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Selective Liquid-Membrane Transport of Nitro-phenols by a Simple and Costless Carrier. An Application of the Results of Centrifugal Partition Chromatography+

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By applying the separation data of countercurrent type chromatography (centrifugal partition chromatography(CPC)) to liquid-membrane transport system(LMT), an effective simple carrier for selective LMT was found. This observation will be an important suggestion for finding out a costless carrier of selective LMT for weakly ionic or non-ionic substrates.

Artificial liquid-membrane transport[1)] has been obtaining an important position[2)] in chemistry in view of its dual significance. First, it is an experimental technique of biomimetic molecular recognition or a model of cell membrane. Second, it is a potential energy-saving concentration technique. In the studies on the former stand point it is reasonable to employ a carrier compound of relatively complicated but properly designed structures. However, when LMT is studied on the latter viewpoint, it is of value to find out effective and costless carriers suitable for a given substrate mixture.

Despite of recent development it seemed still rather difficult to attain effectively selective transports for non-ionic organic molecules.[2)] Our recent results obtained in separator- or carrier-aided CPC[3)] indirectly suggest that the chromatography is related to LMT, because the values of retention volume (V_R) for the samples were almost linearly correlated with the equilibrium constants obtained by extraction from the closely related two-phase systems.

This paper refers to the selective LMT of p-nitrophenol(NP) and 2,4,6-trinitrophenol(TNP) by an extremely simple carrier compound, i.e., butan-1-ol.

Prior to the experiment of LMT we studied the preparative-scale separation of the two nitrophenols by CPC (Sanki Engineering Co. Ltd., Model L-90 apparatus was used.). In this CPC experiment a mixed solvent ($CHCl_3$/butan-1-ol) was used as the stationary phase and H_2O as the mobile phase (1 cm^3 min^{-1}), under centrifugation with a rotation speed of 700 rev at room temperature. When the amount of butan-1-ol was 0.5% (v/v) of $CHCl_3$(45 cm^3), the mixture of equal amounts of the two nitrophenols was fractionated into NMR-spectroscopically pure compounds (ratio of V_R(PN) to V_R(TNP): 5.4) with the recovering efficiency of 70%(13.0 mg)

+ This paper is dedicated to the late Professor Ryozo Goto, Kyoto University.

and 76%(14.9 mg)(total of 5 runs) for PN and TNP, respectively, with only 150 separating micro-cells (50 micro-cell x 3 cartridges, which correspond to almost identical number of theoretical plate).

LMT experiments were performed by using an armed double cylinder type glass apparatus at room temperature. The source- and receiving-phases were H_2O, and the liquid-membrane was constructed by $CHCl_3$ containing 5% butan-1-ol (v/v) as in the case of CPC separation. The amounts of nitrophenols transported were determined by absorption spectra using a pre-calibrated graphs.

No transport was observed through the liquid-membrane of $CHCl_3$ alone. However, when the membrane containing 5%-butan-1-ol was used, TNP was transported very quickly and PN slowly as expected from the results of CPC. The rate constants of transport per unit concentration, k_{tr}(TNP) and k_{tr}(PN) (corrected for the concentration: 1.0×10^{-3} M and 1.0×10^{-2} M for TNP and PN, respectively), were 2.06×10^{-1} h^{-1} and 2.46×10^{-2} h^{-1}, respectively. The relative rate can be estimated as ca. 8.4.

Our results indicate that the data of CPC are useful to find out an effective carrier of selective LMT system. The fundamental mechanism of CPC is the same4) as classical countercurrent distribution method5) and its improvements including droplet countercurrent chromatography(DCCC)6) or planet-coil centrifugal countercurrent,7) and other partition data by using a variety of two phase system have been accumulated. Hence, researchers in the field of LMT aiming energy-saving concentration of weakly ionic or non-ionic compounds can obtain many guidances also from these countercurrent or partition data. At the same time, preparative-scale separations by the separator-aided CPC can be developed by using the data of LMT systems. Note that the detailed phase transfer mechanisms in CPC and LMT are not fully identical, it is necessary to consider the difference. The studies on the last promlem are underway in our laboratory.

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