_2$ formed via dissolution of the ternary compound is likely to have been small enough to be completely dissolved. Thus, given the presence of NH_4Cl and magnesium methoxide as likely phases in the $MgCl_2-NH_3-CH_3OH$ system, the phase relations shown in Figure 1 should therefore be more accurately described as pseudoternary.

In addition to the phase fields directly determined in the experiments, the additional phase fields, HEX+$Liq_{(17.45\ \%NH3/MeOH)}$+$NH_3$, HEX+TET+T, TET+DI+T, DI+T+$MgCl_2$, $MgCl_2 \cdot 6CH_3OH$+T+T_{Liq}, and $MgCl_2 \cdot 6CH_3OH$+T+$MgCl_2$, are also likely present in the system. The existence of these phase regions is assumed based on the overall phase topology and the presence of TET, DI, $MgCl_2 \cdot 6CH_3OH$, and $MgCl_2$ as stable phases within the ternary (although as noted earlier the existence of TET as a pure, stable phase is unconfirmed). These additional phase stability regions have also been indicated in Figure 1.

The existence of the HEX+TET+T, TET+DI+T, DI+T+$MgCl_2$, and $MgCl_2 \cdot 6CH_3OH$+T+$MgCl_2$ phase fields were not able to be verified experimentally as the high solid:liquid ratios required to produce bulk compositions within these regions would significantly retard the attainment of equilibrium. It was, however, possible to confirm the existence of the $MgCl_2 \cdot 6CH_3OH$+T+T_{Liq} field. An additional three bulk compositions were prepared: two compositions (258A and 258B) were anticipated to equilibrate within the $MgCl_2 \cdot 6CH_3OH$+T+T_{Liq} field, whereas composition 258C was expected to produce the assemblage T+T_{Liq}. Final solid and liquid compositions (including duplicates) are listed in Table 3, and the experimental results have been included on the $MgCl_2-NH_3-CH_3OH$ phase diagram in Figure 1.

3.3. Implications for Producing Anhydrous $MgCl_2$. The thermal decomposition of ammoniated magnesium chloride compounds has been suggested by many workers as a possible way to manufacture anhydrous $MgCl_2$. Most processes involve the formation of the hexammoniate phase; however, the production of deammoniated phases such as TET or DI would be advantageous as the energy costs involved in calcination would be considerably less than for hexammoniate, plus the initial cost of ammonia would be significantly reduced. There would also be a reduced cost associated with recycling ammonia.

Results from the current work in the $MgCl_2-NH_3-CH_3OH$ system indicate that it is possible to produce HEX as a single crystalline phase providing ammonia concentrations are main-

Table 3. Starting Compositions and Results from Additional Solid/Liquid Equilibration Experiments to Locate the $MgCl_2 \cdot 6CH_3OH + T + T_{Liq}$ and $T + T_{Liq}$ Phase Fields[a]

				final assemblage[b]			
	bulk composition % (by weight)				liquid % (by weight)		
sample no.	$MgCl_2$	NH_3	CH_3OH	solid	$MgCl_2$	NH_3	CH_3OH
258A	18.70	1.30	80.00	M[c] + T	14.00	0.98	85.02
258A2				M + T	14.36	1.11	84.53
258B	22.00	3.00	75.00	M + T	17.44	2.27	80.29
258B2				M + T	17.56	2.36	80.08
258C	15.00	5.00	80.00	T[d]	13.45	4.32	82.23
258C2				T[d]	13.66	4.37	81.97

[a] All experiments were conducted at (298 ± 0.5) K. In all liquids, H_2O levels were < 1900 ppm. [b] All XRD scans indicated the presence of NH_4Cl in the final assemblage. [c] M denotes the compound $MgCl_2 \cdot 6CH_3OH$. [d] Contains two low intensity broad peaks ~11° 2θ and ~59° 2θ.

tained at high levels. If, however, the ammonia levels drop below about 8 % (by weight), the formation of a ternary compound of composition $MgCl_2 \cdot 4NH_3 \cdot 2CH_3OH$ is promoted. This results in HEX no longer occur as a single phase, instead crystallizing in association with the ternary compound. The presence of the ternary compound at low ammonia contents also precludes the formation of single-phase TET and/or DI as ammoniated intermediate phase(s) in the production of anhydrous magnesium chloride. A similar situation occurs in the analogous $MgCl_2-NH_3-$ethylene glycol system where low ammonia compositions stabilize the formation of a ternary magnesium chloride diammoniate diglycolate compound of composition $MgCl_2 \cdot 2NH_3 \cdot 2C_2H_4(OH)_2$.

The presence of the ternary compound, if generated, will require additional processing to separate it from the ammoniated magnesium chloride species. This would likely add extra costs to any process through a need to process the ternary phase separately to recover magnesium chloride and reagents, additional materials handling, and increased energy consumption. Thus, in any process using the $MgCl_2-NH_3-CH_3OH$ system to derive feedstock for anhydrous magnesium chloride production, the process operating conditions need to be carefully monitored and controlled so that the ammonia concentration remains high enough to ensure hexammoniate is the ammoniated magnesium chloride phase generated and the formation of the ternary compound is suppressed.

3.4. Comparison with Previous Work. The system $MgCl_2-NH_3-CH_3OH$ was previously investigated by Sivilotti et al.,[3] as a potential process for producing anhydrous magnesium chloride. The Sivilotti et al. study is, however, not strictly comparable to the current study as the former used impure, partially hydrated magnesium chloride ($nH_2O < 6$) as the starting material to produce magnesium chloride hexammoniate. The use of a partially hydrated feed material causes the undesirable formation of $Mg(OH)_2$ according to

$$MgCl_{2(sol)} + 2H_2O_{(sol)} + 2NH_{3(sol)} \leftrightarrow 2NH_4Cl_{(sol)} + Mg(OH)_2 \qquad (6)$$

and results in the production of MgO upon subsequent calcining. To minimize $Mg(OH)_2$ formation, Sivilotti et al.[3] found it necessary to add ammonium chloride to the system. There was no indication in the results of Sivilotti et al. of the possible formation of the ternary compound or its equivalent in aqueous solutions.[15] This suggests either its formation was suppressed by the addition of ammonium chloride or that ammonia levels were kept sufficiently high (i.e., at saturation) to ensure crystallization occurred only within the HEX+Liq phase stability field.

4. Conclusions

The $MgCl_2-NH_3-CH_3OH$ system was investigated at 298 K to determine phase stability fields. Five phase regions were determined experimentally using solid−liquid equilibration experiments. These were: HEX+Liq, $HEX+T+T_{Liq}$, $T+T_{Liq}$, $MgCl_2 \cdot 6CH_3OH+T+T_{Liq}$, and T_{Liq}. The symbol T represents a ternary compound of composition $MgCl_2 \cdot 4NH_3 \cdot 2CH_3OH$; Liq refers to the liquid phase with a composition along, or very close to, the NH_3-CH_3OH binary; and T_{Liq} represents a ternary liquid phase. An additional five phase regions were also predicted based on the existence of known crystalline phases. These were the regions: $HEX+Liq_{(17.45\%NH3/MeOH)}+NH_3$, HEX+TET+T, TET+DI+T, $DI+T+MgCl_2$, and $MgCl_2 \cdot 6CH_3OH+T+MgCl_2$.

The ternary phase was found to be unstable, breaking down to produce ammonium chloride, ammonia, and magnesium methoxide ($Mg(CH_3O)_2$). Ammonium chloride and magnesium methoxide are both soluble in the ternary liquid phase resulting in the T_{Liq} phase region extending into the ternary. The expansion of the T_{Liq} phase field is directly linked to the amount of ternary phase present. The presence of NH_4Cl and magnesium methoxide as separate phases implies the $MgCl_2-NH_3-CH_3OH$ system should be considered as pseudoternary.

The $MgCl_2-NH_3-CH_3OH$ system could potentially be used to produce a magnesium chloride hexammoniate feedstock for anhydrous magnesium chloride production provided the ammonia concentration is high enough to prevent formation of the ternary compound.

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