

Acknowledgment. Support from the National Science Foundation Polymers Program (DMR-8712428) and the NSF Science and Technology Center for High Performance Polymeric Adhesives and Composites is gratefully acknowledged. We also acknowledge Mr. Kim C. Harich at Virginia Tech and MCMS at University of Nebraska for their help in mass spectroscopic analysis.

Registry No. 1, 90030-13-0; 2, 88498-43-5; 3, 15418-29-8; 4, 88478-97-1; 5, 134153-40-5; 6, 134153-41-6; 7, 134153-42-7.

High Potassium Ion Selectivity on Sodium-Substituted Taeniolite

Michihiro Miyake,* Toshiyuki Yoshida, Hiroaki Uchida,[†] Masasi Ozawa,[‡] and Takashi Suzuki

Department of Applied Chemistry and Biotechnology
Faculty of Engineering, Yamanashi University
Takeda, Kofu 400, Japan

Received February 19, 1991

Revised Manuscript Received April 5, 1991

There are only a few inorganic cation exchangers able to efficiently separate specific cations from systems in which analogous cations coexist. For example, it is difficult to selectively take up K^+ ions in the presence of a large excess of Na^+ ions¹ although the effective ionic size of a K^+ ion in aqueous solution is different from that of a Na^+ ion. In this paper, we report the discovery of an outstanding K^+ ion sieve effect of Na-substituted taeniolite (NaT), comparing with the K^+ ion selectivity of Na-substituted hectorite (NaH) and terasilicic mica (NaTS). NaT, NaH, and NaTS, which are fluormicas, are swellable with water, and their basal spacings are 12.3 Å at 25 °C in 70% relative humidity [chemical compositions are ideally as follows: NaT, $NaMg_2LiSi_4O_{10}F_2 \cdot 2H_2O$; NaH, $Na_{1/3}Mg_{8/3}Li_{1/3}Si_4O_{10}F_2 \cdot 2H_2O$; NaTS, $NaMg_{2.5}Si_4O_{10}F_2 \cdot 2H_2O$].²⁻⁴ The structure of taeniolite [$KMg_2LiSi_4O_{10}F_2$] is built by the stacking of the complex layer made by two SiO_4 tetrahedral sheets and one $(Mg,Li)(O,F)_6$ octahedral sheet.⁵ The complex layers are connected by interlayer Na^+ ions and water molecules in NaT. Although the fundamental structures of NaT, NaH, and NaTS are similar to one another, the atomic ratios of Li/Mg in the octahedral sheet are different among them.

NaT, NaH (Topy Ind. Co.), and NaTS (Coop Chemical Ind. Co.) were repeatedly washed with distilled water, and most impurities, namely small amounts of α -cristobalite and other nonswelling particles, were removed by centrifugation prior to cation-exchange experiments. The specimens were dried at 80 °C under vacuum and stored in a desiccator with 70% relative humidity. The $Na^+ \rightleftharpoons K^+$ exchange experiments were made by the normal batch method with shaking at 25 °C, described elsewhere.⁶ Each specimen of 0.1 g was equilibrated in 40 cm³ of NaCl + KCl solution with various ratios of the two salts for 24 h in order to determine the exchange isotherms at constant total

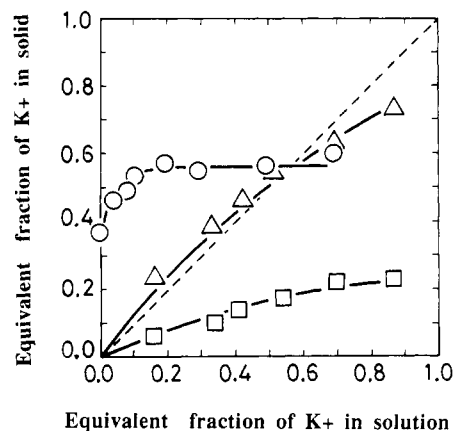
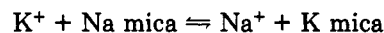


Figure 1. $Na^+ \rightleftharpoons K^+$ exchange isotherms on NaT (O), NaH (Δ), and NaTS (\square) at a constant total molarity of 1.0×10^{-2} M.

molarities of 2.5×10^{-2} , 1.0×10^{-2} , and 2.5×10^{-3} M. NaT (0.1 g) was also equilibrated in 40 cm³ of NaCl + KCl solutions with Na^+/K^+ ratios of 10, 20, and 30 at K^+ ion concentrations of 200, 300, 400, and 500 ppm for 24 h in order to further clarify K^+ ion selectivity in the presence of a large excess of Na^+ ions. After the reaction, the solid and solution phases were separated by centrifugation, and an aliquot of supernatant was collected for chemical analyses. The solutions were analyzed for Li, Na, and K by atomic absorption spectroscopy. At least three replications were carried out in the cation-exchange experiments with concurrent results.

The exchange reaction of NaT, NaH, and NaTS of 1 g with 1.0×10^{-2} M KCl solutions attained steady states within 24 h, and the molar ratios of Na^+/K^+ during the reactions were found to be close to 1.0. The interlayer Na^+ ions of ca. 55% in NaT, 75% in NaH, and 25% in NaTS, whose theoretical cation exchange capacities are 235, 78, and 233 mequiv/100 g, respectively, were exchanged for K^+ ions at an equilibrium state. The cation exchanges that occurred were incomplete. This was considered to be due to the fact that it is impossible to synthesize solid solutions between Na and K substitutions over the entire composition range.⁷

The exchange isotherms on NaT, NaH, and NaTS at a constant total molarity of 1×10^{-2} M are shown in Figure 1. The $Na^+ \rightleftharpoons K^+$ exchange process on mica is represented by



K^+ ions are preferable to Na^+ ions if the exchange isotherm lies above the diagonal line, whereas Na^+ ions are preferable to K^+ ions if the exchange isotherm lies below the diagonal line, and the diagonal line represents no preference between these ions.⁸ The $Na^+ \rightleftharpoons K^+$ exchange isotherm on NaT rises steeply and attains a plateau above the diagonal line in the initial stages, which reveals that K^+ ions are extremely preferred over Na^+ ions in the low-concentration region of K^+ ions. The $Na^+ \rightleftharpoons K^+$ exchange isotherm on NaH lies just above the diagonal line in the low-concentration region of K^+ ions, which reveals that K^+ ions are moderately preferred over Na^+ ions. The $Na^+ \rightleftharpoons K^+$ exchange isotherm on NaTS lies below the diagonal line over the concentration range, which reveals that Na^+ ions are preferred over K^+ ions. The order of K^+ ion selectivity was, therefore, concluded to be NaTS < NaH << NaT in

* Present address: Oki Electric Co., Ltd, Tokyo, Japan.

[†] Present address: Nippon Kemikon Co., Ltd, Tokyo, Japan.

(1) Suzuki, T.; Miyake, M.; Yoshikawa, Y.; Yoshida, T. *Bull. Soc. Seawater Sci. Jpn.* **1990**, *44*, 185-188.

(2) Kitajima, K.; Sugimori, K.; Daimon, N. *J. Chem. Soc. Jpn.* **1973**, 1885-1892.

(3) Kitajima, K.; Daimon, N. *J. Chem. Soc. Jpn.* **1974**, 685-689.

(4) Kitajima, K.; Daimon, N. *J. Chem. Soc. Jpn.* **1975**, 991-995.

(5) Toraya, H.; Iwai, S.; Marumo, F.; Hirao, M. *Z. Kristallogr.* **1977**, *146*, 73-83.

(6) Suzuki, T.; Hatsushika, T.; Miyake, M. *J. Chem. Soc., Faraday Trans. 1*, **1982**, *78*, 3605-3611.

(7) Kondo, R.; Daimon, M.; Asaga, K.; Nishikawa, T.; Kitajima, K.; Daimon, N. *J. Am. Ceram. Soc.*, **1980**, *63*, 41-43.

(8) Rees, L. V. C. *The Properties and Applications of Zeolites*; The Chemical Society: London, 1979; pp 218-243.

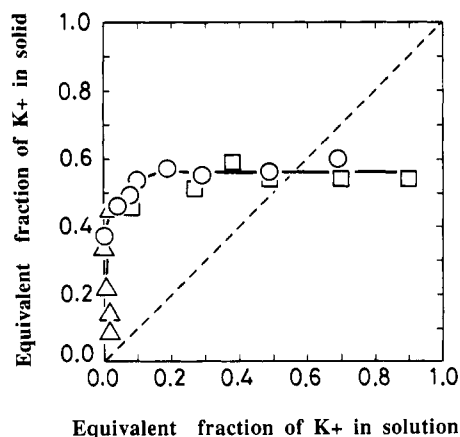


Figure 2. $\text{Na}^+ \rightleftharpoons \text{K}^+$ exchange isotherms on NaT at constant total molarities of 1.0×10^{-2} (○), 2.5×10^{-3} (Δ), and 2.5×10^{-2} M (□).

Table I. K^+ Ion Selectivity (K^+ Uptake, ppm) on NaT (1 g) in 40 cm^3 of NaCl + KCl Solutions with an Excess of Na^+ Ions

Na^+/K^+	initial K^+ concn, ppm			
	200	300	400	500
10	110.8	120.7	112.3	125.9
20	112.2	120.7	114.8	123.2
30	112.2	110.0	120.5	124.1

the low-concentration region of K^+ ions. The superior preference for K^+ ions over Na^+ ions on NaT was found to be independent on the total molarity as is shown in Figure 2. The characteristics for the selective K^+ ion uptake of NaT were further examined in the presence of a large excess of Na^+ ions. From the results, NaT was found to selectively take up a regular amount of K^+ ions without depending on the concentrations of Na^+ and K^+ ions as is seen in Table I.

In conclusion, these basic studies suggest that NaT can be utilized in the separation and immobilization of K^+ ions from the system which has a large quantity of Na^+ ions and a small quantity of K^+ ions, for example, seawater (Na^+ , 10 500 ppm; and K^+ , 380 ppm). The relation between the selectivity and structural change on fluormicas will be discussed in detail in a following paper.

Potential Dependence of the Conductivity of Polyacetylene: Finite Potential Windows of High Conductivity

David Ofer, Lee Y. Park, Richard R. Schrock,* and Mark S. Wrighton*

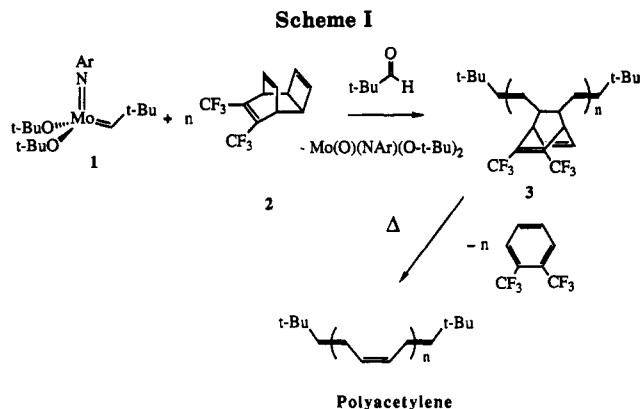
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received May 28, 1991

We wish to communicate that polyacetylene, the "prototypic" conducting polymer, exhibits a finite potential

* To whom correspondence should be addressed.

(1) (a) Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 1441. (b) Chao, S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 6627.



window of high conductivity upon oxidation in liquid SO_2 or upon reduction in tetrahydrofuran. These findings are analogous to those obtained for other conjugated polymers (polyaniline,¹ polythiophenes,^{2,3} and polypyrroles²) and establish that a finite potential window is a general feature of conductivity in such polymers. The observation of finite potential windows of high conductivity in conjugated polymers is in accord with theoretical studies⁴⁻⁶ that indicate it should be possible to oxidize or reduce them sufficiently to render them nonconducting.

Polyacetylene samples were prepared via a controlled version⁷ of the Durham route,⁸ as shown in Scheme I.⁹ Samples of 3 were prepared by using a 60:1 ratio of monomer to catalyst; polydispersities were ≤ 1.18 .¹⁰ Films of 3 were cast onto arrays of individually addressable platinum macro- and microelectrodes¹¹ having a total area of $\sim 0.04 \text{ cm}^2$, and the arrays were heated to 120°C for 3 min to generate the polyacetylene films. Two individually addressable electrodes connected by a redox active polymer can be operated in a transistor-like configuration to reveal the potential dependence of the conductivity of the polymer. When a small fixed-potential difference (drain voltage V_D) is applied between the two electrodes, the magnitude of the current, I_D , between the electrodes is directly proportional to the conductivity of the polymer, which changes as the electrochemical potential (V_G) is changed. Therefore, a plot of I_D vs V_G gives relative conductivity vs potential.¹²

Figure 1a shows the cyclic voltammogram for a polyacetylene film in liquid $\text{SO}_2/0.1 \text{ M } [(n\text{-Bu})_4\text{N}]\text{AsF}_6$ at -70°C . At potentials negative of $\sim 0.7 \text{ V}$ vs poly(vinyl-

(2) Ofer, D.; Crooks, R. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 7869.

(3) Crooks, R. M.; Chyan, O. M. R.; Wrighton, M. S. *Chem. Mater.* **1989**, *1*, 2.

(4) Brédas, J. L.; Elsenbaumer, R. L.; Chance, R. R.; Silbey, R. *J. Chem. Phys.* **1983**, *78*, 5656.

(5) Chance, R. R.; Boudreau, D. S.; Brédas, J. L.; Silbey, R. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Chapter 24.

(6) Chance, R. R.; Brédas, J. L.; Silbey, R. *Phys. Rev. B* **1984**, *29*, 4491.

(7) Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 7989.

(8) Edwards, J. H.; Feast, W. J. *Polymer* **1980**, *21*, 595.

(9) (a) Schrock, R. R. *Acc. Chem. Res.* **1990**, *24*, 158. (b) Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378. (c) Bazan, G. C.; Schrock, R. R.; Cho, H.-N. *Macromolecules*, in press.

(10) Park, L. Y.; Schrock, R. R.; Stieglitz, S. G.; Crowe, W. E. *Macromolecules*, in press.

(11) The platinum arrays will be described fully in a future publication. For the purposes of the I_D - V_G , current passes between two platinum electrodes, $\sim 0.1 \mu\text{m}$ high, $\sim 1.5 \text{ mm}$ long, $\sim 1.2 \text{ mm}$ wide, and separated from each other by $\sim 35 \mu\text{m}$. Four microelectrodes, $\sim 1.5 \text{ mm}$ long \times $\sim 4 \mu\text{m}$ wide, which lie between the two larger electrodes, are used for four-point probe measurements when the polymer is maximally conducting.

(12) Natan, M. J.; Wrighton, M. S. *Prog. Inorg. Chem.* **1989**, *37*, 391.