

# STUDY OF THE EQUILIBRIA IN THE $\text{MCl}_2\text{-H}_2\text{O-ROH}$ SYSTEMS ( $\text{M} = \text{Co, Ni}$ ; $\text{ROH} = \text{CH}_3\text{OH, C}_2\text{H}_5\text{OH}$ ) AT 25 °C

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The solubility isotherms of the  $\text{CoCl}_2\text{-H}_2\text{O-CH}_3\text{OH}$  ( $\text{C}_2\text{H}_5\text{OH}$ ) and  $\text{NiCl}_2\text{-H}_2\text{O-CH}_3\text{OH}$  ( $\text{C}_2\text{H}_5\text{OH}$ ) systems at 25 °C have been studied. Crystallization fields of the equilibrium existence of the salts  $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 4 \text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 2 \text{CH}_3\text{OH}$ ,  $\text{CoCl}_2 \cdot 2.5 \text{C}_2\text{H}_5\text{OH}$ ,  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 4 \text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 2 \text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 3 \text{CH}_3\text{OH}$  and  $\text{NiCl}_2 \cdot 2 \text{C}_2\text{H}_5\text{OH}$  have been found. The dehydration and solubility processes of the studied systems have been discussed.

The present work extends our study on the  $\text{MX}_2\text{-H}_2\text{O-ROH}$  systems<sup>1</sup> at 25 °C, where  $\text{M} = \text{Co, Ni}$ ;  $\text{X} = \text{Cl, Br}$  and  $\text{ROH} = \text{CH}_3\text{OH, C}_2\text{H}_5\text{OH}$ . The subject of this communication is behaviour of  $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$  and  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$  in the  $\text{H}_2\text{O-CH}_3\text{OH}$  ( $\text{C}_2\text{H}_5\text{OH}$ ) mixed solvents. Our aim is to discuss the dehydration and solubility processes which the salts undergo in the saturated solution depending on the nature and concentration of the alcohols.

The experimental procedure is described elsewhere<sup>1</sup>. All chemicals used,  $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ , and  $\text{C}_2\text{H}_5\text{OH}$  were of analytical grade. The thermally dehydrated salts<sup>2</sup> and anhydrous alcohols<sup>3</sup> were used in the low water concentration regions of the solubility diagrams.

## RESULTS AND DISCUSSION

### *Equilibria in the $\text{CoCl}_2\text{-H}_2\text{O-CH}_3\text{OH}$ ( $\text{C}_2\text{H}_5\text{OH}$ ) Systems at 25 °C*

The results concerning the equilibria in the  $\text{CoCl}_2\text{-H}_2\text{O-CH}_3\text{OH}$  ( $\text{C}_2\text{H}_5\text{OH}$ ) systems are given in Table I. The solubility isotherms show the existence of equilibrium solid phases  $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 4 \text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 2 \text{CH}_3\text{OH}$  and  $\text{CoCl}_2 \cdot 2.5 \text{C}_2\text{H}_5\text{OH}$ . Crystalline hydrate  $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$  undergoes the stepwise dehydration  $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O} \rightarrow \text{CoCl}_2 \cdot 4 \text{H}_2\text{O} \rightarrow \text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$  in the mixed  $\text{H}_2\text{O-CH}_3\text{OH}$  ( $\text{C}_2\text{H}_5\text{OH}$ ) solvents. In the system with methanol, the last process is accompanied with the increase of  $\text{CoCl}_2$  solubility about 14.60 mass% compared to the binary  $\text{CoCl}_2\text{-H}_2\text{O}$  system. The

salting out process and the minimum of the solubility isotherm of the equilibrium field of  $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$  are observed in the ethanolic system. The low crystalline hydrate  $\text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$  transforms to the crystalline solvates  $\text{CoCl}_2 \cdot 2 \text{CH}_3\text{OH}$  (ref.<sup>4</sup>) and  $\text{CoCl}_2 \cdot 2.5 \text{C}_2\text{H}_5\text{OH}$  with the increase of the concentration of  $\text{CH}_3\text{OH}$  and  $\text{C}_2\text{H}_5\text{OH}$ , respectively. These crystalline solvates can be found in the binary  $\text{CoCl}_2\text{-CH}_3\text{OH}$  ( $\text{C}_2\text{H}_5\text{OH}$ ) systems<sup>5</sup>. The solvation process in the methanolic system is accompanied with salting out process of  $\text{CoCl}_2 \cdot 2 \text{CH}_3\text{OH}$  and its solubility increases about 19.16 mass%  $\text{CoCl}_2$  compared to the eutonic point.

### Equilibria in the $\text{NiCl}_2\text{-H}_2\text{O-CH}_3\text{OH}$ ( $\text{C}_2\text{H}_5\text{OH}$ ) Systems at 25 °C

The results concerning the equilibria in the  $\text{NiCl}_2\text{-H}_2\text{O-CH}_3\text{OH}$  ( $\text{C}_2\text{H}_5\text{OH}$ ) systems (Table I) indicate the existence of the following equilibrium solid phases  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 4 \text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 2 \text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 3 \text{CH}_3\text{OH}$  and  $\text{NiCl}_2 \cdot 2 \text{C}_2\text{H}_5\text{OH}$ . The dehydration process  $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O} \rightarrow \text{NiCl}_2 \cdot 4 \text{H}_2\text{O} \rightarrow \text{NiCl}_2 \cdot 2 \text{H}_2\text{O}$  takes place in the mixed  $\text{H}_2\text{O-CH}_3\text{OH}$  ( $\text{C}_2\text{H}_5\text{OH}$ ) solvents. Solubility of  $\text{NiCl}_2$  in the methanolic system changes negligibly with the increase of the methanol concentration during the dehydration process. The solubility of  $\text{NiCl}_2$  in ethanolic system decreases about 15.80 mass%

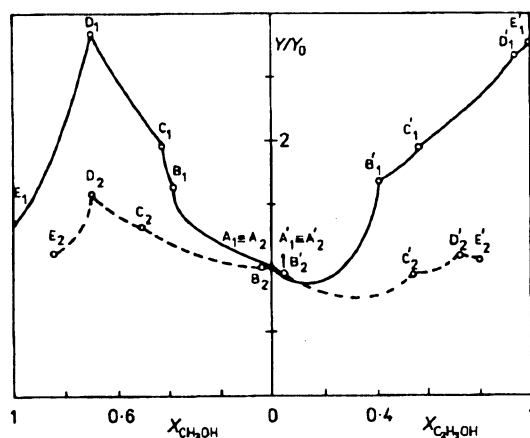


Fig. 1

Solubility processes in the  $\text{MCl}_2\text{-H}_2\text{O-ROH}$  systems ( $\text{M} = \text{Co, Ni}$ ;  $\text{ROH} = \text{CH}_3\text{OH, C}_2\text{H}_5\text{OH}$ ) at 25 °C.  $X_{\text{ROH}}$  is molar ratio of alcohol in the mixed solvent;  $Y$  is amount of substance of salt in 100 mol of mixed solvent (or water (subscript 0)). —  $\text{CoCl}_2\text{-H}_2\text{O-CH}_3\text{OH}$  ( $\text{C}_2\text{H}_5\text{OH}$ ),  $\text{A}_1\text{B}_1 = \text{A}'_1\text{B}'_1 = \text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ ;  $\text{B}_1\text{C}_1 = \text{B}'_1\text{C}'_1 = \text{CoCl}_2 \cdot 4 \text{H}_2\text{O}$ ;  $\text{C}_1\text{D}_1 = \text{C}'_1\text{D}'_1 = \text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$ ;  $\text{D}_1\text{E}_1 = \text{CoCl}_2 \cdot 3 \text{CH}_3\text{OH}$ ,  $\text{D}'_1\text{E}'_1 = \text{CoCl}_2 \cdot 2 \text{C}_2\text{H}_5\text{OH}$ . - - -  $\text{NiCl}_2\text{-H}_2\text{O-CH}_3\text{OH}$  ( $\text{C}_2\text{H}_5\text{OH}$ ),  $\text{A}_2\text{B}_2 = \text{A}'_2\text{B}'_2 = \text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$ ;  $\text{B}_2\text{C}_2 = \text{B}'_2\text{C}'_2 = \text{NiCl}_2 \cdot 4 \text{H}_2\text{O}$ ;  $\text{C}_2\text{D}_2 = \text{C}'_2\text{D}'_2 = \text{NiCl}_2 \cdot 2 \text{H}_2\text{O}$ ;  $\text{D}_2\text{E}_2 = \text{NiCl}_2 \cdot 3 \text{CH}_3\text{OH}$ ;  $\text{D}'_2\text{E}'_2 = \text{NiCl}_2 \cdot 2 \text{C}_2\text{H}_5\text{OH}$

TABLE I  
Solubility isotherms for the  $\text{MCl}_2\text{-H}_2\text{O-ROH}$  ( $\text{M} = \text{Co, Ni}$ ;  $\text{ROH} = \text{CH}_3\text{OH, C}_2\text{H}_5\text{OH}$ ) systems at 25 °C

| No.                                                                  | Liquid phase, mass%              |                  | Wet residue, mass% |                  | Equilibrium solid phase |                                                                                   |
|----------------------------------------------------------------------|----------------------------------|------------------|--------------------|------------------|-------------------------|-----------------------------------------------------------------------------------|
| CoCl <sub>2</sub> -H <sub>2</sub> O-CH <sub>3</sub> OH               |                                  |                  |                    |                  |                         |                                                                                   |
|                                                                      | CH <sub>3</sub> OH               | H <sub>2</sub> O | CoCl <sub>2</sub>  | H <sub>2</sub> O | CoCl <sub>2</sub>       |                                                                                   |
| 1                                                                    | 0.00                             | 64.00            | 36.00              | —                | —                       | CoCl <sub>2</sub> · 6 H <sub>2</sub> O                                            |
| 2                                                                    | 1.7                              | 62.6             | 35.65              | 46.0             | 53.13                   |                                                                                   |
| 3                                                                    | 12.4                             | 51.1             | 36.50              | 47.0             | 50.10                   |                                                                                   |
| 4                                                                    | 22.0                             | 40.7             | 37.28              | 45.0             | 53.02                   |                                                                                   |
| 5                                                                    | 31.1                             | 30.0             | 38.90              | 42.0             | 51.16                   |                                                                                   |
| 6                                                                    | 31.0                             | 28.0             | 41.00              | 41.0             | 51.20                   |                                                                                   |
| 7                                                                    | 30.6                             | 27.5             | 41.82              | 37.5             | 53.00                   | CoCl <sub>2</sub> · 6 H <sub>2</sub> O + CoCl <sub>2</sub> · 4 H <sub>2</sub> O   |
| 8                                                                    | 30.4                             | 26.9             | 42.70              | 35.0             | 60.52                   | CoCl <sub>2</sub> · 4 H <sub>2</sub> O                                            |
| 9                                                                    | 31.3                             | 25.0             | 43.67              | 34.0             | 58.28                   |                                                                                   |
| 10                                                                   | 30.8                             | 24.2             | 44.97              | 27.5             | 50.18                   |                                                                                   |
| 11                                                                   | 31.1                             | 23.5             | 45.32              | 25.0             | 55.00                   | CoCl <sub>2</sub> · 4 H <sub>2</sub> O + CoCl <sub>2</sub> · 2 H <sub>2</sub> O   |
| 12                                                                   | 32.4                             | 22.5             | 45.10              | 22.0             | 58.10                   | CoCl <sub>2</sub> · 2 H <sub>2</sub> O                                            |
| 13                                                                   | 33.0                             | 21.0             | 46.00              | 21.0             | 51.02                   |                                                                                   |
| 14                                                                   | 35.4                             | 16.0             | 48.58              | 19.1             | 62.50                   |                                                                                   |
| 15                                                                   | 36.1                             | 14.9             | 48.93              | 18.2             | 64.10                   |                                                                                   |
| 16                                                                   | 38.7                             | 11.1             | 50.20              | 19.0             | 70.10                   |                                                                                   |
| 17                                                                   | 39.9                             | 9.5              | 50.60              | 7.5              | 68.32                   | CoCl <sub>2</sub> · 2 H <sub>2</sub> O + CoCl <sub>2</sub> · 2 CH <sub>3</sub> OH |
| 18                                                                   | 41.4                             | 9.0              | 49.52              | 6.5              | 54.21                   | CoCl <sub>2</sub> · 2 CH <sub>3</sub> OH                                          |
| 19                                                                   | 44.0                             | 8.7              | 47.22              | 6.5              | 53.11                   |                                                                                   |
| 20                                                                   | 46.6                             | 7.2              | 46.11              | 3.5              | 56.23                   |                                                                                   |
| 21                                                                   | 60.6                             | 4.1              | 35.24              | 2.5              | 49.50                   |                                                                                   |
| 22                                                                   | 63.7                             | 3.2              | 33.10              | 1.5              | 52.20                   |                                                                                   |
| 23                                                                   | 67.2                             | 1.5              | 31.22              | 1.0              | 50.31                   |                                                                                   |
| 24                                                                   | 69.64                            | 0.00             | 30.36              | —                | —                       |                                                                                   |
| CoCl <sub>2</sub> -H <sub>2</sub> O-C <sub>2</sub> H <sub>5</sub> OH |                                  |                  |                    |                  |                         |                                                                                   |
|                                                                      | C <sub>2</sub> H <sub>5</sub> OH | H <sub>2</sub> O | CoCl <sub>2</sub>  | H <sub>2</sub> O | CoCl <sub>2</sub>       |                                                                                   |
| 1                                                                    | 0.00                             | 64.00            | 36.00              | —                | —                       | CoCl <sub>2</sub> · 6 H <sub>2</sub> O                                            |
| 2                                                                    | 4.8                              | 62.0             | 33.11              | 51.0             | 48.40                   |                                                                                   |
| 3                                                                    | 6.9                              | 60.0             | 33.03              | 46.0             | 53.09                   |                                                                                   |
| 4                                                                    | 9.8                              | 58.3             | 31.87              | 48.0             | 49.50                   |                                                                                   |
| 5                                                                    | 12.8                             | 56.0             | 31.20              | 47.8             | 50.01                   |                                                                                   |
| 6                                                                    | 14.0                             | 55.5             | 30.44              | 45.0             | 54.00                   |                                                                                   |
| 7                                                                    | 20.5                             | 50.0             | 29.50              | 45.0             | 50.00                   |                                                                                   |
| 8                                                                    | 20.1                             | 49.4             | 30.44              | 45.2             | 52.08                   |                                                                                   |
| 9                                                                    | 23.1                             | 47.7             | 29.19              | 45.2             | 51.84                   |                                                                                   |
| 10                                                                   | 23.2                             | 46.8             | 29.98              | 45.0             | 50.54                   |                                                                                   |
| 11                                                                   | 31.9                             | 39.9             | 28.14              | 44.0             | 53.05                   |                                                                                   |
| 12                                                                   | 32.1                             | 38.8             | 29.01              | 44.0             | 52.06                   |                                                                                   |
| 13                                                                   | 34.1                             | 37.4             | 28.42              | 44.0             | 51.00                   |                                                                                   |
| 14                                                                   | 35.2                             | 35.0             | 29.76              | 44.0             | 50.63                   |                                                                                   |
| 15                                                                   | 36.0                             | 34.6             | 29.39              | 42.0             | 48.78                   |                                                                                   |

TABLE I  
(Continued)

| No.                                                                  | Liquid phase, mass%              |                  | Wet residue, mass% |                  | Equilibrium solid phase |                                                                                                   |
|----------------------------------------------------------------------|----------------------------------|------------------|--------------------|------------------|-------------------------|---------------------------------------------------------------------------------------------------|
| CoCl <sub>2</sub> -H <sub>2</sub> O-C <sub>2</sub> H <sub>5</sub> OH |                                  |                  |                    |                  |                         |                                                                                                   |
|                                                                      | C <sub>2</sub> H <sub>5</sub> OH | H <sub>2</sub> O | CoCl <sub>2</sub>  | H <sub>2</sub> O | CoCl <sub>2</sub>       |                                                                                                   |
| 16                                                                   | 39.6                             | 32.1             | 28.27              | 40.0             | 45.80                   | CoCl <sub>2</sub> · 6 H <sub>2</sub> O                                                            |
| 17                                                                   | 40.4                             | 30.5             | 29.04              | 43.0             | 52.24                   |                                                                                                   |
| 18                                                                   | 41.2                             | 28.9             | 29.82              | 45.4             | 54.41                   |                                                                                                   |
| 19                                                                   | 42.3                             | 26.3             | 31.33              | 42.5             | 51.92                   |                                                                                                   |
| 20                                                                   | 40.2                             | 23.9             | 35.81              | 39.0             | 49.01                   |                                                                                                   |
| 21                                                                   | 41.0                             | 22.5             | 36.50              | 38.0             | 53.00                   | CoCl <sub>2</sub> · 6 H <sub>2</sub> O + CoCl <sub>2</sub> · 4 H <sub>2</sub> O                   |
| 22                                                                   | 42.9                             | 21.0             | 36.10              | 35.0             | 60.07                   | CoCl <sub>2</sub> · 4 H <sub>2</sub> O                                                            |
| 23                                                                   | 44.1                             | 20.0             | 35.88              | 31.0             | 54.46                   |                                                                                                   |
| 24                                                                   | 46.4                             | 17.4             | 36.20              | 32.0             | 56.24                   |                                                                                                   |
| 25                                                                   | 47.2                             | 16.7             | 36.09              | 32.5             | 57.00                   |                                                                                                   |
| 26                                                                   | 48.1                             | 15.0             | 36.81              | 27.0             | 60.32                   | CoCl <sub>2</sub> · 4 H <sub>2</sub> O + CoCl <sub>2</sub> · 2 H <sub>2</sub> O                   |
| 27                                                                   | 48.6                             | 14.7             | 36.70              | 19.3             | 62.81                   | CoCl <sub>2</sub> · 2 H <sub>2</sub> O                                                            |
| 28                                                                   | 49.9                             | 13.4             | 36.64              | 19.0             | 64.58                   |                                                                                                   |
| 29                                                                   | 52.3                             | 10.6             | 37.10              | 19.1             | 64.73                   |                                                                                                   |
| 30                                                                   | 54.8                             | 9.0              | 36.20              | 18.0             | 65.60                   |                                                                                                   |
| 31                                                                   | 54.9                             | 8.2              | 36.82              | 17.2             | 66.22                   |                                                                                                   |
| 32                                                                   | 55.6                             | 7.0              | 37.36              | 21.0             | 76.05                   |                                                                                                   |
| 33                                                                   | 56.1                             | 6.0              | 37.86              | 17.5             | 67.33                   |                                                                                                   |
| 34                                                                   | 57.9                             | 4.2              | 37.90              | 17.0             | 67.05                   |                                                                                                   |
| 35                                                                   | 59.0                             | 3.0              | 38.00              | 18.1             | 69.30                   |                                                                                                   |
| 36                                                                   | 60.8                             | 1.6              | 37.60              | 13.0             | 60.87                   |                                                                                                   |
| 37                                                                   | 59.5                             | 2.0              | 38.50              | 6.0              | 60.01                   | CoCl <sub>2</sub> · 2 H <sub>2</sub> O + CoCl <sub>2</sub> · 2.5 C <sub>2</sub> H <sub>5</sub> OH |
| 38                                                                   | 60.7                             | 1.3              | 38.00              | 0.8              | 50.95                   | CoCl <sub>2</sub> · 2.5 C <sub>2</sub> H <sub>5</sub> OH                                          |
| 39                                                                   | 61.0                             | 1.0              | 37.92              | 0.5              | 48.00                   |                                                                                                   |
| 40                                                                   | 62.2                             | 0.00             | 37.80              | —                | —                       |                                                                                                   |
| NiCl <sub>2</sub> -H <sub>2</sub> O-CH <sub>3</sub> OH               |                                  |                  |                    |                  |                         |                                                                                                   |
|                                                                      | CH <sub>3</sub> OH               | H <sub>2</sub> O | NiCl <sub>2</sub>  | H <sub>2</sub> O | NiCl <sub>2</sub>       |                                                                                                   |
| 1                                                                    | 0.00                             | 60.7             | 39.30              | —                | —                       | NiCl <sub>2</sub> · 6 H <sub>2</sub> O                                                            |
| 2                                                                    | 0.4                              | 61.0             | 38.58              | 50.8             | 49.00                   |                                                                                                   |
| 3                                                                    | 0.8                              | 60.4             | 38.80              | 47.0             | 52.60                   |                                                                                                   |
| 4                                                                    | 2.1                              | 59.0             | 38.82              | 49.0             | 50.10                   |                                                                                                   |
| 5                                                                    | 2.9                              | 58.1             | 39.00              | 43.0             | 56.10                   | NiCl <sub>2</sub> · 6 H <sub>2</sub> O + NiCl <sub>2</sub> · 4 H <sub>2</sub> O                   |
| 6                                                                    | 4.0                              | 57.3             | 38.73              | 46.7             | 51.04                   | NiCl <sub>2</sub> · 4 H <sub>2</sub> O                                                            |
| 7                                                                    | 8.4                              | 53.0             | 38.60              | 44.0             | 51.24                   |                                                                                                   |
| 8                                                                    | 9.8                              | 51.8             | 38.43              | 46.5             | 46.48                   |                                                                                                   |
| 9                                                                    | 19.8                             | 41.8             | 38.44              | 39.5             | 47.94                   |                                                                                                   |
| 10                                                                   | 21.5                             | 40.5             | 38.00              | 37.5             | 52.02                   |                                                                                                   |
| 11                                                                   | 23.6                             | 38.4             | 38.00              | 37.2             | 51.24                   |                                                                                                   |
| 12                                                                   | 25.0                             | 37.8             | 37.16              | 36.0             | 56.36                   |                                                                                                   |
| 13                                                                   | 27.9                             | 35.1             | 36.98              | 35.0             | 54.46                   |                                                                                                   |

TABLE I  
(Continued)

| No.                                                                  | Liquid phase, mass%              |                  | Wet residue, mass% |                  |                   | Equilibrium solid phase                                                                         |
|----------------------------------------------------------------------|----------------------------------|------------------|--------------------|------------------|-------------------|-------------------------------------------------------------------------------------------------|
| NiCl <sub>2</sub> -H <sub>2</sub> O-CH <sub>3</sub> OH               |                                  |                  |                    |                  |                   |                                                                                                 |
|                                                                      | CH <sub>3</sub> OH               | H <sub>2</sub> O | NiCl <sub>2</sub>  | H <sub>2</sub> O | NiCl <sub>2</sub> |                                                                                                 |
| 14                                                                   | 28.6                             | 34.2             | 37.20              | 34.8             | 56.00             | NiCl <sub>2</sub> · 4 H <sub>2</sub> O                                                          |
| 15                                                                   | 33.2                             | 29.1             | 37.70              | 34.1             | 55.35             |                                                                                                 |
| 16                                                                   | 36.0                             | 27.7             | 36.30              | 33.0             | 56.50             |                                                                                                 |
| 17                                                                   | 38.9                             | 24.0             | 37.10              | 31.2             | 55.12             |                                                                                                 |
| 18                                                                   | 39.4                             | 22.5             | 38.13              | 27.3             | 53.44             | NiCl <sub>2</sub> · 4 H <sub>2</sub> O + NiCl <sub>2</sub> · 2 H <sub>2</sub> O                 |
| 19                                                                   | 40.8                             | 22.2             | 37.00              | 22.0             | 55.50             | NiCl <sub>2</sub> · 2 H <sub>2</sub> O                                                          |
| 20                                                                   | 42.2                             | 20.4             | 37.35              | 21.0             | 56.00             |                                                                                                 |
| 21                                                                   | 48.5                             | 12.3             | 39.23              | 16.0             | 53.38             |                                                                                                 |
| 22                                                                   | 48.7                             | 11.5             | 39.80              | 5.5              | 59.24             | NiCl <sub>2</sub> · 4 H <sub>2</sub> O + NiCl <sub>2</sub> · 3 CH <sub>3</sub> OH               |
| 23                                                                   | 51.4                             | 11.0             | 37.51              | 8.4              | 43.37             | NiCl <sub>2</sub> · 3 CH <sub>3</sub> OH                                                        |
| 24                                                                   | 52.0                             | 11.2             | 36.72              | 6.9              | 43.66             |                                                                                                 |
| 25                                                                   | 59.0                             | 9.3              | 31.65              | 4.5              | 43.78             |                                                                                                 |
| 26                                                                   | 60.8                             | 8.0              | 31.20              | 4.0              | 45.42             |                                                                                                 |
| 27                                                                   | 63.0                             | 6.1              | 30.81              | 3.2              | 45.42             |                                                                                                 |
| NiCl <sub>2</sub> -H <sub>2</sub> O-C <sub>2</sub> H <sub>5</sub> OH |                                  |                  |                    |                  |                   |                                                                                                 |
|                                                                      | C <sub>2</sub> H <sub>5</sub> OH | H <sub>2</sub> O | NiCl <sub>2</sub>  | H <sub>2</sub> O | NiCl <sub>2</sub> |                                                                                                 |
| 1                                                                    | 0.00                             | 60.7             | 39.30              | —                | —                 | NiCl <sub>2</sub> · 6 H <sub>2</sub> O                                                          |
| 2                                                                    | 1.3                              | 60.6             | 38.01              | 49.1             | 50.21             |                                                                                                 |
| 3                                                                    | 0.8                              | 61.6             | 37.59              | 49.0             | 50.89             |                                                                                                 |
| 4                                                                    | 1.4                              | 60.6             | 37.93              | 50.0             | 47.60             |                                                                                                 |
| 5                                                                    | 4.1                              | 59.0             | 36.84              | 49.0             | 49.60             | NiCl <sub>2</sub> · 6 H <sub>2</sub> O + NiCl <sub>2</sub> · 4 H <sub>2</sub> O                 |
| 6                                                                    | 4.3                              | 58.5             | 37.07              | 48.4             | 48.47             | NiCl <sub>2</sub> · 4 H <sub>2</sub> O                                                          |
| 7                                                                    | 5.0                              | 58.2             | 36.75              | 49.2             | 46.14             |                                                                                                 |
| 8                                                                    | 14.6                             | 53.2             | 32.14              | 44.1             | 49.00             |                                                                                                 |
| 9                                                                    | 16.1                             | 51.9             | 32.00              | 43.5             | 48.35             |                                                                                                 |
| 10                                                                   | 20.6                             | 50.0             | 29.39              | 37.0             | 61.02             |                                                                                                 |
| 11                                                                   | 21.6                             | 48.5             | 29.88              | 38.1             | 55.72             |                                                                                                 |
| 12                                                                   | 23.8                             | 47.1             | 29.02              | 40.2             | 48.92             |                                                                                                 |
| 13                                                                   | 26.0                             | 46.5             | 27.50              | 38.2             | 53.37             |                                                                                                 |
| 14                                                                   | 28.1                             | 45.0             | 26.85              | 37.0             | 57.25             |                                                                                                 |
| 15                                                                   | 35.0                             | 37.0             | 27.96              | 35.8             | 58.94             |                                                                                                 |
| 16                                                                   | 46.6                             | 25.8             | 27.55              | 32.2             | 50.26             |                                                                                                 |
| 17                                                                   | 52.5                             | 22.0             | 25.48              | 32.8             | 54.73             |                                                                                                 |
| 18                                                                   | 53.5                             | 21.5             | 25.00              | 31.2             | 53.00             |                                                                                                 |
| 19                                                                   | 54.5                             | 20.1             | 25.31              | 26.0             | 61.00             |                                                                                                 |
| 20                                                                   | 56.2                             | 18.8             | 25.00              | 20.5             | 61.20             |                                                                                                 |
| 21                                                                   | 62.7                             | 13.0             | 24.21              | 18.0             | 57.12             |                                                                                                 |
| 22                                                                   | 69.2                             | 7.9              | 22.85              | 13.0             | 43.00             |                                                                                                 |
| 23                                                                   | 69.5                             | 7.0              | 23.50              | 8.0              | 42.21             | NiCl <sub>2</sub> · 2 H <sub>2</sub> O + NiCl <sub>2</sub> · 2 C <sub>2</sub> H <sub>5</sub> OH |
| 24                                                                   | 70.5                             | 6.5              | 23.0               | 3.4              | 41.52             | NiCl <sub>2</sub> · 2 C <sub>2</sub> H <sub>5</sub> OH                                          |
| 25                                                                   | 72.6                             | 4.9              | 22.5               | 3.2              | 41.80             |                                                                                                 |

compared to the  $NiCl_2$ - $H_2O$  system. The crystalline solvates  $NiCl_2 \cdot 3 CH_3OH$  (ref.<sup>6</sup>) and  $NiCl_2 \cdot 2 C_2H_5OH$  (ref.<sup>7</sup>) exist in the mixed solvents as a result of the solvation of  $NiCl_2 \cdot 2 H_2O$ . These solvates are known to be present in the binary  $NiCl_2$ - $CH_3OH$  ( $C_2H_5OH$ ) systems<sup>5</sup> as well. The crystalline solvates are highly hygroscopic and once isolated from the saturated solutions they are easily converted to crystalline hydrates in a short time. The viscosity of their saturated solution is high in the region with low concentration of water. It is thus difficult to isolate solid phases using common filtration procedure and/or centrifugation<sup>6</sup>. This was the main difficulty in studying the systems containing less than 5 mass%  $H_2O$ .

*Comparison of the Dehydration and Solubility Properties of Alcohols in the Saturated Solutions*

The dehydration properties of  $CH_3OH$  and  $C_2H_5OH$  in the saturated solution of  $CoCl_2$  ( $NiCl_2$ )- $H_2O$ - $CH_3OH$  ( $C_2H_5OH$ ) are compared to the thermal dehydration of crystalline hydrates in the binary  $CoCl_2$ ( $NiCl_2$ )- $H_2O$  systems in Table II. The dehydration processes in the mixed solvent take place in a stepwise manner just as in the case of their thermal dehydration in water solutions, and it is seen the methanol is a little better dehydration agent than ethanol. It is notable fact that the phase transition  $NiCl_2 \cdot 6 H_2O \rightarrow NiCl_2 \cdot 4 H_2O$  takes place at very low concentrations of both used alcohols. The solubility properties of the two alcohols are compared in Fig. 1. The curves are drawn on the basis of the experimental data given in Table I. A quantitative measure for the solubility effects of the alcohols is the ratio of  $Y/Y_0$  which was discussed in the previous paper<sup>8</sup>. A marked complexation reflected in the increase in the solubility of  $CoCl_2$  in the mixed  $H_2O$ - $CH_3OH$  ( $C_2H_5OH$ ) solvent.

TABLE II

Dehydration of the  $CoCl_2 \cdot 6 H_2O$  and  $NiCl_2 \cdot 6 H_2O$  crystalline hydrates in the  $H_2O$ - $CH_3OH$  ( $C_2H_5OH$ ) mixed solvents at 25 °C

| Phase transitions                                     | $MCl_2$ - $H_2O$<br>$t$ , °C | $X_{CH_3OH}$<br>m. f. | $X_{C_2H_5OH}$<br>m. f. |
|-------------------------------------------------------|------------------------------|-----------------------|-------------------------|
| $CoCl_2 \cdot 6 H_2O \rightarrow CoCl_2 \cdot 4 H_2O$ | 49                           | 0.38                  | 0.42                    |
| $CoCl_2 \cdot 4 H_2O \rightarrow CoCl_2 \cdot 2 H_2O$ | 58                           | 0.43                  | 0.56                    |
| $NiCl_2 \cdot 6 H_2O \rightarrow NiCl_2 \cdot 4 H_2O$ | 28.8                         | 0.03                  | 0.03                    |
| $NiCl_2 \cdot 4 H_2O \rightarrow NiCl_2 \cdot 2 H_2O$ | 64.3                         | 0.50                  | 0.51                    |

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