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Transport Properties of Cation-Exchange Membrane-Aqueous Electrolyte System

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Transport properties of a cation-exchange membrane-aqueous sodium chloride solution system have been studied. The membrane used was a sulfonated styrene-divinyl benzene copolymer, Neosepta C66-5T. The salt concentration was kept at 10^{-1} mol dm^{-3} on one side of the membrane and varied from 10^{-3} to 10^{-2} mol dm^{-3} on the other. The six elements of a conductance matrix have been experimentally determined according to the previous theory[1] and the membrane properties were discussed in terms of conductance elements. All the elements of the conductance matrix were positive within the concentration range studied. This would be characteristic of a cation-exchange membrane. The electrical ion conductance was greater than the diffusional ion conductance by a factor of 10 to 100. The ion-solvent coupling coefficient was much less than the interionic one, although the electroosmotic conductance was ten-times greater than the membrane conductance. The reflection coefficient was close to unity. The electroosmotic properties were also discussed in terms of the conductance matrix.

In the preceding papers,[1,2] six elements of a conductance matrix (phenomenological coefficients) were experimentally determined with the amphoteric ion-exchange membrane–aqueous electrolyte systems and the membrane properties were discussed in terms of the conductance matrix. All the transport properties in these systems could be explained in terms of the six elements. This indicates that six phenomenological coefficients are required for a characterization of a membrane–aqueous electrolyte system. It is, therefore, of interest to determine the phenomenological coefficients by using a variety of membranes and to understand how the coefficients reflect the membrane characters. Thus, a determination of the coefficients in the cation-exchange membrane-aqueous electrolyte system has been attempted. This paper describes the experimental results.

Experimental

Materials. The cation-exchange membrane used in the present study was a sulfonated styrene-divinyl benzene copolymer developed by Tokuyama Soda Co., Ltd. and coded as Neosepta C66-5T. The ion-exchange capacity was 2.45 meq. (g dry membrane)$^{-1}$, the water content 0.4 gH$_2$O (g dry membrane)$^{-1}$ and the thickness 0.15 mm. A pure specimen of sodium chloride as well as sucrose and twice-distilled water were used for preparing salt and sucrose solutions.

Procedures of Experiments. The experimental procedures were described elsewhere.[1] Regarding the aqueous phases separated by a membrane, the salt concentration of phase II was kept at 10^{-1} mol dm^{-3} and that of phase I was varied from 10^{-3} to 10^{-2} mol dm^{-3}. The sucrose concentration used for an osmotic flux measurement was 8.176×10^{-2} mol dm^{-3}. In the present study, current densities of 0.902×10^{-2}, 1.981×10^{-1}, and 2.971×10^{-1} mA cm^{-2} were passed through the paired Ag/AgCl electrodes of each system. The experiments were carried out at a regulated temperature of 25.0±0.1 °C.

Results and Discussion

The aim of the present work was to determine the phenomenological coefficients, g_{NaNa}—g_{ww}, in the phenomenological equation[1]

$$\begin{bmatrix} i_{\mathrm{Na}} \\ i_{\mathrm{Cl}} \\ Fj_{\mathrm{w}} \end{bmatrix} = -\begin{bmatrix} g_{\mathrm{NaNa}} & g_{\mathrm{NaCl}} & g_{\mathrm{Naw}} \\ g_{\mathrm{ClNa}} & g_{\mathrm{ClCl}} & g_{\mathrm{Clw}} \\ g_{\mathrm{wNa}} & g_{\mathrm{wCl}} & g_{\mathrm{ww}} \end{bmatrix} \begin{bmatrix} V-V_{\mathrm{Na}} \\ V-V_{\mathrm{Cl}} \\ -V_{\mathrm{w}} \end{bmatrix}, \tag{1}$$

and to discuss the membrane properties in terms of the conductance matrix. In Eq. 1, the suffixes Na, Cl, and w refer to sodium and chloride ions and water, respectively. Also i denotes the ion current, j the flux, V the membrane potential, V_{Na} and V_{Cl} the pseudoequilibrium potential for sodium and chloride ions, respectively, and V_{w} the effective driving potential for water or the water potential. V_{Na}, V_{Cl}, and V_{w} are defined by

$$Z_\gamma F V_\gamma = RT \ln a_\gamma^{\mathrm{I}}/a_\gamma^{\mathrm{II}} - \bar{v}_\gamma \Delta P \quad (\gamma = \mathrm{Na,\ Cl}) \tag{2}$$

and

$$FV_{\mathrm{w}} = RT \ln a_{\mathrm{w}}^{\mathrm{I}}/a_{\mathrm{w}}^{\mathrm{II}} - \bar{v}_{\mathrm{w}} \Delta P = \bar{v}_{\mathrm{w}}(\Delta\pi - \Delta P), \tag{3}$$

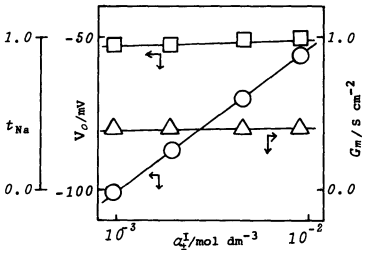

Fig. 1. Membrane potential at zero electric current, V_0, membrane conductance G_{m} and cationic transport number, t_{Na}, vs. mean electrolyte activity of phase I. ○: V_0, △: G_{m}, □: t_{Na}.

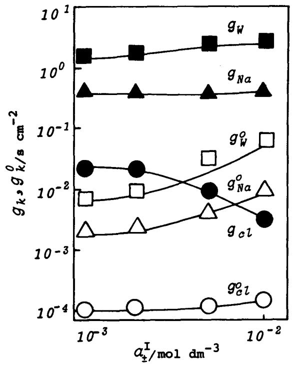

Fig. 2. Electrical ion and water conductances (g_{Na}, g_{Cl}, g_w) and diffusional ion and water conductances (g_{Na}^0, g_{Cl}^0, g_w^0) vs. mean electrolyte activity of phase I. ▲: g_{Na}, ●: g_{Cl}, ■: g_w, △: g_{Na}^0, ○: g_{Cl}^0, □: g_w^0.

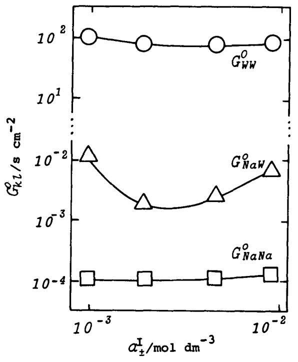

Fig. 3. G_{NaNa}^0, G_{Naw}^0, and G_{ww}^0 as a function of mean electrolyte activity in phase I. □: G_{NaNa}^0, △: G_{Naw}^0, ○: G_{ww}^0.

respectively, where the superscripts I and II refer to phases I and II, respectively. Here, F, R, and T denote the Faraday constant, the gas constant and the absolute temperature, respectively. Also, Z is the charge number, a the activity, $\bar{v}_\gamma$ (γ=Na, Cl, w) the partial molar volume of species γ (assumed to be constant for a given system), $\Delta\pi$ the osmotic pressure and ΔP ($=P^{II}-P^{I}$) the external pressure difference.

The equation for the membrane current, I, is obtained from Eq. 1 as follows[1)]

$$\begin{aligned} I = i_{Na} + i_{Cl} &= -G_m(V-V_0) \\ &= -g_{Na}(V-V_{Na}) - g_{Cl}(V-V_{Cl}) + g_w V_w, \end{aligned} \tag{4}$$

where g_{Na}, g_{Cl}, and g_w denote the electric conductances for the permeating species Na, Cl, and w, respectively,

$$g_k = g_{kNa} + g_{kCl} \quad (k=\text{Na, Cl, w}) \tag{5}$$

G_m, the membrane conductance is given by

$$G_m = g_{Na} + g_{Cl}. \tag{6}$$

V_0, the membrane potential at zero membrane current is

$$V_0 = t_{Na}V_{Na} + t_{Cl}V_{Cl} + t_w V_w, \tag{7}$$

and t_k, the transport number of a species k, is

$$t_k = g_k/G_m. \tag{8}$$

The transport numbers can be estimated from fluxes and the membrane currents according to the relations[1)]

$$i_{Na} - i_{Na}^0 = t_{Na}I$$

and

$$F(j_w - j_w^0) = t_w I, \tag{9}$$

where the superscript 0 refers to the fluxes at zero membrane current. The transport number of the cation t_{Na} is plotted in Fig. 1 together with the membrane potential V_0 and the membrane conductance G_m. This figure indicates that the membrane is selective to cations and that G_m is constant in the concentration range studied. The apparent transport number $(t_{Na})_{app.}$ estimated from the membrane potential vs. the logarithmic activity relation was close to t_{Na}.

The chloride ion conductance g_{Cl} was evaluated by subtracting g_{Na} ($=G_m t_{Na}$) from G_m. The conductances, g_{Na}, g_{Cl}, and g_w ($=G_m t_w$), are plotted against the salt activity as shown in Fig. 2. In the absence of a membrane current in the external solution, Eq. 1 is reduced to

$$\begin{bmatrix} i_{Na}^0 \\ Fj_w^0 \end{bmatrix} = -\begin{bmatrix} G_{NaNa}^0 & G_{Naw}^0 \\ G_{wNa}^0 & G_{ww}^0 \end{bmatrix} \begin{bmatrix} V_{Cl} - V_{Na} \\ -V_w \end{bmatrix}, \tag{10}$$

where

$$G_{NaNa}^0 = g_{NaNa} - G_m t_{Na}^2,$$

$$G_{Naw}^0 = g_{Naw} - G_m t_{Na} t_w = G_{wNa}^0,$$

and

$$G_{ww}^0 = g_{ww} - G_m t_w^2. \tag{11}$$

A change in the water potential, ΔV_w, under constant values of V_{Na} and V_{Cl} gives rise to changes in the fluxes, Δi_{Na}^0 and Δj_w^0, which are given as

$$\Delta j_{Na}^0 = G_{Naw}^0 \Delta V_w$$

and

$$F\Delta j_w^0 = G_{ww}^0 \Delta V_w, \tag{12}$$

provided that there is no appreciable change in the activity coefficients of ions as well as the phenomenological coefficients due to the addition of sucrose into one of the two aqueous phases. G_{NaNa}^0 and G_{wNa}^0 may be determined by using Eq. 10 provided G_{Naw}^0 and G_{ww}^0 are known. The result showed that G_{wNa}^0 and G_{Naw}^0 are close to each other, an indication of a reciprocal relation. Figure 3 shows G_{NaNa}^0, G_{Naw}^0, and G_{ww}^0 as a function of the salt concentration in phase I. The diffusional conductances g_k^0 (k=Na, Cl, w), calculated according to the relation

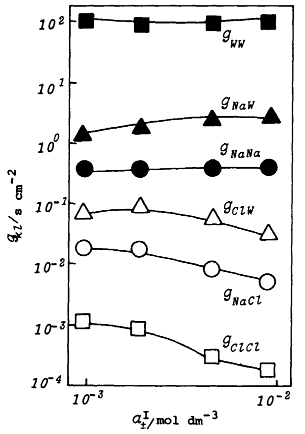

Fig. 4. Element of conductance matrix vs. mean electrolyte activity of phase I.
●: g_{NaNa}, □: g_{ClCl}, ○: g_{NaCl}, ▲: g_{Naw}, △: g_{Clw}, ■: g_{ww}.

$$g_k^0/g_k = (g_{\mathrm{NaNa}}g_{\mathrm{ClCl}} - g_{\mathrm{NaCl}}^2)/g_{\mathrm{Na}}g_{\mathrm{Cl}} \tag{13a}$$

$$= G_{\mathrm{NaNa}}^0/G_{\mathrm{m}}t_{\mathrm{Na}}t_{\mathrm{Cl}}\,, \tag{13b}$$

are plotted in Fig. 2 together with the conductances g_k as functions of the electrolyte activity in the external solution. The value of g_k^0 can be estimated according to Eq. 13b, provided that g_k, G_m, and G_{NaNa}^0 are known.

Comparing Eqs. 11 and 5, we obtain a set of relations for estimating the elements of the conductance matrix as follows[2)]

$$\begin{aligned} g_{\mathrm{NaNa}} &= G_{\mathrm{m}}t_{\mathrm{Na}}^2 + G_{\mathrm{NaNa}}^0, & g_{\mathrm{Naw}} &= G_{\mathrm{m}}t_{\mathrm{Na}}t_{\mathrm{w}} + G_{\mathrm{Naw}}^0 \\ g_{\mathrm{NaCl}} &= G_{\mathrm{m}}t_{\mathrm{Na}}t_{\mathrm{Cl}} - G_{\mathrm{NaNa}}^0, & g_{\mathrm{Clw}} &= G_{\mathrm{m}}t_{\mathrm{Cl}}t_{\mathrm{w}} - G_{\mathrm{Naw}}^0 \\ g_{\mathrm{ClCl}} &= G_{\mathrm{m}}t_{\mathrm{Cl}}^2 + G_{\mathrm{NaNa}}^0, & g_{\mathrm{ww}} &= G_{\mathrm{m}}t_{\mathrm{w}}^2 + G_{\mathrm{ww}}^0 \end{aligned} \tag{14}$$

Thus, the six elements of the conductance matrix can be estimated according to Eq. 14 after measurements of G_m, t_{Na}, t_{w}, G_{NaNa}^0, G_{Naw}^0, and G_{ww}^0. Figure 4 shows the six elements as functions of the mean electrolyte activity of phase I.

It can be seen in Fig. 4 that $g_{\mathrm{ww}} > g_{\mathrm{Naw}} > g_{\mathrm{NaNa}} > g_{\mathrm{Clw}} > g_{\mathrm{NaCl}} > g_{\mathrm{ClCl}}$ and that all the conductance elements are positive. This result is similar to that in the cation-exchange membrane-barium chloride system,[3)] but differs from that in the amphoteric ion-exchange membrane-aqueous sodium chloride system,[1)] $g_{\mathrm{ww}} > g_{\mathrm{Naw}} > |g_{\mathrm{Clw}}| > g_{\mathrm{NaNa}} \simeq g_{\mathrm{ClCl}} > |g_{\mathrm{NaCl}}|$, where g_{Clw} and g_{NaCl} are negative.

The lines in Fig. 2 indicate the values of g_k and g_k^0 calculated from g_{kl}'s (k,l=Na, Cl, w) in Fig. 4 according to Eqs. 5 and 13b, respectively. The calculated values are in good agreement with those obtained experimentally. This figure also indicates that the electrical ion conductance g_γ (γ=Na, Cl) is much greater than g_γ^0. This result agreed with that observed with the cation-exchange membrane-aqueous calcium chloride system[4)] and can be ascribed to the small co-ion concentration in the membrane. In contrast, it was also reported that g_γ is much smaller than g_γ^0 in the amphoteric ion-exchange membrane-aqueous electrolyte system.[1,2)] Rewriting Eq. 13a we have[1)]

$$g_\gamma - g_\gamma^0 = g_{\mathrm{NaCl}}/(1-t_\gamma). \tag{15}$$

Thus, it is seen that the positive value of g_{NaCl} in the cation-exchange membrane and the negative value of g_{NaCl} in the amphoteric ion-exchange membrane[2)] are correlated to the difference between the conductive and diffusional ion conductances. Assuming the membrane controlling, we have from Eq. 15 an equation for the equivalent ion conductance[1)]

$$\lambda_\gamma - \lambda_\gamma^0 = g_{\mathrm{NaCl}}\,\delta/|Z_\gamma|\bar{C}_\gamma(1-t_\gamma), \tag{16}$$

where λ_γ denotes the equivalent ion conductance and λ_γ^0, that calculated from the diffution coefficient according to the Nernst-Einstein relation; δ the membrane thickness; and $\bar{C}_\gamma$, the concentration of γ ions within the membrane. Despić and Hills[5)] ascribed the difference, $\lambda_\gamma - \lambda_\gamma^0$, to an electroosmotic effect. Since g_{NaCl} exhibits an interionic correlation, Despic and Hills' theory is not theoretically valid in view of nonequilibrium thermodynamics. Furthermore, the fact that the negative value of $(\lambda_\gamma - \lambda_\gamma^0)$ is observed in an amphoteric ion-exchange membrane can not be explained by Despić and Hills' theory, because the electroosmotic term is always positive.[5)]

The reason why the positive and negative values of g_{NaCl} are observed in the cation-exchange membrane and the amphoteric ion-exchange membrane, respectively, has not yet been clear. However, it is of interest to point out that the negative value of g_{NaCl} in the amphotoric ion-exchange membrane is conformable with the positive cross term in phenomenological coefficients observed in an aqueous sodium chloride solution.[6)]

The difference between the membrane conductance G_m and that without the electroosmotic effect, G_m' has been expressed as[1)]

$$G_{\mathrm{m}} - G_{\mathrm{m}}' = g_{\mathrm{v}}^2/g_{\mathrm{p}}\,, \tag{17}$$

where g_v and g_p denote the electroosmotic volume-flow conductance and the hydrodynamic volume-flow conductance, respectively. Since the transport number of cations in the cation-exchange membrane is close to unity, Eq. 17 can be rewritten as

$$\lambda_{\mathrm{Na}} - \lambda_{\mathrm{Na}}' = \delta g_{\mathrm{v}}^2/g_{\mathrm{p}}\bar{C}_{\mathrm{Na}}\,, \tag{18}$$

where δ is the membrane thickness and $\bar{C}_{\mathrm{Na}}$, is the sodium ion concentration in the membrane. It has been shown in a preceding paper that under several assumptions Eq. 18 can be reduced to Despić and Hills' equation[1)]

$$\lambda - \lambda' = (Fr)^2\bar{X}/8\eta, \tag{19}$$

where F denotes Faraday constant, r the capillary radius, $\bar{X}$ the counter-ion concentration in the membrane and η the solvent viscosity. It can be seen by comparing Eq. 16 with Eqs. 18 and 19 that the failure of Despic and Hills' theory lies in the replacement of λ_y' by λ_y^0. The electroosmotic contribution to the membrane conductance can be evaluated according to Eq. 17. The values of g_v and g_p can be estimated from g_{kl}'s given in Fig. 4 by using the relations given in the preceding paper.[1] The values of g_v and g_p were found to be almost the same as those of g_w and g_{ww}, respectively. The observed value of G_m was 0.39 S cm^{-2} in the range of concentration studied and the values of G_m' calculated according to Eq. 18 were 0.35—0.30 S cm^{-2}. On the other hand $g_y(\lambda_y)$ was greater than $g_y^0(\lambda_y^0)$ by a factor of 2 as shown in Fig. 2. These results indicate that the electroosmotic effect is not so appreciable as the diffusional effect.

The charge concentration per unit volume of the pore liquid X can be evaluated according to the relation[1]

$$X = g_v/g_p\bar{v}_w. \tag{20}$$

The value of X is given in Fig. 5. Equation 20 is equivalent to the effective charge density of a membrane proposed by Staverman.[7] The values of X were found to be 1—1.6 mol dm^{-3}, while the counter-ion concentration, $\bar{X}$, in the pore liquid evaluated from the exchange capacity and water content of the membrane was ca. 6 mole/KgH$_2$O. This might indicate that the counter-ions accompanying the electroosmotic flow are not all counter-ions within the membrane, as assumed in classical membrane theory.[8] The relation $X=\bar{X}$ was also assumed in Despić and Hills' theory.[5] It is interesting to note here that the ratio, $X/\bar{X}$, is near to the contribution of the electroosmotic effect in membrane conductance, $(G_m-G_m')/G_m$.

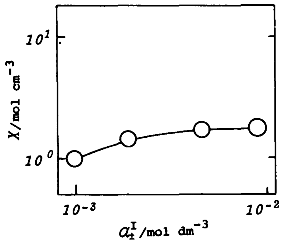

Fig. 5. Charge concentration per unit volume of the pore liquid vs. mean electrolyte activity of phase I.

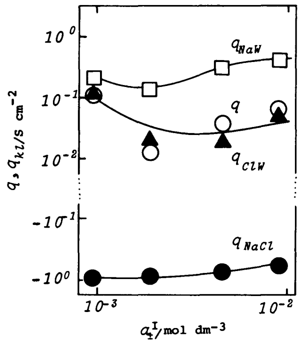

Fig. 6. Coupling coefficient vs. mean electrolyte activity of phase I.
○: q, ●: q_{NaCl}, □: q_{Naw}, ▲: q_{Clw}.

The present study deals with the three processes expressed by Eq. 1. The degree of coupling among these processes can be demonstrated by a coupling coefficient[1]

$$q_{kl} = -|g|_{kl}/(|g|_{kk}|g|_{ll})^{1/2}, \tag{21}$$

where $|g|_{kl}$ is the cofactor of an element g_{kl} in the conductance matrix. The coupling coefficients q_{NaCl}, q_{Naw}, and q_{Clw} calculated according to Eq. 21 is shown in Fig. 6. It is shown in this figure that q_{NaCl} is close to -1 while q_{Naw} and q_{Clw} are the order of 10^{-1} and 10^{-2}, respectively. This indicates that the ionic processes are more strongly coupled to each other than the coupling between ion and water transports. The remarkable difference between the diffusional and electric ion conductances reflects a strong interionic coupling. On the other hand, the ion-solvent interaction is weaker as shown in the electroosmotic effect, although it is appreciable. These facts indicate the importance of the cross coefficients in the membrane process. Thus, the cross coefficients in the phenomenological equation can not be ignored unless doing so is verified experimentally. The coupling coefficient q for the salt flow-volume flow coupling in the absence of an electric current is also shown in Fig. 6. The coefficient q is defined by

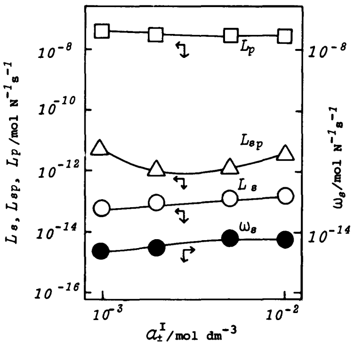

Fig. 7. Solute permeability(ω_s), thermodynamic permeability(L_s), mechanical filtration coefficient(L_{sp}) and hydrodynamic permeability(L_p) vs. mean electrolyte activity of phase I.
●: ω_s, ○: L_s, △: L_{sp}, □: L_p.

$$q = L_{sp}/(L_s L_p)^{1/2}, \tag{22}$$

where L_{sp} and L_s, and L_p are the phenomenological coefficients in the equation[1)]

$$\begin{bmatrix} \bar{v}_s J_s^0 \\ J_v^0 \end{bmatrix} = -\begin{bmatrix} L_s & L_{sp} \\ L_{sp} & L_p \end{bmatrix} \begin{bmatrix} \Delta\pi - \Delta\pi_s \\ \Delta p - \Delta\pi \end{bmatrix}. \tag{23}$$

This can be derived from Eq. 1 at a zero membrane current.[1)] In Eq. 23, the superscript 0 refers to a case where there is no membrane current; $\bar{v}_s$ denotes the partial molar volume of the salt; J_s^0 the salt flux; J_v^0 the volume flow; $\Delta\pi$ the osmotic pressure difference; Δp the external pressure difference; and $\Delta\pi_s$ the osmotic pressure difference of the salt. It is defind by[1)]

$$\bar{v}_s \Delta\pi_s = -2RT \ln a_{\pm}^{\mathrm{II}}/a_{\pm}^{\mathrm{I}}. \tag{24}$$

Here, $a_{\pm}$ denotes the mean activity of salt. It should be noted that the factors determining the correlation among the flow processes are not the relative magnitudes of the flows, but the coupling coefficients. For example, g_{ww} and g_w are greater than 100 and 10 times the membrane conductance, respectively, while the effects of the solvent flow on the interionic correlations are small as illustrated in the electro-osmotic effect on the membrane conductance. The ion fluxes can also be expressed by

$$\begin{bmatrix} i_{Na} \\ i_{Cl} \end{bmatrix} = -\begin{bmatrix} (g_{NaNa})_{app} & (g_{NaCl})_{app} \\ (g_{ClNa})_{app} & (g_{ClCl})_{app} \end{bmatrix} \begin{bmatrix} V - V_{Na} \\ V - V_{Cl} \end{bmatrix}, \tag{25}$$

where the subscript app refers to the apparent values, including the solvent effect.[1)] The deviation of $(g_{NaCl})_{app}$ from g_{NaCl} was comparable with that of G_m from G_m', although $(t_{Na})_{app}$ is close to t_{Na}.

Since the conductance matrix characterizes the system, all the transport properties of the membrane can be calculated from the elements of the conductance matrix. The thermodynamic solute permeability L_s, the mechanical filtration coefficient L_{sp}, the hydrodynamic permeability L_p and the solute permeability coefficient ω_s[1)] are related by

$$\omega_s = (L_s - L_{sp}^2/L_p)/\bar{v}_s. \tag{26}$$

These quantities were estimated for the present system as shown in Fig. 7. The reflection coefficient

$$\sigma = 1 - L_{sp}/L_p \tag{27}$$

was close to unity, 0.9998—0.9999, and is not plotted in this figure.

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