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COMPARISON OF EXPERIMENTAL AND THEORETICAL RATES OF ION EXCHANGE

STEPHEN C. DUFFY

Kodak Ltd., Harrow, Middlesex (Great Britain)

and

LOVAT V. C. REES

Physical Chemistry Laboratories, Imperial College of Science and Technology, London, SW7 2AY (Great Britain)

SUMMARY

The theoretical rates of the forward and backward ion-exchange reactions



have been calculated. In these calculations the concentration dependencies of D_{Na}^* and D_{K}^* , the respective self-diffusion coefficients of sodium and potassium in (Na,K)-chabazites, have been taken into account. When these theoretical rates are compared with rates determined experimentally for these two reactions, the introduction of concentration-dependent self-diffusion coefficients has been shown to be of prime importance.

INTRODUCTION

For spherical symmetry the diffusion equation can be written as:

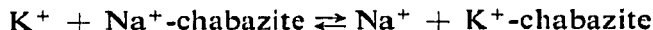
$$\frac{\partial C_A}{\partial t} = \frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left(r^2 D_{AB} \frac{\partial C_A}{\partial r} \right) \quad (1)$$

where t is time, r is the distance from the centre of the sphere, and C_A is the concentration in mole fractions of the ion A in the sphere. This diffusion equation has been solved for a binary ion-exchange system using a finite difference method^{1,2}. The inter-diffusion coefficient, D_{AB} , used includes activity gradient terms and is given by

$$D_{AB} = \frac{D_A^* D_B^* \left(C_A Z_A^2 \frac{\partial \ln a_B}{\partial \ln C_B} + C_B Z_B^2 \frac{\partial \ln a_A}{\partial \ln C_A} \right)}{D_A^* C_A Z_A^2 + D_B^* C_B Z_B^2} \quad (2)$$

D_A^* , D_B^* are the self-diffusion coefficients of the ions A and B in the exchanger phase whose valencies and activities are Z_A , Z_B and a_A , a_B , respectively.

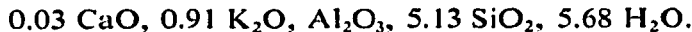
In this paper the theoretical rates of the forward and backward ion-exchange reactions



have been calculated and are compared with the corresponding experimental rates. Chabazite is a zeolite whose composition in the Na^+ form was



and in the K^+ form was



RESULTS AND DISCUSSION

To calculate theoretical rates it is necessary to determine the concentration dependencies of D_{Na}^* and D_{K}^* in the chabazite exchanger. The coefficients were determined using radiochemical techniques with ^{24}Na and ^{42}K as tracers³. The results obtained are shown in Fig. 1. This figure shows that there is a smooth decrease in both D_{Na} and D_{K}^* as the K^+ content of the exchanger decreases.

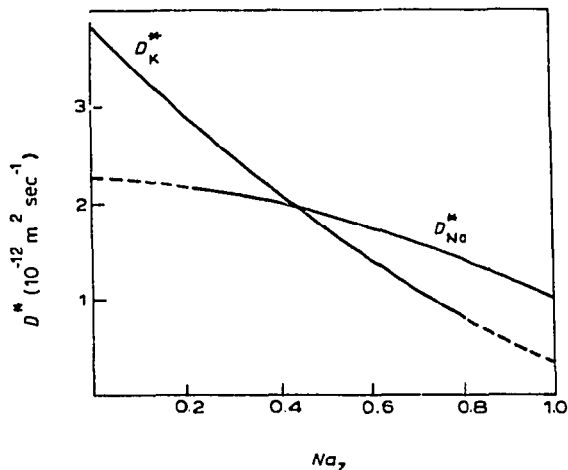


Fig. 1. Concentration dependence of self-diffusion coefficients.

The $(\partial \ln a)/(\partial \ln C)$ terms were obtained from a thermodynamic analysis⁴ of the equilibrium isotherm shown in Fig. 2a. This isotherm shows that K^+ is the preferred ion in the chabazite lattice. In Fig. 2b the plot of $\log_{10} K_C$ against K_Z is shown, where

$$K_C = \frac{K_Z \cdot m_{\text{NaCl}} \cdot \gamma_{\text{NaCl}}^2}{Na_Z \cdot m_{\text{KCl}} \cdot \gamma_{\text{KCl}}^2} \quad (3)$$

Na_Z and K_Z are the mole fractions of Na^+ and K^+ ions in the chabazite phase, respectively; m and γ represent the molality and mean molal activity coefficient of the subscripted electrolyte in the mixed solution phase.

In previous theoretical studies D_A and D_B have always been assumed constant equal to their values in the respective pure A and B forms of the exchanger. In one of these studies¹ it was found that the introduction of the $(\partial \ln a)/(\partial \ln C)$ terms reversed the predicted rates of exchange and produced kinetics which were in qualitative agreement with experiment.

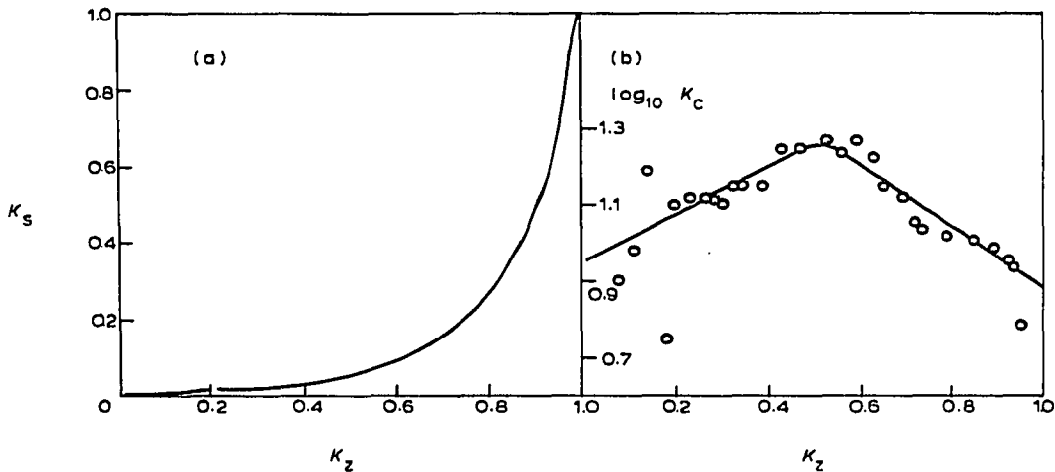


Fig. 2. (a) Na/K equilibrium exchange isotherm in chabazite (K_s and K_z represent the mole fraction of K^+ in the solution and zeolite phase, respectively). (b) Plot of $\log_{10} K_c$ against K_z (*i.e.* Kjelland plot).

In the present study, however, Fig. 3 shows that if the self-diffusion coefficients are held constant and only activity corrections applied, the theoretical rates are the reverse of the experimental rates.

When, however, allowance is made for the concentration dependence of the self-diffusion coefficients as well as the non-ideality of the exchanger, the theoretical rates are reversed and these rates now agree qualitatively with the experimental rates. The introduction of concentration-dependent self-diffusion coefficients into the theoretical equations is obviously of prime importance.

In Fig. 4, D_{AB} as a function of Na_z is shown for the case (a) where the self-diffusion coefficients are constant but the zeolite is thermodynamically non-ideal and (b) where these coefficients are concentration dependent in the non-ideal zeolite.

The exchange in the peripheral layers contributes principally to the overall exchange rate because, for spherical particles, the spherical shell of thickness dr and volume $4\pi r^2 \cdot dr$ is greatest at the periphery and contains, therefore, the largest fraction of the exchangeable cations. Secondly, in the exchange $A^+ \rightarrow B^+$ the outward passage of A^+ ions through the B^+ -rich outer layers is rate controlling.

When the exchange Na-chabazite \rightarrow K-chabazite is considered, the D_{AB} values in the rate-controlling peripheral layers are the high values shown in Fig. 4 around the 100% K^+ region. The rate-controlling D_{AB} values for the reverse exchange are the low values of the 100% Na^+ region. Thus, when concentration-dependent self-diffusion coefficients are used, the above argument indicates that the exchange

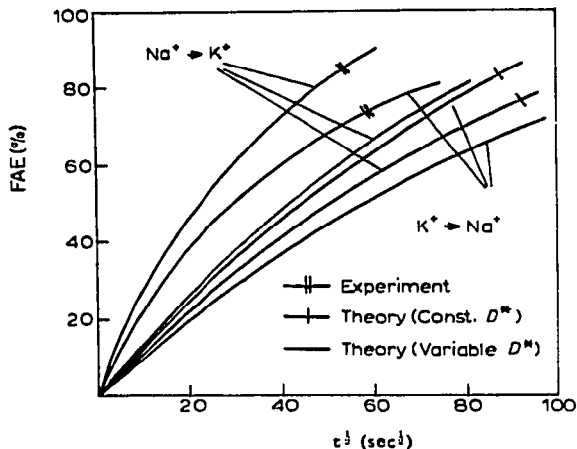


Fig. 3. Comparison of theoretical and experimental rates of forward and backward exchange. (Fractional attainment of equilibrium vs. $t^{1/2}$).

Na-chabazite \rightarrow K-chabazite should be the faster of the two. Similar analysis of the D_{AB} values for the situation where the self-diffusion coefficients are assumed constant indicates that the reverse exchange should now be the faster. This is also the situation for a thermodynamically ideal exchanger phase and constant self-diffusion coefficients, *i.e.* the conditions of the simple theory of Helfferich and Plesset⁵.

The smooth decrease in both D_{Na}^* and D_K^* as the K^+ content of the exchanger decreases as shown in Fig. 1 can be explained as follows. As Na^+ ions replace K^+ ions in the K-chabazite these Na^+ ions are forced to occupy sites least favourable to K^+ ions since the isotherm shows that K^+ is the preferred cation of the two in the chabazite lattice. Thus D_K^* decreases as this replacement proceeds since the K^+ ions remaining and participating in the diffusion process are occupying the most favourable

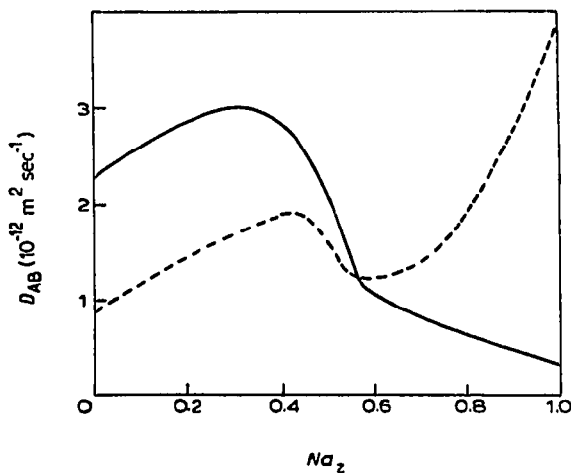


Fig. 4. D_{AB} as a function of concentration for constant (---) and concentration-dependent D_{AB} and D_K^* (—).

sites and require a larger and larger activation energy for their movement. The converse situation explains the increase in D_{Na}^* as Na^+ ions are replaced by K^+ ions.

It is interesting to note that similar behaviour to that found for Na^+/K^+ exchange in chabazite has been observed in all ion-exchange reactions in zeolites so far studied. In all cases the faster rate of exchange has always been obtained when the cation with the higher affinity for the lattice is diffusing into the exchanger from the solution phase. The rates are not dependent on whether $D_A^* > D_B^*$ or not (where D^* here refers to the homoionic form of the exchanger). The elementary theory of Helfferich and Plesset always predicts that the exchange $A \rightarrow B$ should be the faster if $D_A^* > D_B^*$. It would be interesting, therefore, to measure the concentration dependence of the self-diffusion coefficients of many more binary exchange systems to see if they behave similar to the Na/K-chabazite system.

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