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# Thermo-osmosis in Membrane Systems: A Review

DOI 10.1515/jnet-2016-0088

Received December 22, 2016; revised February 15, 2017; accepted March 22, 2017

**Abstract:** We give a first review of experimental results for a phenomenon little explored in the literature, namely thermal osmosis or thermo-osmosis. Such systems are now getting increased attention because of their ability to use waste heat for separation purposes. We show that this volume transport of a solution or a pure liquid caused by a temperature difference across a membrane can be understood as a property of the membrane system, i. e. the membrane with its adjacent solutions. We present experimental values found in the literature of thermo-osmotic coefficients of neutral and hydrophobic as well as charged and hydrophilic membranes, with water and other permeant fluids as well as electrolyte solutions. We propose that the coefficient can be qualitatively explained by a formula that contains the entropy of adsorption of permeant into the membrane, the hydraulic permeability, and a factor that depends on the interface resistance to heat transfer. A variation in the entropy of adsorption with hydrophobic/hydrophilic membranes and structure breaking/structure making cations could then explain the sign of the permeant flux. Systematic experiments in the field are lacking and we propose an experimental program to mend this situation.

**Keywords:** thermo-osmosis, membrane structure, electrolyte structure, entropy of adsorption

## 1 Introduction

The renewed interest in thermo-osmosis and its technical importance has motivated us to give this review of experimental results in the field. The aim is to better understand the underlying mechanisms giving rise to its magnitude and sign, and to foster a development of interesting new technological applications. For instance, thermo-osmosis is considered important for fuel cell operation [1–4], but also in other applications where water management is important [5]. The recovery of water from organic waste-water by thermal osmosis was analysed [6], and it was concluded that thermo-osmosis is less costly than other processes. Equally interesting, the MemPower Concept of Kuipers et al. [7, 8] can make use of thermo-osmosis, not only to clean contaminated water but also to generate power, through build-up of a thermo-osmotic pressure. In addition, Bregulla et al. [9] have suggested that a thermo-osmotic flux could be relevant for particle motion through hot nanostructures, and be harnessed for microfluidic applications.

A review on this class of phenomena has, to the best of our knowledge not yet been done. The present review may therefore be timely. We aim to bring to focus experimental studies reported in the literature, and seek out the most important properties that govern thermo-osmosis in membranes, its direction and magnitude. As explained above, the understanding of these relations is crucial for water management of non-isothermal membrane systems and may enhance a development that takes advantage of the earth's large resources of waste heat.

### 1.1 The pioneer studies

The first works about thermo-osmosis date back to the early twentieth century. Lippmann in 1907 and Aubert in 1912 [10, 11] observed the passage of water through membranes of gelatine, pig's-bladder, etc.,

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under the influence of a temperature gradient. The flow depended on the presence of water-soluble electrolytes in the membrane, and they explained the process to be of electrical origin. In 1952 Denbigh and Raumann [12] published a theoretical study of thermal osmosis of gas through a membrane. They defined thermo-osmosis as fluid diffusion through a membrane under the influence of a temperature gradient. There was no experimental evidence yet to verify the existence of thermo-osmosis of liquids in membranes, although various investigations had been done to examine the possible thermal migration of water and other liquids through porous materials [13].

The pioneer papers suggested that non-isothermal transport was only possible with electrolyte solutions and charged membranes. In 1932, Carr and Sollner studied non-isothermal systems where the same outer solutions were kept at different temperatures and reported that the thermo-osmotic flow was proportional to the temperature difference. Their experimental work was published much later, in 1962 [14], and analysed by Kobakate and Fujita [15]. The proportionality factor depended strongly on the concentration of solute in the outer solution. Carr and Sollner stated that any thermo-osmotic flow of electrolyte solutions across the neutral cellophane membranes was undetectable. This was also the conclusion of Hutchinson et al. [16] after a careful analysis of the pioneering experiments of Derjaguin and Sidorenko [17]. Haase et al. [18–21] obtained, however, marked thermo-osmotic effects in experiments with cellophane membranes, demonstrating that thermo-osmosis existed, also with non-electrolytes in neutral membranes.

Although the first papers on the subject explained that thermal osmosis existed only with suitable dense membranes, several later contributions demonstrated that thermal osmosis can also occur in porous walls. We shall naturally use the term to cover the wider class of phenomena; all volume transport caused by a thermal driving force across a membrane.

## 1.2 The field becomes established

After the early works, extensive, but not very systematic studies were done [22–33]. A comparison of published results of a large number of authors, the majority of whom employed cellophane or cellulose acetate membranes, reveals qualitative and quantitative differences between the transport coefficients. Inspection of the literature also reveals contradictory results for analogous membranes. Some differences were explained by Bellucci [34] using the concept of thermal polarization, first suggested by Vink and Chisthi [28], and used implicitly by Dariel and Kedem [25]. Other discrepancies were resolved by Fernández-Pineda and Vázquez-González [35]. The temperature dependence of the membrane absorption enthalpy and of the phenomenological coefficient were important factors. During the 1980s and 1990s, many studies were carried out on ion-exchange membranes and hydrophobic membranes with electrolyte solutions as permeants [36–51].

## 1.3 State-of-the art

Thermo-osmosis is now an accepted membrane phenomenon. Over the last years, there has been a resurgence in the interest of thermo-osmosis, for instance, as mentioned, in relation to polymer electrolyte fuel cells (PEMFC) [1–4, 52]. Usually, fuel cells operate under isothermal conditions. Nevertheless, temperature gradients can arise during cell operation [53], affecting both water and thermal management; critical factors for the overall cell performance. These studies have revealed that the presence of a temperature difference across the cell can cause a significant flow of water through the membrane-electrode-assembly in the direction towards the colder side. Despite a consensus on the existence of thermo-osmosis, one can find experimental disagreement in the literature on the direction and magnitude of thermo-osmotic flux for different fuel cell materials. The need to consider the through-plane temperature profiles in water management design and operation in PEMFCs [3] and the need to understand the

origin of the phenomenon become then imminent. In non-isothermal direct alcohol fuel cells, a thermo-osmotic flux of alcohol could, for instance, promote fuel crossover, which is detrimental [4]. The aim is thus that the present review can contribute to better experiments and understanding.

The outline of the review is as follows. After some general comments (Section 2) we discuss transport of pure fluids through neutral or weakly charged membranes (Section 3). A similar analysis is next be carried out for electrolyte transport (Section 4). Experiments will be explained using non-equilibrium thermodynamics [54, 55]. The theory will enable us to point out the factors that govern the transport. They are hydraulic permeability, the adsorption entropy of the permeant, and the surface thermal resistance.

## 2 The system

An overall comment on the origin of thermo-osmosis is in order. According to the second law of thermodynamics, a transport process is spontaneous, if it leads to an increase in the entropy of the system. Clearly, by system in this context, is meant *the membrane plus the permeant solutions*. The system can be denoted

$$(T) \text{ solution} | \text{membrane} | \text{solution} (T + \Delta T)$$

Both phases, the solution as well as the membrane phase, are decisive for the origin and mechanism of transport. Transport will always occur in a direction which increases the *entropy of the system*. Clearly, in the absence of other driving forces, heat will diffuse down a thermal gradient. But permeant can flow against a thermal gradient, if this on the whole produces more entropy in the system. The entropy production of the system is therefore central and was used all the time from the beginning, from Derjaguin and Sidorenkov [17], Hutchinson et al. [16], and Katchalsky and Curran [56]. In recent years, Kjelstrup and Bedeaux [54] gave the entropy production of thermo-osmosis of a two-component *membrane-solution system* (flux  $J_j$ , with  $j = 0$  (solvent) and  $s$  (solute)) under chemical and thermal driving forces by

$$\sigma = J_q^o \Delta \left[ \frac{1}{T} \right] + \sum_{1,2} J_j \left[ - \frac{1}{T^i} \Delta \mu_j(T^i) \right] > 0 \quad (1)$$

Special about this equation is that it refers more precisely than before to the actual position and condition for evaluation of the fluxes and forces. This follows from the authors consideration of the heterogeneity of the system. The expression applies to a membrane of thickness  $d_m$ . As variable fluxes are chosen the heat flux,  $J_q^o$ , measured *on the outgoing side*,  $o$ , of the membrane, and the component fluxes. Their conjugate forces are the difference in the inverse temperature  $T$ , and minus the difference in the chemical potential,  $\mu_j$ , divided by  $T$  and *evaluated at the temperature at the incoming side*  $1$ ,  $T^i$ . For further details on sub- and superscripts, see Ref. [54]. The details have a bearing on the interpretation of coefficients (see eqs. (4)–(6) below). When the solution on the two sides has the same composition, but allows for a pressure difference across the membrane, the contribution to the last driving force is:

$$\Delta \mu_j(T^i) = V_j \Delta p \quad (2)$$

Here  $T^i$  is the temperature of side  $i$ ,  $p$  is the pressure and  $V_j$  is the partial molar volume. The symbol  $\Delta$  refers to the membrane only, no diffuse boundary layers. Alternative equivalent choices of variables exist.

From eqs. (1) and (2) we obtain  $\sigma = J_q^\circ \Delta \left[ \frac{1}{T} \right] + J_V \left[ -\frac{1}{T} \Delta p \right]$ . The fluxes are now the measurable heat flux on the right-hand (outgoing) side and the volume flux. The corresponding flux–force relations for the whole membrane are

$$\begin{aligned} J_q^\circ &= -l_{qq} \frac{\Delta T}{T^2} - l_{qV} \frac{1}{T} \Delta p \\ J_V &= -l_{Vq} \frac{\Delta T}{T^2} - l_{VV} \frac{1}{T} \Delta p \end{aligned} \quad (3)$$

The temperature difference,  $\Delta T$ , and the pressure difference,  $\Delta p$ , apply to the whole membrane and  $l_{qV} = l_{Vq}$  (Onsager relations). The equations predict that the volume flux for two components,  $J_V = J_1 V_1 + J_2 V_2$ , is proportional to the temperature difference across the membrane when  $\Delta p = 0$ .

Before reduction of experimental data can take place according to these equations or others (see below eq. (4)), one must make sure that there is no thermal polarisation of diffuse boundary layers next to the membrane. In general, at a given average temperature, the thermo-osmotic flux is proportional to the temperature difference between both sides of the membrane. However, in some cases, the behaviour ceased to be linear after a certain temperature difference was reached. With highly selective membranes, Villaluenga et al. [4] observed water fluxes from the cold to the hot side of Nafion 117 membranes, confirming Tasaka's observations in Nafion 417 [45]. The flux of water was proportional to the temperature difference in both works, but only when the temperature polarization was taken into account. Vink and Chisthi [28] obtained thermo-osmotic effects in experiments with cellophane membranes. They took thermal polarization into account and obtained a linear relation between the thermo-osmotic flux and the temperature difference across the membrane. Rastogi and Singh [23] found that the thermo-osmotic coefficient was independent of the temperature difference up to 20 °C for water, and up to 15 °C for methanol, when measurements were made at a constant average temperature. In this case, the solutions in contact with the membrane were not stirred, however, so polarization effects were probably present. Clearly, it is important for the outcome of the experiment to control polarization. Many authors [42, 46, 48–50] plotted the volume flux against the temperature difference and found deviations from a straight line [26, 29, 42–45]. In all these cases, the thermo-osmotic flux increased with the stirring rate. Stirring of the solutions adjacent to the membrane will decrease the thickness of diffusive layers and increase the overall thermal driving force across the membrane. The higher the stirring rate, the larger becomes the thermal force, and the larger is the flux.

### 3 Thermo-osmosis of pure fluids

Thermo-osmotic studies of transport of pure fluids have been carried out mostly with cellophane and weakly charged cellulose acetate membranes, and mainly with water or alcohols [20–23, 25, 28, 30, 38, 39] as permeants. More recently, also transport in ion-exchange membranes, such as Nafion or Neosepta membranes [4, 41, 45] has been investigated. Studies of thermo-osmosis of pure non-aqueous permeants in highly charged membranes are practically non-existent. As the only group Villaluenga et al. [4] measured the methanol thermo-osmotic coefficient. The reports on thermo-osmosis with pure liquids in membranes are few, but there are also qualitative and quantitative discrepancies in the results reported. In some cases, operating conditions are not sufficiently detailed.

In order to examine the reported results, let us rewrite equations (3) in a more convenient form; i. e. per unit of membrane thickness:

$$J_q^\circ = -\frac{\lambda}{d_m} \Delta T + q^* J_V \quad (4a)$$

$$J_V = -\frac{D_T}{d_m} \Delta T - \frac{L_p}{d_m} \Delta p \quad (4b)$$

Here  $d_m$  is the membrane thickness and  $\lambda$  is the Fourier type stationary state thermal conductivity. We see from eq. (4b) that the volume flux is proportional to the pressure difference, in the absence of a temperature difference, and with the hydraulic permeability  $L_p$  as proportional factor. Similarly, the volume flux is proportional to the temperature difference, only in the absence of a pressure difference. The coefficient  $L_p$  is the hydraulic permeability of the permeant, defined by

$$L_p = -(J_V d_m / \Delta p)_{\Delta T=0} \quad (5a)$$

The heat of transfer,  $q^*$ , is the reversible heat carried by the volume flux.

$$q^* = (J_q^0 / J_V)_{\Delta T=0} \quad (5b)$$

The thermo-osmotic coefficient is defined by

$$(D_T)_{\Delta p=0} = -J_V d_m / \Delta T \quad (5c)$$

The coefficients depend on the membrane system. The hydraulic permeability is for instance a function of the membrane pore diameter, tortuosity and water content. With the volume flux measured in  $\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ , the proportionality factor  $D_T$  has units  $\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$ , given per unit length of membrane.

The heat transported by a mass flux as in eq. (4a) bears the name Dufour effect while the mass transported by a temperature gradient is called the Soret effect. These effects are related due to Onsagers reciprocal relations where  $l_{qV} = l_{Vq}$ . We obtain

$$q^* = \left[ \frac{J_q^0}{J_V} \right]_{\Delta T=0} = \frac{D_T T}{L_p}; \quad D_T = \frac{q^*}{T} L_p \quad (6)$$

While the hydraulic permeability is always positive, the heat of transfer,  $q^*$ , may change in sign. Experimental results are often expressed in terms of the thermo-osmotic coefficient,  $D_T$ , but we shall also find values for the heat of transfer  $q^*$ . Our thesis will be, that  $q^*$  provides a way to understand the sign of the thermo-osmotic coefficient. Equation (6) predicts that the thermo-osmotic coefficient depends on the pore radius and liquid viscosity, as the hydraulic permeability depends on this value. The coefficient,  $D_T$ , is probably also temperature sensitive, like the normal diffusion coefficient.

In their analysis of the membrane interfaces, Kjelstrup and Bedeaux [54] argued that the heat of transfer for interface transport is a fraction of the enthalpy of the phase change when the permeant enters the membrane,

$$q^* = k(\bar{H}_0 - H_0) \quad (7)$$

For water, this means that the enthalpy of adsorption of water is the partial molar enthalpy of water in the membrane,  $\bar{H}_0$ , minus the (partial) molar enthalpy of water in the solution,  $H_0$ . The factor  $k$  was derived from the assumption that the thermal resistance of the interface is composed of two resistances in series, one on the solution side, and one on the membrane side [54]. The factor is the ratio of the thermal resistance of the solution side to total thermal resistance of the membrane-solution interface. The factor is equal to 0.2 in kinetic theory for the vapour-liquid interface. It is likely much higher here, as the liquid and the membrane sides on the interface are more comparable in their thermal resistance. The enthalpy of adsorption can be replaced by the entropy of adsorption when there is local equilibrium at the interface.

$$\bar{H}_0 - H_0 = T(\bar{S}_0 - S_0) \quad (8)$$

Here the entropy of the permeant in the membrane is  $\bar{S}_0$ , while the entropy of the pure permeant is  $S_0$ . Using these relations in combination with eq. (6), we obtain a new expression for  $D_T$

$$D_T = q^* L_p / T = k(\bar{S}_0 - S_0) L_p \quad (9)$$

This equation will be used below to explain the sign and magnitude of the thermo-osmotic coefficient. A formula that supports the form of eq. (9) was given by Tasaka and co-workers [45, 46] and Suzuki and co-workers [48–50].

The results found in the literature are summarised in Table 1 for water and some other pure liquids. The membranes listed in this table can be characterized as hydrophobic or neutral (Cellophane, Millipore), and hydrophilic or weakly charged (Cellulose acetate) and charged (Neosepta). The fuel cell membranes (Nafion, Flemion, Gore-Select) are membranes with hydrophilic as well as hydrophobic regions. The thermo-osmotic coefficient  $D_T$  was computed for all.

Inspection of the results in Table 1 reveals that thermo-osmotic coefficient for water varies enormously, by five orders of magnitude (between  $10^{-8}$  and  $10^{-13}$   $\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$ ) depending on the membrane system. The coefficient can be negative as well as positive.

Our hypothesis is now that it is possible to explain qualitatively all results in Table 1 by eq. (9). The variation in magnitude and sign may be then related to variations in hydraulic permeability, to the factor  $k$ , or to the entropy difference. Bregulla et al. [9] give some experimental support for a relation between  $D_T$  and a heat source or sink. They reported that a velocity field derived from a non-uniform heat production along a solid–liquid boundary. They concluded that the resulting excess positive enthalpy change lead to liquid flow towards the cold side. The effect was reported for glass capillaries, clay and silica gels. The authors concluded that the enthalpy excess in the boundary layer governs the direction of the thermo-osmotic flux. This fits with an application of eqs. (8) and (9) and will now be further discussed.

### 3.1 Impact of the membrane system

#### 3.1.1 The order of magnitude of the thermo-osmotic coefficient

A dramatic variation in  $D_T$  by five orders of magnitude was seen in Table 1. According to eq. (9), thermo-osmosis depends on three properties of the membrane–fluid system, not more. Not all of these can explain the observed variation in magnitude. The  $k$ -factor is a number between minus one and one. The molar entropies may vary, but again it is unlikely that the molar entropies vary by several orders of magnitude. They are likely in the range of a few  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  to some tens  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . An explanation must then be sought in the remaining property; the hydraulic permeability. The hydraulic permeability depends on the membrane structure and on the nature of the permeant [57–59], and may really vary by several orders of magnitude. This is shown in the compilation of data in Table 2, column 5. The data are too few to allow for a systematic examination. Viscosity data are few but the thermo-osmotic coefficient increases toward large positive values when the permeant viscosity increases, in Nafion [4], in cellophane membranes, and in cellulose acetate membranes [20, 28]. This gives some support to our idea. More experiments will be needed to document the dependency in a systematic manner, however.

#### 3.1.2 The sign of the thermo-osmotic coefficient

The most surprising finding in Tables 1 and 2 is perhaps the fact that the thermo-osmotic coefficient varies in sign. We see that water transport by a temperature gradient is, broadly speaking, directed from the hot to the cold side in hydrophobic membranes (e. g. Cellophane, Millipore) and from the cold to the hot side in hydrophilic membranes (e. g. Cellulose acetate, Nafion). There is only one factor in eq. (9) that can explain a change in sign, namely the entropy term. This term must then be able to explain the observed signs of  $D_T$  in Table 1 or  $q^*$  in Table 2.

Can the sign be explained by changes in the molar entropy of water when it passes the membrane interface? Consider first a hydrophilic membrane (Figure 1(a)). In such a membrane, it is reasonable to

**Table 1:** Thermo-osmotic coefficient per unit length of membrane,  $D_T$ , for single fluid transport in various membranes. The dry membrane thickness is used for  $d_m$  and the average temperature is  $\bar{t}$ .

Membrane [Reference]	$d_m/10^{-3}$ m	Liquid	$\bar{t}/^\circ\text{C}$	$D_T/\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$	Thermo-osmotic flux direction
<b>Cellophane 600P</b> Rastogi et al. [22]	0.062	water	40	$3.5 \times 10^{-11}$	from hot to cold
<b>Cellophane 600P</b> Rastogi and Singh [23]	0.062	water	46	$4.6 \times 10^{-10}$	from hot to cold
		methanol	42	$2.2 \times 10^{-8}$	from hot to cold
<b>Cellophane 600P</b> Haase et al. [20]	0.062	water	25	$1.8 \times 10^{-11}$	from hot to cold
			60	$-3.6 \times 10^{-12}$	from cold to hot
<b>Cellophane 600P</b> Haase and Greiff [21]	0.062	methanol	25	$-7.4 \times 10^{-12}$	from cold to hot
			60	$-5.7 \times 10^{-12}$	from cold to hot
<b>Dense cellulose acetate</b> Dariel and Kedem [25]	0.077	water	25	$3.8 \times 10^{-11}$	from hot to cold
<b>Cellophane</b> Vink and Chishti [28]	0.076	water	25	$1.4 \times 10^{-10}$	from hot to cold
		methanol		$-4.5 \times 10^{-11}$	from cold to hot
		acetone		$-6.1 \times 10^{-10}$	from cold to hot
		toluene		$-1.7 \times 10^{-10}$	from cold to hot
<b>Cellulose acetate</b> Vink and Chishti [28]	0.104	water		$3.8 \times 10^{-12}$	from hot to cold
		methanol		$-1.0 \times 10^{-10}$	from cold to hot
		toluene		$-1.5 \times 10^{-10}$	from cold to hot
		cyclohexane		$-3.4 \times 10^{-11}$	from cold to hot
<b>Cellulose acetate</b> Mengual et al. [30]	0.130	water	35	$5.4 \times 10^{-16}$	from hot to cold
<b>Cellulose acetate</b> Mengual and García-López [37]	0.012	water	38	$2.2 \times 10^{-12}$	from hot to cold
<b>TF1000 Gelman</b> Paglicua et al. [36]	0.150	water	30	$3.7 \times 10^{-9}$	from hot to cold
<b>LCWP Millipore</b> Paglicua et al. [36]	0.125			$2.2 \times 10^{-9}$	
<b>AP-20 Millipore</b> Paglicua et al. [36]	0.300			$1.4 \times 10^{-8}$	
<b>Cellophane 500P</b> Fernández-Pineda and Vázquez-González [38]	0.051	water	40	$8.5 \times 10^{-12}$	from hot to cold
<b>Cellophane 600P</b> Fernández-Pineda and Vázquez-González [38]	0.062			$6.7 \times 10^{-12}$	
<b>Cellulose acetate</b> Mengual and García-López [39]	0.027	water	30	$3.8 \times 10^{-11}$	from hot to cold
		methanol		$3.9 \times 10^{-10}$	
		ethanol		$8.1 \times 10^{-10}$	
<b>TF-1000 Gelman</b> Ortiz de Zárate et al. [51]	0.178	water	35	$8.5 \times 10^{-8}$	from hot to cold
<b>FGLP Millipore</b> Ortiz de Zárate et al. [51]	0.130			$2.5 \times 10^{-8}$	

(continued)

Table 1: (continued)

Membrane [Reference]	$d_m/10^{-3}$ m	Liquid	$\bar{t}/^\circ\text{C}$	$D_T/\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$	Thermo-osmotic flux direction
<b>Nafion 417</b> Tasaka et al. [45]	0.43	water	35	$-1.5 \times 10^{-9}$	from cold to hot
<b>Neosepta CM-2</b> Tasaka et al. [45]	0.12			$-1.6 \times 10^{-8}$	
<b>Nafion 117</b> Villaluenga et al. [4]	0.183	water methanol	26	$-1.4 \times 10^{-10}$ $-2.7 \times 10^{-10}$	from cold to hot
<b>Nafion 112</b> Kim and Mench [1]	0.050	water	65	$-2.0 \times 10^{-13}$	from cold to hot
<b>Flemion SH50</b> Kim and Mench [1]	0.050			$-3.0 \times 10^{-13}$	
<b>Gore-Select</b> Kim and Mench [1]	0.018			$-1.3 \times 10^{-13}$	

expect that water is *relatively more ordered* inside than outside the membrane. This makes  $\bar{S}_0 < S_0$  and  $D_T < 0$  from eq. (9) and explains that the fluid moves against the temperature gradient, from the cold to the hot side. It follows that water adsorption on the cold side means heat release on this side, and desorption on the hot side means that heat is consumed at this location. There is heat transferred by water in the opposite direction, from hot to cold in this case. Table 1 shows that this is the case for all cases of water transport in charged, predominantly hydrophilic membranes (Neosepta, Nafion, Flemion, GoreSelect). All is in agreement with the second law.

According to the same line of thinking, the transport direction should be the reverse in a hydrophobic membrane; namely from hot to cold (Figure 1(b)). This is indeed, observed in many Cellophane membranes. Also hydrophobic PTFE membranes [36, 51] follow this pattern, with heat and water flux from the hot side to the cold side. In all cases, one may say that the water transport enhances the heat transport by conduction only.

These arguments explain in a qualitative manner why charged membranes have transport of water mostly from the cold to the hot side, while non-charged or weakly charged membranes have a water flux mostly directed from the hot to the cold side. But in most of studies with cellophane membranes, the thermo-osmotic flux direction was from the hot side to the cold side. Haase et al. [20, 21] observed an inversion of the water thermo-osmotic flux for a Cellophane 600P membrane at the average temperature of  $60^\circ\text{C}$  by replacing water with methanol. A similar inversion of the flux was observed by Vink and Chishti [28] in cellophane and cellulose acetate membranes, again with methanol as permeant. In order to explain these findings along the lines given by eq. (9), the entropies in the membrane and in the solution must vary with temperature in different ways. This is a point amenable to experimental tests. We propose that this is done. Methanol was not able to bring about an inversion of the flux in highly charged membranes, however [4]. Regrettably, we do not have available enthalpies or entropies of adsorption for the fluids in their respective membranes.

The actual values computed for  $q^*$  (see Table 2) are not large. They vary between 1 and 2,000 J/mol. The smallest values imply small adsorption enthalpies, or small changes in energy or entropy as the permeant crosses the membrane interface. One may imagine that experiments become increasingly inaccurate as the value goes down.

There are only few other results, reported for thermo-osmosis of alcohols. An exception is the work of Vink and Chishti [28] who measured acetone and toluene in cellophane membranes and toluene and cyclohexane in cellulose acetate membranes. In all cases, the flux was in the same direction as for methanol, from hot to cold; and opposite to the water flux. It would be interesting to know the enthalpy



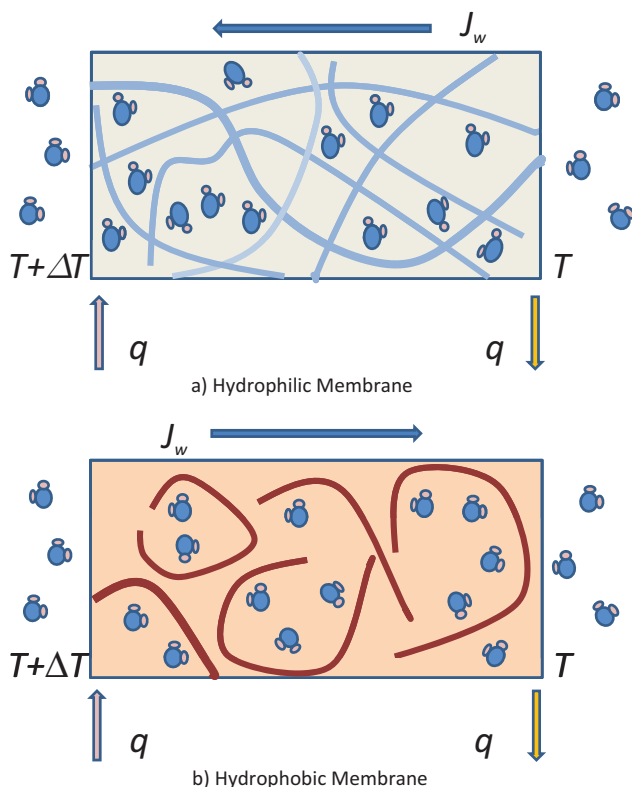
**Table 2:** Hydraulic permeation coefficient per unit length of membrane,  $L_p$ , and heat of transfer,  $q^*$ , for single fluid transport in various membranes. The dry membrane thickness is used for  $d_m$  and the average temperature is  $\bar{t}$ .

Membrane [Reference]	$d_m / 10^{-3} \text{ m}$	Liquid	$\bar{t} / ^\circ\text{C}$	$L_p / \text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$	$q^* / \text{J}\cdot\text{mol}^{-1}$
<b>Cellophane 600P</b> Rastogi and Singh [23]	0.062	water	46	$5.5 \times 10^{-12}$	0.5
		methanol	42	$5.0 \times 10^{-11}$	6
<b>Cellophane 600P</b> Haase et al. [20]	0.062	water	25	$1.3 \times 10^{-14}$	7
			60	$2.3 \times 10^{-14}$	-1
<b>Cellophane 600P</b> Haase and Greiff [21]	0.062	methanol	25	$1.7 \times 10^{-14}$	-5
			60	$3.2 \times 10^{-14}$	-3
<b>Dense cellulose acetate</b> Dariel and Kedem [25]	0.077	water	25	$1.1 \times 10^{-16}$	1900
<b>Cellophane</b> Vink and Chishti [28]	0.076	water	25	$5.8 \times 10^{-14}$	13
		methanol		$5.5 \times 10^{-14}$	-10
		acetone		$1.1 \times 10^{-13}$	-125
		toluene		$4.5 \times 10^{-14}$	-120
<b>Cellulose acetate</b> Vink and Chishti [28]	0.104	water		$7.1 \times 10^{-14}$	0.3
		methanol		$5.9 \times 10^{-14}$	-20
		toluene		$3.7 \times 10^{-14}$	-128
		cyclohexane		$1.1 \times 10^{-14}$	-100
<b>Cellulose acetate</b> Mengual et al. [30]	0.130	water	35	$5.1 \times 10^{-18}$	0.6
<b>Cellulose acetate</b> Mengual and García-López [37]	0.012	water	38	$1.2 \times 10^{-14}$	1
<b>TF1000 Gelman</b> Paglicua et al. [36]	0.150	water	30	$8.3 \times 10^{-12}$	2
<b>LCWP Millipore</b> Paglicua et al. [36]	0.125			$2.4 \times 10^{-12}$	5
<b>AP-20 Millipore</b> Paglicua et al. [36]	0.300			$1.4 \times 10^{-10}$	0.6
<b>Cellophane 500P</b> Fernández-Pineda and Vázquez-González [38]	0.051	water	40	$1.1 \times 10^{-13}$	0.4
<b>Cellophane 600P</b> Fernández-Pineda and Vázquez-González [38]	0.062			$4.0 \times 10^{-14}$	1
<b>Nafion 417</b> Tasaka et al. [45]	0.43	water	35	$3.2 \times 10^{-14}$	-265
<b>Nafion 117</b> Villaluenga et al. [4] Barragán and Muñoz [60]	0.183	water	26	$3.3 \times 10^{-14}$	-23
		methanol		$3.7 \times 10^{-14}$	-89

of adsorption of these polar or polarizable liquids in these membranes, to understand better why they differ from water transport.

### 3.2 The effect of average temperature

At a given temperature difference, most of the studies have shown an increase of the thermo-osmotic coefficient with increasing average temperature. In cellophane membranes [20, 21] the direction of thermo-



**Figure 1:** Schematic diagram of water flux across hydrophilic (a) and hydrophobic (b) membranes. In both cases there is heat transport from the hot to the cold side.

osmosis depended also on the average temperature. Rastogi et al. [22] found that for cellophane membranes and a given difference of 14 K, thermo-osmosis decreased with average temperature up to a minimum value and thereafter it increased with temperature. The minimum value was in the 40–55 °C interval, near 51 °C. This behaviour was contrary to that reported by Haase and Greif [20, 21] with cellophane membranes and water as permeant. In their works, the thermo-osmotic coefficient was found to decrease with average temperature with the flux going from the hot to the cold side of the membrane, but the direction of the flux changed above 55 °C, i. e. water went from the cold to the warm compartment. A difference of 1.3 °C was used in that case. Some of the discrepancies between the works of Haase et al. [20, 21] and Rastogi et al. [22, 23] could be explained by temperature polarization [34], and temperature variation in the overall coefficient [35, 38]. The transport of one solute under steady-state conditions driven by a temperature gradient was investigated. The thermo-osmotic coefficient was, in their model, a function of the temperature-dependent permeant adsorption enthalpy, molar volume, enthalpy of transfer and phenomenological coefficient, assuming that the membrane-permeant system was without single charges. Interesting is that an Arrhenius behaviour in  $D_T$  has been observed with water and methanol in Nafion membranes [4] as well as in other membrane systems [30, 34, 39]. One possibility is to ascribe this to the hydraulic permeability.

The thermo-osmotic coefficients of Table 1 are given per unit length of membrane. Nevertheless, they seem to increase with increasing membrane thickness given the same temperature, see results for Nafion membranes of different thicknesses [1, 4, 45]. The thermo-osmotic coefficient of charged membranes increased with increasing membrane thickness. The temperature was not the same in these experiments, making it difficult to conclude. A possible unknown factor contributing to such a variation could be the factor  $k$  in eq. (8). The surface resistance to heat transfer, may be a function of the membrane thickness.

## 4 Thermo-osmosis of electrolyte solutions

Thermo-osmosis of electrolyte solutions was first reported by Carr and Sollner early in 1935. The data were published in 1962 [14]. The thermo-osmotic flux through oxidized collodion membranes in KCl solutions occurred from the hot to the cold side. The volume flow across the membrane varied in proportion to the temperature difference. They concluded that thermo-osmosis of electrolyte solutions through charged membranes was an electrokinetic phenomenon, possibly related to electro-osmosis in isothermal systems. Kobatake and Fujita [15] gave a theoretical description of the works of Carr and Sollner, similar to what they did for anomalous osmosis. They concluded that thermo-osmosis was like electro-osmosis caused by the electric field set up in the membrane, justifying a dependence of the electro-osmotic coefficient on salt concentration. This gave the primary influence of the electrolyte on thermo-osmosis in charged membranes. Thus the thermo-osmotic volume flow had two contributions. One of them depended on the membrane charge, and tended to zero when the charge diminished. The other term was independent of the membrane charge, and represented volume transported by thermal diffusion, which is present also when the membrane was uncharged.

Using eq. (1) with the same electrolyte concentrations on the two sides of the membrane of thickness  $d_m$ , we obtain

$$\sigma = J_q^0 \Delta \left[ \frac{1}{T} \right] + (J_w V_w + J_s V_s) \left[ -\frac{1}{T_i} \Delta p \right] = J_q^0 \Delta \left[ \frac{1}{T} \right] + J_V \left[ -\frac{1}{T_i} \Delta p \right] \quad (10)$$

The form of the entropy production becomes the same as before, the only change being a change in the definition of the volume flow, which is  $J_V = J_w V_w + J_s V_s$ . Otherwise the flux equations and the coefficient relations are the same as above in eqs. (2)–(9), the only difference being that electrolyte transport may be included.

Tasaka and Nagasawa [26] studied thermo-osmosis, and measured thermoelectric potentials across heterogeneous cation exchange membranes and oxidized collodion membranes. The electrolyte was aqueous KCl solutions of varying concentrations. The thermo-osmotic flow was, contrary to the observation of Carr and Sollner, from the cold to the hot side in all experiments. Later, many papers appeared, in which the direction of the thermo-osmotic flux through different types of membranes was also from the cold to the warm solution. A series of important works about thermo-osmosis in electrolyte solutions were published in 80's and 90's by Tasaka and Suzuki and co-workers [41–50]. Since then, experimental reports about thermo-osmosis have been basically non-existent.

A summary of results for electrolyte transport is shown in Table 3. The thermo-osmotic coefficient  $D_T$  ( $\text{kg.m}^{-1}.\text{s}^{-1}.\text{K}^{-1}$ ) was calculated. Rather than eq. (9) which applies to a pure permeant, we now have the coefficient

$$D_T = q^* L_p / T \approx k [c_0(\bar{s}_0 - s_0) + c_s(\bar{s}_s - s_s)] L_p \quad (11)$$

The entropy of adsorption has now to take into account that the permeant is an electrolyte solution. The magnitude and the direction of the thermo-osmotic flux depend like before, on the membrane via the hydraulic permeability, the scaling factor for thermal resistances, and the entropies of adsorption. Via these variables there is also a dependence on the temperature and the electrolyte nature and concentration.

### 4.1 Impact of membrane-system

The main picture of the results in Table 3 is that thermo-osmosis again appears from the hot to the cold side in hydrophobic membranes, and from the cold to the hot side in hydrophilic membranes. This is so, with few exceptions, regardless of the presence or the type of electrolyte solutions in contact with the membrane. The sign of the results in Table 1 were explained by eq. (9). The signs of the thermo-osmotic coefficients in

**Table 3:** Thermo-osmotic coefficients per unit length of membrane,  $D_T$ , for selected electrolyte solutions in membranes of dry thickness  $d_m$  at the average temperature  $\bar{t}$ .

Membrane	$d_m$ /mm	Electrolyte	$\bar{t}/^\circ\text{C}$	$D_T / \text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$	Thermo-Osmotic flux Direction	Reference
<b>Collodion Oxidized</b>	0.53	KCl	25?	$-7.7 \times 10^{-10}$	from cold to hot	Tasaka et al. [29]
<b>Collodion</b>	0.63	$(10^{-3} \text{ mol}\cdot\text{kg}^{-1})$		$-3.7 \times 10^{-10}$		
<b>Collodion-sulfonate interpolymer</b>	0.30			$-6.0 \times 10^{-10}$		
				$-4.2 \times 10^{-10}$		
<b>Collodion Oxidized</b>	0.53	KCl	25?	$-7.9 \times 10^{-10}$	from cold to hot	Tasaka et al. [26, 29]
<b>Collodion</b>	0.53	$(0.02 \text{ mol}\cdot\text{kg}^{-1})$		$-6.6 \times 10^{-10}$		
<b>AP-20 Millipore</b>	0.32	$\text{CH}_3\text{COONa}$ , 0.02 M NaCl, 0.02 M KCl, 0.05 M	30	$1.6 \times 10^{-8}$ $1.5 \times 10^{-8}$ $1.8 \times 10^{-8}$	from hot to cold	Belluci et al. [33] Mita et al. [40]
<b>Cation-exchange membranes</b>						
<b>MC 3470</b>	0.51	NaCl $(0.10 \text{ mol}\cdot\text{l}^{-1})$ $(\text{CH}_3)_4\text{NCl}$ $(0.10 \text{ mol}\cdot\text{l}^{-1})$	25?	$-3.4 \times 10^{-12}$ $-9.2 \times 10^{-12}$	from cold to hot	Goldstein and Verhoff [27]
<b>Flemion S</b>	0.21	HCl $(0.01 \text{ mol}\cdot\text{kg}^{-1})$ LiCl $(0.01 \text{ mol}\cdot\text{kg}^{-1})$ NaCl $(0.01 \text{ mol}\cdot\text{kg}^{-1})$ KCl $(0.01 \text{ mol}\cdot\text{kg}^{-1})$	25	$-3.1 \times 10^{-9}$ $7.7 \times 10^{-10}$ $-4.4 \times 10^{-11}$ $8.3 \times 10^{-11}$	from cold to hot from hot to cold from cold to hot from hot to cold	Suzuki et al. [48]
<b>Aciplex K-181</b>	0.094	HCl $(0.01 \text{ mol}\cdot\text{kg}^{-1})$ LiCl $(0.01 \text{ mol}\cdot\text{kg}^{-1})$ NaCl $(0.01 \text{ mol}\cdot\text{kg}^{-1})$ KCl $(0.01 \text{ mol}\cdot\text{kg}^{-1})$	25	$-1.8 \times 10^{-10}$ $1.4 \times 10^{-10}$ $-5.5 \times 10^{-11}$ $4.4 \times 10^{-11}$	from cold to hot from hot to cold from cold to hot from hot to cold	Suzuki et al. [50]
<b>Aciplex K-181</b>	0.094	$\text{NH}_4\text{Cl}$	25	$1.7 \times 10^{-10}$	from hot to cold	
<b>Aciplex K-182</b>	0.093	$(0.01 \text{ mol}\cdot\text{kg}^{-1})$		$1.4 \times 10^{-10}$		
<b>Neosepta C66-5T</b>	0.140			$2.2 \times 10^{-11}$		
<b>Flemion S</b>	0.21			$7.2 \times 10^{-10}$		Suzuki et al. [48]
<b>Nafion 417</b>	0.43	LiCl $(0.001 \text{ mol}\cdot\text{kg}^{-1})$ LiCl $(0.1 \text{ mol}\cdot\text{kg}^{-1})$ LiCl $(10 \text{ mol}\cdot\text{kg}^{-1})$	35	$3.9 \times 10^{-10}$ $3.7 \times 10^{-10}$ $2.6 \times 10^{-11}$	from hot to cold	Tasaka et al. [45]
<b>Flemion AR1 25</b>	0.10	LiCl $(10 \text{ mol}\cdot\text{kg}^{-1})$		$3.0 \times 10^{-12}$	from hot to cold	
<b>Neosepta C66-10F</b>	0.36	HCl $(0.001 \text{ mol}\cdot\text{kg}^{-1})$ KCl $(0.001 \text{ mol}\cdot\text{kg}^{-1})$	35	$-5.3 \times 10^{-10}$ $-4.7 \times 10^{-11}$	from cold to hot	
<b>Anion-exchange membranes</b>						
<b>A1</b>	0.69	HCl, LiCl, KCl $(0.01 \text{ mol}\cdot\text{kg}^{-1})$ $\text{KIO}_3$ $(0.01 \text{ mol}\cdot\text{kg}^{-1})$	–	$-1.0 \times 10^{-9}$ $-1.4 \times 10^{-9}$	From cold to hot	Tasaka et al. [41]

(continued)

Table 3: (continued)

Membrane	$d_m/\text{mm}$	Electrolyte	$\bar{t}/^\circ\text{C}$	$D_T / \text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$	Thermo-Osmotic flux Direction	Reference
Neosepta AM-1	0.123	LiCl (0.001 mol.kg <sup>-1</sup> )	30	$-8.9 \times 10^{-11}$	from cold to hot	Suzuki et al. [49]
		LiCl (0.01 mol.kg <sup>-1</sup> )		$-8.9 \times 10^{-11}$		
		LiCl (0.1 mol.kg <sup>-1</sup> )		$-1.1 \times 10^{-10}$		
		LiCl (5 mol.kg <sup>-1</sup> )		$-3.9 \times 10^{-11}$		
		KCl (0.001 mol.kg <sup>-1</sup> )		$-1.1 \times 10^{-10}$		
		KCl (0.01 mol.kg <sup>-1</sup> )		$-9.4 \times 10^{-11}$		
		KCl (0.1 mol.kg <sup>-1</sup> )		$-8.9 \times 10^{-11}$		
Aciplex A-201	0.281	KF	30	$-4.4 \times 10^{-10}$	from cold to hot	Suzuki et al. [49]
		(0.01 mol.kg <sup>-1</sup> )				
		KCl		$-2.2 \times 10^{-10}$		
		(0.01 mol.kg <sup>-1</sup> )				
		KNO <sub>3</sub>		$-1.6 \times 10^{-10}$		
		(0.01 mol.kg <sup>-1</sup> )				
		KIO <sub>3</sub>		$-6.7 \times 10^{-10}$		
(0.01 mol.kg <sup>-1</sup> )						
Neosepta AFN	0.160	KF	30	$-6.3 \times 10^{-10}$	from cold to hot	Tasaka et al. [46]
		KCl		$-2.1 \times 10^{-10}$		
		KNO <sub>3</sub>		$-2.0 \times 10^{-10}$		
		KClO <sub>3</sub>		$-2.1 \times 10^{-10}$		
		KIO <sub>3</sub>		$-4.0 \times 10^{-10}$		
		HCOONa		$-3.2 \times 10^{-10}$		

Table 3 can be explained correspondingly by eq. (11). The dominant term in this equation must be the term due to the solvent.

Mita et al. [40] observed that the thermo-osmotic flux in AP-20 Millipore membranes went from the hot to the cold side of the membrane in the presence of alkali chloride solutions, similar to the case of pure water. Tasaka et al. [44] observed for all hydrophobic membranes (Fluoropore, Hipore and Yumicron) a flux direction from hot to cold. For similar membrane thicknesses, the volume flux increased with increasing average pore diameter. We may understand this as an effect of increasing hydraulic permeability.

According to Table 3, the presence of an electrolyte in the external solutions does not have much impact on the direction of the flow, eq. (11), but there are exceptions. The ion selectivity of the counter-ion could change the direction of the thermo-osmotic flow. This is not the case for any of the anion-selective membranes, where the direction of the thermo-osmosis flux is always from the cold to the hot side, independent of the electrolyte nature, concentration or average temperature. But results from cationic selective membranes, show that the counter-ion may have an impact on both the magnitude as well as the direction of the thermo-osmotic flux. This effect must be understood from the differences in ability to include salt (counter-ions, co-ions) in the membrane, contributing differently to the last term in eq. (11).

With unselective porous membranes, the water flux was always in the direction of decreasing temperature. Belluci et al. [33] and Mita et al. [40] found sharp minima in the coefficient for water in A-20 Millipore in the presence of NaCl-, KCl- and CH<sub>3</sub>COONa solutions. The qualitative behaviour was similar for all solutions, but the position of the minimum depended on the type of solvent. Mita et al. observed a displacement of the minimum at lower concentration with increasing average temperature. They explained

this by an increased solute concentration in the membrane with increasing temperature. The entropy difference for water in eq. (11) may be negligible.

In hydrophobic membranes, Tasaka et al. [44] did not observe, within experimental errors, any dependence on the electrolyte concentration in the presence of KCl solutions. With charged membranes, the general trend was an increase of the thermo-osmotic flux with increasing the electrolyte concentration. Tasaka et al. [26, 29, 31, 43] measured the thermo-osmotic coefficient in collodion membranes as a function of the KCl concentration in the interval ( $10^{-3}$ – $1$  mol.kg $^{-1}$ ) and found no dependence on the KCl concentration below  $10^{-1}$  mol.kg $^{-1}$ . But a larger concentration produced a strong increase in the thermo-osmotic coefficient. For oxidized collodion membranes, smaller values were obtained. An increase was observed also at lower concentrations, in the  $10^{-3}$  to  $10^{-2}$  mol.kg $^{-1}$  interval, with a plateau where the coefficient did not depend on the concentration. When collodion sulfonated membranes were used, the plateau practically disappeared and the thermo-osmotic coefficient increased with concentration in all studied concentration intervals. In all cases of this membrane, the direction of the flux was from the cold to the hot side, and no inversion of the flux was observed. Goldstein and Verhoff [27] analysed the dependence of the thermo-osmotic flux with the concentration of NaCl and (CH $_3$ ) $_4$ NCl in the sulfonic cation-exchange membrane MC 3470. Thermo-osmosis occurred from the cold to the warm solution, with a maximum at a concentration of 0.10 moldm $^{-3}$ .

The works carried out by Tasaka et al. [45] and Suzuki et al. [48, 50] with highly selective cation-exchange membranes, showed that the direction of the thermo-osmotic flux depended on the cation type. Sulfonic acid-type membranes in the H $^+$ -form gave a higher flux than for membranes in alkali metal forms. For carboxylic acid-type membranes in the H $^+$ -form, the flux was very small. In strong acid-type membranes, the membrane may bind water, reducing the permeability. Suzuki et al. observed that the thermo-osmotic flux in hydrocarbon-sulfonic acid-type cation-exchange membranes with the H $^+$  and Na $^+$  forms was from the cold to the hot side, whereas the direction was from the hot side to the cold side with the Li $^+$ - and K $^+$ - forms of the membranes, as well as with the ammonium and the alkylated ammonium ion forms. An exception was observed for Neosepta membranes. An inversion of the flux took place with pure water in a membrane in the Li $^+$ -form. The inversion was observed for all membranes in the Li $^+$ -form, and for some membranes in the K $^+$ -form.

For anion-exchange membranes, the direction of the flux was always from the cold side to the hot side, regardless the nature and concentration of the electrolyte. Tasaka et al. [41] measured thermo-osmosis with anion-exchange membrane A1 for  $10^{-3}$  to 2 mol.kg $^{-1}$  of aqueous KCl, LiCl and NH $_4$ Cl and for  $10^{-3}$  to 0.3 mol.kg $^{-1}$  of aqueous KIO $_3$  and K $_2$ SO $_4$ . The trend with the concentration was similar than the previously described for collodion membranes. The results were similar with all the electrolytes with the exception of KIO $_3$ , for which larger values were found. The authors suggested that it was due to the larger ionic radius of IO $_3^-$  than of Cl $^-$ , so that the pore volume fraction of the membrane was larger for IO $_3^-$ . Suzuki et al. [49], however, found significant influence of the electrolyte nature on the thermo-osmotic coefficient when hydrocarbon-type and fluorocarbon-type anion exchange membranes were used. Neosepta membranes with KCl solutions have a thermo-osmotic coefficient, which is constant at low concentrations and decreases with increasing concentration. But LiCl has the opposite effect; the value decreased with increasing concentration. The authors concluded that the thermo-osmotic coefficient depended largely on the mobility of water in the membrane and the water content. However, we cannot find a simple relationship between the thermo-osmotic coefficient and the reciprocal of the mobility of counter-ions in free solutions. Also, the presence of organic anions seems to have a small effect on the water structure small compared with that of cations. Other explanations of thermo-osmosis in charged membranes have invoked the electric double layer. While this is present, it is not expected to provide a net driving force in electroneutral membrane systems.

Rather than all these various explanations above, we favour the explanations based on eq. (11) where the entropy of adsorption of permeant(s) is changing with electrolyte composition and type, as well as with temperature and hydraulic conductivity. So far, it seems possible to explain all results in a qualitative manner using this expression.

We know that the hydration of the counter-ion is important for the water structure, and therefore for the entropy of water in the membrane. Electrolytes interact in general strongly with water, breaking or making its structure [61–63]. Ions in water are surrounded by water molecules, which differ in their degree of freedom or order, depending upon their size and charge. Frank and Wen [61] suggested that ions could be classified as being either structure-makers, such as  $\text{Li}^+$ ,  $\text{F}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{OH}^-$ , *etc.*, or structure-breakers, such as  $\text{H}^+$ ,  $\text{Cs}^+$ ,  $\text{Rb}^+$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , *etc.*, and proposed a mechanism by which this occurred based on ion hydration. Structure-maker ions are ions that induce order within the bulk water structure, thereby increasing the numbers of H-bonds (which again increases the water-water interaction energy). These different effects of the electrolytes, may thus explain also the inversion of the thermo-osmotic flux in some electrolytes. When structure-maker ions are present in water, as is the case with LiCl, water can acquire a more ordered state also outside the membrane, thereby reversing the thermo-osmotic flux. If this is correct, the structure breaking or making ions should be investigated for a possible systematic impact on the thermo-osmotic flux. At present this is not more than an hypothesis, conclusive evidence would be provided with independent information on enthalpies or entropies of adsorption.

## 5 The thermo-osmotic pressure

The thermo-osmotic coefficients given in Tables 1 and 3, together with the corresponding hydraulic permeability in Table 2, can be used to estimate the expected pressure rise across a membrane from a temperature difference. Such values may be of interest for separation purposes or for power production [7]. They have been used to describe frost heave phenomena [64]. The maximum pressure obtainable per degree, with heat available from waste heat reservoirs is given from eq. (3)

$$(\Delta p)_{J_V=0} = -q^* \frac{\Delta T}{T} \quad (13)$$

By introducing the expression for the heat of transfer, eq. (9), we obtain

$$\left(\frac{\Delta p}{\Delta T}\right)_{J_V=0} = -\frac{q^*}{T} = -\frac{D_T}{L_p} \quad (14)$$

In descriptions of frost heave, a value near the enthalpy of freezing for water was able to predict the maximum heaving pressure [64]. The typical value of  $q^*$  of an exothermic adsorption process ( $\sim -2\text{kJ/mol}$  at 300 K), gives a pressure difference of 7 bar per degree. This is a relatively impressive number! The results in Table 2 indicate that the value in general is smaller. But a large value indicates a potential for application of thermo-osmotic effects [7, 54]. For a Nafion 117 membrane, the values of the hydraulic permeability coefficient per unit length of membrane obtained with water and methanol at 25 °C were, respectively,  $3.3 \times 10^{-14}$  and  $3.7 \times 10^{-14} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$  [60]. Values of 40 and 70  $\text{mbar} \cdot \text{K}^{-1}$  were computed for the thermo-osmotic pressure for water and methanol, respectively, from eq. (14). From eq. (13), for a water-Nafion 117 membrane system the estimated heat of transfer at 25 °C would be  $23 \text{ J} \cdot \text{mol}^{-1}$ , and  $88 \text{ J} \cdot \text{mol}^{-1}$  for a methanol-Nafion 117 membrane system (see Table 2). From the entropy values estimated by Tasaka et al. [45], an enthalpy of adsorption for Nafion 417 membrane was estimated to  $268 \text{ J} \cdot \text{mol}^{-1}$  at 308 K. From eq. (7) the heat of transfer for this membrane would then be  $54 \text{ J} \cdot \text{mol}^{-1}$ , of the same order of magnitude than the value obtained for Nafion 117. From the data of Rastogi and Singh [23], lower heats of transfer were obtained for Cellophane 600P membranes with water and methanol, 0.5 and  $5.6 \text{ J} \cdot \text{mol}^{-1}$ , respectively, at 40 °C. For a cellulose acetate membrane, low heats of transfer, about  $1 \text{ J} \cdot \text{mol}^{-1}$  at 37.5 °C, can be estimated from the values of thermo-osmotic and hydraulic permeability coefficients given by Mengual and García-López [37]. Clearly, given eq. (7), the enthalpies of adsorption in these membranes must be small, but possibly within the limit of detection.

Thermo-osmotic fluxes are often small, making them difficult to measure. From eq. (3), thermo-osmotic pressure and hydraulic permeability can be defined, respectively, as

$$\left(\frac{\Delta p}{\Delta T}\right)_{J_V=0} = -\frac{l_{Vq}}{l_{VV}} \quad (15)$$

$$\left(\frac{J_V}{\Delta p}\right)_{\Delta T=0} = -\frac{l_{VV}}{T} \quad (16)$$

For an experiment starting with a temperature gradient, but initially no gradient in concentration or pressure, the initial volume flux is

$$(J_V)_{t=0} = -\left(\frac{\Delta p}{\Delta T}\right)_{J_V=0} \left(\frac{J_V}{\Delta p}\right)_{\Delta T=0} \Delta T \quad (17)$$

To measure the hydraulic permeability and the thermo-osmotic pressure would then be equivalent to measure the initial volume flux in a thermo-osmosis experiment. Hydraulic flux per bar is typically several order of magnitude larger than the corresponding thermo-osmotic flux per degree. Vink and Chisthti [28] measured thermo-osmotic pressures to study thermal osmosis in different membrane systems. Values of 24 and 0.5 mbar · K<sup>-1</sup> were obtained for a water-cellophane membrane and a water-cellulose acetate membrane systems, respectively, at a average temperature of 25 °C. In some works thermo-osmotic coefficient was determined with experiments running by maintaining constant the temperature difference and allowing the pressure difference to change with time [30, 37, 38].

## 6 Thermal osmosis – relation to other phenomena

Thermal osmosis has been compared to anomalous osmosis. Anomalous osmosis (negative or positive) is defined as volume flow in excess (negative or positive) of the flow predicted by the solute concentration. In order to see the possible equivalence, we write the entropy production for the isothermal transport of a solvent (0) and solute (s) through a membrane [55]

$$\sigma = J_0 \left[ -\frac{1}{T} \Delta \mu_0 \right] + J_s \left[ -\frac{1}{T} \Delta \mu_s \right] = -J_V \frac{1}{T} \Delta p - J_D \frac{c_s}{T} \Delta \mu_s(c) \quad (18)$$

The conjugate flux-force pairs are (1) the volume flux and minus the pressure difference over the temperature, and the relative velocity of components times the concentration-dependent part of the chemical potential and the solute concentration. The relative velocity of the two components is

$$J_D = \left( \frac{J_s}{c_s} - \frac{J_0}{c_0} \right) \quad (19)$$

The relative velocity of the components can be negative (velocity of s is largest) or positive (velocity of 0 is largest). When this relative flux is zero, the membrane is equally permeable to both components. For ideal conditions, the driving force simplifies to

$$-\frac{c_s}{T} \Delta \mu_s(c) \approx -R \Delta c_s \quad (20)$$

The flux equations on local form (per unit length of membrane)

$$\begin{aligned} J_D &= -l_{cc} R \frac{\Delta c_s}{d_m} - l_{cV} \frac{\Delta p}{T d_m} \\ J_V &= -l_{Vc} R \frac{\Delta c_s}{d_m} - l_{VV} \frac{\Delta p}{T d_m} \end{aligned} \quad (21)$$



The pressure is not included in the definition of anomalous osmosis. We express the pressure difference by eq. (18a) and introduce the result in eq. (18b) and obtain

$$\begin{aligned} J_D &= -l_{cc}R \frac{\Delta c_s}{d_m} - l_{cV} \frac{\Delta p}{T d_m} \\ J_V &= -\left(l_{Vc} - \frac{l_{cc}l_{VV}}{l_{cV}}\right)R \frac{\Delta c_s}{d_m} + \frac{l_{VV}}{l_{cV}}J_D \end{aligned} \quad (22)$$

In terms of these equations, we can see that the volume flux is proportional to the concentration difference only when  $J_D = 0$ . The coefficient in front of the second term in the last line is negative, because the matrix of coefficients obeys  $(l_{cc}l_{VV} - l_{Vc}l_{cV}) \geq 0$ .

Therefore, one may observe a volume flux against a concentration gradient. In this sense one may compare anomalous osmosis to thermal osmosis.

Goldstein and Verhoff [27] measured anomalous osmosis and thermo-osmosis of different permeants in polystyrene–divinyl benzene-sulfonic membranes. They observed a solvent water flux in direction opposite to the thermal driving force. The nature of the cation had a significant effect. They concluded that thermo-osmosis was caused by the same general effect as *anomalous osmosis*, an extra driving force leading to enhanced or retarded flow. The sign of thermo-osmotic effect is, however, as we have seen above, given by the sign of the adsorption entropy. The sign of the effect leading to anomalous osmosis, does not depend on this parameter. Moreover, anomalous osmosis does not occur with electroneutral membranes.

## 7 Conclusions and perspectives

Thermo-osmotic phenomena have been reviewed for the first time. Experimental results show that the magnitude and direction of the thermo-osmotic flux depends on the membrane, the solutions to be transported, as well as on operating parameters, like the average temperature. The phenomenon, which is a property of the *membrane-permeant system*, can be described with non-equilibrium thermodynamics. Only this theory provides the correct coupling of fluxes and forces.

We have found that thermo-osmosis in hydrophobic membranes always was directed from the hot to the cold side, regardless of the permeant used (water, alcohol, electrolyte solutions). In hydrophilic membranes, the direction of the thermo-osmotic flux depended on the permeant type, possible solutes and the average temperature. The direction of transport seems in most cases to be explainable by the sign of the entropy of adsorption of the permeant in the membrane. We have proposed a new relation between the thermo-osmotic coefficient, the entropy of permeant adsorption, the hydraulic permeability, and a factor related to thermal resistivities. The relation has its basis in the Onsager relations. Systematic studies in the field are lacking, and could be useful for independent controls of this relation, and for further applications of this interesting process.

Given the importance of water management of non-isothermal systems, an increased understanding of the thermo-osmotic phenomena in membrane systems and could be important for applications of electro-chemical systems like fuel cells, saline power plants, reverse electro-dialysis cells, as well as for membrane separation processes like membrane distillation, carbon capture and sequestration. We have pointed at more experiments that may bring such insight.

**Acknowledgements:** Kim Roger Kristiansen is thanked for discussions on the thermo-osmotic pressure. V. María Barragán wishes to thank the Norwegian University of Science and Technology (NTNU) for financial and support from the Research Council of Norway – grant no 197598 during her stay. ENERSENSE is thanked for support of the Open Access publication.

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