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THE DETERMINATION OF DYNAMIC CHARACTERISTICS OF ION-EXCHANGE COLUMNS BY THE APPLICATION OF ONE-DIMENSIONAL MATHEMATICAL MODELS

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SUMMARY

The one-dimensional mathematical models describing the processes in ion-exchange columns with packed bed and counter-current phase motion are compared. The exchange of Li^+ with H^+, Na^+ with H^+ and K^+ with H^+ was studied on a sulphonated cation exchanger KU-2 × 8. The parameters of the models were determined by the method of random search from the experimental curves showing the responses to pulse perturbations of the hydrogen-ion concentration. Under the experimental conditions, the diffusion model (ED) and the plug-flow (PF) model are equally adequate. A more complicated model (LD) which takes into account the interphase non-equilibrium and axial dispersion in the liquid phase was also studied. The ranges of parameters for which the LD model reduces to the ED and PF models are established. It is shown that the LD model has no advantages over the ED and PF models, because axial dispersion and interphase non-equilibrium are additive.

INTRODUCTION

The determination of dynamic characteristics, such as height equivalent to a theoretical plate (HETP), height of transfer unit, etc., of separation columns with fixed sorbent beds or with counter-current motion of the phases is one of the key issues in choosing the conditions for separation of mixtures and purification of substances. The most convenient method is to calculate the parameters of a mathematical model of a column from the curves representing the response to a disturbance of the concentration of the substance exchanging between the phases.

As known from the work of Glueckauf[1], the HETP value can be found from the broadening of a chromatographic peak in a packed bed. The possibility of using the pulse method to determine the parameters of counter-current exchange columns was considered previously[2-6]. This method can be based upon various mathematical models, such as the equilibrium diffusion (ED) model which was used in calculations of HETP by Glueckauf

$$(1-\chi)\, m_0 \cdot \frac{\partial N}{\partial t} + \chi c_0 \cdot \frac{\partial n}{\partial t} = S \cdot \frac{\partial N}{\partial Z} - L \cdot \frac{\partial n}{\partial Z} + E_s \cdot \frac{\partial^2 N}{\partial Z^2} + E_L \cdot \frac{\partial^2 n}{\partial Z^2} \quad (1)$$

where $N = \alpha n$, the non-equilibrium model of plug flow (PF)

$$(1-\chi)\, m_0 \cdot \frac{\partial N}{\partial t} = S \cdot \frac{\partial N}{\partial Z} + K_L\, (n - N/\alpha)$$

$$\chi\, c_0 \cdot \frac{\partial n}{\partial t} = -L \cdot \frac{\partial n}{\partial Z} - K_L\, (n - N/\alpha) \tag{2}$$

and the more complicated diffusion model (LD) in which, in contrast to PF, the liquid phase axial dispersion is taken into account:

$$(1-\chi)\, m_0 \cdot \frac{\partial N}{\partial t} = S \cdot \frac{\partial N}{\partial Z} + K_L\, (n - N/\alpha)$$

$$\chi c_0 \cdot \frac{\partial n}{\partial t} = -L \cdot \frac{\partial n}{\partial Z} + E_L \cdot \frac{\partial^2 n}{\partial Z^2} - K_L\, (n - N/\alpha) \tag{3}$$

The present work demonstrates the possibility of simultaneous determination of several parameters of ion-exchange columns from the experimental curves representing the responses to pulse concentration disturbances of one of the exchanging components. Also, the PF, ED and LD models are compared.

SOLUTIONS OF THE EQUATIONS

The solution of eqn. 1 describing the broadening of a δ-shaped pulse applied to a solid phase at a location remote from the end of the column is (within the ED model)[2,4]

$$n(Z,t) = n_0 + \frac{Q}{2\sqrt{\pi\alpha\rho h_{ED} L t}} \cdot \exp\left[-\alpha\rho \cdot \frac{(Z - Z_0 - ut)^2}{4\, h_{ED}\, L\, t} \right] \tag{4}$$

where $\rho = (1-\chi)m_0 + \chi c_0/\alpha$, $u = (L - \alpha S)/\alpha\rho$ and $h_{ED} = (\alpha E_s + E_L)/L$. In the PF model, the solution of eqn. 2 for a very narrow signal and on condition that $\chi c_0/(1-\chi)m_0$ is very small is[5]

$$n(Z,t) = n_0 + \frac{Q}{\alpha\, (1-\chi)\, m_0\, h_{PF}} \cdot$$

$$\exp\left[-\frac{Z - Z_0 + w\, t}{h_{PF}} - \frac{L\, t}{\alpha\, (1-\chi)\, m_0\, h_{PF}} \right] \cdot \tag{5}$$

$$I_0\left[2 \sqrt{L\, (Z - Z_0 + w\, t)t/\alpha\, (1-\chi)\, m_0\, h_{PF}^2} \right]$$

where I_0 is the zero-order modified Bessel function, $w = S/(1 - \chi)\, m_0$ and $h_{PF} = L/K_L$. For the LD model, the solution of eqn. 3 obtained under the same conditions as that of PF and at $\eta > 0$ is[6]

$$n \, (\eta > 0) = n_0 + \frac{Q \, (1 + \gamma\mu/\alpha)}{h_{LD} \, (1 - \chi) \, m_0 \, 2\alpha \, \sqrt{\pi\mu}} \, \cdot$$

$$\exp \left[- \frac{St \, (1 + \gamma\mu/\alpha)}{\alpha \, (1 - \chi) \, m_0 \, h_{LD}} \right] \cdot$$

$$\int_0^\infty I_0 \left(2 \, \sqrt{\frac{St \, \omega \, (1 + \gamma\mu/\alpha)}{\alpha \, (1 - \chi) \, m_0 \, h_{LD}}} \right) \cdot$$

$$\frac{1}{\sqrt{\omega}} \cdot \exp \left[-\omega - \frac{(\eta - \omega)^2}{4 \, \mu\omega} \right] d\omega$$

(6)

where $\mu = K_L E_L/L^2$, $\gamma = L/S$, $h_{LD} = (L/K_L) \, (1 + \gamma\mu/\alpha)$, $\eta = (K_L/L) \, (Z - Z_0 + \omega t)$, $\omega = \alpha \, (1 - \chi) \, m_0 \xi/\chi \, c_0$ and ξ is the integration variable.

EXPERIMENTS WITH PULSE INJECTION OF H$^+$

The experiments were carried out with sulphonated polystyrene–divinylbenzene resin KU-2 × 8 (particle diameters 0.25–0.50 mm, exchange capacity 4.93 mg-equiv. per 1 g of dry exchanger in the hydrogen form). The exchange of Li$^+$ with H$^+$, Na$^+$ with H$^+$ and K$^+$ with H$^+$ was studied from chloride solutions with a total concentration of 0.2 M. Since there was a reliable and fast technique to determine H$^+$ in small-volume samples using an antimony electrode[7], the H$^+$ was taken as the microcoponent. The concentration of H$^+$ was determined from a calibration curve of the dependence of the potential of the electrode system on log c_H. To obtain this curve we used a series of standard solutions containing M$^+$ and H$^+$ with the total concentration of those ions 0.2 M.

When planning the experiment, it was envisaged that the equilibrium separation coefficient, α (for the microcomponent $\alpha = N/n$), should be constant. Preliminary studies of the M$^+$–H$^+$ exchange indicated that at low contents of H$^+$ a decrease in their fraction results in a change in α[8]. That is why a "slug" was introduced into the column packed with the exchanger that was not in the pure metal form, but was first equilibrated with a solution containing 0.2 M MCl and 0.001 M (or 0.0005 M) hydrochloric acid. In this case, the experimental value of α changed by no more than 20–30%. The values of α used in the calculations were $\alpha_{Li}^H = 1.67$, $\alpha_{Na}^H = 1.04$ and $\alpha_K^H = 0.91$ in accordance with the solution compositions.

The experiments were done in glass columns with packed beds (height 120 cm, diameter 1.8 cm) and in a counter-current column (height 218 cm, diameter 2.4 cm) in which the solution ascends while the resin descends and is withdrawn by a screw-conveyer (Fig. 1). This set-up is similar to that described previously[9,10].

The "slug" —1 ml of the exchanger suspension in hydrogen form— was introduced homogeneously over the cross-section at a point in the counter-column well away from its ends. The conditions in the column were chosen so that the "slug" should move along the column. At certain positions along the column (at 80–135 cm
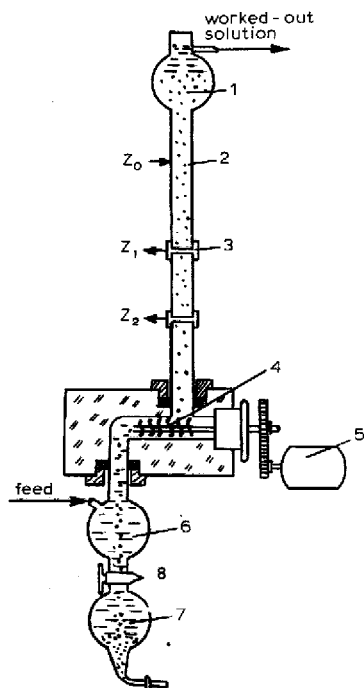
Fig. 1. Counter-current column: 1 = upper tank; 2 = glass column; 3 = rubber sealings; 4 = screw-conveyer; 5 = electromotor; 6,7 = lower exchanger tank; 8 = three-way valve.

from where the "slug" was introduced), 0.1-ml samples for determining the hydrogen-ion concentrations were extracted with a syringe through the rubber seals between the glass sections. The total amount of H^+ taken for measurements was never greater than 3% of that introduced with the "slug".

After the measurements, the resin from the lower tank was put into a gauging tank, where the total capacity of the waste resin was calculated from the volume of the suspension and the known specific capacity of the suspension. This value was then used to calculate the experimental value of the flow-rate of the ions with the ion exchanger, S. The flow-rate of the ions with the solution, L, was calculated from the volume of the solution leaving the column and from the solution volume displaced by the resin from the tank. The experimental values are given in Table I. The results of the experiments at various velocities of the phases are presented in Fig. 2.

In the column with a fixed bed the samples were taken from a cross-section located 95 cm from where the slug was introduced; solution fractions were also taken at the column exit (at 105 cm). After the experiments the solution from the intergrain space and the absorbed electrolyte were displaced with distilled water, the ion exchanger being then transformed into the hydrogen form and its capacity thereby being determined.

The experimental capacity of a unit volume of the column was calculated from the total amount of ions in the column and from the known volume of the suspension. The flow-rate, L, was calculated using the known flow-rate of the solution passed through. These values are given in Table II.

TABLE I

EXPERIMENTAL RESULTS FOR THE Na^+–H^+ SYSTEM WITH THE COUNTER-CURRENT COLUMN

Values in brackets show the confidence interval for a found value with the standard reliability 0.95.

	h_{ED}, h_{PF} (cm)	ρ (mg-equiv./ml)	S (mg-equiv. $cm^2 \cdot min$)	u (cm/min)	Z_0 (cm)
Experiment A					
Obs.	—	2.14*	0.53 (0.49; 0.57)	0.28	0
ED	0.14 (0.12; 0.15)	1.62 (1.52; 1.74)	—	0.284 (0.283; 0.285)	−0.55
PF	0.14 (0.13; 0.17)	1.67 (1.51; 1.75)	0.51 (0.46; 0.53)		−0.39
Experiment B					
Obs.	—	2.14*	0.42 (0.38; 0.46)	0.13	0
ED	0.26 (0.25; 0.27)	1.95 (1.92; 2.00)	—	0.135 (0.134; 0.139)	+0.51
PF	0.26 (0.25; 0.27)	1.95 (1.91; 1.99)	0.44 (0.43; 0.45)	—	+0.6
Experiment C					
Obs.	—	2.14*	1.07 (1.01; 1.13)	0.40	0
ED	0.78 (0.71; 0.84)	1.88 (1.81; 1.97)	—	0.41 (0.40; 0.42)	−6.89
PF	0.77 (0.72; 0.82)	1.88 (1.82; 1.89)	1.14 (1.11; 1.16)	—	−6.13

* The value determined for a column with a fixed bed (diameter 1.8 cm).

The elution curves for the three systems at the same feeding rate of the solution are shown in Fig. 3.

TREATMENT OF EXPERIMENTAL RESULTS

The parameters of the models 1 and 2 were determined from the experimental response curves by numerically solving the inverse problem. The function

$$\psi = \sum_{i=1}^{K} (n_{i,e} - n_{i,t})^2 / n_{i,e} n_{i,t} \qquad (7)$$

was minimized by the method of random search[11], where $n_{i,e}$ and $n_{i,t}$ are the experimental and calculated (using eqns. 4, 5) values of the fraction of the component in the ith sample (at given t and Z), and K is the total number of experimental points in an experiment. The errors in each parameter were estimated by the method of linearization[2].

On treating the curves obtained in experiments with the counter-current col-
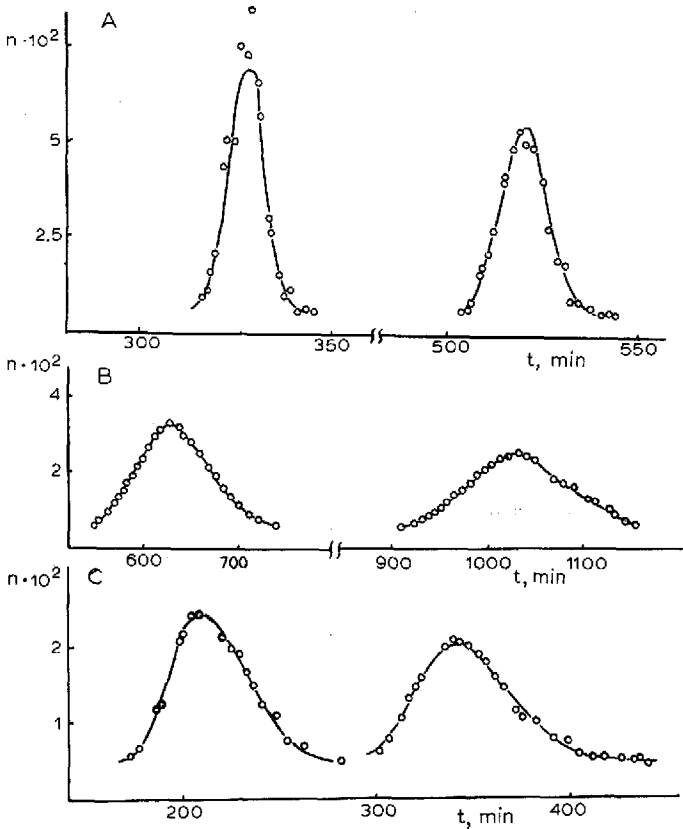
Fig. 2. Elution curves for experiments with the counter-current column: (A) $Q = 0.366$ mg-equiv./cm^2, $v = 0.4$ cm/min, $w = 0.3$ cm/min; (B) $Q = 0.709$ mg-equiv./cm^2, $v = 2.1$ cm/min, $w = 0.2$ cm/min; (C) $Q = 0.741$ mg-equiv./cm^2, $v = 4.4$ cm/min, $w = 0.6$ cm/min. ○, Experimental values; ——, calculated according to the models.

umn, the parameters determined were h_{ED}, ρ, u and the coordinate Z_0, where the "slug" was introduced, for the ED model and h_{PF}, $(1 - \chi)m_0$, S and Z_0 for the PF model. The values of Q, L, α, n_0 and the coordinates Z_1 and Z_2 were known. For the experimental points obtained at the exit of a fixed bed column, three parameters were determined for both models: h_{ED} (or h_{PF}), ρ [or $(1 - \chi)m_0$] and L. Here, Q, α, n_0 and the height of the exchanger bed were known.

DISCUSSION

The response curves consisting of about 40 experimental points allowed the determination of the four parameters of each system. Under the conditions mentioned above, the curves calculated by the ED and FP models practically coincide and are in good agreement with the experimental results for both types of columns (see Figs. 2 and 3). The experimental and calculated parameters are also in agreement (see Tables I and II and Figs. 4 and 5). (Of note is that the parameters determined from the elution curves and response curves obtained from the cross-section of a

TABLE II

RESULTS OF EXPERIMENTS WITH THE FIXED BED COLUMN

Values in brackets show the confidence interval for a found value with the standard reliability 0.95.

	h_{ED}, h_{PF} (cm)	ρ (mg-equiv./ml)	L (mg-equiv./cm² · min)
Li^+-H^+ system			
Obs.	—	1.95	0.505
		(1.91; 1.99)	(0.50; 0.51)
ED	0.213	1.76	0.52
	(0.206; 0.220)	(1.71; 1.80)	(0.51; 0.54)
PF	0.212	1.75	0.53
	(0.203; 0.221)	(1.70; 1.81)	(0.51; 0.54)
Na^+-H^+ system			
Obs.	—	2.14	0.494
		(2.10; 2.18)	(0.489; 0.500)
ED	0.41	1.75	0.51
	(0.38; 0.43)	(1.70; 1.82)	(0.50; 0.53)
PF	0.42	1.75	0.51
	(0.39; 0.45)	(1.68; 1.82)	(0.49; 0.53)
K^+-H^+ system			
Obs.	—	2.28	0.512
		(2.23; 2.33)	(0.507; 0.517)
ED	0.29	1.62	0.48
	(0.26; 0.32)	(1.51; 1.78)	(0.45; 0.53)
PF	0.29	1.62	0.48
	(0.25; 0.32)	(1.51; 1.83)	(0.45; 0.54)

fixed bed are very similar.) In experiments with the fixed bed column, the calculated value of ρ was smaller than the experimental one, possibly because the isotherm deviates from linearity.

For the ion-exchange system involved the complicated PF model has no advantages over the simpler ED model, at least in the range of phase velocities studied.

Figs. 6 and 7 for the two types of columns show the dependences of h_{ED} and h_{PF} on the solution velocity, v, and on the relative velocity of the phases, $v + w$. The dependences are similar to those revealed earlier for these types of columns by the methods of broadening and stationary fronts[9], the characteristic scales h_{ED} and h_{PF} being practically independent of the ionic species.

In order to estimate separately the contributions of two factors, E_L and K_L, to broadening of the concentrational signal, an attempt was made to treat the experimental data using the LD-model. In accordance with theoretical additivity of the axial dispersion and the resistance to interphase transfer[6], the characteristic scale of the model was taken as $h_{LD} = L/K_L + E_L/\alpha S$. In the calculations, four parameters were determined: $(1 - \chi) m_0$, γ, μ and h_{LD}; the values of α, n_0, Q, L and Z_0, Z_1, Z_2 were known. At $\mu > 30$ the solution of the LD model (eqn. 6) is very similar to that of the ED model (eqn. 4) in which $E_s \ll E_L$. At $\mu < 0.05$ the solution of the LD model almost coincides with that of the PF model (eqn. 5). When the parameters ρ, γ, h_{LD} were evaluated at values of μ within the interval 0.05–30 serious errors were
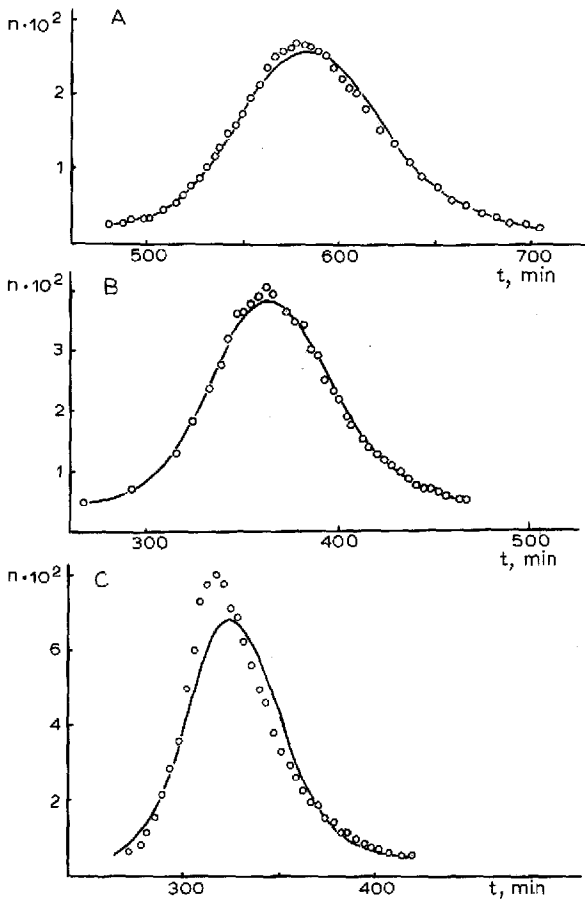
Fig. 3. Elution curves for experiments with the fixed bed column: (A) Li^+–H^+ system, Q = 1.15 mg-equiv./cm², v = 6.4 cm/min; (B) Na^+–H^+ system, Q = 1.36 mg-equiv./cm², v = 6.4 cm/min; (C) K^+–H^+ system, Q = 1.82 mg-equiv./cm², v = 6.9 cm/min. ○, Experimental values; ——, calculated according to the models.
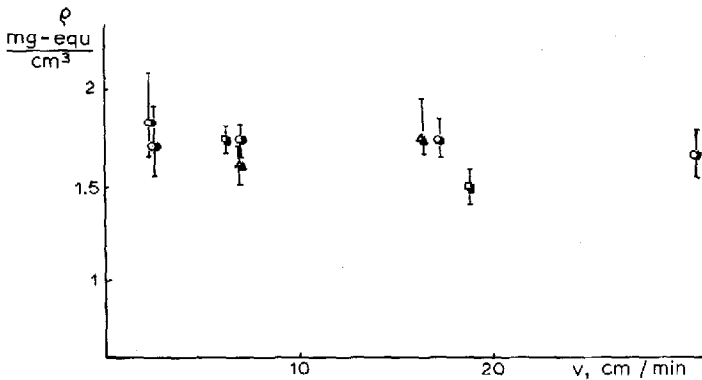

Fig. 4. Values of ρ at different solution velocities, v, in experiments with the fixed bed column: □, ■, Li^+–H^+; ○, ●, Na^+–H^+; △, ▲, K^+–H^+; □, ○, △, calculated according to the ED model; ■, ●, ▲, calculated according to the PF model.
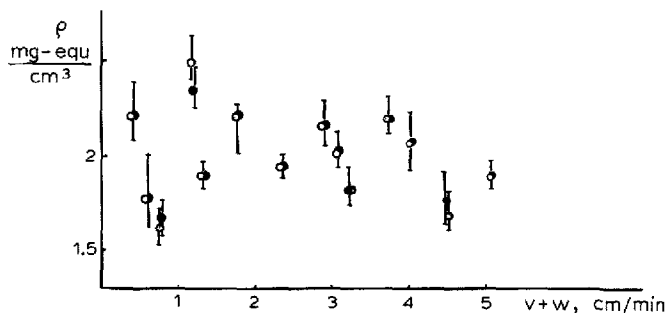
Fig. 5. Values of ρ for different relative velocities of the phases $v + w$. Na$^+$–H$^+$ system: O, calculated according to the ED model; ●, calculated according to the PF model.
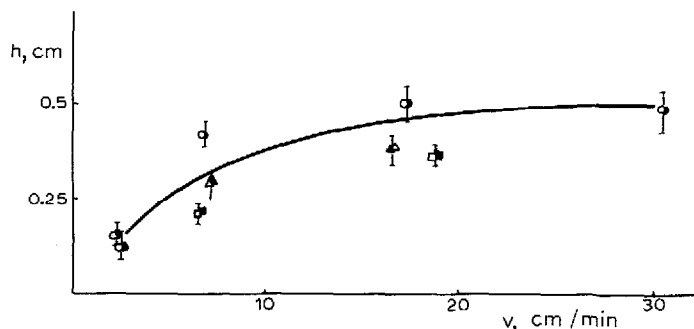

Fig. 6. Dependence of h_{ED}, h_{PF} on the velocity, v, of the solution in experiments with the fixed bed column. Notation as in Fig. 4.

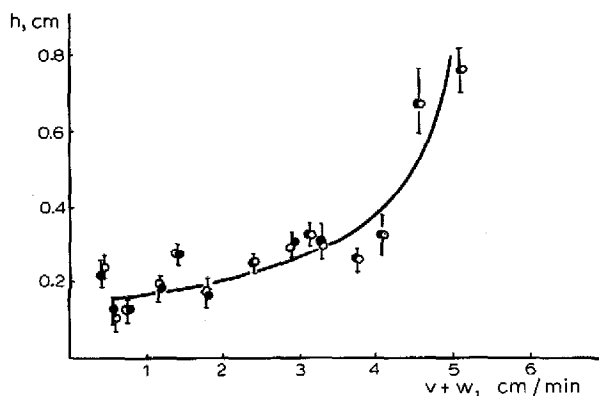Fig. 7. Dependence of h_{ED}, h_{PF} on the relative velocity of the phases. Na$^+$–H$^+$ system. Notation as in Fig. 5.

found and the value of the function ψ (eqn. 7) was larger than that for the ED and PF models. When trying to determine simultaneously the four parameters ρ, γ, h_{LD} and μ, the value of μ rapidly went out of the above interval.

The method of moments[12], which is widely used to determine dynamic parameters, was also not applicable in our case because the obtained peaks are almost symmetric, which results in a large error in calculations of the third moment which is essential in determining E_L and K_L.

In conclusion, the obtained results show that, for the systems involved, broadening of a concentration wave is, first of all, determined by superposition of the effects of axial dispersion and interphase non-equilibrium and practically does not depend on the relative contributions of these factors. The two limiting models (ED and PF) are equally applicable, but the more complicated LD model seems to be redundant in our case.

SYMBOLS

N, n	Equivalent fractions of the component in the exchanger and in solution
N_0, n_0	Initial concentrations of the component (H^+) in the exchanger and in solution
m_0, c_0	Total concentrations (mg-equiv./ml) of the exchanging ions in the exchanger and in solution
S, L	Flow-rates (mg-equiv./cm^2 · min) of the mixtures of ions with the ion exchanger and with the solution
E_s, E_L	Coefficients (mg-equiv./cm · min) of axial dispersion in the solid and liquid phases
K_L	Liquid side mass-transfer coefficient (mg-equiv./ml · min)
Q	Amount (mg-equiv./cm^2) of the component introduced in a pulse per unit cross-section of the column
u	Velocity (cm/min) of the pulse motion along the column
v	Linear velocity (cm/min) of the solution
w	Linear velocity (cm/min) of the ion exchanger
h_{ED}, h_{PF}	Characteristic scales of the models (cm)
α	Equilibrium separation coefficient
ρ	Capacity of the column per unit volume (mg-equiv./ml)
χ	External void fraction
Z	Longitudinal coordinate directed along the solution motion (cm)

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