Proc. Indian Acad. Sci., Vol. 87 A (Chemical Sciences-6). No. 12, December 1978, pp. 435-441,

Thermo-osmosis of water through composite clay membranes—The parallel arrangement

R C SRIVASTAVA, M GEORGE ABRAHAM and ABHAY K JAIN
Chemistry Department, Birla Institute of Technology & Science, Pilani 333 031

MS received 20 May 1978

Abstract. Thermo-osmosis of water through a composite clay membrane consisting of kaolinite and crysotile clay membrane elements in a parallel array has been studied. Water flux in presence of both pressure difference and temperature difference for the parallel composite clay membrane and also for the constituent clay membrane elements has been shown to be adequately described by the usual linear and homogeneous phenomenological equation. The combination rules for the phenomenological coefficients L_{11} and L_{12}, representing hydraulic permeability and thermo-osmotic permeability, as deduced from the theory of Kedem and Katchalsky, have been found to be valid. The validity of the combination rules for L_{11} and L_{12}, in the case of parallel composite membrane has yielded a relationship between the heat of transport of water for the parallel composite membrane and the heat of transport of water for the constituent clay membrane elements.

Keywords. Thermo-osmosis; composite-clay membranes.

1. Introduction

The non-equilibrium thermodynamic theory for the permeability of composite membranes developed by Kedem and Katchalsky (1963 a, b, c) was primarily intended for biological membranes. To what extent can this theory be helpful in analysing the data on flow through composite porous media that one comes across in geosystems e.g. porous soils or rocks having layered structure, has been explored recently by Srivastava and Jain (1975 a, b) who have studied the electro-osmotic permeability of water through composite clay membranes consisting of parallel and series arrangements of two different clay membrane elements.

In the present paper the studies have been extended to the case of thermo-osmosis of water through a composite clay membrane consisting of kaolinite and crysotile clay membrane elements arranged in a parallel array. The hydraulic permeability and the thermo-osmotic permeability measurements for the parallel composite clay membrane and also for its constituent clay membrane elements have been made. The data have been utilised to test the validity of the combination rules as deduced by Kedem and Katchalsky (1963 b) connecting the various phenomenological coefficients for the total parallel composite clay membrane and the corresponding phenomenological coefficients for its constituent clay membrane elements.

2. Phenomenological relations for thermo-osmosis

When two chambers containing a single fluid (say water) are separated by a porous barrier, the pore size of which is comparable to the mean free path of the permeating fluid and difference of temperature is maintained across the porous plug, migration of fluid occurs and a pressure difference $\triangle P$ sets up in the steady state corresponding to the temperature difference $\triangle T$. For such a situation the equation for entropy production σ can be written as (de Groot 1956).

$$\sigma = J_w\left(-\frac{v\triangle P}{T}\right) + J_q\left(-\frac{\triangle T}{T^2}\right), \quad (1)$$

where J_w and J_q represent the mass flow of water and the heat flow respectively, v is the specific volume of water. The linear phenomenological relations for the simultaneous transport of water and heat across the porous plug can be written as

$$J_w = L_{11}\left(-\frac{v\triangle P}{T}\right) + L_{12}\left(-\frac{\triangle T}{T^2}\right), \quad (2)$$

$$J_q = L_{21}\left(-\frac{v\triangle P}{T}\right) + L_{22}\left(-\frac{\triangle T}{T^2}\right). \quad (3)$$

In (2) and (3) L_{ik} are the phenomenological coefficients and the equality

$$L_{12} = L_{21}, \quad (4)$$

holds among them on account of Onsager's reciprocity theorem. From (2) and (3) it follows that

$$(J_q | J_w)_{\triangle T = 0} = \frac{L_{21}}{L_{11}} = Q^*. \quad (5)$$

The quantity Q^* is known as heat of transport and is defined as the heat transported per unit mass transport when there is no temperature difference across the porous plug. In the steady state when J_w=0, the equation

$$\left(\frac{\triangle P}{\triangle T}\right)_{J_{w=0}} = -\frac{L_{12}}{L_{11}vT}, \quad (6)$$

for thermo-osmotic pressure difference can be deduced from (2). The relationship

$$\left(\frac{\triangle P}{\triangle T}\right)_{J_{w=0}} = -\frac{Q^*}{vT}, \quad (7)$$

between thermo-osmotic pressure difference and the heat of transport follows as a consequence of Onsagaer's reciprocal relation (4). If in the given system pressure is not allowed to develop the equation

$$(-J_w)_{\triangle P = 0} = \frac{L_{12}}{T^2}\triangle T, \quad (8)$$

for thermo-osmotic velocity can be deduced from eq. (2) by imposing the restriction $\triangle P$=0.

3. Experimental

3.1. *Apparatus*

The thermo-osmotic cell used in the present studies has been depicted in figure 1. It consisted of six parts. Parts I, II, III and IV consisted individually of glass tubes A_1A_2, B_1B_2, C_1C_2 and D_1D_2 of length 12 cm and diameter 1 cm. Each of the tubes A_1A_2, B_1B_2, C_1C_2 and D_1D_2 contained an outer jacket, through which water at desired temperature could be circulated, and each of them was fitted with a B_{14} socket at one end and a sliding standard ground glass joints at the other. Parts I and III or parts II and IV could be joined with or detached from each other through these sliding ground glass joints. Part V of the apparatus consisted of a glass tube bent twice at right angles with B_{14} cones at the ends E_1 and E_2. The tube G_1G_2 provided in part V could be connected to the pressure head. Part VI of the apparatus was also a glass tube bent twice at right angles with B_{14} cones at the ends F_1 and F_2 and a capillary L_1L_2 of length 20 cm and diameter 0·232 cm. The water flux was measured by noting the rate of advancement of water miniscus in the capillary L_1L_2. The purpose of the two stopcocks T_1 and T_2 in part VI of the apparatus was to connect or disconnect the two halves of the thermo-osmotic cell (i.e. parts (I + III) and (II + IV) with each other as and when required. The purpose of the other stopcocks T_3, T_4 and T_5 was simply to remove the air bubbles if any while filling the apparatus with water.

3.2. *Procedure*

After a thorough cleaning of the apparatus, compressed kaolinite and crysotile clay plugs were placed at the ends A_2 and B_2 of the tubes A_1A_2 and B_1B_2. Part I was then joined with part III and part II with part IV through the sliding ground glass joints. These two portions i.e. parts (I+III) and (II+IV) were then joined together through

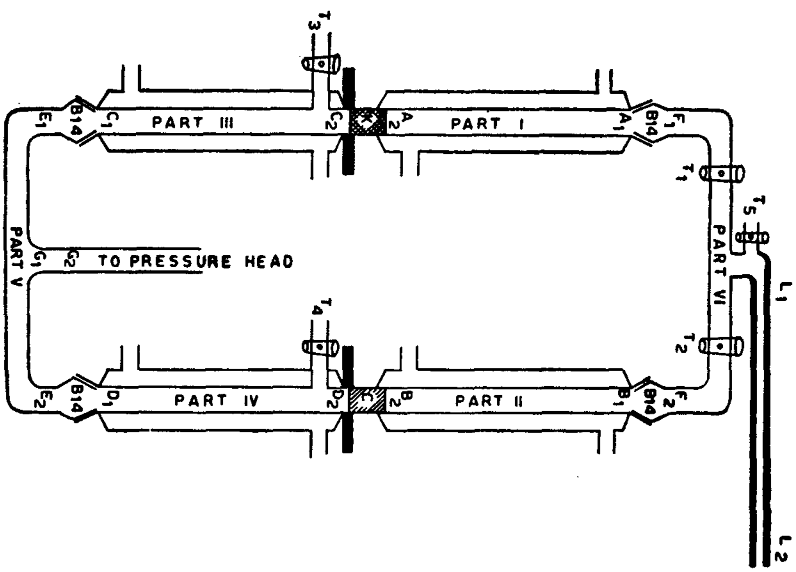

Figure 1. Thermo-osmotic cell

parts V and VI. The arrangement thus obtained (figure 1) was used for measurements on the parallel composite membrane. The thermo-osmotic cell (figure 1) was then filled with double distilled water and was allowed to stand for several days so that the clay plugs were completely wet with water. In order to test whether the clay plugs were completely saturated with water or not hydraulic permeability measurements were made. When reproducible values were obtained, it was concluded that the clay plugs were completely wet with water.

For the measurements of hydraulic permeabilities through kaolinite crysotile and the parallel composite clay membrane systems known pressure differences were applied across the clay plugs by connecting the tube G_1G_2 to a pressure head and the movement of water in the capillary L_1L_2 was noted with time using a cathetometer with a least count of 0·001 cm and a stop watch reading upto 0·1 seconds.

For the measurement of thermo-osmotic velocities, temperature difference $\triangle T$ across the clay plugs was created by circulating water at different temperatures in the outer jackets of parts I, II, III and IV of the apparatus and water flux induced by the temperature difference thus created were measured by noting the movement of water miniscus in the capillary L_1L_2. In all measurements of thermo-osmotic velocity the condition $\triangle P=0$ was enforced by adjusting the pressure head. The temperature differences in the measurements of thermo-osmotic velocity were so adjusted that the mean temperature did not vary. The mean temperature was kept constant at 45°C. The hydraulic permeability measurements were also made at 45°C. For this the entire thermo-osmotic cell was placed in a thermostat set at 45°C.

It may be pointed out that for the measurement of both hydraulic permeability and thermo-osmotic velocity through kaolinite plug the stop cock T_2 was closed and T_1 was kept open. Similarly for the measurements through crysotile plug the stopcock T_1 was closed and T_2 was kept open whereas for the measurements through the parallel composite clay membrane both stopcocks T_1 and T_2 were kept open. The stopcocks T_3, T_4 and T_5 were kept closed throughout all measurements.

4. Results and discussion

The data on hydraulic permeability and thermo-osmotic velocity for the parallel composite clay membrane, and its constituent clay membrane elements are plotted in figures 2 and 3. It may be mentioned that the thermo-osmotic movement of water as observed in the present studies was always from warmer to the colder side. The straight line plots in figures 2 and 3 confirm the validity of the linear phenomenological equation (2) for the parallel composite-membrane and also for its constituent clay membrane elements. The values of the phenomenological coefficients L_{11} and L_{12} obtained from the slope of the straight line plots shown in figures 2 and 3, for the various systems studied are recorded in table 1.

4.1. *The parallel composite membrane*

The treatment of Kedem and Katchalsky (1963 b) for the parallel composite membrane assumes that linear phenomenological relations between fluxes and forces are valid for the parallel composite membrane and also for the constituent membrane elements. It is also assumed that flows are normal to the membrane surface, parallel

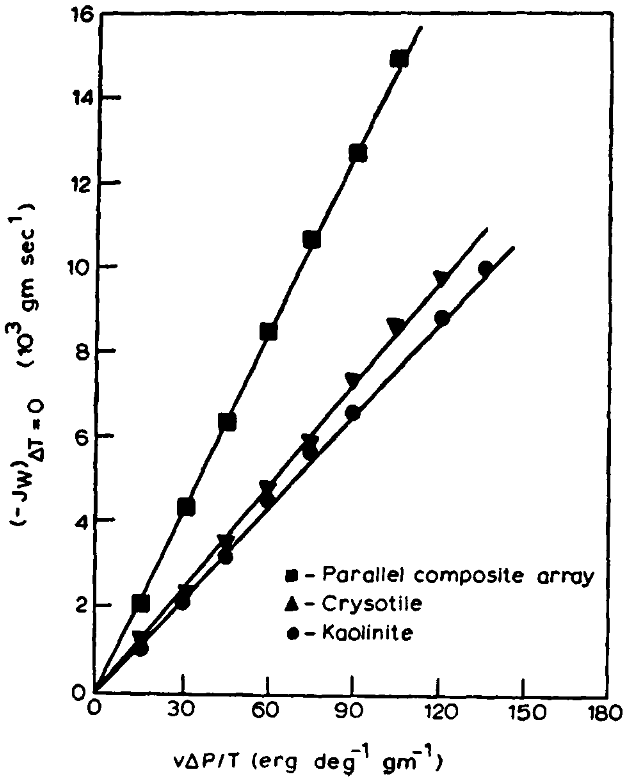

Figure 2. Hydraulic permeability data

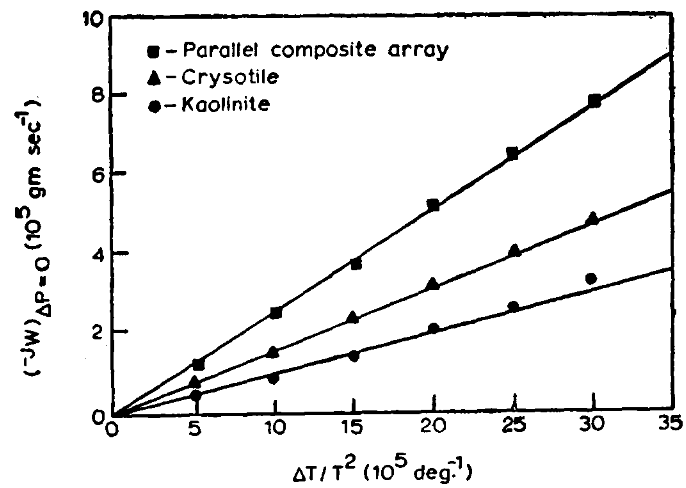

Figure 3. Thermo-osmotic velocity data

Table 1. Values of the phenomenological coefficients

	Kaolinite (1)	Crysotile (2)	Composite parallel array (Experimental)
$L_{11} \times 10^5$ g^2 deg erg^{-1} sec^{-1}	7·163 ± 0·104	8·092 ± 0·122	15·026 ± 0·437
$L_{12} \times 10$ g deg sec^{-1}	1·010 ± 0·022	1·546 ± 0·020	2·550 ± 0·045

to the x-axis and independent of x. The forces considered are differences of the potentials acting across the membrane. Since the same compartment maintains contact with all elements on each side of the membrane, the same force which acts on the parallel composite membrane also operates on the constituent membrane elements. This implies that the forces are perpendicular to the membrane surface and no lateral forces creating internal circulation need be considered. Thus the total flow through the parallel composite membrane is assumed to be sum of the total flows through the constituent membrane elements. This in the present case would mean

$$(J_w)^p_{\Delta T=0} = (J_w)^k_{\Delta T=0} + (J_w)^c_{\Delta T=0}, \tag{9}$$

$$(J_w)^p_{\Delta P=0} = (J_w)^k_{\Delta P=0} + (J_w)^c_{\Delta P=0}, \tag{10}$$

where the superscripts p, k and c represent the parallel composite membrane, kaolinite clay membrane element and crysotile clay membrane element. In view of the validity of the linear phenomenological equation (2) for the parallel composite clay membrane and its constituent clay membrane elements (figures 2 and 3) and the fact that the same force which acts across the parallel composite membrane also acts across the constituent clay membrane elements, (9) and (10) would in turn imply

$$L^p_{11} = L^k_{11} + L^c_{11}, \tag{11}$$

and
$$L^p_{12} = L^k_{12} + L^c_{12}. \tag{12}$$

Values of the phenomenological coefficients given in table 1 confirm the validity of the combination rules given by (11) and (12). In view of the validity of the combination rules given by (11) and (12) the thermo-osmotic pressure difference for the composite parallel membrane can be shown to be related to the thermo-osmotic pressure differences for the constituent clay membrane elements by the equation

$$\left(\frac{\Delta P}{\Delta T}\right)^p_{J_w=0} = \left(\frac{\Delta P}{\Delta T}\right)^k_{J_w=0}\left(\frac{L^k_{11}}{L^k_{11}+L^c_{11}}\right) + \left(\frac{\Delta P}{\Delta T}\right)^c_{J_w=0}\left(\frac{L^c_{11}}{L^k_{11}+L^c_{11}}\right). \tag{13}$$

Equation (13) on account of (7) can be rewritten as

$$(Q^*)^p = (Q^*)^k\left(\frac{L^k_{11}}{L^k_{11}+L^c_{11}}\right) + (Q^*)^c\left(\frac{L^c_{11}}{L^k_{11}+L^c_{11}}\right), \tag{14}$$

which gives a relationship between the heat of transport for composite parallel clay membrane and the constituent clay membrane elements.

Acknowledgement

Financial support received from CSIR, New Delhi is gratefully acknowledged.

References

de Groot S R, 1956 *Thermodynamics of irreversible processes* (Amsterdam; North Holland).
Kedem O and Katchalsky A 1963a *Trans. Faraday Soc.* **59** 1918
Kedem O and Katchalsky A 1963b *Trans. Faraday Soc.* **59** 1931
Kedem O and Katchalsky A 1963c *Trans. Faraday Soc.* **59** 1941
Srivastava R C and Jain A K 1975a *J. Hydrol.* **25** 307
Srivastava R C and Jain A K 1975b *J. Hydrol.* **25** 325