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TRANSPORT OF CARBON MONOXIDE FACILITATED BY A Cu^I-TETRAETHYLENEPENTAMINE SYSTEM

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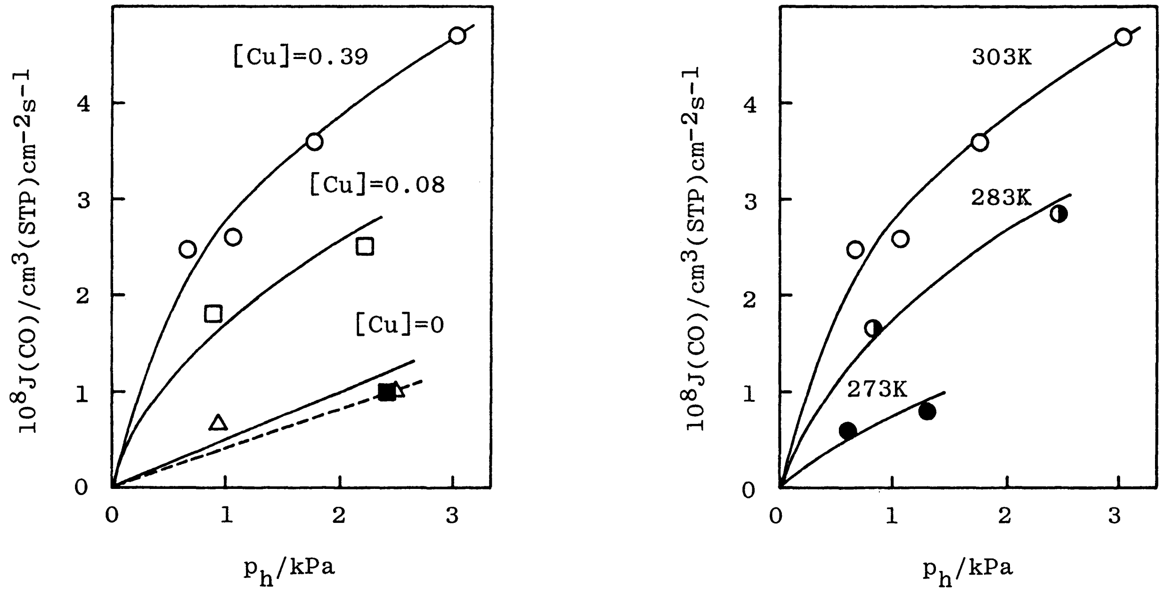
The transport of CO through a thin layer of tetraethylenepentamine was found to be enhanced by the presence of Cu^I ion. The CO uptake measurement and the i.r. study suggested that the facilitated transportation of CO was mediated by the reversible formation of a Cu^I-carbonyl complex.

The transport of gas molecules through a membrane mediated by a carrier has attracted much attention in connection with enhanced interests in the simulation of biological systems and in the application to membrane separation processes.[1,2] However, only a few investigations have so far been undertaken on the carrier-mediated transport of CO.[3,4] Although many copper(I) compounds are known to absorb CO reversibly, they are usually liable to be oxidized by oxygen to copper(II) compounds and easily disproportionate ($2Cu^+ \rightleftarrows Cu + Cu^{2+}$) in aqueous media.[5,6] This unstability of Cu^I compounds has frustrated the investigation of the facilitated transport of CO with Cu^I complexes. In the present letter, we wish to report that the transport of CO can be facilitated by a Cu^I-tetraethylenepentamine(tetren) system which is not so oxygen-sensitive and do not undergo the disproportionation reaction within the present experimental conditions.

No other solvents or diluents were here employed. The tetren molecule acts not only as a multidentate ligand but also as a diffusion medium. Thus, Cu(SCN) was dissolved in a large excess of tetren in vacuo and resulting liquid complex was used for transport and equilibrium CO uptake measurements. The molar ratio of Cu^I: tetren was less than 1:12 (0.39 mol/kg) and a colorless liquid was obtained. It would be noteworthy that when the preparation of Cu^I-tetren system was carried out in air the resulting system became blue colored, but on evacuation at 313 K the blue one turned into a colorless liquid and the properties of the resultant for CO were essentially the same as those prepared in vacuum.

The method and procedure for the preparation of liquid membranes and the transport experiments are the same as reported earlier.[7,8] The liquid layer of ca. 0.32 cm in thickness was retained on a microporous poly(tetrafluoroethylene) membrane fixed horizontally in the transport measurement cell. The CO gas was introduced in the upstream side of the cell and the pressure increase in the downstream side due to gas transport through the liquid film was followed with a Pirani gauge. The transport rate of nitrogen was also determined for comparison.



(a) (b)

Fig. 1. Variation of flux J(CO) with upstream pressure p_h for Cu(SCN)-tetren liquid membranes. (a) Effect of Cu^I concentration in tetren (mol/kg) at 303 K. (Closed square and broken line denote $J(N_2)$ in pure tetren.) (b) Effect of temperature ([Cu] = 0.39 mol/kg).

The permeation flux of CO, J(CO), is plotted against the upstream pressure, p_h in Fig. 1(a) as a function of the concentration of Cu^I ion, [Cu]. The relation between J(CO) and p_h for pure tetren ([Cu]=0) is almost linear within the experimental error, indicating the diffusion to obey Fick's law. For Cu^I-containing systems, on the other hand, the relation becomes nonlinear and J(CO) increases with increasing [Cu]. The concavity to p_h axis displayed by these systems probably arises from the finite amount of CO transport mediated by Cu^I ion. In contrast, $J(N_2)$ was almost equal to J(CO) in pure tetren and scarecely changed with the addition of Cu^I ion. Thus, the flux ratio $J(CO)/J(N_2)$ increased with increasing [Cu] or decreasing p_h to attain to ca. 6 at [Cu]=0.39 mol/kg and p_h=0.7 kPa. These results demonstrate the facilitated transport of CO molecules in the presence of Cu^I ion.

As illustrated in Fig. 1(b), J(CO) increased with the rise of temperature. In contrast, $J(CO)/J(N_2)$ was found to become larger at a lower temperature. For example, the ratio came up to 8.5 at 273 K and p_h=0.7 kPa. These temperature dependences would be explained by considering that J(CO) consists of two transportation mode; the CO flux attributable to the diffusion in tetren matrix, $J_D(CO)$, and the transportation mediated by Cu^I ion, $J_M(CO)$. A rise in temperature causes increases in both diffusivities of the dissolved CO molecule and the Cu^I-CO adduct, which would bring about the enhancement of J(CO). However, it accompanies, at the same time, an increase in the diffusivity of dissolved N_2 to result in a lowering of $J(CO)/J(N_2)$. The enhanced $J(CO)/J(N_2)$ with lowering temperatures would be attributed to the increasing solubility of CO owing to the complex formation with Cu^I

Table 1. The saturation constant, S, and the affinity constant, K, of the Langmuir type equation($v = KSp(CO)/[1 + Kp(CO)]$) for equilibrium CO uptake, v.

[Cu] / mol/kg	T / K	S / mol CO/mol Cu	10^5K / Pa^{-1}
0.09	313	1.6	1.8
0.40		2.0	1.1
0.08	273	0.8	7.7
0.41		0.8	7.6

ion. A more stable Cu^I-carbonyl complex is formed at a lower temperature as will be discussed below. Taking into account $J(N_2) \simeq J(CO)$ in pure tetren, $J(CO)/J(N_2)$ may be regarded as a measure of the facilitated ratio, $J(CO)/J_D(CO)$.

Equilibrium CO uptake was determined by a volumetric method over the range of CO pressure, p(CO), 0 - 50 kPa. The amount of CO uptake increased more significantly at lower p(CO) and the rate of increase became slower with increasing p(CO). Neither precipitation nor color change was observed upon exposing Cu^I-tetren complex to CO. The CO sorption was thoroughly reversible. The CO dissolution into tetren matrix was negligible. This means the CO uptake in Cu^I-containing system to result from CO addition to Cu^I-tetren complex surrounded by an excess of tetren molecules. The sorption data was found to be characterized satisfactorily by use of a Langmuir expression. The sorption parameters determined are summarized in Table 1. The affinity constant increases with lowering temperature, indicating the formation of more stable copper carbonyl at a lower temperature. On the other hand, the saturation constant increases with elevating temperature and exceeds 1 mol CO/ mol Cu at 313 K. Although the amount of CO uptake of Cu^I complexes so far known is mostly one or half mol per mol of Cu, some instances are known in which the amount of CO uptake increases beyond 1 mol CO/ mol Cu. For example, it is reported that relatively free Cu^I ion in strong acid media can absorb more than 1 mol of CO to give copper polycarbonyl cations such as $Cu(CO)_3^+$ or $Cu(CO)_4^+$.9,10) Then, it seems likely that in the present system the absorption site for CO increases as the binding of tetren molecule would become loose at elevated temperatures.

Among the Cu^I carbonyl species with nitrogen ligands recently studied,11-14) the structures show a pseudotetrahedral geometry about the Cu^I ion with a terminally bound CO, except for five-coordinate complexes with macrocyclic ligands11) and binuclear complexes.14) According to a series of investigations of Pasquali and coworkers on copper-amine-carbonyl chemistry, a suspension of CuCl or CuI in methanol containing ethylenediamine or histamine, absorbs CO reversibly at room temperature, giving a homogeneous solution from which thermally stable carbonyl complexes can be obtained as crystalline solids by addition of $NaBPh_4$.12) These copper(I)-polyamine-carbonyls give the ν(CO) stretching frequencies over the range

2060-2117 cm^{-1} characteristic of a terminally bonded CO. In the present work, the i.r. spectrum of the CO adduct of CuI-tetren (1:33) revealed an intense band at 2064 cm^{-1} which diminished readily upon evacuation at ambient temperature. This suggests presumably the present Cu^{I} carbonyl complex to have a pseudotetrahedral geometry in which the CO molecule adds to a three-coordinated Cu^{I} center. No other direct evidence for the complex structure has been obtained and further investigations are in progress. The findings presented here would provide a novel information on the carrier-mediated transport of CO. It is worthwhile noting that the Cu^{I}-tetren system is a good carrier for not only molecular oxygen$^{7)}$ but carbon monoxide.

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References

1) S.G. Kimura, S.L. Matson, and W.J. Ward,III, "Recent Developments in Separation Science," ed by N.N.Li, CRC Press, Cleaveland, Ohio (1979), p.11.
2) J.D. Way, R.D. Noble, T.M. Flynn, and E.D. Sloan, J. Membr. Sci., 12, 239 (1982).
3) J.S. Schultz, Science, 197, 1177(1977).
4) D.R. Smith and J.A. Quinn, AIChE J., 26, 112(1980).
5) M.I. Bruce, J. Organometal. Chem., 44, 209(1972).
6) F.H. Jardine, Adv. Inorg. Chem. Radiochem., 17, 115(1975).
7) M. Kawakami, H. Iwanaga, M. Iwamoto, and S. Kagawa, J. Chem. Soc., Chem. Commun., 1982, 1396.
8) M. Kawakami, H. Iwanaga, Y. Yamashita, M. Yamasaki, M. Iwamoto, and S. Kagawa, Nippon Kagaku Kaishi, 1983, 847.
9) Y. Matsushima, T. Koyano, T. Kitamura, and S. Wada, Chem. Lett., 1973, 433.
10) Y. Souma, J. Iyoda, and H. Sano, Inorg. Chem., 15, 968(1976).
11) R.R. Gagne, R.S. Gall, G.C. Lisensky, R.E. Marsh, and L.M. Speltz, Inorg. Chem., 18, 771(1979); R.R. Gagne, D.M. Ingle, and G.C. Lisensky, Inorg. Chem., 20, 1991(1981); and references cited therein.
12) M. Pasquali, G. Marini, C. Floriani, A. Gaetani-Manfredotti, and C. Guastini, Inorg. Chem., 19, 2525(1980); M. Pasquali, C. Floriani, and A. Gaetani-Manfredotti, Inorg. Chem., 19, 1191(1980); and references cited therein.
13) J.J. Grzybowski and F.L. Urbach, Inorg. Chem., 19, 2604(1980).
14) S. Kitagawa and M. Munakata, Inorg. Chem., 20, 2261(1981).

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