Carbon Monoxide Absorption by Aqueous CuCl–$MgCl_2$ Absorbent

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Carbon monoxide absorption characteristics of an aqueous CuCl–$MgCl_2$ solution system are clarified. A CuCl 3.7 mol/l–$MgCl_2$ 4.7 mol/l solution is found to absorb 2.2 mol of CO per liter at 30 °C and $P_{CO}=2\times10^4$ Pa. This is 8 times greater than a CuCl 3.2 mol/l–HCl 8.2 mol/l solution and 16 times greater than a CuCl 4.8 mol/l–KCl 5.9 mol/l solution. The CO absorption of the concentrated aqueous solution of CuCl–$MgCl_2$ is accompanied with fine particle precipitation. This precipitate, which consists of CO, Cu^+, Mg^{2+}, Cl^-, and H_2O, is estimated to be $CO\cdot CuMgCl_3\cdot nH_2O$. The complex completely releases CO at 70 °C or above. Chloride ion influence on the formation of $CO\cdot CuMgCl_3\cdot nH_2O$ is discussed.

The carbon monoxide absorption properties of an aqueous copper(I) chloro-complex solution and aqueous CuCl-MCl_n ($M=H^+$, NH_4^+, metal ion and $n=1$—3) suspension systems have long been known.[1,2] Among these systems, the CuCl-$MgCl_2$ suspension was reported by Deringer[3] as absorbing a larger amount of CO at relativey low CO partial pressure region (above 20 kPa) than the aqueous solution of copper(I) chlorocomplex. Decomposition pressure of the CO complex was said to be lowered only in the CuCl-$MgCl_2$ suspension absorbent, which contains solid $MgCl_2\cdot 6H_2O$.[3,4] The solid CO complex thus formed may contain $MgCl_2$, since the appearance of solid $MgCl_2\cdot 6H_2O$ changes after CO absorption.[3] However, neither the details of these phenomena nor the absorption behavior of CuCl-$MgCl_2$ solution has been clarified.

Aqueous absorbent that does not contain an acid or alkali, is quite promising for industrial use in recovering carbon monoxide from gas mixtures containing H_2O and CO_2. It includes no inflammable organic solvent and requires no pre-dehydration or pre-decarbonation of gas mixtures.[5,6]

The present work clarifies the CO absorption phenomena of the aqueous CuCl-$MgCl_2$ solution system.

Experimental

Materials. Copper(I) chloride and other chloride salts listed in Table 1 were purchased as reagent grade (Kanto Chemical Co., Inc.) and used as received. Carbon monoxide gas (99% pure) was used without further purification.

Copper(I) solutions were prepared by the following procedure. The desired amounts of chloride salts were weighed and transferred into a flask in a nitrogen box. Oxygen-free deionized water was added to the flask. Then, the flask was sealed and stirred. The flask was permitted to stand at 30 °C overnight to settle either the excess chloride or the impurities. The upper portion was used as a solution absorbent.

Metal ion concentration of the solution was determined by atomic absorption analysis. Chloride ion concentration was determined by spectrophotometry using mercury(II) thiocyanate and iron(III) ion,[7] after eliminating the metal ion as hydroxide precipitates.

The copper(II) ion content was checked by redox titration, using $TiCl_3$ standard solution as the reductant and monitoring the redox potential, for several solutions prepared as described above. Copper(II) ion content was always below 1% of the total copper ion concentration. Copper(II) ion does not form a compound with CO, and was ignored in the following discussion.

CO Absorption Measurement. Carbon monoxide absorption was measured using a constant pressure apparatus. The absorption vessel was connected to the apparatus *via* a tapered joint and immersed in temperature regulated water. The solution or suspension was rigorously stirred with a magnetic stirrer.

The amount of CO absorbed at $P_{CO}=1.01\times10^5$ Pa was determined as follows. Twenty ml of copper(I) solution or suspension was transferred to an absorption vessel. The apparatus was degassed quickly to the vapor pressure of the solution, and then CO gas was introduced to the apparatus. Pressure decrease due to absorption was detected by manometric pressure sensor and more CO gas was fed automatically to keep the pressure constant.

Dependence of the amount of CO absorbed on the CO pressure was determined as follows. After evacuation to a vapor pressure, measured quantities of CO were added. After each addition of CO, the equilibrium pressure and amount of CO absorbed were determined. The absorption equilibrium was attained within 1 h when the amount of CO absorbed was below 1.5 mol/l, after the precipitation occurred. It was considered that the maximum CO absorption under given conditions was obtained when the pressure change was less than 133 Pa within 30 min. No precipitation was observed before the CO absorption occurred.

To separate fine particles or a flake precipitate formed by

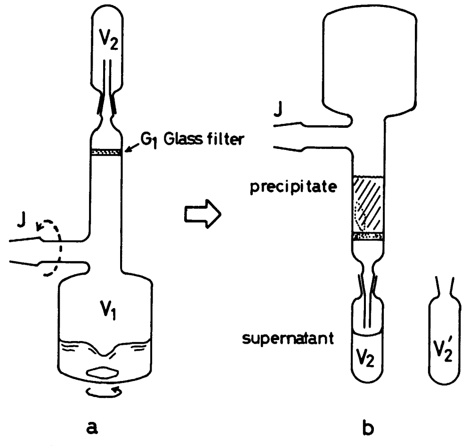

Fig. 1. Apparatus and procedure for precipitate separation from supernatant liquid.
V_1: Absorption vessel, V_2 and V_2': vessel for recuperation of liquid obtained after CO release, J: ground glass joint, a: CO absorption, b: separation of precipitate.

CO absorption in some cases, a vessel V_1, equipped with a glass filter (Fig. 1) was used. After CO absorption, V_1 was rotated around joint J. The supernatant portion dropped to vessel V_2, leaving the fine particles or flakes on the glass filter. Then, V_2 was replaced by V_2', previously filled with CO. The fine particles or the flakes remained on the glass filter were warmed and the quantity of CO released was measured with a gas buret. The liquid, obtained after CO release from the fine particles, dropped into vessel V_2'. During these procedures, the supernatant liquid and the precipitate were kept under an atmosphere of CO ($P_{\mathrm{CO}}=1.01\times10^5$ Pa). This was done because the CO complex formed in the liquid phase as well as in the solid phase releases CO when the partial pressure of CO decreases. The white solid remained after CO release from the flake was dissolved in HCl solution. The total amount of CO released from the supernatant liquid and the precipitate corresponds to the amount of CO absorbed within the experimental errors.

Results and Discussion

Comparison of CO Absorption Behavior. The characteristics of CO absorption by aqueous CuCl-$MgCl_2$ solution (not including solid $MgCl_2 \cdot 6H_2O$) are compared with those of other CuCl-MCl_n solutions in terms of the maximum amount of CO absorbed, the molar ratio of CO absorbed to Cu^+, CO/Cu^+, and the appearance of precipitate. Results are summarized in Table 1.

Maximum Amount of CO Absorbed: The maximum amount of CO absorbed under given conditions increases with the dissolved CuCl concentration. It is noteworthy that the maximum amount of CO absorbed by the concentrated CuCl-$MgCl_2$ solution is larger than that by CuCl-MCl_n solution which contain nearly the same amount of dissolved CuCl as the CuCl-$MgCl_2$ solution.

CO/Cu^+ Ratio: The CO/Cu^+ ratio decreases as the dissolved CuCl concentration increases in the CuCl-HCl system.[1)] All systems, except CuCl-$MgCl_2$, show the same tendency at 30 °C, regardless of whether flakes of CuCl-CO complex are formed.[1,8)] The CO/Cu^+ ratio of the CuCl-$MgCl_2$ system decreases in the low concentration region. In high concentration region, the ratio increases with the dissolved CuCl concentration.

Appearance of Precipitate: When the concentration of CuCl and $MgCl_2$ was high, the precipitation of fine particles, which were considered as the CO complex, was observed. This kind of precipitate with a fine particle form has not been previously reported. This precipitate differs from the flake of CuCl-CO solid complex in both size and shape. The former is much smaller (about one-tenth that of the latter). It is also more spherical as opposed to flaky.

These observations clearly indicate that the CO absorption characteristics of the CuCl-$MgCl_2$ system are quite different from other CuCl-MCl_n systems.

Composition of the Precipitate with Fine Particle Form: The composition of supernatant solution, the content of precipitates, and the amount of CO released from the supernatant solution and the precipitate are summarized in Table 2.

Table 1. Maximum amount of CO absorbed by CuCl-MCl_n solutions (30 °C, $P_{\mathrm{CO}}=1.01\times105$ Pa)

Concentration mol l^{-1} CuCl	Concentration mol l^{-1} MCl_n	Amount of CO absorbed mol l^{-1}	CO/Cu^+	Appearance of precipitate
CuCl-$MgCl_2$				
0.79	1.95	0.32	0.40	—
2.20	3.27	0.62	0.28	—
2.57	3.46	1.03	0.40	Fine particle
2.61	3.64	1.24	0.47	Fine particle
2.30	3.93	1.43	0.62	Fine particle
2.80	3.92	1.86	0.66	Fine particle
3.00	4.80	1.83	0.61	Fine particle
		(3×10^4 Pa)	(3×10^4 Pa)	
3.70	4.70	2.23	0.60	Fine particle
		(2×10^4 Pa)	(2×10^4 Pa)	
CuCl-HCl				
0.26	2.00	0.15	0.57	—
0.98	4.62	0.40	0.48	—
2.24	6.77	0.91	0.41	—
3.15	8.15	1.30	0.41	Flake
CuCl-LiCl				
0.54	3.50	0.23	0.43	—
1.90	6.10	0.47	0.25	—
2.70	7.60	0.68	0.25	Flake
3.50	9.20	0.88	0.25	Flake
CuCl-NaCl				
0.76	3.24	0.28	0.37	—
2.20	5.40	0.44	0.20	—
3.20	6.40	0.95	0.29	Flake
CuCl-NH_4Cl				
0.77	2.33	0.30	0.39	—
2.04	4.16	0.62	0.28	—
4.31	6.97	0.65	0.15	—
5.30	7.71	0.64	0.12	—
CuCl-KCl				
0.23	1.34	0.12	0.52	—
1.53	3.32	0.38	0.24	—
2.61	4.44	0.56	0.22	—
3.93	5.52	0.88	0.22	Flake
4.84	5.88	1.07	0.22	Flake
CuCl-$CaCl_2$				
0.16	0.75	0.08	0.53	—
1.65	2.84	0.53	0.31	Flake
2.77	3.64	0.73	0.26	Flake
CuCl-$SrCl_2$				
0.26	0.93	0.16	0.63	—
1.02	1.97	0.35	0.34	—
2.69	3.30	0.78	0.29	Flake
CuCl-$CoCl_2$				
0.22	0.93	0.13	0.59	—
1.42	3.07	0.41	0.29	—
1.90	4.58	0.57	0.30	Flake
CuCl-$NiCl_2$				
0.26	1.04	0.14	0.53	—
1.65	3.05	0.43	0.26	Flake
2.17	3.80	0.53	0.25	Flake

For the CuCl-$MgCl_2$ and CuCl-$MgCl_2$-MCl_n solutions, the following results were obtained.

(1) About 80% of CO absorbed, was released from the fine particles.

(2) CO/Cu^+ ratio was about 0.8 for the precipitate and 0.2 for the supernatant solution.

TABLE 2. COMPOSITION OF SUPERNATANT LIQUID AND FINE PARTICLE PRECIPITATE
(30 °C, $P_{CO}=1.01\times10^5$ Pa, volume of absorbent: 20 ml)

Absorbent (mol/l)			Supernatant							Precipitate					
			Composition (mol/l)				volume (ml)	CO released (mmol)	$\frac{CO}{Cu^+}$	Content (mmol)				CO released (mmol)	$\frac{CO}{Cu^+}$
CuCl	$MgCl_2$	MCl_n	Cu^+	Mg^{2+}	M^{n+}	Cl^-				Cu^+	Mg^{2+}	M^{n+}	Cl^-		
2.9	4.0	—	2.2	3.6	—	9.4	10	4.4	0.2	37	44	—	131	28.3	0.76
2.4	3.1	$CrCl_3$ 0.6	1.9	2.6	0.75	9.8	13.5	5.3	0.2	23	26	2.9	83	19.6	0.73
3.1	3.1	$CaCl_2$ 1.0	2.5	2.6	1.3	10.3	13	5.9	0.2	28	28	5.3	95	23.2	0.83
2.8	3.3	$CoCl_2$ 1.1	2.1	2.6	1.2	10.2	12	5.3	0.2	28	29	6.7	106	21.4	0.77
3.0	3.1	LiCl 2.0	2.4	2.4	2.3	10.1	12	5.9	0.2	31	32	11	104	24.8	0.80
4.8	—	KCl 5.1	4.4	—	5.0	10.0	18.5	7.9	0.1	15	—	8.9	a)	10.2	0.66

a) Amount of Cl^- could not be determined because the solid remaining after CO release was dissolved in HCl solution.

(3) The amount of chloride ion A_{Cl^-}, was expressed as $A_{Cl^-}=A_{Cu^+}+2\,A_{Mg^{2+}}+n\,A_{M^{n+}}$ where A_{Cu^+}, $A_{Mg^{2+}}$, and $A_{M^{n+}}$ are Cu^+, Mg^{2+}, and M^{n+} content in mol/l, respectively.

(4) As much Mg^{2+} as Cu^+ was contained in the precipitate.

(5) The Mg^{2+} concentration of the supernatant solution was always lower than that of the absorbent before CO absorption, while the M^{n+} concentration was always higher despite the rough separation process.

These results indicate that the precipitate with fine particle form consists of CO, Cu^+, Mg^{2+}, Cl^-, and H_2O. Since the M^{n+} distribution between a supernatant and a precipitate is opposite that of Mg^{2+}, M^{n+} is not considered as a precipitate compounent.

This precipitate might be expressed as the rational formula: $CO\cdot CuMgCl_3\cdot nH_2O$.

Flake formed when CO is absorbed by a concentrated CuCl–KCl solution, was analyzed in a simillar way. In this case, residue remained after release of CO from the flake was dissolved in HCl solution and the ratio of K^+ to Cu^+, K^+/Cu^+, was determined. As this ratio is much smaller than unity (0.58), the flake appears to be composed essentially of CuCl-CO as previously reported.[2,8]

Partial Pressure Dependence of CO Absorption. Pressure dependene of CO absorption by CuCl 3 mol/l-$MgCl_2$ 4.8 mol/l solution is shown in Fig. 2 (curve A). The amount of CO absorbed, A_{CO}, increases abruptly when CO partial pressure surpasses the threshold pressure, P^*_{CO}; and CO absorption above P^*_{CO} is accompanied with fine particle precipitation.

The pressure dependence of CO absorption by CuCl-$MgCl_2$ suspension and that by CuCl-KCl solution are also shown in Fig. 2. Curves C and D show the results obtained by Deringer.[3] This figure clearly shows that the dependence of the amount of CO absorbed on CO partial pressure is substantially the same for each CuCl-$MgCl_2$ system, regardless of whether it is a solution or a suspension. Furthermore, when CO was absorbed by CuCl 3 mol/l-$MgCl_2$ 5 mol/l suspension absorbent above P^*_{CO}, precipitate with fine particle form was also observed at the wall of the absorption vessel, in the vicinity of gas-liquid interface. Therefore, the CO complex pointed out by Deringer, which might contain $MgCl_2\cdot6H_2O$, is considered to be $CO\cdot CuMgCl_3\cdot nH_2O$.

The amount of CO absorbed by the concentrated CuCl-KCl system changes gradually with increasing CO partial pressure (curve E) in quite a different

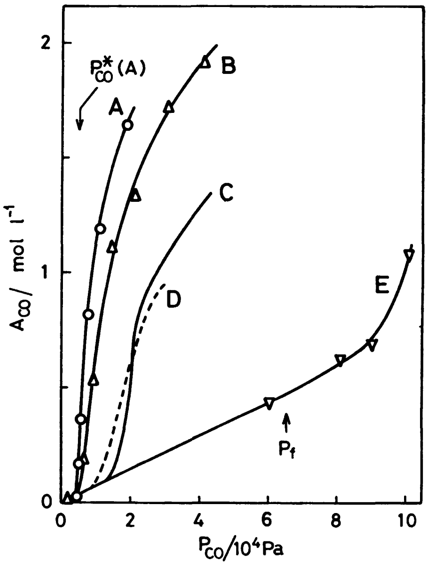

Fig. 2. Pressure dependence of CO amount absorbed, A_{CO}, by CuCl-$MgCl_2$ and CuCl-KCl (30 °C).
A: CuCl 3 mol/l-$MgCl_2$ 4.8 mol/l, B: CuCl 3 mol/l-$MgCl_2$ 5 mol/l (suspension), C: CuCl 1 g+3 ml of $MgCl_2$ suspension (Deringer[3]), D: CuCl 1 g+3 ml of Carnallite suspension (Deringer[3]), E: CuCl 4.8-KCl 5.9 mol/l.
P^*_{CO} (A): Threshold pressure for absorbent A above the amount of CO absorbed increases remarkably with increased CO partial pressure. CO absorption above P^*_{CO} is accompanied with fine particle precipitation. P^f_{CO}: Flake formation pressure for absorbent E. CO absorption above P^f_{CO} is accompanied with flake formation.

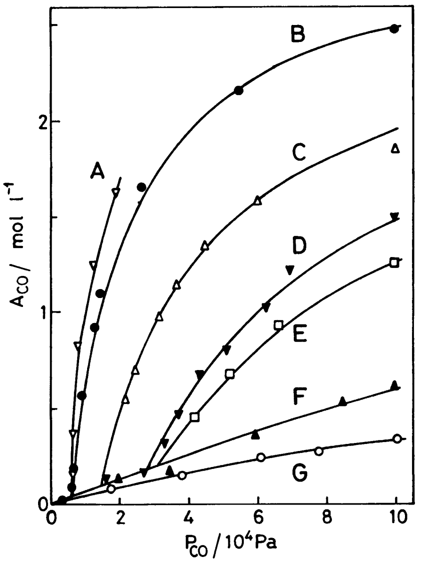

Fig. 3. Pressure dependence of CO amount absorbed, A_{CO}, for several CuCl-MgCl$_2$ solutions and suspensions (30 °C).
A: CuCl 3 mol/l-MgCl$_2$ 4.8 mol/l, B: CuCl 3 mol/l-MgCl$_2$ 5 mol/l (suspension), C: CuCl 2.8 mol/l-MgCl$_2$ 3.9 mol/l, D: CuCl 3 mol/l-MgCl$_2$ 4 mol/l (suspension), E: CuCl 2.7 mol/l-MgCl$_2$ 3.7 mol/l, F: CuCl 2.2 mol/l-MgCl$_2$ 3.3 mol/l, G: CuCl 0.8 mol/l-MgCl$_2$ 2.0 mol/l.
Solid lines A to E were calculated using Eq. 4 with $K_2=8.86\times10^{-5}$ Pa^{-1} and $P^*_{CO}=5\times10^3$ Pa for A, $K_2=5.196\times10^{-5}$ Pa^{-1} and $P^*_{CO}=5\times10^3$ Pa for B, $K_2=2.625\times10^{-5}$Pa^{-1} and $P^*_{CO}=1.16\times10^4$Pa for C, $K_2=1.26\times10^{-5}$ Pa^{-1} and $P^*_{CO}=2.33\times10^4$ Pa for D, and $K_2=1.191\times10^{-5}$ Pa^{-1} and $P^*_{CO}=2.43\times10^4$ Pa for E. Solid lines F and G were calculated using Eq. 2 with $K_1=3.725\times10^{-6}$ Pa^{-1} for F and $K_1=6.771\times10^{-6}$ Pa^{-1} for G.

manner than with CuCl-MgCl$_2$ system.

The partial pressure dependence of CO absorption by several CuCl-MgCl$_2$ solutions and suspensions are summarized in Fig. 3. There, P^*_{CO} increases as either CuCl or MgCl$_2$ content decrease, in either solution or suspension. Furthermore, the change in amount of CO absorbed with the CO pressure above P^*_{CO}, is smaller for more dilute absorbents.

These phenomena can be explained as follows. In solutions F and G, CO absorption proceeds *via* Reaction 1 as previously reported.[1,8)]

$$\text{Cu(I)}\cdot\text{chloro-complex(dissolved)} + \text{CO}$$
$$\longrightarrow \text{CO}\cdot\text{Cu(I)}\cdot\text{chloro-complex(dissolved)} \tag{1}$$

The physical solubility of CO in this system is expected to be very low as in the case of the CuCl–HCl system.[8)] Thus, the amount of CO absorbed, *i.e.* amount of CO·Cu(I)·chloro-complex dissolved, α in mol/l, is expressed by Eq. 2:

$$\alpha = \frac{K_1 P_{CO} A^\circ_{Cu^+}}{(1+K_1 P_{CO})}, \tag{2}$$

where K_1 denotes the absorption coefficient in Pa^{-1}, which depends on the absorbent composition and the temperature, and $A^\circ_{Cu^+}$, the total concentration of Cu$^+$ in mol/l.

The solid lines, F and G in Fig. 3, calculated using Eq. 2 and K_1, agree with the experimental results (K_1 was determined with the amount of CO absorbed at $P_{CO}=1.01\times10^5$ Pa).

For absorbents A to E, the amount of CO absorbed increases gradually with CO partial pressure below P^*_{CO}, in the same manner as for solutions F and G. Therefore, CO absorption in this region also proceeds *via* Reaction 1 .

Above P^*_{CO}, fine particle precipitation might occur *via* Reaction 3:

$$\text{CO}\cdot\text{Cu(I)}\cdot\text{chloro-complex(dissolved)} + \text{Mg}^{2+}$$
$$+ m\text{Cl}^- + n\text{H}_2\text{O} \longrightarrow \text{CO}\cdot\text{CuMgCl}_3\cdot n\text{H}_2\text{O}\downarrow. \tag{3}$$

The pressure dependence of CO absorption in this region is expressed by Eq. 4:

$$A_{CO} = \frac{K_2(P_{CO}-P^*_{CO})A^\circ_{Cu^+}}{1+K_2(P_{CO}-P^*_{CO})}, \tag{4}$$

where K_2 is the absorption coefficient above P^*_{CO}, which depends on absorbent composition and temperature. Solid lines A to E of Fig. 3 calculated using Eq. 4, agree with the experimetal results. Values for K_2 and P^*_{CO}, used in the calculation are summarized in the figure caption.

To precipitate CO·CuMgCl$_3$·nH$_2$O a certain concentration of CO·Cu(I)·chloro-complex (dissolved) as well as Mg^{2+} and/or Cl$^-$, may be required. Once CO·CuMgCl$_3$·nH$_2$O precipitation occurs, the concentration of CO·Cu(I)·chloro-complex (dissolved), Mg^{2+} and Cl$^-$ decrease. When CO partial pressure increases, the concentration of CO·Cu(I)·chloro-complex increases *via* Reaction 1. Then, precipitation occurs again *via* Reaction 3.

Temperatre Dependence of CO Absorption. The changes in the amount of CO absorbed, A_{CO}, by the CuCl 3 mol/l-MgCl$_2$ 5 mol/l suspension absorbent at $P_{CO}=4\times10^4$ Pa and at 1.01×10^5 Pa are shown in Fig. 4. The amount of CO absorbed decreases especially above

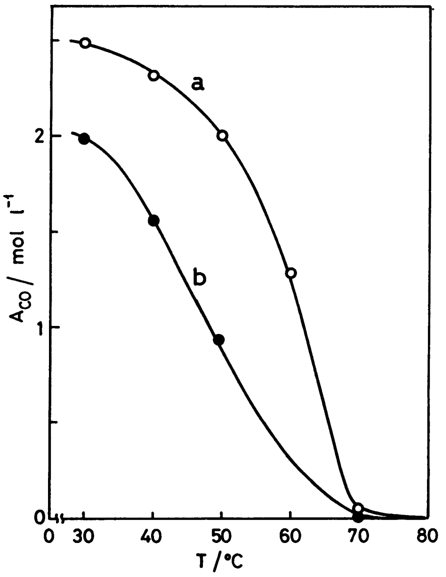

Fig. 4. Temperature dependence of amount of CO absorbed, A_{CO}, by CuCl 3 mol/l-MgCl$_2$ 5 mol/l (suspension).
a: $P_{CO}=1.01\times10^5$ Pa, b: $P_{CO}=4\times10^4$ Pa.

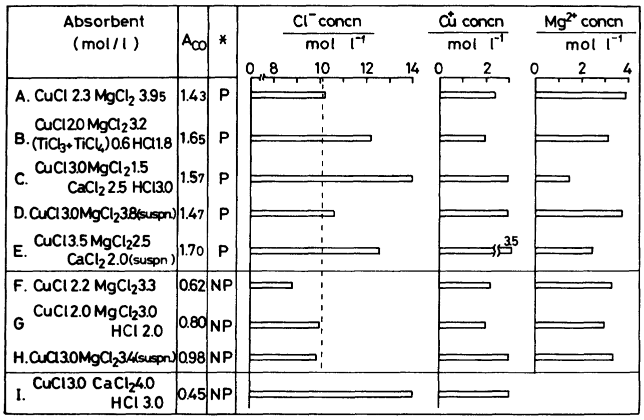

Fig. 5. Dependence of CO absorption behavior on ion concentration of solutions (30 °C: $P_{CO}=1.01\times10^5$ Pa).
* P : Precipitation was observed. NP : No precipitation was observed.

50 °C, becoming nearly zero at 70 °C. This means that the decomposition temperatre of the CO·$CuMgCl_3 \cdot nH_2O$ complex at $P_{CO}=1.01\times10^5$ Pa is around 70 °C.

Influences of Chloride Ion Concentration on CO·$CuMgCl_3 \cdot nH_2O$ Formation. Deringer claimed that only CuCl–$MgCl_2$ suspension absorbent containing solid $MgCl_2 \cdot 6H_2O$ absorbs a large amount of CO in the relatively low CO partial pressure range. As mentioned above, the amount of CO absorbed increases drastically above P^*_{CO} for both the CuCl–$MgCl_2$ solution and suspension absorbents. Therefore, the conditions proposed by Deringer are not always necessary for absorption of large amounts of CO by the CuCl–$MgCl_2$ system. Furthermore, this absorption of CO above P^*_{CO} closely relates to the formation of CO·$CuMgCl_3 \cdot nH_2O$.

The dependence of the absorption behavior of the CuCl–$MgCl_2$ system on the concentration of Cu^+, Mg^{2+}, and Cl^- is shown in Fig. 5. There is no threshold value for Cu^+ and Mg^{2+}, above that CO absorption accompanied with CO·$CuMgCl_3 \cdot nH_2O$ precipitation.

On the contrary, absorbents containing more than 10 mol/l chloride ions manifest the CO absorption characteristic that is accompanied with the precipitation of CO·$CuMgCl_3 \cdot nH_2O$. Solution I, which contains 14 mol/l of chloride ion but no Mg^{2+}, absorbs only 0.45 mol/l of CO and no precipitation is observed.

Summary

The CO absorption by the concentrated aqueous CuCl-$MgCl_2$ solution system is characterized by (i) a large amount of CO absorbed per unit volume of absorbent, and (ii) precipitation of fine particles different from the flake complex of CuCl-CO. A chloride ion concentration of more than 10 mol/l in the CuCl-$MgCl_2$ system results in the formation of fine particles estimated to be CO·$CuMgCl_3 \cdot nH_2O$.

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