Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Ion-Exchange Selectivities of Periderm and Cuticular Membranes toward Alkali Cations

Mustafa Ersoz[a]; Harry J. Duncan[b]
[a] DEPARTMENT OF CHEMISTRY, FACULTY OF ARTS AND SCIENCES, UNIVERSITY OF SELCUK, KONYA, TURKEY [b] AGRICULTURAL, FOODS AND ENVIRONMENTAL CHEMISTRY SECTION, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF GLASGOW, GLASGOW, SCOTLAND, UK

To cite this Article Ersoz, Mustafa and Duncan, Harry J.(1994) 'Ion-Exchange Selectivities of Periderm and Cuticular Membranes toward Alkali Cations', Separation Science and Technology, 29: 13, 1719 — 1731
To link to this Article: DOI: 10.1080/01496399408002167
URL: http://dx.doi.org/10.1080/01496399408002167

SEPARATION SCIENCE AND TECHNOLOGY, 29(13), pp. 1719–1731, 1994

Ion-Exchange Selectivities of Periderm and Cuticular Membranes toward Alkali Cations

MUSTAFA ERSOZ*
DEPARTMENT OF CHEMISTRY
FACULTY OF ARTS AND SCIENCES
UNIVERSITY OF SELCUK
42079, KONYA, TURKEY

HARRY J. DUNCAN
AGRICULTURAL, FOODS AND ENVIRONMENTAL CHEMISTRY SECTION
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF GLASGOW
GLASGOW, G12 8QQ, SCOTLAND, UK

ABSTRACT

The ion-exchange selectivities of lithium, sodium, potassium, and cesium on isolated potato periderm (*Solanum tuberosum*) and pear fruit cuticular membranes were investigated; the general order of preference both for cation selectivities and ion-exchange capacities was lithium > sodium > potassium > cesium. The potato periderm and pear fruit cuticular membranes exhibited a behavior typical of ion-exchange resins of the weak acid type. At constant pH 7, the ion-exchange capacities of periderm and cuticular membranes increased with hydrated ionic radius, and also with increasing pH and neutral salt concentration, and decreased with crystal ionic radius. Counterion selectivities also exhibited the same behavior. The ion-exchange properties are discussed in terms of the structure and function of potato periderm and pear fruit cuticular membranes.

INTRODUCTION

Transport properties of membranes depend strongly on the nature and density of the charges fixed to the membrane matrix (1, 2). Plant cuticles are biological polymer membranes of heterogeneous composition (3) and are bipolar polyelectrolytes (4).

* To whom correspondence should be addressed.

Isolated cuticles or periderms, which represent the prime barrier to penetration, provide a physical system by which transport studies can be conducted under well-defined and highly controlled conditions. Most studies with isolated cuticles have focused on sorption, desorption, and infinite-dose cuticular transport of chemical compounds in aqueous systems.

Indirect evidence suggests that cuticular membranes can be considered to possess some properties of weak acid cation-exchange membranes, as has been pointed out by various workers (5–7). Kolattukudy (8) described cutin and suberin as biopolyester membranes. Cutin and suberin are closely related chemical compounds. Both are polymers with a high proportion of fatty acids. The cuticular membrane exhibits a behavior typical of highly crosslinked, high capacity ion-exchange resins of the weak acid type (6). The inner surfaces of cuticular membranes are more highly charged due to the pectin materials present, and this has been noted to have an effect on the penetration and binding of cations to isolated cuticle membranes (9, 10).

Plant cuticles are potential sorption compartments for lipophilic compounds (11). In this study the emphasis is toward quantitative analytical and physicochemical procedures for chemicals adsorbed by periderms and cuticles. There is a need to know the behavior of chemical substances in plant materials, i.e., their sorption, accumulation, and desorption in cuticles. Fundamental knowledge of the morphology and properties of plant cuticles is crucial to the design formulations for agrochemicals, especially in explaining their behavior and performance following spray application to foliage (12). This information is also relevant to any sorption studies with pesticides and adjuvants which might be undertaken in vitro using isolated cuticle preparations.

While the information available at present on the selectivity and interaction of alkali metal ions with sulfonic, inorganic, and other types of exchangers is abundant, nothing is known about the selectivity and interaction of alkali metal ions with periderm and cuticular membranes. Therefore, in these studies the ion-exchange properties and counterion selectivities of potato periderm membranes (PM) and pear fruit cuticular membranes (PFCM) toward alkali cations were studied.

EXPERIMENTAL

Materials

The salts were Analytical grade NaCl, KCl, standard NaOH and HCl solutions from BDH Ltd., LiCl from Hopkin & Williams, CsCl from

Formachem Ltd., cellulose from Sigma Chemical Co., pectinase from ICN Biomedicals Ltd., and sodium acetate and acetic acid from May & Baker Ltd.

Salt solutions were prepared using deionized water without further purification by dissolving a weighed quantity of Analar grade salts. Standard solutions were prepared using standard concentration solutions. The indicator used was phenolphthalein.

Isolation of Periderms and Cuticles

Periderms were isolated from potatoes cultivar (cv.) Record, and pears were purchased at the local market. Sampled potatoes and pears were washed carefully by hand before several cores 17 and 22 mm in diameter were taken from each potato and pear. Isolation was carried out using a modification of a published method (13, 14). The cores were placed in a suspension of 0.1% cellulase and 2% pectinase buffered (0.2 M sodium acetate/0.2 M acetic acid) at pH 3.8. The suspensions were stored at 25°C for 14 days before isolating the periderms and cuticles from the remaining attached flesh.

Exchange Capacity

The ion-exchange properties of the isolated periderm and cuticular membranes were investigated using various salt concentrations. The ion-exchange capacities of the isolated PM and PFCM were determined potentiometrically. In this experiment the progressive batch titration method was used (6) to determine the exchange capacities of various salt concentrations using the same pieces of periderm and cuticle. Between solute changes the cuticle was rinsed thoroughly with dilute nitric acid (10% v/v) (15) and then washed with deionized water to remove sorbed cations.

Selectivity Coefficient

Each membrane in M^+- or H^+-form was usually equilibrated with a mixed HCl + MCl (M: Li, Na, K, and Cs) solution of total composition 0.05 M. After equilibrium (generally 24 hours), the equilibrated membrane was removed from solution. The change in composition of the equilibrated solution was determined by titration of H^+ ions. The membrane composition was also determined by conversion to the M^+-form and titration of the released H^+ ion. The concentrations of metal cations in the solution and in the membrane phase were determined by atomic absorption spectrophotometry (Perkin Elmer 1100 B). In all cases a mass balance was confirmed. Selectivity coefficients were calculated from the results of

these experiments by using the equation

$$K_H^M = \frac{X_M}{X_H}\frac{C_H}{C_M}$$

where X_M and X_H represent the equivalent ionic fractions of the counterions in the membrane phase, and C_M and C_H are the corresponding equivalent fractions of these ions in the solution phase.

RESULTS AND DISCUSSION

The ion-exchange capacities dependent on different ionic Li^+, Na^+, K^+, and Cs^+ forms at constant pH 7 as a function of the nature and concentration of counterions are listed in Table 1. The titration curves of the PM and PFCM obtained with NaOH in the presence of 0.1 M NaCl dependent on pretreatment are given in Fig. 1. Isolated PM and PFCM pretreated with 1 M HCl gave the following ion-exchange capacities: 0.415 meq·g^{-1} for PM and 0.25 meq·g^{-1} for PFCM. When pretreated with 2 M HCl, the ion-exchange capacities were increased to the following values: 0.435 meq·g^{-1} for PM and 0.265 meq·g^{-1} for PFCM. Repeating the 2 M HCl pretreatment had no further effect. Pretreatment with a stronger acid concentration was not attempted due to the possibility of damaging the cuticle samples. The titration curves of the isolated periderm and cuticular membranes exhibited a behavior typical of weak acid resins. The initial pH of the aqueous phase is slightly higher. The ion-exchange capacities of PM and PFCM toward alkali metal cations followed the sequence $Li^+ > Na^+ > K^+ > Cs^+$. At constant pH the ion-exchange capacity increased with increasing pH and the concentration of neutral salt, and it decreased with decreasing crystal radius. This sequence was apparent over the pH

TABLE 1
Exchange Capacity of the Periderm and Pear Fruit Cuticular Membranes at pH 7.0 as a Function of Nature and Counterion

	Exchange capacity (meq·g^{-1})	
Counterion	Periderm	Pear
Li	0.433	0.255
Na	0.410	0.238
K	0.398	0.215
Cs	0.370	0.203

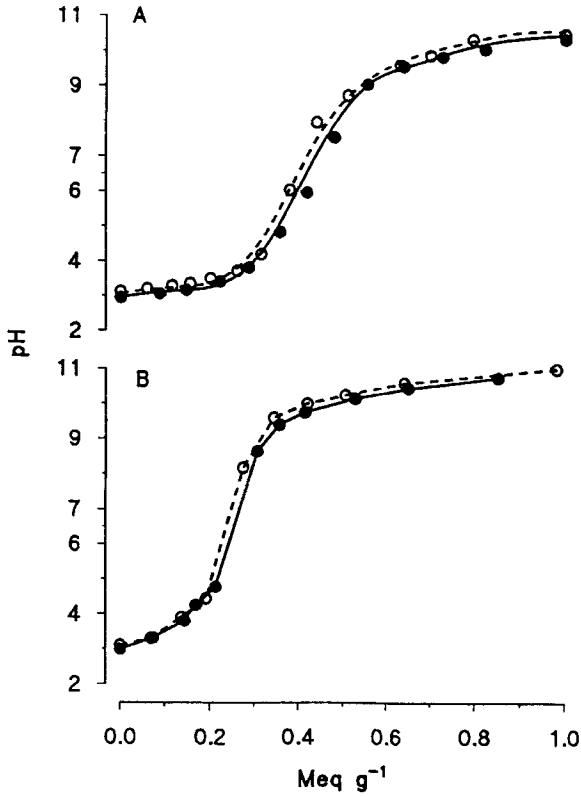

FIG. 1 Titration of PM (A) and PFCM (B) with NaOH in the presence of 0.1 N NaCl as affected by pretreatment: (●) pretreatment with 2.0 M HCl, (○) pretreatment with 1.0 M HCl.

3–9 ranges. This order follows the sequence of hydration energies, which is also the sequence of hydrated radii.

Three separate groups can be distinguished over the pH range studied, the first between pH 3 and 5.5 and the second between pH 5.5 and 9. The endpoint of the third group was not observed in some experiments, but it could be estimated from some titration curves and covered the pH range between 9 and 11.5 or 12. Schonherr and Bukovac (6) observed three dissociable groups in the pH ranges 3–6 (0.2 meq·g^{-1}), 6–9 (0.3 meq·g^{-1}), and 9–12 (0.55 meq·g^{-1}) for tomato cuticular membranes. These investigators reported that the first group was tentatively assigned to the —COOH group of pectic material and protein embedded in the membrane,

the second to nonesterified —COOH groups of the cutin polymer, and the third to phenolic —OH groups, such as nonextractable flavenoids present in the membrane, and to a small amount of $—NH_3^+$ groups of proteins.

It has been found that the exchange capacity of PM is higher than that of PFCM. Kolattukudy (8) reported that the major aliphatic components of suberin are ω-hydroxy fatty acids and dicarboxylic acids. He proposed a model for cutin and suberin; the composition of the monomers in cutin shows that hydroxyl groups are in excess of the number of carboxyl groups, whereas the composition of the monomers in suberin suggests that hydroxyl groups are not in excess of the number of carboxyl groups. It can be concluded here that the carboxyl groups of PM are in excess over those of PFCM, therefore the exchange capacity of PM is higher than that of PFCM.

The selectivity of a cation-exchange resin for alkali cations is affected by the nature and effect of the neutral salt and the acidity of the exchange group. The apparent acid strength increased with increasing concentration of neutral salt and decreasing crystal radius of counterions. This behavior is typical for polyelectrolytes of the weak acid type (16, 17), and the main reason is the electrostatic free energy arising from the mutual repulsion of neighboring fixed charges (6, 18). Schonherr and Bukovac (6) observed that as the electrostatic potential increases during titration, the tendency to form more negative groups will diminish, and the apparent acid strength therefore decreases as the degree of ionization and exchange capacity increase.

Generally, smaller ions have larger heats of hydration and a small ion contains a more concentrated charge, leading to a greater electrostatic interaction between the ion and polar water molecules. The hydration of ions in aqueous solutions is frequently represented as the strong binding of nearby molecules. The concept of a more or less strong bond among molecules of water and ions is justified only in the case of strongly hydrated ions. The hydration number is directly proportional to the charge and inversely proportional to the size of the ion.

According to electrostatic theory, the electric field at the surface of a charged sphere of radius r is proportional to ze/r^2, where z is the number of charges and e is the electronic charge. The ion–dipole interaction between dissolved ions and water molecules can affect a number of bulk properties of water, hence small ions such as Li^+ and Na^+ are called structure-making ions (19). The high electric fields exerted by these ions can polarize the water molecules, producing additional order beyond the first hydration layer. This interaction leads to an increase in the solution's viscosity. Large monovalent ions such as K^+ and Cs^+ are structure-breaking ions.

As a result of their diffuse surface charges and hence weak electric fields, these ions are unable to polarize water molecules beyond the first layer of hydration.

The electrostatic free energy can be reduced by association between fixed charges and counterions, and by screening of neighboring fixed charges (16). The smaller the crystal radius of a counterion, the greater the interaction with the fixed charge, the lower the electrostatic free energy, and the greater the apparent acid strength (6). The decreasing order of crystal radii of counterions used in this study is $Li^+ < Na^+ < K^+ < Cs^+$, which is also the order of decreasing acid strength observed. The fact that ions are hydrated in solution means that their effective radii can be appreciably greater than their crystal or ionic radii. Ionic hydration plays a role in exchange capacity. Gregor et al. (16, 17) observed the following sequence for the insolubility of dicarboxylic acids: $Li^+ > Na^+ > K^+$. In this work the observed sequence at pH 7 is the same as the hydration energies, $Li^+ > Na^+ > K^+ > Cs^+$.

The counterion selectivity was studied by titrating PM and PFCM in solutions of various M^+/H^+ ratios. Alkali metal–hydrogen exchange on isolated PM and PFCM is characterized by ion-exchange isotherms (Fig. 2). Selectivity coefficient isotherms for alkali metal–hydrogen ion exchange of isolated PM and PFCM at 25 ± 1°C are shown to be functions of equivalent fractions of alkali metal ions in solutions of HCl + MCl of 0.05 M (Fig. 3). The selectivity coefficient integrated over all ionic compositions is the value obtained at an ionic fraction of 0.5 (20). These values for PM and PFCM, obtained by interpolation of the data shown in Fig. 3(B), are Li^+, 1.03; Na^+, 0.95; K^+, 0.62; and Cs^+, 0.28 for PM, and Li^+, 0.99; Na^+, 0.83; K^+, 0.76; and Cs^+, 0.46 for PFCM.

For exchange of two ions of equal ionic charge, the selectivity coefficient defines the relative affinity of the two counterions. It is seen from Fig. 2 that the selective uptake of alkali metal ions in isolated PM and PFCM follows the general order of preference $Li^+ > Na^+ > K^+ > Cs^+$. The $K_{M/H}$ values for K^+ and Cs^+ are lower than unity when the ionic fraction of the membrane phase is less than 0.8, and the membrane shows a preference for hydrogen over potassium and cesium. The selectivity coefficients for lithium and sodium ions are higher than those for potassium and cesium ions (Fig. 3).

The selectivity coefficient isotherms for alkali metal–hydrogen ion exchange in isolated periderm and cuticular membranes show preference for hydrogen over alkali metal ions when the membrane phase is rich in hydrogen. With alkali-metal ion-rich membranes, this preference is reversed, and the membranes prefer alkali metal ions over hydrogen to a marked degree.

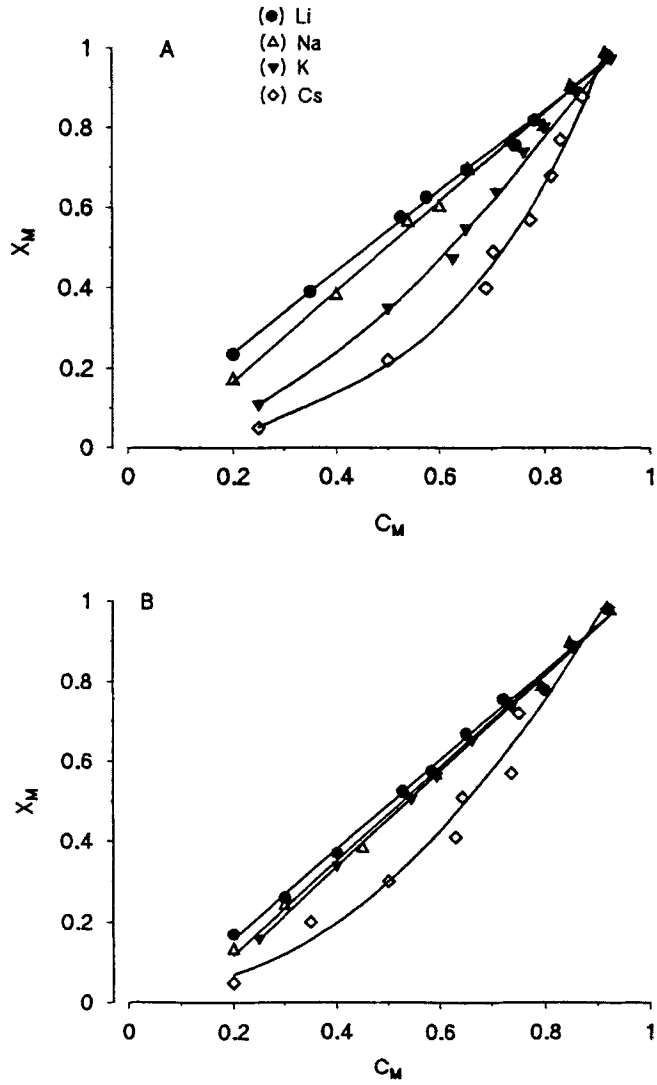

FIG. 2 M^+/H^+ exchange isotherms for isolated PM (A) and PFCM (B) membranes equilibrated with mixed alkali metal chloride and hydrochloric acid solutions of total concentration 0.05 M.

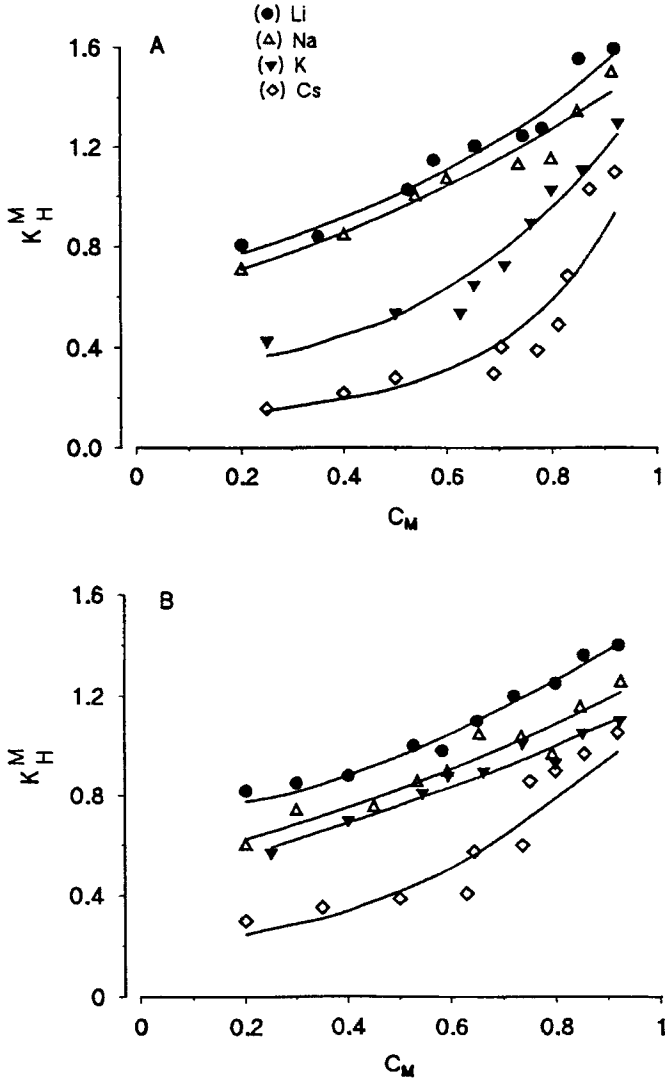

FIG. 3 Selectivity coefficients $K_{M/H}$ for isolated PM (A) and PFCM (B) membranes as a function of the equivalent fraction of alkali cations in a solution of (MCl + HCl) of total concentration 0.05 M.

With carboxylic acid resins, the hydrogen ion exhibits the highest exchanging power (21) because it forms covalent compounds due to its being a weak acid exchanger (22). This ion exchanger prefers the counterion which forms the stronger ion pairs or bonds with the fixed ionic groups. If the counterions are available, the polymer preferentially exchanges that ion in an attempt to minimize free energy; therefore, the polymer prefers the counterion that associates more closely with the fixed charges of the polymer (minimizing the electrostatic free energy) and which results in the smallest polymer volume (minimizing the free energy of stretching and maximizing the configurational entropy of the polymer chains) (6, 17). The attracting interactions between the metal ion and the water molecules are primarily electrostatic in character. Most theories of ion-exchange studies attach key importance to ionic solvation phenomena. Carboxylic acid groups are proton acceptors, thus these fixed groups prefer the larger and more strongly hydrated spaces. There is agreement between these findings and the affinity sequence of the hydrated ionic radius.

The selectivity of a cation-exchange resin for alkali cations is affected by the nature and acidity of the exchange groups. The carboxylic and phenolic resins require high pH values for their efficient utilization. pH has an important influence on the efficiency of a weakly acidic exchanger. The results obtained here are in agreement with the affinity order for weak acid resins and show inverse selectivities to those of the sulfonic resins (17, 23–25). The selectivity also increases with increasing hydrated ionic radii and decreasing crystal ionic radii of alkali cations.

If a monovalent counterion is taken from the bulk solution and brought into contact with a fixed group, two types of interaction energy are involved (24): 1) The electrostatic interaction between the fixed grouping and the ion, and 2) the free energies required to remove from the fixed grouping and the counterion as many water molecules as are necessary to permit contact of the fixed grouping and counterion. Such free energies would be closely related to the standard free energies of hydration of the fixed group and counterion. In the case of a fixed grouping of high field strength, the exchanger will now give preference to the ion with a smaller radius. This is exactly what is found with carboxylate resin, which is regarded as a grouping of high field strength, owing to its small size. Reports by Link (26) deal with the heat, entropy, and free energy of solvation. Selectivity in the "normal" order is governed by the free energies of hydration of the counterion.

Ion exchangers have a very large external surface. In most theoretical studies of ion-exchange equilibria, attempts are made to fit empirical equations to experimental results. The equations used are modifications of either the mass-action law or adsorption isotherms of the Langmuir or

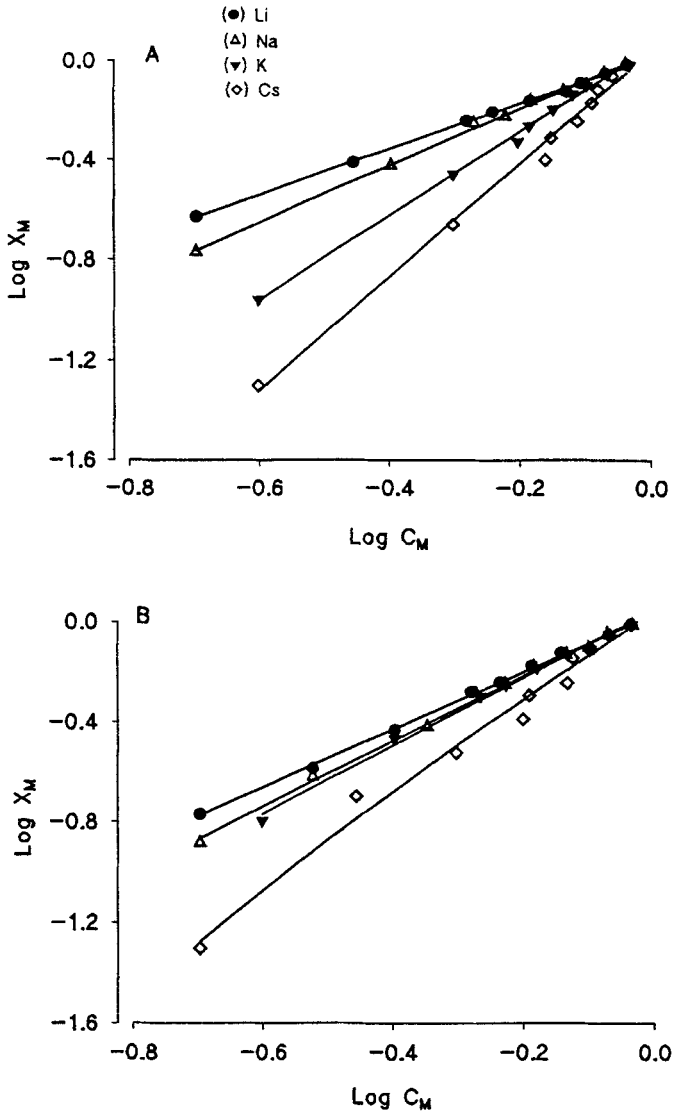

FIG. 4 The Freundlich isotherms of M^+/H^+ exchange systems for PM (A) and PFCM (B).

Freundlich type (1). Cuticles are heterogeneous membranes (27). There is no assurance that the derivation of the Freundlich equation is unique if the data fit the equation; it is likely, but not proven, that the surface is heterogeneous (28). Ion exchange takes place to a great extent at this external surface, and exchangeable cations are held in part as a diffuse double layer, shading off gradually into the solution (22). When the experimental data were examined in terms of either Langmuir or Freundlich isotherm equations, both PM and PFCM were found to exhibit behavior characteristics of the Freundlich isotherm type (Fig. 4).

CONCLUSION

This study examined the possibility of using isolated cuticles or periderms to quantify the selectivities and sorption of alkali cations, and suggested this as a possible approach for studying the uptake of environmental pollutants and gaining knowledge on foliar absorption and the effect of spray additives on pesticide penetration. Knowledge about the dependence of transport, concentration, selectivity, and type of periderm and cuticle is essential for understanding and analyses of the uptake of chemical substances and environmental pollutants into leaves or fruits.

ACKNOWLEDGMENT

The authors gratefully acknowledge the Selcuk University for its financial support.

REFERENCES

1. F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962.
2. N. Lakshminarayanulah, *Transport Phenomena in Membranes*, Academic Press, New York, 1969.
3. J. T. Martin and B. E. Juniper, *The Cuticle of Plants*. Edward Arnold, London, 1970.
4. J. Schonherr and R. Huber, *Plant Physiol.*, *59*, 145 (1977).
5. H. Keppel, in *Isotopes in Plant Nutrition and Physiology*., Proc. Symp. on the use of isotopes in plant nutrition and physiology IAEA Vienna, 329, (1967).
6. J. Schonherr and M. J. Bukovac, *Planta*, *109*, 73 (1973).
7. G. T. Cook and H. J. Duncan, *Aspects Appl. Biol.*, *4*, 371 (1983).
8. P. E. Kolattukudy, *Science*, *208*, 990 (1980).
9. Y. Yamada, M. J. Bukovac, and S. H. Wittwer, *Plant Physiol.*, *39*, 978 (1964).
10. Y. Yamada, S. H. Wittwer, and M. J. Bukovac, *Ibid.*, *39*, 29 (1964).
11. M. Riederer and J. Schonherr, *Ecotoxicol. Environ. Saf.*, *8*, 236 (1984).
12. P. J. Holloway, *Pestic. Sci.*, *37*, 203 (1993).
13. J. Schonherr, *Planta*, *128*, 113 (1976).
14. E. Vogt, J. Schonherr, and H. W. Schmidt, *Ibid.*, *158*, 294 (1983).

15. J. C. McFarlane and W. L. Berry, *Plant Physiol.*, *53*, 723 (1974).
16. H. P. Gregor, M. J. Hamilton, J. Becher, and F. Bernstein, *J. Phys. Chem.*, *59*, 874 (1955).
17. H. P. Gregor, M. J. Hamilton, R. J. Oza, and F. Bernstein, *Ibid.*, *60*, 263 (1956).
18. A. Katchalsky, *J. Polym. Sci.*, *22*, 159 (1954).
19. C. Raymond, *Physical Chemistry with Applications to Biological Systems*, 2nd ed., Macmillan, New York, 1981, p. 206.
20. H. L. Yeager and A. Steck, *Anal. Chem.*, *51*, 862 (1979).
21. R. Kunin, *Ion Exchange Resins*, 2nd ed., Wiley, New York, 1958, p. 320.
22. F. C. Nachod, *Ion Exchange: Theory and Application*, Academic Press, New York, 1949.
23. J. I. Bregman, *Ann. N.Y. Acad. Sci.*, *57*(5), 123 (1953).
24. D. Reichenberg, in *Ion Exchange*, Vol. 1 (J. A. Marinsky, Ed.), Arnold, London; Dekker, New York, 1966, p. 227.
25. R. J. D. Williams, in *Recent Development in Ion Exchange* 2 P. A. Williams and M. J. Hudson, Eds.), (Proceedings of the International Conference "ION-EX'90"), Elsevier Applied Science, London, 1990, p. 3.
26. G. N. Link, *J. Gen. Physiol., Suppl.*, *43*, 149 (1960).
27. J. Schonherr and M. Riederer, *Rev. Environ. Contam. Toxicol.*, *108*, 1 (1989).
28. A. W. Adamson, *Physical Chemistry of Surfaces*, 5th ed., Wiley, New York, 1990.

Received by editor November 29, 1993