Carbon Monoxide Absorption by Solutions of Aluminium Copper(I) Chloride in Various Aromatic Solvents

Hidefumi Hirai,* Masahiro Nakamura, and Makoto Komiyama
Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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Synopsis. Carbon monoxide absorbents composed of aluminium copper(I) chloride and various aromatic solvents are prepared, and their absorbing capacities are determined. The plot of the equilibrium molar ratio of the absorbed carbon monoxide to $AlCuCl_4$ *vs.* the ionization potential of the aromatic solvent indicates that both electronic and steric factors are important in the molecular complex formation between $AlCuCl_4$ and aromatic solvent molecules.

Carbon monoxide, a valuable starting material in industry, is generally separated from gas mixtures of carbon monoxide, hydrogen, carbon dioxide, methane, nitrogen, and others.[1)]

One of the recently developed carbon monoxide-separation methods takes advantage of the molecular complex formation of aluminium copper(I) chloride ($AlCuCl_4$) with carbon monoxide in a toluene solution.[2)] On contact with gas mixtures, toluene interacting with aluminium copper(I) chloride is replaced by carbon monoxide. This absorbent is readily deactivated with water in the feed gas. The present authors have now exploited a water-resistant carbon monoxide absorbent by protecting aluminium copper(I) chloride with polystyrene.[3,4)] Here, the water resistance has been attributed to the interactions of $AlCuCl_4$ with adjacent aromatic rings of polystyrene.

This paper will describe the preparation of carbon monoxide absorbents composed of aluminium copper(I) chloride and various aromatic solvents. The dependence of their absorbing capacities on the electronic and steric properties of the aromatic solvents will be shown.

Experimental

The aluminium chloride (guaranteed grade, Kishida Chemical Co.) was purified by sublimation. The copper(I) chloride (guaranteed grade, Koso Chemical Co.) was used without further purification. All the aromatic solvents were dried with calcium hydride immediately before use. The triethylbenzene, obtained from the Nakarai Chemical Co., was a mixture of the 1,3,5- and 1,2,4-isomers in a molar ratio of about 2 : 1. The carbon monoxide gas and nitrogen gas, which had purities of 99.95 and 99.999% respectively, were passed through the columns of a 3A molecular sieve.

The carbon monoxide absorbents were prepared by heating 35 mmol of copper(I) chloride and 35 mmol of aluminium chloride in 20 ml of an aromatic solvent in a 100 ml flask for 5 h at 100 °C (for 1,2,3,4-tetrahydronaphthalene, triethylbenzene, and triisopropylbenzene) or 40 °C (for others).

The carbon monoxide–nitrogen mixture, which had an initial volume of 1400 ml and an initial molar ratio of 0.84 : 0.16, was placed in contact with the absorbents, and then the mixture was continuously stirred with a magnetic stirrer (at 20 °C; 1 atm). The absorptions of carbon monoxide were followed by reading the uptake of carbon monoxide with a gas burette. During the first 10 min, the carbon monoxide–nitrogen mixture was made to flow over the absorbent at rate of 30 ml/s by the use of a gas pump.

Results and Discussion

Homogeneous solutions of aluminium copper(I) chloride were prepared for all the aromatic solvents investigated, *i.e.*, benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, 1,2,3,4-tetrahydronaphthalene, mesitylene, triethylbenzene, and 1,3,5-triisopropylbenzene.

On contact with carbon monoxide-nitrogen mixtures at 20 °C, all of these solutions exhibited a rapid absorption of carbon monoxide. The molar ratios of the carbon monoxide absorbed to $AlCuCl_4$ attained equilibrium values within 1 h. By raising the temperature from 20 °C to 90 °C, almost all of the absorbed carbon monoxide was rapidly released.

Table 1 lists the equilibrium molar ratios of the absorbed carbon monoxide to $AlCuCl_4$ for all the absorbents. The molar ratio varies considerably with the aromatic solvent used; this fact seems to indicate the significant roles played by the aromatic solvents in these absorbents.

Figure 1 depicts the plot of the molar ratio *vs.* the ionization potential of the aromatic solvent.[5,6)] The molar ratio decreases almost linearly with the decrease in the ionization potential from benzene to 1,2,3,4-tetrahydronaphthalene. This is attributable to the fact that the charge-transfer complex between $AlCuCl_4$ and the aromatic-solvent molecule becomes more stable with the decrease in the ionization potential. The absorption of carbon monoxide by the absorbent should be more favorable for the aromatic solvent forming the less stable molecular complex with aluminium copper(I) chloride, since it involves the substitution of the ligand on aluminium copper(I) chloride from the aromatic-solvent molecule to carbon monoxide.

As may clearly be seen from Fig. 1, the molar ratio

Table 1. Equilibrium molar ratios of the absorbed carbon monoxide to $AlCuCl_4$ in various aromatic solvents[a)]

Aromatic solvent	Equilibrium molar ratio
Benzene	0.87
Toluene	0.81
o-Xylene	0.70
m-Xylene	0.74
p-Xylene	0.72
1,2,3,4-Tetrahydronaphthalene	0.63
Mesitylene	0.87
Triethylbenzene	0.85
1,3,5-Triisopropylbenzene	0.91

a) At 20 °C: total pressure, 1 atm; initial partial pressures of carbon monoxide and nitrogen, 0.84 and 0.16 atm respectively.

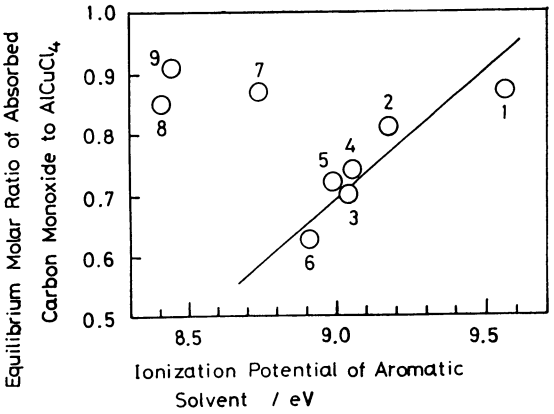

Fig. 1. Plot of equilibrium molar ratio of the absorbed carbon monoxide to $AlCuCl_4$ *vs.* ionization potential of aromatic solvent: benzene(1), toluene(2), *o*-xylene(3), *m*-xylene(4), *p*-xylene(5), 1,2,3,4-tetrahydronaphthalene (6), mesitylene (7), triethylbenzene(8), and 1,3,5-triisopropylbenzene(9).

for mesitylene, triethylbenzene, or triisopropylbenzene is much higher than the value estimated from the ionization potential alone. The molecular complex formation of these trisubstituted benzenes with aluminium copper(I) chloride in the absorbents is largely suppressed by steric hindrance, resulting in feasible ligand substitutions from the aromatic solvents to carbon monoxide. Thus, both electronic and steric factors are important in molecular-complex formation in the absorbents.

In the molecular complexes, the copper atoms, the electron-accepting centers in aluminium copper(I) chloride, are probably located on one of the six C–C bonds of the aromatic rings of the solvents. Under these circumstances, alkyl substitution at an aromatic carbon atom of the solvent molecule should hinder to a large extent the interactions of aluminium copper(I) chloride with aromatic rings at the two C–C bonds involving the substituted carbon. This is in accord with Fig. 1, which shows that the contributions of steric factors in the molecular-complex formation of trisubstituted benzenes with aluminium copper(I) chloride are larger than those for the benzenes with two, one, or no substituents. If the copper were located near the center of the aromatic ring, such large contributions of steric factors should not be observed. The proposed conformations of the molecular complexes in solutions are consistent with that of the $AlCuCl_4$–benzene complex in a solid.[7]

The above arguments are supported by the fact[8] that the equilibrium constants for the formation of molecular complexes of the silver ions with aromatic compounds, which involved silver ions located on one of the six C–C bonds of the aromatic rings,[9] were in the following order: xylenes>benzene≫mesitylene.

In conclusion, the capacities of the carbon-monoxide absorbents composed of aluminium copper(I) chloride and aromatic solvents are governed by both electronic and steric factors in the molecular-complex formation between aluminium copper(I) chloride and the aromatic compounds.

References

1) A. L. Kohl and F. C. Riesenfeld, "Gas Purification," 3rd ed, Gulf Publishing Co., Houston (1979).

2) D. J. Haase, *Chem. Eng. News*, **1975**, August 4, 52.

3) H. Hirai, M. Komiyama, and S. Hara, *Makromol. Chem., Rapid Commun.*, **2**, 495 (1981).

4) H. Hirai, M. Komiyama, and S. Hara, *Chem. Lett.*, **1982**, 1685.

5) The ionization potentials for benzene, toluene, *o*-xylene, *m*-xylene, and mesitylene were taken from G. F. Crable and G. L. Kearns, *J. Phys. Chem.*, **66**, 436 (1962).

6) The ionization potentials for 1,2,3,4-tetrahydronaphthalene was taken to be identical with that for *o*-diethylbenzene reported in "Kagaku Binran, Kiso-hen," ed by the Chemical Society of Japan, Maruzen, Tokyo (1966), p. 1127; Monograph Ser. Res. Instit. Appl. Elect. Hokkaido Univ. No. 4 (1954—1957), Appendix. The ionization potentials for triethylbenzene and triisopropylbenzene were estimated by assuming that the differences in values between these trialkylbenzenes and mesitylene were 3 times as large as the difference between toluene and ethylbenzene or that between toluene and cumene. According to J. D. Morrison and A. J. C. Nicholson (*J. Chem. Phys.*, **20**, 1021 (1952)); the difference in ionization potential between toluene and ethylbenzene is 0.11 eV, while that between toluene and cumene is 0.10 eV.

7) R. W. Turner and E. L. Amma, *J. Am. Chem. Soc.*, **88**, 1877 (1966).

8) N. Ogimachi, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **78**, 2210 (1956).

9) H. G. Smith and R. E. Rundle, *J. Am. Chem. Soc.*, **80**, 5075 (1958).