

THE TRANSFERENCE NUMBERS OF THE COUNTER-IONS IN MONTMORILLONITE PASTE AS A FUNCTION OF WATER FILM THICKNESS AND ELECTROLYTE CONCENTRATION

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Abstract—The transference numbers of the counter ions in montmorillonite paste are determined as a function of the thickness of the water film (h) and of the diffuse double layer ($1/\kappa$).

From measured E.M.F. values of a cell with two liquid junction potentials (C_{KCl}^I solution-paste- C_{KCl}^{II} solution) and by applying the Henderson equation, the transference numbers t_+ were calculated. It is shown that the transference numbers of the counter-ions, $t_+ \rightarrow 1$ if $h\kappa \rightarrow 0$.

INTRODUCTION

IT IS known (Michaelis *et al.*, 1972) that the transference numbers of the counter-ions are greater and of the co-ions are less in membrane pores than in the surrounding bulk solution. The first study of the dependence of the transference numbers of ions in charged membranes on the size of the membrane pores was that of Manegold and Solf (1931), whereas more detailed studies were those of Zhukov (1943) and his collaborators (Grigorov and Prikhod'ko, 1949). These latter workers established that the transference numbers of K^+ in $10^{-2}N$ solution depend on the pore size (radius) such that transference numbers of 0.8, 0.7, 0.62, 0.58, 0.56 correspond to pore radius of 15, 30, 60,

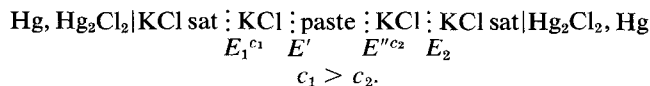
the water film on the surface and $1/\kappa =$ thickness of the diffuse double layer.

The transference number of the counter-ion in gel (or paste) can not be equal exactly to 1, because of hydrolysis and the mobility of the particles.

This note contains a report of our study of the dependence of t_+ of the counter-ion on the concentration of KCl solution and the thickness (h) of water film on the surface.

THEORY

The transference numbers of the monovalent counter-ions of montmorillonite paste (Li^+ , Na^+ , and K^+) were calculated from EMF measurements of the following cell with two liquid junctions:



150 and 240 Å, respectively (interpolated values from the data given by Zhukov and Grigorov and Prikhod'ko for t_{Cl^-}). For membranes it is possible to assume that $t_{K^+} = 1 - t_{\text{Cl}^-}$.

Zhukov and Grigorov observed only low values of t_{K^+} . That is the t_{K^+} values never increased to 1 although their membranes possessed pores < 30 Å, the thickness of the diffuse double layer ($1/\kappa$) in the $10^{-2}N$ KCl solutions used by them.

Due to the surplus of the counter-ions in the double layer above the bulk concentration (Overbeek, 1952) the current in the double layer is principally conducted by the counter-ions. Therefore, the transference number of the counter-ions must $\rightarrow 1$ at $h < 1/\kappa$, where: $h =$ thickness of

The potential of this cell is given by the sum of all liquid junction potentials:

$$E = E_1 + E' + E'' + E_2. \quad (1)$$

But, since the liquid junction potentials E_1 and E_2 are negligible (< 0.1 mV), the potential of the cell is given practically by the sum of the two other liquid potentials:

$$E = E' + E''. \quad (2)$$

To avoid the change of concentration of KCl in the chambers due to the escape of KCl from calomel electrodes, the electrodes were submerged

in funnels which contained the same concentrations of KCl as the chambers.

The exact thermodynamic treatment of this cell is not yet known. However, consider replacement of the paste in the above cell by a solution. If the conductivity of such a solution is many times greater than the conductivity of the KCl solutions (c' or c''), the calculated transference numbers of ions of the solution in question will coincide with the actual values (Grazán *et al.*, 1972). This condition (i.e. conductivity difference) is fulfilled for obtaining the t_+ values of the counter-ions for pastes. Notwithstanding the lack of the theory of this cell, it has been used by many authors; for example, Schlumberger *et al.* (1934); Wyllie (1955); Tschapek (1962) and Subrahmanyam and Lakshminarayanaiah (1962).

An approximate treatment of this cell is possible by applying the known Henderson (1907) equation for liquid junction potential. To integrate the mixture boundary potential, Henderson postulated that "the junction consists of a continuous series of solutions produced by mixing the two solutions initially brought into contact" (MacInnes, 1961). After Henderson, the mixtures are free from the effects of diffusion, but "since diffusion of one solution into the other is inevitable, however, this type of boundary is probably unstable" (Glasstone, 1962).

$$E_j = \frac{RT}{F} \times \frac{\sum_n (u_i/z_i)(c'_i - c''_i)}{\sum_n u_i(c'_i - c''_i)} \times \ln \frac{\sum_n c'_i u'_i}{\sum_n c''_i u''_i} \quad (3)$$

where: u_i = mobility of the ion i ;
 \sum_n = summation of all terms;
 c' and c'' = concentrations in equivalents;
 z_i = valencies (retaining the signs).

Let us suppose that between two dilute solutions of different concentrations of KCl (i.e. 1×10^{-4} and 2×10^{-4} N) is a K^+ -montmorillonite paste. The liquid junction potentials E' and E'' after Henderson would be as follows:

$$E'_j = \frac{RT}{F} \frac{\left(u''' - \frac{v'''}{z}\right)c''' - (u' - v')c'}{(u''' + v''')c''' - (u' + v')c'} \times \ln \frac{(u' + v')c'}{(u''' + v''')c'''} \quad (4)$$

$$E''_j = \frac{RT}{F} \frac{\left(u''' - \frac{v'''}{z}\right)c'''}{(u' + v'')c'' - (u''' + v''')c'''} \times \ln \frac{(u''' + v''')c'''}{(u' + v'')c''}$$

where: u' , u'' and u''' = mobilities of K^+ of KCl (1), KCl (2) and clay particles, respectively.

v' , v'' and v''' = mobilities of Cl^- of KCl (1), KCl (2) and clay particles, respectively.

c' , c'' and c''' = concentrations of KCl (1), KCl (2) and of exchangeable cations or particles, respectively

z = valence of particles.

At $cc''' \gg c''$ or c' the $(u' - v')c'$, $(u' + v')c'$, $(u'' - v'')c''$ and $(u'' + v'')c''$ present insignificant values in comparison with $(u''' - v''')c'''$ and $(u''' + v''')c'''$. Therefore, they can be eliminated and we obtain:

$$E = E'_j + E''_j = \frac{RT}{F} \frac{\left(u''' - \frac{v'''}{z}\right)}{(u''' + v''')} \ln \frac{(u' + v')c'}{(u' + v'')c''} \quad (5)$$

When c' is not very different from c'' , then the mobilities of K^+ and of Cl^- are equal in both KCl solutions and we can also eliminate $(u'' + v'')$ and $(u' + v')$. After substitution of t_+ for $u'''/(u''' + v''')$ and t_- for $v'''/(u''' + v''')$ the equation becomes:

$$-E = \frac{RT}{F} (2t_+ - 1) \ln \frac{c_{KCl(2)}}{c_{KCl(1)}} \quad (6)$$

The value of $(2t_+ - 1)$ is derived from the assumption that:

$$t_{K^+} + t_{p^-} = 1$$

where: t_{K^+} = transference number of counter-ions;
 t_{p^-} = transference number of particles.

At $t_+ = 1$ ($t_{p^-} = 0$), the paste acts as a perfect membrane and the cell becomes without transport:

$$-E_{\max} = \frac{RT}{F} \ln \frac{a_{KCl(2)}}{a_{KCl(1)}} \quad (7)$$

From the relation $E/E_{\max} = (2t_+ - 1)$ (equations 6 and 7) is found the values of t_+ and t_- :

$$t_+ = 0.5 + E/2E_{\max} \quad (8)$$

$$t_- = 0.5 - E/2E_{\max} \quad (9)$$

EXPERIMENTAL

The monocationic montmorillonite gels were obtained by five successive treatments of Volclay bentonite with 0.1N solutions of the corresponding chlorides. By using the Sharples supercentrifuge the free electrolytes and coarse particles were eliminated. The paste with a given concentration was used as a membrane (thickness 5-7 mm) between two KCl solutions of different concentration. The EMF of the cell was measured with a Keithley 662 differential voltmeter which permits infinite impedance at null for potentiometric measurements from 0 to 500V. The theoretical calculated value of 750m².g⁻¹ is used for the specific surface area (*A*) to obtain values of the water film thickness (*h*). The water content (*W*) in the paste was determined by drying at 105°C after each experiment.

RESULTS AND DISCUSSION

From the specific surface and the water content it is easy to calculate the thickness of the film:

$$\frac{w}{Ad} = h$$

where: *d* = density of water film (≈ 1).

The value of *h* so obtained is a minimum value for a given water content. The effective surface area was probably less than the theoretical and *h* would be greater than the calculated value.

In 10⁻²N KCl solution, exchange of K⁺ for Li⁺ and Na⁺ probably takes place. Therefore, the determined transference numbers of these latter cations correspond to their mixtures with K⁺. In more dilute KCl solutions (10⁻³ and 10⁻⁴N) the extent of such exchange is considered insignificant.

For negatively charged montmorillonite paste we can put:

$$\lim_{t_+ \rightarrow 1} E = E_{\max} \tag{11}$$

and

$$\lim_{n_f/n_c \rightarrow 0} t_+ = 1 \tag{12}$$

where: *n_f* = number of the free ions in paste per 1 cm² of surface;

n_c = number of the counter-ions (≈ 10¹⁴ ions cm⁻²).

The *n_f/n_c* depends on the ratio *h/1/κ*: if *h* > 1/κ, then *n_f/n_c* > 0 and *t₊* → 1, whereas at *h* < 1/κ the *n_f/n_c* → 0 and also *t₊* → 1.

Equation (12) therefore can be presented as follows:

$$\lim_{h\kappa \rightarrow 0} t_+ = 1. \tag{13}$$

The following two numerical examples will facili-

tate understanding of the above discussion. Let us suppose that K⁺-montmorillonite paste (20 per cent) is used as a membrane (diaphragm) between two KCl solutions of different concentration:

- (a) 1 × 10⁻⁴N KCl: paste: 2 × 10⁻⁴N KCl
- (b) 1 × 10⁻¹N KCl: paste: 2 × 10⁻¹N KCl

The film thickness is 5.3 × 10⁻⁷ cm i.e.

$$h = \frac{80}{20 \times 7.5 \times 10^6} = 5.3 \times 10^{-7} \text{ cm.}$$

For case (a) 1/κ = 3 × 10⁻⁶ cm; κ = 0.33 × 10⁶ cm⁻¹
hκ = 0.16; log 0.16 = -0.8.

Due to the fact that *h* < 1/κ, no diffusion of KCl will take place. Therefore, current will be transported only (not taking into consideration transport by particles) by the K⁺ counter-ions, i.e. *t_{K+}* → 1.

For case (b) 1/κ = 1 × 10⁻⁷ cm; κ = 10⁷ cm⁻¹
hκ = 5.3; log 5.3 = 0.72.

Due to the fact that *h* > 1/κ, diffusion of KCl will take place. Therefore, current will be transported by the K⁺ counter-ions and by Cl⁻, i.e. 0.5 < *t_{K+}* < 1 (0.5 is its value in bulk solution). In general, for the relation between *hκ* and *t_{K+}* we have:

$$h\kappa > 1 (\log h\kappa > 0); 0.5 < t_{K^+} < 1$$

$$h\kappa < 1 (\log h\kappa < 0); t_K \rightarrow 1.$$

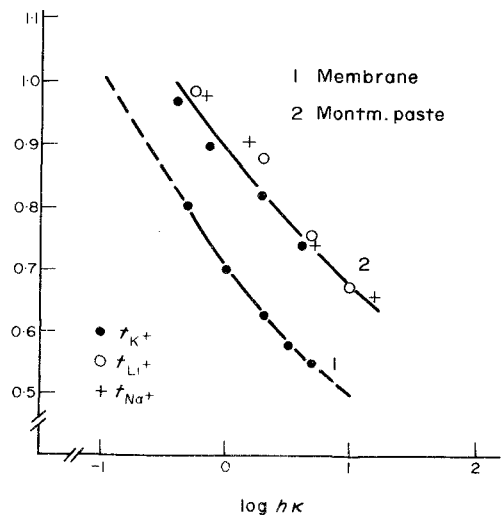


Fig. 1. The *t₊* curves for montmorillonite paste (1) and for membrane (2), (after Zhukov and Grigorov data). Ordinate: *t₊* = transference number of the counter-ions. Abscissa: log *hκ*, where *h* = thickness of water film and 1/κ = thickness of the diffuse double layer.

Table 1. The observed E and calculated t_+ , h and $1/\kappa$ values

KCl concentrations $C''(N)C'$	$1/\kappa \approx 3/\sqrt{I}$ (Å)	$h = W/Ad$ (Å)	E (observed) $h\kappa$ (mV)		t_+ calculated	E_{\max} for $C'f'/C''f''$ at 25°C (mV)	Note
K⁺-montmorillonite paste							
1. 10 ⁻⁴ -2. 10 ⁻⁴	305	69	0.2	16.1	0.966	17.28	I = ionic strength W = water content A = surface area $t_+ = 0.5 + 0.5E/E_{\max}$ $d \approx 1$ f = activity coefficient c = concentration in N
1. 10 ⁻³ -2. 10 ⁻³	96	65	0.7	13.6	0.897	17.11	
1. 10 ⁻² -2. 10 ⁻²	30	55	1.8	10.6	0.820	16.54	
1. 10 ⁻¹ -2. 10 ⁻¹	10	43	4.3	7.5	0.739	15.70	
Na⁺-montmorillonite paste							
1. 10 ⁻⁴ -2. 10 ⁻⁴	305	188	0.6	17.0	0.992	17.28	
1. 10 ⁻³ -2. 10 ⁻³	96	160	1.7	5.1	0.915	17.11	
1. 10 ⁻² -2. 10 ⁻²	30	148	4.9	8.1	0.745	16.54	
1. 10 ⁻¹ -2. 10 ⁻¹	10	148	14.8	14.2	0.662	15.70	
Li⁺-montmorillonite paste							
1. 10 ⁻⁴ -2. 10 ⁻⁴	305	220	0.7	17.1	0.995	17.28	
1. 10 ⁻³ -2. 10 ⁻³	96	192	2	12.9	0.877	17.11	
1. 10 ⁻² -2. 10 ⁻²	30	160	5.3	7.8	0.736	16.54	
1. 10 ⁻¹ -2. 10 ⁻¹	10	120	12.0	5.8	0.685	15.70	

To compare our values of t_+ with that of Zhukov and Grigorov, the pore radius of their membrane was taken as equivalent to the film thickness (h). In Fig. 1 the t_+ values for a montmorillonite paste and an organic membrane are presented as a function of $\log h\kappa$.

As may be seen, $t_+ \rightarrow 1$ when $\log h\kappa < 0$, i.e. when $1/\kappa > h$.

Zhukov and Grigorov obtained lower t_+ values because of their use of more concentrated KCl solutions (10⁻²N) than ours (10⁻⁴N) and probably because of the low charge density of the membrane. The main experimental values are presented in Table 1.

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Résumé— Les nombres de transfert des ions compensateurs dans des pâtes de montmorillonite ont été déterminés en fonction de l'épaisseur du film d'eau (h) et de celle de la double couche diffuse ($1/\kappa$).

A partir des valeurs de la F E M mesurée dans une cellule comportant deux potentiels de jonction liquide (C'/C_{KCl} solution-pâte C'' solution) et en appliquant l'équation d'Henderson, on a calculé les nombres de transfert t_+ . On montre que les nombres de transfert des cations compensateurs t_+ tendent vers 1 si $h\kappa$ tend vers 0.

Kurzreferat— Die Überführungszahlen der Gegenionen in Montmorillonitpaste wurden als Funktion der Dicke der Wasserfilme (h) und der diffusen Doppelschicht ($1/\kappa$) bestimmt.

Aus den gemessenen E.M.K.-Werten einer Zelle mit zwei Grenzflächenpotentialen (C'_{KCl} -Lösung-

Paste- C_{KCl}'' -Lösung) und durch Anwendung der Henderson-Gleichung wurden die Überföhrungszahlen t_+ berechnet. Es wird gezeigt, daß für $h\kappa \rightarrow 0$ die Überföhrungszahlen der Gegenionen gegen 1 gehen ($t_+ \rightarrow 1$).

Резюме — Определяются числа переноса контрионов в монтмориллонитовой пасте в качестве функции толщины пленки воды (h) и диффузного двойного слоя ($1/\kappa$).

Из вымеренных значений Е.М.Ф. ячейки с двумя потенциалами жидкостной границы (C_{KCl} раствор-паста- C_{KCl}' раствор) и посредством применения уравнения Хендерсона были высчитаны числа переноса t_+ . Нашли, что числа переноса контрионов следующие: $t_+ \rightarrow 1$, если $h\kappa \rightarrow 0$.