The Transport of Oxygen facilitated by a Cu^{I}–Tetraethylenepentamine System

Mitsuyasu Kawakami, Hideaki Iwanaga, Masakazu Iwamoto, and Shuichi Kagawa *

Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852, Japan

The transport of oxygen is facilitated by a thin liquid layer of the title system which absorbs molecular oxygen reversibly with a stoicheiometry of $Cu : O_2 = 1 : 1$ accompanied by a $Cu^{I} \rightleftharpoons Cu^{II}$ cycle, causing the flux ratio of oxygen to nitrogen to be as high as 20 : 1.

Much interest has been shown in the membrane separation of oxygen from air and extensive studies have been undertaken to develop highly functional membranes.[1] Although recent advances in the development of ultra-thin polymeric membranes have resulted in increased gas flux,[2] their permeable selectivities for O_2 remain low (usually the flux ratio of O_2/N_2 is *ca.* 2—5). Carrier-mediated transport has the potential to solve this problem. In living systems, oxygen molecules

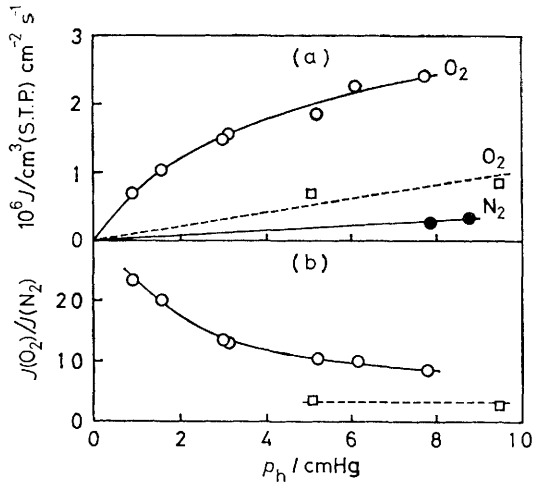

Figure 1. Variations of flux (a) and flux ratio (b) with upstream pressure p_h for Cu(SCN)–tetren 1 : 12 liquid membranes at 313.2 K. The broken lines denote the results for the pure tetren system.

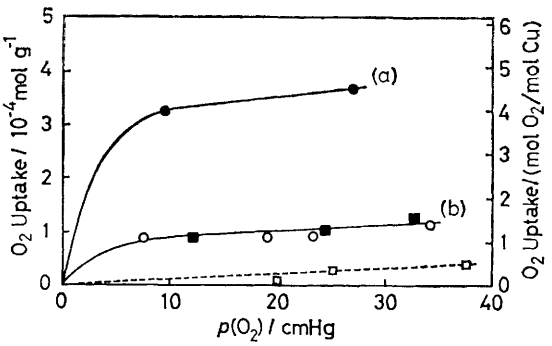

Figure 2. Sorption isotherms for O_2–[Cu(SCN)–tetren (1 : 64)] obtained from repeated measurements at 313.2 K: (a) first run [●], (b) second [■] and third runs [○]. The broken line denotes the results for the pure tetren system.

are transported efficiently with the aid of oxygen-carrying proteins such as haemoglobin, myoglobin, and haemocyanin. In order to elucidate the function of biological systems and the mechanism of carrier-mediated transport, many kinds of synthetic metal complexes have been presented as model compounds.[3] However, only a few attempts have been made to apply these complexes to the separation of oxygen from air (N_2).[4,5] Here, we report a novel Cu^I–polyamine system which is the first example of the Cu^I ion assisting the transport of oxygen.

A homogeneous liquid complex was prepared under an N_2 atmosphere by dissolving Cu(SCN) in tetraethylenepentamine (tetren) which had been distilled twice under reduced pressure; no other diluents or solvents were used. The molar ratio of Cu(SCN) : tetren was less than 1 : 12 and a colourless or pale amber liquid was obtained. The colour changed to greenish-blue on exposure to oxygen or air and reverted to the original colour on evacuation at 313 K.

The method and the apparatus for transport measurements are as reported previously.[6] The Cu^I–tetren liquid complex was poured onto a microporous poly(tetrafluoroethylene) membrane, with an average pore size of 0.2 μm, fixed horizontally in the transport measurement cell. This resulted in a thin layer of the complex, *ca.* 0.32 cm in thickness, on the membrane. The liquid complex did not come through the microporous membrane under the upstream pressure applied. Evacuation was continued for 2 or 3 days before each measurement.

The results of the transport experiments, as a function of upstream pressure (p_h), are illustrated in Figure 1(a). The flux of nitrogen [$J(N_2)$] was almost constant regardless of the presence or absence of the Cu^I ion and gave a single straight line, shown in Figure 1(a). It is noticeable that the transport rate of oxygen [$J(O_2)$] in the Cu^I–tetren 1 : 12 system was greater than that for the tetren system alone and that it increased nonlinearly with p_h whereas that in pure tetren showed a linear relationship with p_h. The straight lines imply that the transport mechanism is a simple Fickian type. On the other hand, the nonlinear relation in the Cu^I-containing system and the considerable increase in the flux ratio [$J(O_2)/J(N_2)$] induced by adding the Cu^I ion [Figure 1(b)] demonstrate that the transport of oxygen is mediated by the Cu^I ion. The increase of $J(O_2)$ compared with that for the pure tetren system represents the contribution of carrier-mediated transport;† this became saturated above a p_h of *ca.* 10 cmHg.

In the present system, the tetren molecule acts not only as a diffusion medium but also as a multidentate ligand. The Cu^I–tetren complex surrounded by an excess of tetren molecules functions as an oxygen-carrying species. To elucidate the interaction between the oxygen molecule and the Cu^I ion, oxygen uptake was examined by a volumetric method. Typical results of repeated measurements are shown in Figure 2 for the Cu–tetren 1 : 64 system. The decrease in oxygen uptake between the first and subsequent runs can be taken to be irreversible consumption of O_2.‡ Evidently the oxygen uptake is reversible except for the first run. The reversible uptake consists of contributions from the oxygenation of the Cu^I-complex(v_{oxy}) and from the dissolution into the tetren matrix. Assuming the Langmuir type equation for v_{oxy}, $v_{oxy} = KSp(O_2)/[1 + Kp(O_2)]$, where $p(O_2)$ is the pressure of oxygen and K and S are the affinity constant and the saturation constant, respectively, the value of S was found to be 0.8—1.0 mol O_2/mol Cu. This indicates that the reversible oxygenation has the stoicheiometry Cu : O_2 = 1 : 1 for the present system.§ The oxygenation gave rise to an absorption spectrum in the visible region (*ca.* 630 nm) and an e.s.r. signal ($g_\parallel = 2.19$, $g_\perp = 2.04$, $A_\parallel = 150$ G), both attributable to the Cu^{II} species and both of which disappeared reversibly upon evacuation, suggesting that the oxygenation–deoxygenation cycle accompanies the reversible $Cu^I \rightleftharpoons Cu^{II}$ redox cycle.

In the light of current interest in synthetic oxygen carriers containing the Cu^I ion,[7] it is of great importance that the facilitation of oxygen transport has been confirmed practically for this Cu^I-based artificial membrane.

† The increase of $J(O_2)$ for the Cu–tetren 1 : 64 system was reduced to *ca.* 1/5 in comparison with that for the Cu–tetren 1 : 12 system.

‡ This irreversible oxygen uptake may arise from the oxidation of tetren molecules, catalysed by Cu^I ions; unambiguous evidence for this has not yet been obtained.

§ The value of S was reduced to 0.13 mol O_2/mol Cu with an increase in the Cu^I concentration to Cu–tetren 1 : 6, suggesting that this stoicheiometry is valid only for fairly dilute concentrations of the Cu^I ion.

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