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CHARGE-TRANSFER INTERACTIONS OF ALUMINUM COPPER(I) CHLORIDE WITH POLYSTYRENE AND RELATED COMPOUNDS

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ABSTRACT

Interactions between polystyrene and aluminum copper(I) chloride (AlCuCl_4) were investigated by various spectroscopic measurements in order to elucidate the structure of polystyrene- AlCuCl_4 complex in solution and the mechanism of water resistance of the complex as a carbon monoxide absorbent. The chemical shift (101 ppm) and

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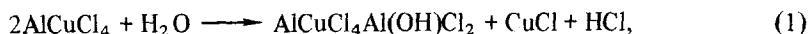
half line width (145 Hz) of AlCuCl_4 in benzene by ^{27}Al -NMR suggest a dimer structure bridged by two chlorine atoms, which is almost identical with that of aluminum chloride. The coordination of benzene or other aromatic compounds to AlCuCl_4 was confirmed by charge-transfer bands in UV and visible absorptions. The equilibrium constants (K) for complex formation of AlCuCl_4 with various aromatic compounds were determined by ^{13}C -NMR spectroscopy. In the case of AlCuCl_4 and benzene in 1,2-dichloroethane, for example, K is 2.2 M^{-1} at 303 K. For the polymer complex solution and 1,3-diphenylpropane solution, strong charge-transfer bands have been observed in the wavelength region at about 380 to 500 nm, where no band is observed in benzene derivatives. This strong charge-transfer band is considered to be due to the strong interaction of AlCuCl_4 with adjacent aromatic rings of polystyrene or 1,3-diphenylpropane of a chelate type, which, as a result, causes the water resistance of the present carbon monoxide absorbent system.

INTRODUCTION

Carbon monoxide, which is a valuable raw material in the chemical industry, is usually obtained in gaseous mixtures with hydrogen, nitrogen, oxygen, methane, carbon dioxide, water, and so on. Therefore, technical improvements in separation of carbon monoxide are necessary for their effective utilization [1]. The cryogenic separation process, taking advantage of the differences in boiling points of the gases, is well known as a separation method for carbon monoxide [1]. This method, however, requires large amounts of energy for achievement of the needed extreme low temperatures, and requires complete removal of carbon dioxide and water which can cause blockade in the refrigeration unit. This holds not only for separation of carbon monoxide but also for separation of other gaseous molecules like ethylene.

Recently, a selective carbon monoxide separation method has been proposed which uses a toluene solution of aluminum copper(I) chloride (AlCuCl_4) [2, 3]. This method takes advantage of the fact that AlCuCl_4 , a double salt composed of copper(I) chloride and aluminum chloride, is made soluble by formation of a molecular complex with aromatic compounds [4]. The selective complex formation with carbon monoxide occurs by means of ligand exchange at the central Cu(I) ion. With this absorbent, carbon monoxide can be separated with high selectivity with less energy. However, as the gas mixtures

are usually saturated with water vapor, the activity for absorption of carbon monoxide is decreased rapidly by the water vapor due to the irreversible decomposition of the double salt with water [5, 6]:



Thus, the water content of gas mixtures must be reduced to less than 1 ppm prior to carbon monoxide separation with this absorbent.

The present authors recently reported that toluene solutions of AlCuCl_4 or AgAlCl_4 containing linear polystyrene reversibly absorb carbon monoxide and ethylene under mild conditions and, in addition, are stable toward water vapor [7, 8]. Furthermore, water-resistant solid adsorbents for carbon monoxide and ethylene have also been prepared in similar systems by using macroreticularly crosslinked polystyrene instead of linear polystyrene as the liquid absorbent [9-11].

In the present paper we show the results of a spectroscopic investigation of complex formation of AlCuCl_4 with polystyrene and related compounds. The role of polystyrene in the water resistance of the absorbents will also be compared with various model compounds of low molecular weight.

EXPERIMENTAL

Materials

Aluminum chloride (Kishida Chemical Co.) was purified by vacuum sublimation. Copper(I) chloride (Koso Chemical Co.) was reprecipitated from an aqueous hydrochloric acid solution by addition of distilled water, washed successively with ethanol and diethyl ether, and then dried *in vacuo* at 100°C for 24 h.

Benzene, toluene, and *p*-xylene were washed with concentrated sulfuric acid, followed by distillation over metallic sodium. Mesitylene was distilled after being dried over metallic sodium. 1,2-Dichloroethane was dried over diphosphorus pentoxide and distilled. 1,2-Diphenylethane was recrystallized from hexane. 1,3-Diphenylpropane was prepared by reduction of 1,3-diphenylpropan-2-one with hydrazine [12] and purified by distillation over metallic sodium. 1,4-Diphenylbutane was prepared by hydrogenation of 1,4-diphenyl-1,3-butadiene (Tokyo Chemical Industry Co.) over an active

carbon-supported palladium catalyst (10%, Kojima Chemical Co.) [13] in methylcyclohexane and recrystallized from ethanol.

Carbon monoxide (99.95% purity, Takachiho Kagakugogyo K.K.) was passed through a column of Molecular Sieve 3A before use.

Linear polystyrene, purchased from Wako Pure Chemical Co. (\bar{M}_w 1.5×10^5), was mainly used in the present experiments. The molecular weight dependence experiments were performed by using polystyrenes with \bar{M}_w 4000, 9000, 6.0×10^5 , and 2.0×10^7 , which were purchased from Toyo Soda Manufacturing Co., as standard polystyrenes for molecular weight measurement. These polystyrenes were reprecipitated several times by using chloroform and methanol and dried *in vacuo* at 60°C for 24 h.

Preparation of Polymer Complex Solutions

Polymer complex solutions were prepared by heating mixtures of polystyrene, copper(I) chloride, aluminum chloride, and an aromatic compound at 50°C for 4 h under dry nitrogen. The charged molar ratio of copper(I) chloride to aluminum chloride was kept at 1.1. Aromatic solutions of AlCuCl_4 without polystyrene were prepared as reference solutions in a similar manner as above, except for the absence of polystyrene. The complex solutions for ^{13}C -NMR spectral measurement were prepared by using 1,2-dichloroethane as a solvent.

NMR Spectral Measurement

^{27}Al - and ^{13}C -NMR spectra were recorded using a JNM FX-90Q at 23.29 and 22.49 MHz, respectively. ^{13}C -NMR spectra were measured at 273, 303, 313, and 323 K. ^{27}Al chemical shifts were referred to aqueous aluminum nitrate. Dichloromethane- d_2 in a capillary tube was used as an internal lock in both ^{27}Al - and ^{13}C -NMR measurements.

Ultraviolet and Visible Absorption Spectrum Measurement

Ultraviolet and visible absorption spectra were measured with a Hitachi Model 340 spectrometer at 25°C, with the complex solutions in a 1-mm quartz cell with a shielding cap under dry nitrogen.

RESULTS

Preparation of AlCuCl_4 Complex Solutions

The mixtures of polystyrene, copper(II) chloride, and aluminum chloride (charged molar ratios of copper(II) chloride and phenyl residue of polystyrene relative to aluminum chloride were 1.1 and 1.0, respectively) became homogeneous on being stirred in toluene at 50°C for about 10-30 min, with a small remaining excess copper(II) chloride. Without polystyrene, most liquid aromatic compounds also gave homogeneous solutions by similar stirring with copper(II) chloride and aluminum chloride. In the case of 1,3-diphenylpropane as the aromatic compound, it took more time to dissolve the inorganic salts completely. These results indicate that the double salt composed of copper(II) chloride and aluminum chloride forms molecular complexes with various aromatic compounds.

In general, the color of the complex solutions was reddish brown, but careful purification of the starting materials led to yellow solutions in almost all cases. For example, the color of the solution of the polystyrene- AlCuCl_4 complex was mostly light yellow. As the molecular weight of polystyrene increased, however, the yellow color became deeper. The color of the solution of the AlCuCl_4 -aromatic compound complex without polystyrene was light brown for benzene, light yellow-green for toluene, faint reddish yellow for *p*-xylene, and deep yellow for 1,3-diphenylpropane.

NMR Spectral Measurement

Table 1 shows the ^{27}Al -chemical shifts and half line width of various aromatic compound- AlCuCl_4 complexes. In all cases a single peak appeared at about 100 ppm from the aluminum nitrate as standard. Line widths of the peaks of AlCuCl_4 in benzene, toluene, and mesitylene increased in this order, and became extremely wide in 1,3-diphenylpropane. On the other hand, no remarkable change in the line width was observed in the ^{27}Al -NMR spectra of aluminum acetylacetonate in various aromatic solvents (Table 1). Appreciable line width broadening was also observed for the polystyrene- AlCuCl_4 complex solution compared with aluminum acetylacetonate solution.

The results of ^{13}C -NMR spectroscopy for various aromatic compounds with AlCuCl_4 are listed in Table 2. The chemical shift of carbon atoms of benzene shifted toward higher magnetic field by complexation with AlCuCl_4 .

TABLE 1. ^{27}Al -NMR Data of AlCuCl_4 and Tris(2,4-Pentanediono)aluminum ($\text{Al}(\text{acac})_3$) with Various Aromatic Compounds and of the Polystyrene- AlCuCl_4 Complex in Toluene

Aromatic compound	Chemical shift, ^a ppm, AlCuCl_4 ^b	Half line width, Hz	
		AlCuCl_4 ^b	$\text{Al}(\text{acac})_3$ ^c
Benzene	101.0	145.1	156.3
Toluene	101.1	224.6	122.1
Toluene-polystyrene ^d	103.0	416.8	178.2
Mesitylene	100.7	357.4	105.0
1,3-Diphenylpropane	103.0	1807	571.3

^aChemical shift with respect to aqueous aluminum nitrate.

^b $[\text{AlCuCl}_4]_0 = 0.5 \text{ mol/L}$.

^cSaturated.

^d $[\text{Polystyrene}]_0 = 1.0 \text{ mol phenyl residue/L}$.

In the case of toluene, the chemical shifts of carbon atoms of the methyl group and the aromatic ring carbon substituted by the methyl group shifted toward lower magnetic field by the complexation, while those of the aromatic ring carbon at the *meta* and *para* positions shifted to higher magnetic field. Similar results were observed for other aromatic compounds. On contact with carbon monoxide, the chemical shifts of aromatic compounds in the presence of AlCuCl_4 came close to those of the free aromatic compounds.

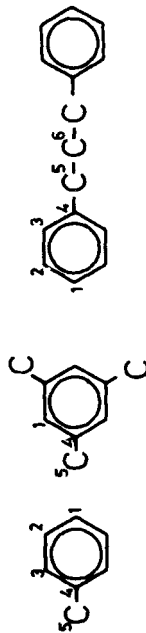
Ultraviolet and Visible Absorption Spectra

Figure 1 shows the ultraviolet and visible absorption spectra of toluene solutions of AlCuCl_4 with polystyrene of various molecular weights. The polymer complex solutions show a charge-transfer band in the region from 380 to 500 nm. This charge-transfer band is composed of several overlapping bands, having major peaks at 380 and 460 nm. As the molecular weight of polystyrene increases, the absorbance of the charge-transfer band increases and the band shape changes with relative increase of the absorbance at 460 nm (Fig. 1). In contrast, the solutions of AlCuCl_4 in monoaromatic ring compounds, such as benzene, toluene, and *p*-xylene, without polystyrene exhibit no bands in the region from 380 to 500 nm, as shown in Fig. 2.

TABLE 2. Changes of ^{13}C -NMR Chemical Shift (in ppm) of Various Aromatic Compounds on Complex Formation with AlCuCl_4^a

No.	Benzene	Toluene ^b	Mesitylene ^c	1,3-Diphenylpropane ^d
C(1)	-0.108	-1.625 (-1.192)	-1.569 (-0.755)	-0.625 (-0.702)
C(2)	-	-1.325 (-0.919)	-	-1.034 (-0.339)
C(3)	-	0 (+0.160)	-	+0.161 (+0.349)
C(4)	-	+2.384 (+2.167)	+1.249 (+1.329)	+1.569 (+1.240)
C(5)	-	+0.704 (+0.596)	+0.758 (+0.589)	+0.217 (+0.163)
C(6)	-	-	-	+0.054 (+0.217)

^aA positive sign shows a shift toward lower magnetic field with respect to the signal of each aromatic compound without AlCuCl_4 . $[\text{AlCuCl}_4]_0 = 0.63 \text{ mol/L}$. The carbon atoms are numbered as follows:



^{b-d}The values in parentheses are the changes of chemical shift after contact of the complex solution with carbon monoxide. Molar ratio of absorbed carbon monoxide to $\text{AlCuCl}_4 = 0.27$ (b), 0.59 (c), and 0.56 (d).

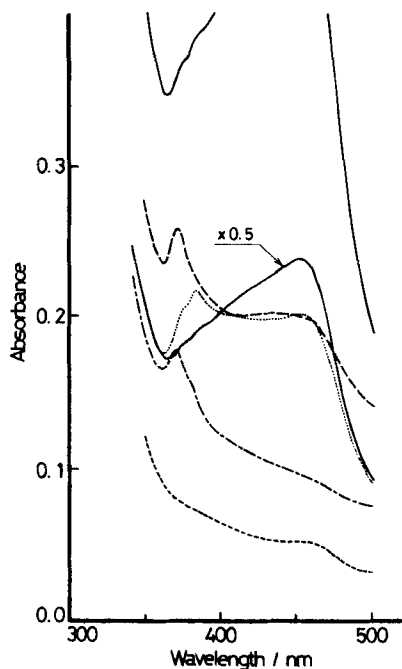


FIG. 1. Electronic absorption spectra of toluene solutions of polystyrene- AlCuCl_4 complexes of various molecular weights: MW = 4000 (---), 9000 (- · -), 1.5×10^5 (···), 6.0×10^5 (---), and 2.0×10^7 (—); $[\text{AlCuCl}_4]_0 = 0.63 \text{ mol/L}$, $[\text{polystyrene}]_0 = 0.63 \text{ mol phenyl residue/L}$; cell length, 1 mm; 25°C .

The solution of AlCuCl_4 in 1,3-diphenylpropane, a low molecular weight model of polystyrene, shows a band shape similar to that of the polymer complex solution (Fig. 2). To investigate the dependence of the absorption spectra on the number of methylene carbon atoms between two aromatic rings, the absorption spectra of benzene solutions of AlCuCl_4 containing various two-aromatic ring compounds were measured, and the results are shown in Fig. 3. For 1,2-diphenylethane and 1,4-diphenylbutane (2 and 4 methylene carbon atoms between two aromatic rings), no charge-transfer band was observed in the 380 to 500 nm region, in contrast to the strong charge-transfer band for 1,3-diphenylpropane in this region.

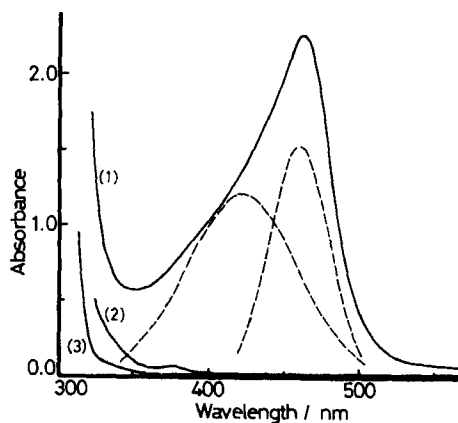


FIG. 2. Ultraviolet and visible absorption spectrum of AlCuCl_4 in 1,3-diphenylpropane (1), toluene (2), and benzene (3) under nitrogen: $[\text{AlCuCl}_4]_0 = 0.63 \text{ mol/L}$; the dashed lines show the resolved absorption bands for the spectrum (Line 1 of the 1,3-diphenylpropane solution of AlCuCl_4); cell length, 1 mm.

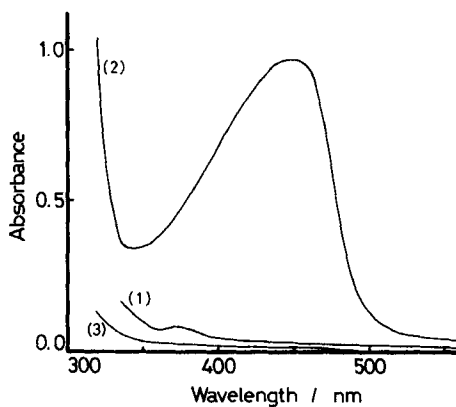


FIG. 3. Ultraviolet and visible absorption spectra of benzene solutions of AlCuCl_4 containing various two-aromatic ring compounds: 1,2-diphenylethane (1), 1,3-diphenylpropane (2), and 1,4-diphenylbutane (3); $[\text{AlCuCl}_4]_0 = 0.63 \text{ mol/L}$, $[\text{aromatic compound}]_0 = 1.26 \text{ mol/L}$; cell length, 1 mm.

DISCUSSION

Structure of AlCuCl_4 in Solution

It has already been reported that aluminum copper(I) chloride (AlCuCl_4), which is active for carbon monoxide absorption, has the structure depicted in Fig. 4(1) in the crystalline state [4]. However, the structure in solution has not been known. Generally speaking, ^{27}Al -NMR chemical shifts reflect the coordination number of the aluminum atom [14]. For example, the spectra of hexa-coordinated, penta-coordinated, and tetra-coordinated aluminum complexes appear at about 0, 50, and 100 ppm, respectively. The ^{27}Al -NMR chemical shifts of AlCuCl_4 in the aromatic solvents appear at about 100 ppm (Table 1). Thus, the coordination number of the aluminum atom of AlCuCl_4 is four in all cases. As the frame structure of AlCuCl_4 possesses tetra-coordinated aluminum atoms, two kinds of structures shown in Fig. 4(1) and (2) will be supposed.

The ^{27}Al -NMR line width, on the other hand, reflects the symmetry around aluminum atoms, that is, the less the symmetry around the aluminum atom, the wider the line width. For example, regular tetrahedral aluminum complexes show narrow spectra of several Hz in half line width, while organo-aluminum compounds, which have considerably distorted bond angles, show extremely broad spectra with more than 1000 Hz [14]. The structure of aluminum chloride in organic solvents is well known to be dimeric, with two aluminum atoms connected through two chlorine bridges, as shown in Fig. 4(3) [15]. It has also been reported that the ^{27}Al -NMR chemical shift and half line width of the spectrum for a benzene solution of aluminum chloride are 100 ppm and 185 Hz, respectively [16], almost identical with those of benzene solutions of AlCuCl_4 . It is considered that the half line width for

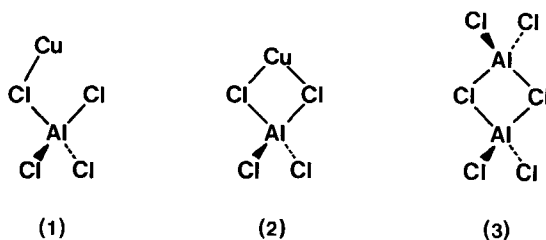


FIG. 4. Supposed structures of AlCuCl_4 (1 and 2) and dimer structure of AlCl_3 (3) in benzene.

the compounds with one chlorine bridge as shown in Fig. 4(1) is much smaller than that for the compound with two chlorine bridges as shown in Fig. 4(2), because the former is closer to regular tetrahedral in structure than the latter. For these reasons, AlCuCl_4 in benzene is proposed to have the structure illustrated in Fig. 4(2), which is similar to the dimeric structure of aluminum chloride.

Coordination of Aromatic Compounds to AlCuCl_4

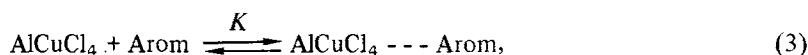
It has been established that AlCuCl_4 in aromatic solvents has the frame structure shown as Fig. 4(2). The next problem is to elucidate how the aromatic molecules coordinate to AlCuCl_4 . ^{13}C -NMR spectra of the aromatic compounds were measured to solve this problem. As shown in Table 2, addition of AlCuCl_4 to benzene makes the chemical shift of the carbon atoms of benzene move toward higher magnetic fields. This suggests that benzene molecules coordinate to AlCuCl_4 . In the case of toluene, the chemical shifts of the *meta* and *para* carbons move toward a higher magnetic field, while those of the methyl carbon and the aromatic carbon substituted by the methyl group move toward a lower magnetic field. The higher magnetic field shift of *meta* and *para* carbons suggests that their sp^3 character increases by coordination of toluene molecules to AlCuCl_4 at these three carbon atoms. Along with the coordination of toluene molecules to the double salts, the electric charge moves onto the aromatic rings. This change in electronic density makes the shifts of the methyl carbon and aromatic carbon substituted by methyl move toward a lower magnetic field.

The ligand exchange must take place from the aromatic compound to carbon monoxide when carbon monoxide is added to a solution of AlCuCl_4 in the aromatic compound because the magnitude of the change in chemical shift due to complex formation decreases on addition of carbon monoxide.

Equilibrium Constants for Complex Formation of AlCuCl_4 with Aromatic Compounds

In order to estimate the strength of interaction between AlCuCl_4 and aromatic compounds, the equilibrium constants (K) for complex formation were calculated. The double salt AlCuCl_4 dissolves in aromatic compounds by forming molecular complexes with the aromatic molecules. There are no solvents for AlCuCl_4 other than aromatic compounds. In the present experiments, 1,2-dichloroethane was used as a solvent to dissolve AlCuCl_4 -aromatic compound complexes. With small amounts of aromatic com-

pounds, however, the double salts did not dissolve sufficiently. Thus, K was calculated by a curve-fitting method for the relations between the ^{13}C -NMR chemical shifts and the concentrations of AlCuCl_4 , by assuming AlCuCl_4 forms a 1:1 complex with an aromatic compound (Arom) in the range of 0 to about 0.5 mol fraction of AlCuCl_4 (Eqs. 3-5) [17]. If the chemical shifts of the free aromatic compound and of the complex with AlCuCl_4 are δ_{arom} and δ_{comp} , respectively, the observed chemical shift of the complex solution, δ_{obsd} , can be written as Eq. (4) in terms of the equilibrium constant K and the initial molar fraction of AlCuCl_4 (c).



$$\delta_{\text{obsd}} = \delta_{\text{arom}} + (\delta_{\text{comp}} - \delta_{\text{arom}}) \sqrt{1 - \frac{4K}{1+K} c(1-c)} \times \frac{1}{2(1-c)}, \quad (4)$$

$$c = \frac{[\text{AlCuCl}_4]_0}{[\text{AlCuCl}_4]_0 + [\text{Arom}]_0}. \quad (5)$$

With benzene, toluene, *p*-xylene, and mesitylene as the aromatic compound, and 1,2-dichloroethane as the solvent, K was calculated at various temperatures (Table 3). Since the ionization potential of the aromatic compounds decreases in the order benzene (9.245 eV), toluene (8.82 eV), *p*-xylene (8.445 eV), and mesitylene (8.39 eV) [18], K increases in the same order, consistent with the general case of charge-transfer complexes of alkylbenzenes [19]. The changes in enthalpy ($-\Delta H$) and entropy ($-\Delta S$) for the complex formation of AlCuCl_4 were also determined by Arrhenius plotting of K (Table 4). A linear relationship between K and ΔH is commonly observed

TABLE 3. Equilibrium Constants for Complex Formation between AlCuCl_4 and Various Aromatic Compounds in 1,2-Dichloroethane

Aromatic compounds	K , mol/L			
	273 K	303 K	313 K	323 K
Benzene	2.5	2.2	2.1	2.0
Toluene	3.8	3.0	2.8	2.6
<i>p</i> -Xylene	6.3	3.9	3.5	3.0
Mesitylene	11	9.7	8.5	7.6

TABLE 4. Thermodynamic Parameters for Complex Formation of AlCuCl_4 with Various Aromatic Compounds in 1,2-Dichloroethane

Aromatic compounds	$-\Delta H$, kJ/mol	$-\Delta S$, $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
Benzene	3.4	4.7
Toluene	5.5	9.1
<i>p</i> -Xylene	11	24
Mesitylene	9.9	14

in a series of analogous complexes [20]. In the series of the AlCuCl_4 complex, this common rule was almost true. However, an inverse relationship was observed for the AlCuCl_4 complexes of *p*-xylene and mesitylene, probably due to steric hindrance. Since the steric hindrance of methyl groups is greater for mesitylene than for the other compounds, the binding energy of mesitylene with AlCuCl_4 is probably lowered.

It has been reported that the carbon monoxide absorbing capacities are governed by both electronic and steric factors in the molecular complex formation between AlCuCl_4 and aromatic compounds [21]. In other words, the carbon monoxide absorbing capacities decrease with the decrease in the ionization potential of aromatic compounds from benzene to *p*-xylene, which is attributable to the more stable complex formation with AlCuCl_4 in benzene than in *p*-xylene. However, the absorbing capacity is larger in mesitylene than *p*-xylene although the ionization potential of mesitylene is smaller than that of *p*-xylene. This result is attributable to the lower complex stability in mesitylene due to steric hindrance by the three methyl groups. These carbon monoxide absorbing capacities are consistent with the $-\Delta H$ values in the present experiment. Thus, as the binding energy of an aromatic compound with AlCuCl_4 increases in the order benzene, toluene, and *p*-xylene, the carbon monoxide absorbing capacity decreases in the same order. This inverse relationship between the binding energy and the carbon monoxide absorbing capacity is also true for mesitylene and *p*-xylene.

Formation of Chelate-Type Complexes of Polyaromatic Ring Compounds with AlCuCl_4 and Their Water Resistance

As can be seen clearly by comparing Figs. 1 and 2, the shape of the ultraviolet and visible absorption spectra of the polystyrene- AlCuCl_4 complex is quite different from that of the AlCuCl_4 complex without polystyrene.

For the polymer complex solution, the charge-transfer bands are composed of several overlapping bands and appear in the region of about 380 to 500 nm, where no band is observed without polystyrene.

When 1,3-diphenylpropane, a low molecular weight model of polystyrene, is used, a strong charge-transfer band is also observed in the same region. The benzene solutions of AlCuCl_4 containing 1,2-diphenylethane and 1,4-diphenylbutane, however, do not exhibit charge-transfer bands as strong as the complex solution containing 1,3-diphenylpropane does, as shown in Fig. 3. These results indicated that the number of methylene carbon atoms between the two aromatic rings is quite important for two-aromatic ring compounds interacting with AlCuCl_4 in a chelate-type complex. Thus, the most favorable number of methylene carbon atoms between two aromatic rings is three, such as in polystyrene and 1,3-diphenylpropane for this type of interaction.

On the other hand, the band for the complex between AlCuCl_4 and 1,3-diphenylpropane is mainly composed of two portions with absorption maxima at 422 and 460 nm [22]. When the concentration of 1,3-diphenylpropane is varied, however, the shape of the charge-transfer band changes. For example, the band at 380 nm becomes appreciable at some concentrations. The relative intensities of these three bands vary in a complicated way with concentration. These strong charge-transfer bands are considered to be due to chelate-type interactions of the two adjacent aromatic rings of 1,3-diphenylpropane with AlCuCl_4 , as mentioned before. For complexes between AlCuCl_4 and a monoaromatic compound, the absorption bands for the charge-transfer interactions are thought to appear at wavelengths lower than 300 nm, where the weak charge-transfer bands cannot be observed because of the strong absorption bands due to the aromatic compounds. Figure 5 illustrates several types of the supposed chelate-type interactions between AlCuCl_4 and 1,3-diphenylpropane. Determination of the equilibrium constant for the chelate-type complex formation of AlCuCl_4 with 1,3-diphenylpropane by using these relatively strong charge-transfer bands was unsuccessful since the changes in the intensities of these three component bands with varying concentration of 1,3-diphenylpropane were too complicated.

The half line widths of ^{27}Al -NMR spectra of AlCuCl_4 in benzene, toluene, *p*-xylene, and mesitylene were found to be broadened in this order (Table 1). This line width broadening is attributed to the lowering of the symmetry in structure around the aluminum atom. Thus, the interactions with aromatic compounds become greater in the same order [14]. For similar reasons, the great line width broadening for the 1,3-diphenylpropane solution is attributed to the drastic lowering of the symmetry around the aluminum atoms caused by the chelate-type interactions with these two aromatic rings. The remark-

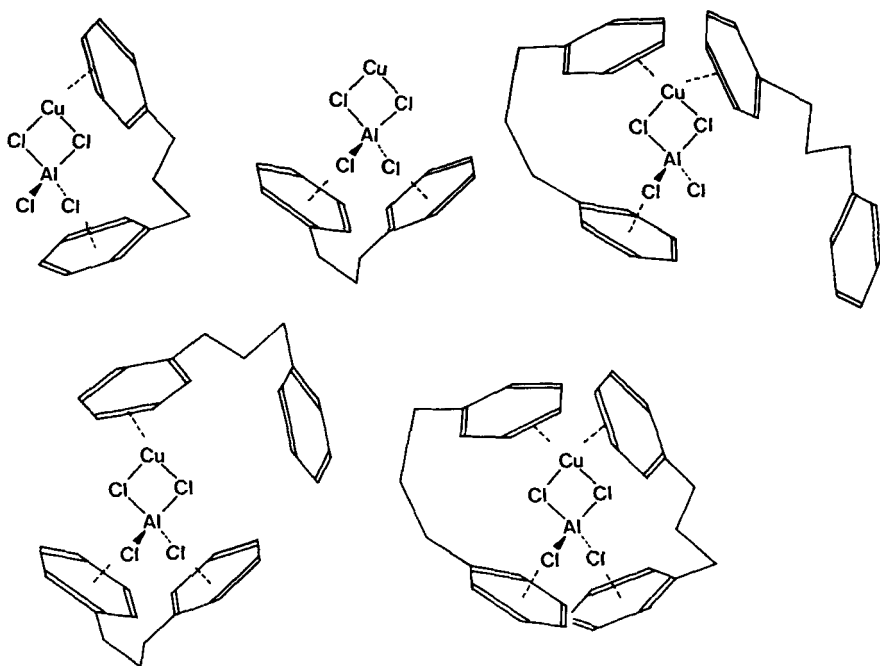


FIG. 5. Chelate-type complex formation of AlCuCl_4 with 1,3-diphenylpropane.

able line width broadening in the polystyrene system strongly suggests chelating interactions of the adjacent aromatic rings of polystyrene with AlCuCl_4 . Though the ^{27}Al -NMR spectra of aluminum acetylacetonate in a series of aromatic compounds were also measured, the broadening of the spectra was not as significant. This result supports the conclusion that the coordination of aromatic compounds to AlCuCl_4 is responsible for broadening of the spectra.

Polystyrene is concluded to coordinate to AlCuCl_4 in a chelate type as illustrated in Fig. 6. This type coordination places the water-sensitive double salt in the strong hydrophobic field of polystyrene. Consequently, the decrease of carbon monoxide-absorbing activity due to the irreversible reaction of AlCuCl_4 with water (Eqs. 1 and 2) does not occur in AlCuCl_4 /polystyrene in contact with a water-containing gas mixture [7]. It was also found that the absorbance of the polymer complex solution increases with increasing molecular weight of polystyrene (Fig. 1), which could be explained by the lowering of the mobility

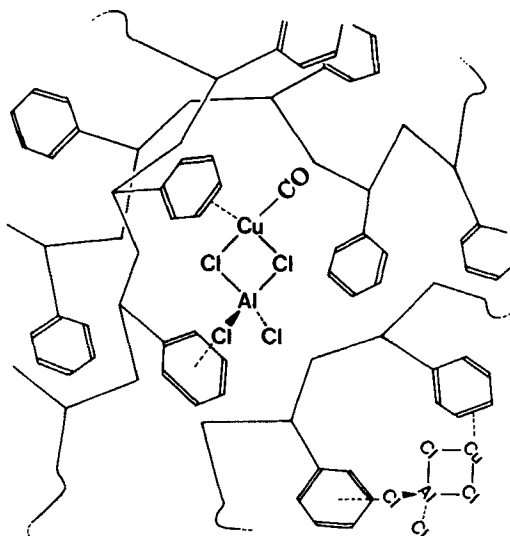


FIG. 6. Proposed structure of the polystyrene- AlCuCl_4 complex with absorbed carbon monoxide.

of the polymer chain with increasing molecular weight. In high molecular weight polystyrene, AlCuCl_4 is liable to be included in the "fixed" domain of polystyrene and, as a result, chelate-type interactions by aromatic rings of polystyrene take place more effectively.

CONCLUSIONS

Polymer-metal complex solutions formed by aluminum copper(I) chloride (AlCuCl_4) and polystyrene in aromatic compounds are significantly more stable toward water than aromatic solutions of AlCuCl_4 without polystyrene. By ^{27}Al -NMR spectroscopy, AlCuCl_4 was found to have a structure similar to that of aluminum chloride dimer in solution. Polymer complex solutions of AlCuCl_4 showed strong charge-transfer bands at about 380 to 500 nm, which were not observed for solutions of monoaromatic ring compounds, but were also found for solutions of 1,3-diphenylpropane, a low molecular model of polystyrene. These strong charge-transfer bands are considered to be due to chelate-type coordination of the adjacent aromatic rings to AlCuCl_4 . This conclusion is supported by the drastic line broadening of ^{27}Al -NMR spectra

of AlCuCl_4 in 1,3-diphenylpropane. From these results the water resistance of the polymer-metal complex of polystyrene and AlCuCl_4 is attributed to the protection of water-sensitive AlCuCl_4 by the hydrophobic field of polystyrene caused by the chelate-type interactions of multiple aromatic rings of polystyrene with AlCuCl_4 .

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REFERENCES

- [1] A. L. Kohl and F. C. Riesenfeld, *Gas Purification*, 3rd ed., Gulf Publishing, Houston, 1983, p. 718.
- [2] D. J. Haase and D. G. Walker, *Chem. Eng. Prog.*, **70**, 74 (1974).
- [3] D. G. Walker, *Chemtech*, p. 308 (May 1975).
- [4] R. W. Turner and E. L. Amma, *J. Am. Chem. Soc.*, **88**, 1877 (1966).
- [5] D. J. Haase, *Chem. Eng.*, p. 52 (August 4, 1975).
- [6] T. Inukai, *Sekiyu Gakkai Shi*, **20**, 317 (1977).
- [7] H. Hirai, S. Hara, and M. Komiyama, *Bull. Chem. Soc. Jpn.*, **59**, 109 (1986).
- [8] H. Hirai, S. Hara, and M. Komiyama, *Chem. Lett.*, p. 257 (1986).
- [9] H. Hirai, S. Hara, and M. Komiyama, *Bull. Chem. Soc. Jpn.*, **59**, 1051 (1986).
- [10] H. Hirai, S. Hara, and M. Komiyama, *Ibid.*, **60**, 385 (1987).
- [11] H. Hirai, S. Hara, and M. Komiyama, *Angew. Makromol. Chem.*, **130**, 207 (1985).
- [12] D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73**, 5691 (1951).
- [13] The Chemical Society of Japan (ed.), *Oxidation and Reduction [II]* (*Shin-Jikkenkagaku-kohza*, Vol. 15), Maruzen, Tokyo, 1977, p. 403.
- [14] P. Laszlo, *NMR of Newly Accessible Nuclei*, Vol. 2, Academic, New York, 1983, p. 153.
- [15] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley, New York, 1980, p. 330.
- [16] H. Nöth, R. Rurländer, and P. Wolfgardt, *Z. Naturforsch.*, **37B**, 29 (1982).
- [17] E. Gore and S. S. Danyluk, *J. Phys. Chem.*, **69**, 89 (1965).

- [18] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).
- [19] L. J. Andrews and R. M. Keefer, *Molecular Complex in Organic Chemistry*, Holden-Day, San Francisco, 1964, p. 19.
- [20] S. Tazuke, H. Tsubomura, J. Tokura, and H. Mikawa, *Charge Transfer Complex (Kagakuzoukan No. 48, Denkaidousakutai)*, Kagakudohjin, Kyoto, 1971, p. 89.
- [21] H. Hirai, M. Nakamura, and M. Komiyama, *Bull. Chem. Soc. Jpn.*, **56**, 2519 (1983).
- [22] H. Hirai, K. Kanaka, and M. Komiyama, *Chem. Lett.*, p. 201 (1986).

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