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DETERMINATION OF THE DENSITY OF THEORETICAL PLATES AND THE MASS EFFECT IN COUNTERCURRENT ELECTROPHORESIS

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SUMMARY

The density of theoretical plates, $n(\text{cm}^{-1}) = v_L/D_{\text{eff}}$, in a countercurrent electrophoretic column is given by the effective diffusion coefficient, D_{eff} , of the ions and the flow-rate, v_L , of the countercurrent solution. Both values and the dependence on each other have been measured.

The mass effect, $1 + \varepsilon$, based on the differences in ionic mobilities, was determined for the isotope mixture ^{22}Na – ^{23}Na in 1 *N* acetic acid as the countercurrent solution as a function of the ionic concentration.

It was found that experimentally determined separation factors, $Q = (1 + \varepsilon)^{n \cdot x}$, obtained in the stationary state of the process, are in good agreement with those calculated from the measured values of n and $1 + \varepsilon$.

INTRODUCTION

Countercurrent electrophoresis (CCEP) can easily be used for the separation of ions (mainly in aqueous solution) based on the differences in their migration velocities (for reviews, see refs. 1 and 2). The principle is simple: a countercurrent flow of the solvent is directed against the ionic mixture migrating in an externally applied electric field. If the flow-rate corresponds to the average velocity of the ions, their centre of gravity will remain stationary, while the faster moving ions migrate against the stream, and the slower moving ions are gradually flushed back.

In earlier publications, the results of CCEP have been described quantitatively only in terms of the separation factor, Q , obtained in the stationary state of the process. Indeed, mass effects, $u_1/u_2 = (1 + \varepsilon)$, can be calculated using an absolute³ or a relative method⁴, but the indirect determination of the density of theoretical plates, n , (of the separation column) using the following equation leads to discrepancies:

$$Q = (1 + \varepsilon)^{n \cdot x} \tag{1}$$

In this paper, a method for determining $(1 + \varepsilon)$ and n is described. Calculated and experimental Q values are compared and the densities of theoretical plates in the electrolytic trough⁵, used as the separation column, are given.

THEORETICAL

Transport equation

The self-stabilization mechanism of CCEP that leads to a stationary distribution of the ionic mixture was described by Wagener and co-workers^{1,2,6}. Here, the ionic transport should be considered.

A binary cationic mixture, the mole fractions of the components being γ_1 and γ_2 , is distributed along the separation column at a constant concentration, c_s (mole · cm⁻³), which is due to the equilibrium between the electric transport of the cations and the movement by the countercurrent solvent:

$$E \cdot \bar{u}^+ - v_L = 0 \quad (2)$$

with

$$\bar{u}^+ = \gamma_1 \cdot u_1^+ + \gamma_2 \cdot u_2^+ \quad (3)$$

where E (V · cm⁻¹) is the electric field strength, \bar{u}^+ (cm² · V⁻¹ · sec⁻¹) is the mean mobility of the cationic mixture and v_L (cm · sec⁻¹) is the flow-rate of the countercurrent solvent through the separation column.

The separation is limited by diffusion processes. The effective diffusion coefficient, D_{eff} (cm² · sec⁻¹), has two major contributions: (a) the parabolic velocity pattern of the flowing solvent and (b) the thermal convection within the solvent, while molecular processes can be neglected.

The net transport, T_1 (mole · sec⁻¹), of component 1 is given by the equation

$$T_1 = q \cdot c_s \left[\gamma_1 (E \cdot u_1^+ - v_L) - D_{\text{eff}} \cdot \frac{\partial \gamma_1}{\partial x} \right] \quad (4)$$

where q (cm²) is the cross-section of the separation column and x (cm) is the length of the stationary distribution in the separation column. The total transport is zero over the whole process:

$$T_1 - T_2 = 0 \quad (5)$$

Initial separation

The initial separation of the components starts at the ends of the stationary distribution of the mixture. The transport of component 1, provided that no concentration gradient is present, is given by the equation

$$T_1 = q \cdot c_s [\gamma_{01} (E u_1^+ - v_L)] \quad (6)$$

where the concentration, c_s , is given by (see refs. 1, 2 and 6)

$$c_s = \frac{I \cdot t r^+}{F \cdot \dot{M}} \quad (7)$$

Substitution of eqn. 2 gives:

$$T_1 = \frac{I}{F} \cdot t r_1^+ - \dot{M} c_s \cdot \gamma_{01} \quad (8)$$

where I (A) is the current, tr^+ is the transport number of the mixture of cations in question, F is the Faraday constant, \dot{M} ($\text{cm}^3 \cdot \text{sec}^{-1}$) = $q \cdot v_L$ is the feed rate of counter-current solvent and γ_{01} is the mole fraction of component 1 in the initial mixture.

If V (cm^3) denotes a certain part of the column (e.g. one half), then the mass of component 1 would change in that volume according to

$$\frac{d}{dt} (V \cdot \gamma_1 \cdot c_s) = T_1 \tag{9}$$

Integration over time t (with V and c_s constant) gives:

$$V \cdot c_s (\gamma_{t1} - \gamma_{01}) = \frac{Q(t)}{F} \cdot tr_1^+ - c_s \gamma_{01} M(t) \tag{10}$$

or, in rearranged form:

$$tr_1^+ = \frac{F \cdot c_s}{Q(t)} [V (\gamma_{t1} - \gamma_{01}) + \gamma_{01} \cdot M(t)] \tag{11}$$

where γ_{t1} is the mole fraction of component 1 in the homogeneous mixed volume V at time t , $Q(t)$ (A · sec) is the total charge transfer through the separation column in time t and $M(t)$ (cm^3) is the total solvent flow through the separation column in time t . Using the definition of the transport number:

$$tr_1^+ = \frac{\gamma_1 u_1^+}{\bar{u}^+ + \bar{u}^-} \tag{12}$$

the ratio of the transport numbers, with $\gamma_2 = 1 - \gamma_1$, is given by the equation

$$\frac{tr_1^+}{tr_2^+} = \frac{\gamma_{01} u_1^+}{(1 - \gamma_{01}) u_2^+} \tag{13}$$

Using eqns. 11 and 13, the elementary effect is obtained:

$$\frac{u_1^+}{u_2^+} = \frac{\frac{\gamma_{t1} - \gamma_{01}}{\gamma_{01}} + \frac{M(t)}{V}}{\frac{(1 - \gamma_{t1}) - (1 - \gamma_{01})}{(1 - \gamma_{01})} + \frac{M(t)}{V}} \tag{14}$$

Transport by solvent flow and diffusion

The transport of radioactive tracer ions (N = specific activity) through a stationary distribution of a uniform compound is given by:

$$-J_2 = -\frac{T_2}{q} = N (E \cdot u_2^+ - v_L) - D_{\text{eff}} \cdot \frac{\partial N}{\partial x} \tag{15}$$

From eqn. 2 for a uniform compound 1, we obtain

$$-J_2 = N \cdot V_p - D_{\text{eff}} \cdot \frac{\partial N}{\partial x} \tag{16}$$

with

$$V_p = v_L \left(\frac{u_1^+ - u_2^+}{u_1^+} \right) \tag{17}$$

N is a function of time and space (longitudinal axis). The variation of N is described by Fick's second law of diffusion:

$$\frac{\partial N}{\partial t} = D_{\text{eff}} \cdot \frac{\partial^2 N}{\partial x^2} - V_p \cdot \frac{\partial N}{\partial x} \quad (18)$$

The initial specific activity, N_0 , extends from $x = x_0$ to $x = \pm h$ ($2h$ is the width of one chamber). The distribution is given by

$$N_0 = \text{constant for } -h < x_0 < +h$$

$$N_0 = 0 \text{ for } -\infty < x < -h \text{ and } h < x < \infty$$

and

$$\lim_{h \rightarrow 0} N_0 \cdot 2h = Q$$

Then, the solution of eqn. 18 would be⁷

$$N(x, t) = \frac{Q}{2\sqrt{\pi D_{\text{eff}} t}} \cdot \exp \left[-\frac{(x - V_p t)^2}{4 D_{\text{eff}} t} \right] \quad (19)$$

V_L and D_{eff} can be determined experimentally using eqns. 17 and 19, respectively. These values are needed for the determination of n (see eqn. 23).

Final separation

In the stationary state (final separation) all transports are zero:

$$T_1 = T_2 = 0 \quad (20)$$

Using eqns. 2, 3, 4 and 20, the separation factor, Q , is obtained:

$$Q \equiv \frac{(\gamma_1/\gamma_2)_{x=x}}{(\gamma_1/\gamma_2)_{x=0}} = \exp \left(\frac{\Delta u^+}{\bar{u}^+} \cdot \frac{x \cdot v_L}{D_{\text{eff}}} \right) \quad (21)$$

If $\Delta u^+/\bar{u}^+ \ll 1$, for the correlation between the elementary effect and the density of theoretical plates (eqn. 1) we obtain

$$Q = (1 + \varepsilon)^{n \cdot x} \quad (1)$$

with

$$(1 + \varepsilon) = \frac{u_1^+}{u_2^+} \approx 1 + \frac{\Delta u^+}{\bar{u}^+} \quad (22)$$

and

$$n = \frac{v_L}{D_{\text{eff}}} \quad (23)$$

EXPERIMENTAL

Electrolytic trough

The separation column is an electrolytic trough⁵ of triangular cross-section, which is divided by diaphragms into a series of chambers. The diaphragms are acrylic

sheets with a large opening covered with nylon gauze. The chambers contain glass cooling elements.

The most important parts of the trough are the diaphragms. A flow of solvent as well as electric transport pass through the diaphragms. Separation takes place mainly in the pores of the diaphragms, which restrict thermal convection to directions perpendicular to the longitudinal axis of the trough. The trough used consisted of 30 chambers of a width of 1.2 cm. The cross-section of the column (q_1) was 28.0 cm², with openings (q_2) of 7.1 cm² (with a mean cross-section (q) of 25.4 cm²). The pore size of the nylon gauze was 25 μ m (or 53 and 20 μ m).

The whole separation equipment has been described earlier^{1,2,6}.

Separation mixture

All of the transport equations were tested with a ²²Na–²³Na isotope mixture. The ²²Na activity was 3–4 μ Ci. The mixture was in the acetate form and 1 *N* acetic acid was used as the countercurrent solvent.

The stationary ionic distribution was extended over 19–20 chambers and was attained at the beginning of each experiment. Owing to the special composition of the mixture, only the displacement of ²²Na has to be considered, and this was measured by its γ -activity. Fig. 1 shows a series of displacement profiles.

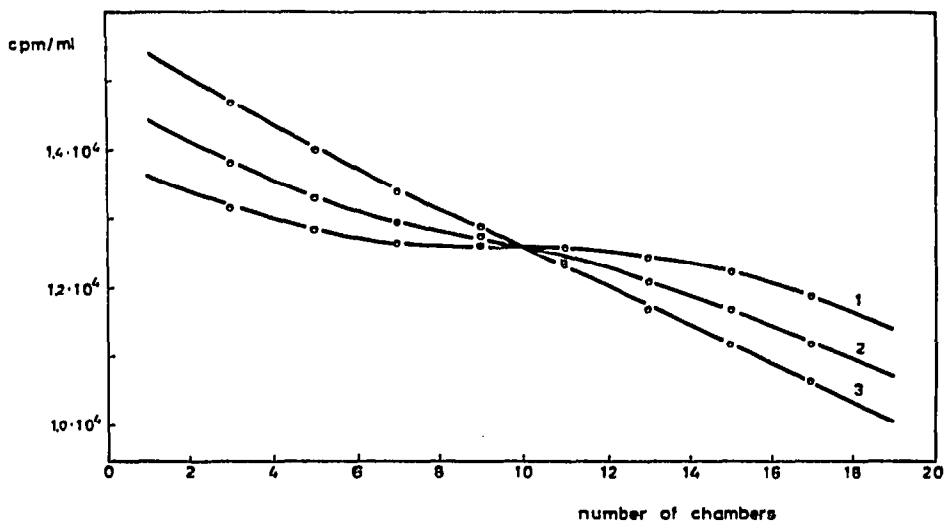


Fig. 1. Displacement profiles of ²²Na in a stationary sodium acetate distribution. The initial composition was homogeneous; the experiments were interrupted after 16 h (curve 1), 50 h (curve 2) and 150 h (curve 3). From evaluating curve 1 with $M(t) = 5769$ cm³, $V = 275$ cm³ and $(N_t - N_0)/N_0 = 41/1260$, the following elementary effect results: $u_{22\text{Na}}/u_{23\text{Na}} = 1.00155$. Experimental parameters: $\dot{M} = 6.01$ cm³·min⁻¹; $U = 725$ V; $I = 0.90$ A; $T_s = 33^\circ$; $c_s = 4.90 \cdot 10^{-2}$ mole·l⁻¹.

Determination of the elementary mass effects

Elementary effects were determined from the displacement profile of ²²Na and the experiments had to be stopped sufficiently early for no concentration gradient of

^{22}Na to have been built up in the centre of the distribution. For the purpose of calculation, eqn. 14 can be reduced to

$$\frac{u_{22\text{Na}}}{u_{23\text{Na}}} = \frac{\frac{N_t - N_0}{N_0} + \frac{M(t)}{V}}{\frac{M(t)}{V}} \quad (24)$$

where $N_0 = N_0^+ = N_0^-$ is the specific activity of the initial solution, $N^+(N^-)$ is the specific activity of the solution in the enrichment (depletion) region and $N_t = N_0 + (N_t^+ - N_t^-)/2$ is the mean specific activity of the solution in the enrichment region after time t .

Determination of the separation factors

Experiments for the determination of separation factors were performed in the same way as for the elementary effects. The experiments were continued until the stationary distribution of ^{22}Na had been attained. According to eqn. 1, the logarithm of the separation factor, Q , is proportional to the length, x , of the separation column (see Fig. 2). Therefore, all values were calculated as $\Delta \log Q / \Delta x$ (cm^{-1}).

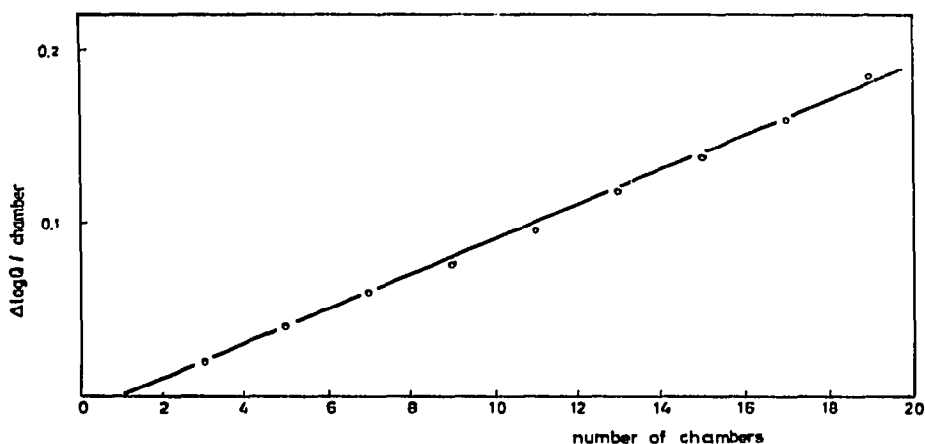


Fig. 2. Logarithm of the separation factor as function of the length of the separation column. From evaluating the curve, the following values result: $\Delta \log Q / \text{chamber} = 0.0101 \pm 0.0007$ or $\Delta \log Q / \Delta x = 0.0084 \pm 0.006 \text{ cm}^{-1}$. Experimental parameters as in Fig. 1 (curve 3).

Determination of the flow-rates

For the determination of the flow-rates, tracer ions were used that have greater ionic mobilities than the stationary ionic species in the separation column. A ^{137}Cs tracer ($1\text{--}2 \mu\text{Ci}$) was placed in one of the end chambers of the stationary sodium acetate distribution. Analogous experiments were carried out with a stationary caesium acetate distribution and ^{22}Na as tracer. The displacement profiles of the tracer ions were measured by their γ -activity several times.

Results are presented in Fig. 3. From these profiles, the velocity of displacement, V_p , was determined and the flow-rate calculated (according to eqn. 17). The relative

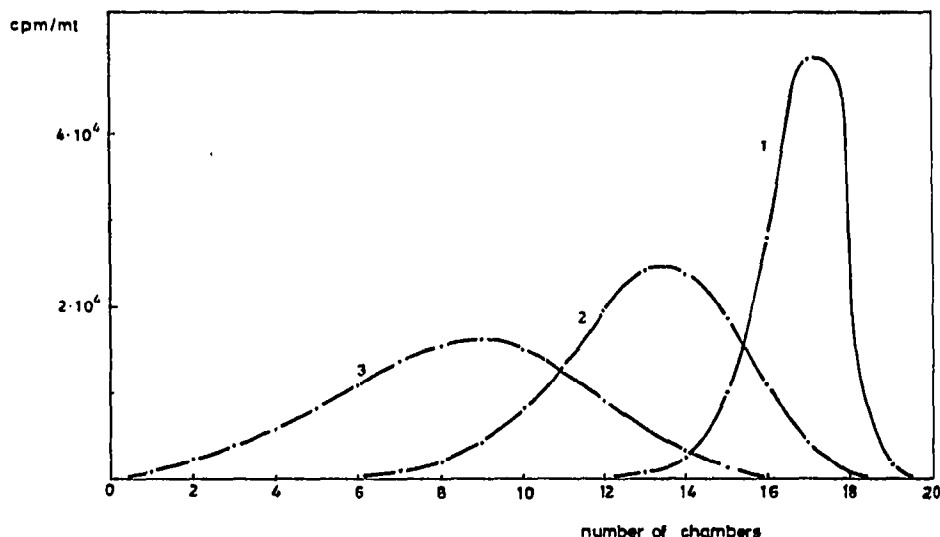


Fig. 3. Displacement profiles of ^{137}Cs in a stationary sodium acetate distribution. The tracer ^{137}Cs was placed in chamber 18; the profiles were measured after 0.5 h (curve 1), 2 h (curve 2) and 3.75 h (curve 3). From evaluating the curves, the velocity of displacement is obtained as $V_p = (0.87 \pm 0.01) \cdot 10^{-3} \text{ cm} \cdot \text{sec}^{-1}$. With $(\lambda_{\text{Cs}} - \lambda_{\text{Na}})/\lambda_{\text{Na}} = 0.565$ [$T_s = 31^\circ$; $c_s = 15.30 \cdot 10^{-2} \text{ mole} \cdot \text{l}^{-1}$] the flow-rate is calculated as $v_L = (1.54 \pm 0.02) \cdot 10^{-3} \text{ cm} \cdot \text{sec}^{-1}$. Calculation of the flow-rate $v_L = \dot{M}/q$ from experimental and geometrical parameters gives the same value $\dot{M} [= 2.35 \text{ cm}^3 \cdot \text{min}^{-1}$; $q = 25.4 \text{ cm}^2]$.

differences in the ionic mobilities, as a function of concentration and temperature, were calculated from equations given by Robinson and Stokes^{8,9}. The equivalent conductance data used for sodium^{8,10} and for caesium¹¹ were measured elsewhere. Fig. 4 shows the calculated $(\lambda_{\text{Cs}} - \lambda_{\text{Na}})/\lambda_{\text{Na}}$ data.

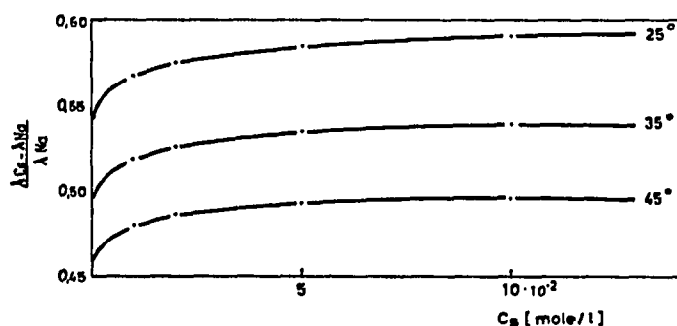


Fig. 4. Relative differences in the ionic mobilities of Cs^+ and Na^+ as a function of concentration and temperature.

Determination of the diffusion coefficients

Experiments on the determination of diffusion coefficients were performed in an analogous manner as for the flow-rates, except that tracer ions (^{22}Na) with ionic mobilities similar to those of the stationary species (sodium acetate) were used in the

separation column. The tracer was introduced into one of the central chambers within the stationary distribution.

Fig. 5 shows diffusion profiles, which are described by eqn. 19. The shift in the profiles relative to each other (during the time of experiment) is negligible ($V_p \cdot t \approx 0$),

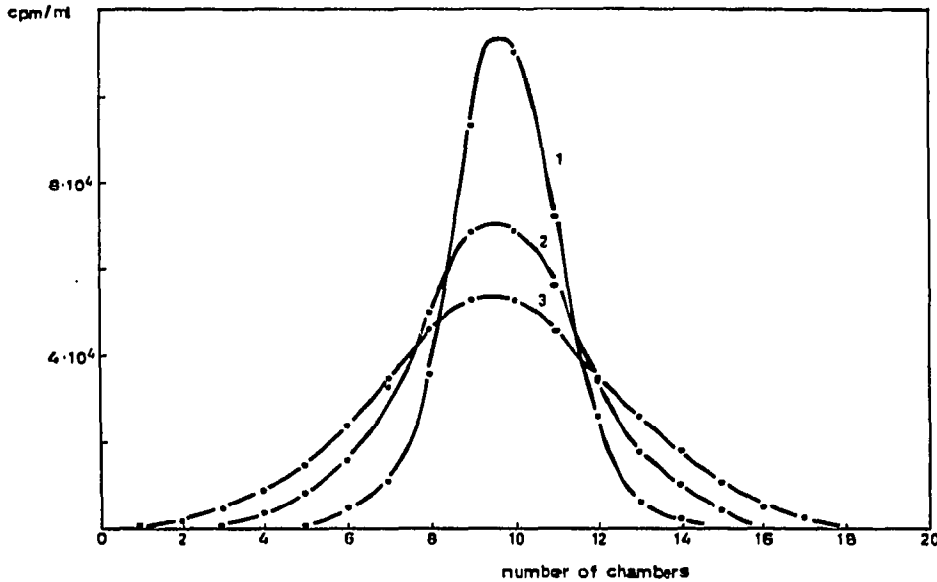


Fig. 5. Diffusion profiles of ^{22}Na in a stationary sodium acetate distribution. The tracer ^{22}Na was placed in chamber 10; the profiles were measured after 1 h (curve 1), 3 h (curve 2) and 5 h (curve 3).

owing to the very small difference in the ionic mobilities of ^{22}Na and ^{23}Na . The profiles fit the Gaussian error function:

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} \cdot \exp\left[-\frac{(x - \varrho)^2}{2\sigma^2}\right] \quad (25)$$

where

$$\sigma = \sqrt{2 \cdot D_{\text{eff}} t} \quad (26)$$

and

$$\varrho = x_0 = 0 \quad (27)$$

The diffusion profiles are converted into probability curves (see Fig. 6), from which σ values at 15.9 or 84.1 % and ϱ values at 50 % can be read. The diffusion coefficients are calculated (according to eqn. 26) from the σ values of the profiles, obtained after different times:

$$D_{\text{eff}} = \frac{\sigma_2^2(t_2) - \sigma_1^2(t_1)}{2(t_2 - t_1)} \quad (28)$$

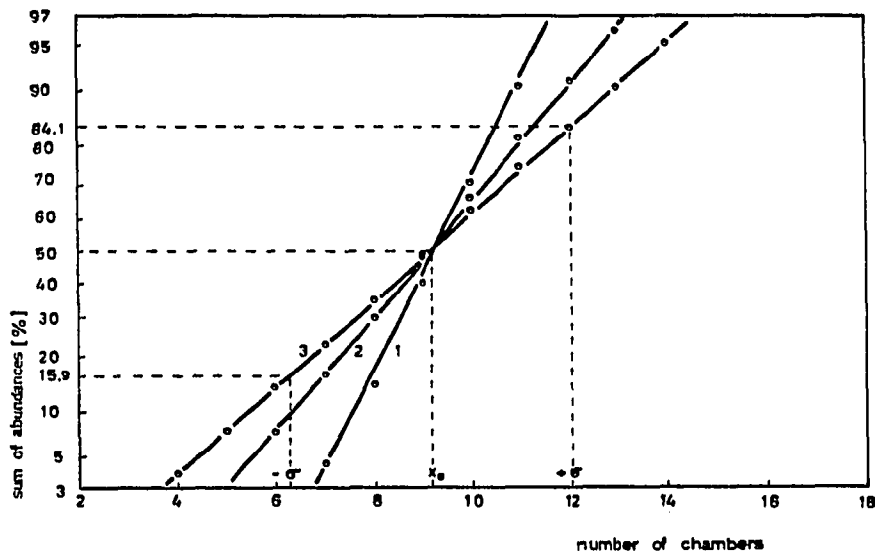


Fig. 6. Diffusion profiles (Fig. 5) as probability curves. From evaluation with $t_1 = 1$ h, $\sigma_1 = 1.53$ cm, $t_2 = 3$ h, $\sigma_2 = 2.64$ cm, $t_3 = 5$ h, $\sigma_3 = 3.45$ cm (chamber width 1.2 cm), the following value is obtained: $D_{\text{eff}} = (3.3 \pm 0.1) \cdot 10^{-4}$ cm²·sec⁻¹.

RESULTS AND DISCUSSION

Correlated data sets of the flow-rate, diffusion coefficients, separation factor and elementary effect, measured under identical conditions, are checked according to eqn. 29:

$$\frac{(\Delta \log Q / \Delta x) \cdot D_{\text{eff}}}{(\log u_1 / u_2) \cdot v_L} = K \equiv 1 \quad (29)$$

The operating conditions for some experiments, together with the results obtained, are given in Table I. The calculated values of K agree well with the expected value of $K = 1$. Therefore, the methods used give reliable results.

For the flow-rates, it has been shown that measured values of v_L are in good agreement with values calculated from experimental data (feed rate of the counter-current solvent and mean cross-section of the liquid column; $v_L = \dot{M}/q$). The densities of theoretical plates can be calculated in a simple manner from the measured diffusion coefficients.

Mass effects

The measured mass effects of the ²²Na–²³Na mixture in 1 *N* acetic acid are given in Fig. 7. Values of $u_{22\text{Na}}/u_{23\text{Na}}$ of 1.0012–1.0029 were found, increasing with increasing salt concentration and temperature. The same dependence has been found in the lithium acetate system⁴.

It was expected that the relative difference in the ionic mobilities, $[(u_1/u_2) - 1]$, of ²²Na–²³Na would be one half of that of ²²Na–²⁴Na. Results for the ²²Na–²⁴Na mixture

TABLE I
MEASURED DATA (EQN. 29) FOR SOME EXPERIMENTS*

Nylon gauze pore size (μm)	$\Delta \log Q / \Delta x$ (cm^{-1})	$D_{eff} \cdot 10^4$ ($\text{cm}^2 \cdot \text{sec}^{-1}$)	$v_L \cdot 10^3$ ($\text{cm} \cdot \text{sec}^{-1}$)	$u_{22\text{Na}}/u_{23\text{Na}}$	$K_{calc.}$
a 53	0.0068 ± 0.0006	3.3 ± 0.1	4.1	1.0012	1.05
b 53	0.0071 ± 0.0004	1.9 ± 0.1	1.5	1.0021	0.99
c 25	0.0086 ± 0.0004	2.2 ± 0.1	2.1	1.0022	0.95
d 20	0.0090 ± 0.0004	2.8 ± 0.1	4.0	1.0015	0.97
e 20	0.0092 ± 0.0008	1.5 ± 0.1	1.5	1.0021	1.01

* Operating conditions in the order given for the first experiment: a: $M = 6.24 \text{ cm}^3 \cdot \text{min}^{-1}$; $U = 750 \text{ V}$; $I = 0.48 \text{ A}$; $T_s = 29^\circ\text{C}$; $c_s = 1.95 \cdot 10^{-2} \text{ mole} \cdot \text{l}^{-1}$. b: 2.33; 570; 0.97; 28° ; $13.20 \cdot 10^{-2}$. c: 3.20; 750; 1.20; 34° ; $12.10 \cdot 10^{-2}$. d: 6.08; 800; 0.65; 31° ; $3.60 \cdot 10^{-2}$. e: 2.34; 600; 0.90; 29° ; $12.90 \cdot 10^{-2}$.

measured by Chemla and co-workers^{12,13} follow this relation and correspond to those of the acetate system at low salt concentrations. The values obtained by Chemla and co-workers were: $u_{22\text{Na}}/u_{24\text{Na}} = 1.0030$ (ref. 12) (in 10%, w/v, aqueous sodium nitrate solution at 20°) and 1.0024 (ref. 13) (in 0.04%, w/v, aqueous sodium chloride solution at 20°). Later values¹⁴ were somewhat higher: $u_{22\text{Na}}/u_{24\text{Na}} = 1.0051$ (in 0.04%, w/v, aqueous sodium chloride solution at 25.5°), 1.0065 (37°) and 1.0079 (49°).

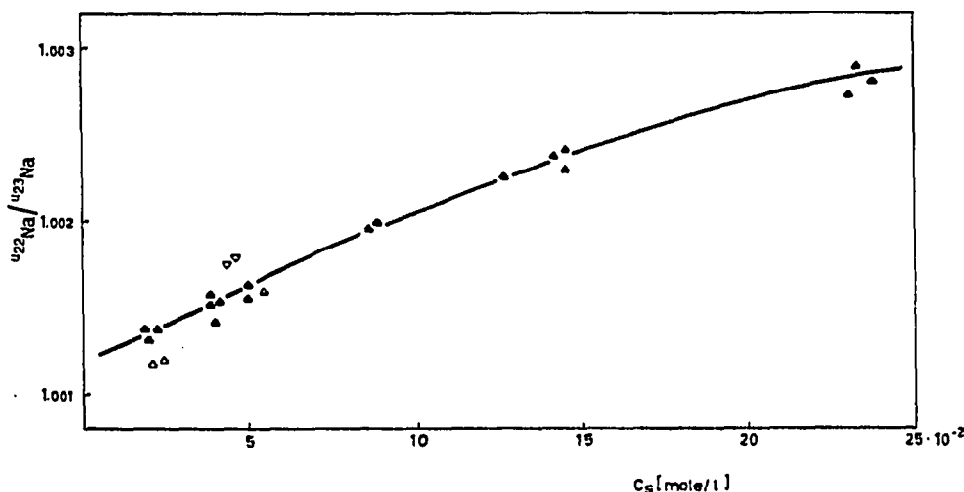


Fig. 7. Mass effects in ionic mobility of the ^{22}Na - ^{23}Na isotopic mixture in 1 *N* acetic acid as a function of salt concentration. \triangle , 26° ; \blacktriangle , 32 - 36° ; ∇ , 44° .

Density of theoretical plates

The effective diffusion coefficient is the sum of a term, D_{conv} , caused by thermal convection, and a term, D_{fl} , caused by the parabolic velocity pattern in the flowing solvent:

$$D_{\text{eff}} = D_{\text{conv}} + D_{\text{fl}} \quad (30)$$

D_{conv} depends on the cross-section, q_2 , of the diaphragm opening and, to the same extent, on the pore size of the nylon gauze. Moreover, D_{conv} depends on the temperature difference, ΔT , between the mean temperature, T_s , of the solution and the temperature, T_c (20°), of the cooling water. D_{conv} can be measured separately in an analogous manner to the total D_{eff} , but without any solvent flow. The convection is generated by heating the solution applying ac. D_{fl} depends mainly on the flow-rate of the solvent. A remixing effect is caused by the parabolic velocity pattern inside the pores of the nylon gauze.

Fig. 8 shows the dependence of D_{conv} and D_{fl} on the cross-section of the diaphragm opening. It can be seen that D_{conv} increases while D_{fl} decreases with increase in q_2 . The same behaviour has been found for different pore sizes of the nylon gauze^{6,15}.

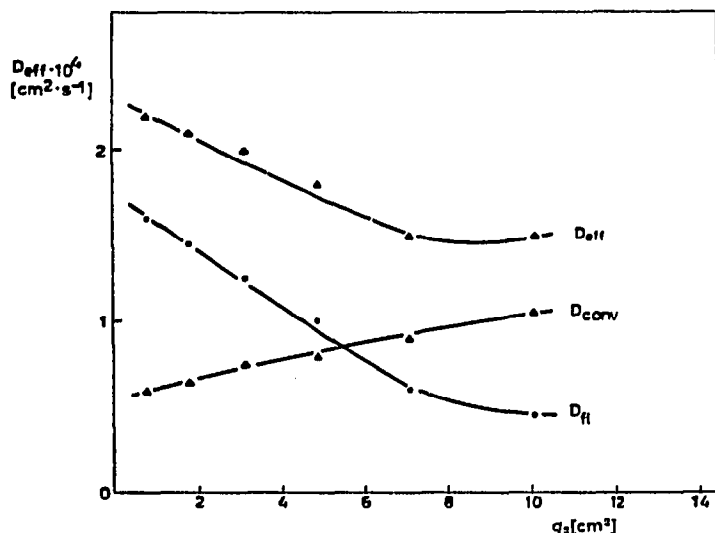


Fig. 8. D_{eff} , D_{conv} and D_{fl} as functions of the cross-section of the diaphragm opening (with nylon gauze of $53 \mu\text{m}$ pore size). The normal cross-section used was $q_2 = 7.1 \text{ cm}^2$. Experimental parameters: $M = 2.52 \text{ cm}^3 \cdot \text{min}^{-1} = \text{constant}$; $c_s = 5.40 \cdot 10^{-2} \text{ mole} \cdot \text{l}^{-1} = \text{constant}$.

Fig. 9 shows the dependence of D_{eff} on v_L and ΔT . This dependence can be described by an empirical relationship (see eqn. 30):

$$D_{\text{eff}} = D_{\text{conv}} + k \cdot \frac{v_L^2}{D_{\text{conv}}} \quad (31)$$

An analogous form was given by Klemm¹⁶.

Using this relationship, the dependence of $n = v_L/D_{\text{eff}}$ on v_L can be derived. At low flow-rates, D_{eff} is determined only by D_{conv} ; D_{fl} can be neglected and n is proportional to v_L . At high flow-rates, D_{eff} is determined by D_{fl} and n is inversely proportional to

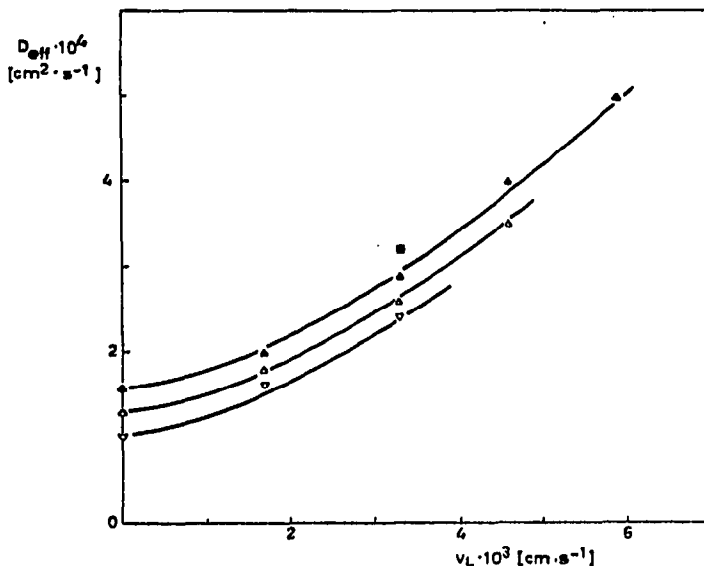


Fig. 9. D_{eff} as a function of flow-rate and temperature difference (normal diaphragm opening with $25 \mu\text{m}$ gauze). ∇ , $\Delta T = 10^\circ$; \triangle , $\Delta T = 15^\circ$; \blacktriangle , $\Delta T = 20^\circ$; \blacksquare , $\Delta T = 27^\circ$.

v_L . Between the two limiting cases, n would be at a maximum. Fig. 10 shows the experimental results. A direct decrease in n with v_L is not observed, because no stationary salt distribution can be established at high v_L values.

In this way, a quantitative characterization of the properties of a CCEP column can be given.

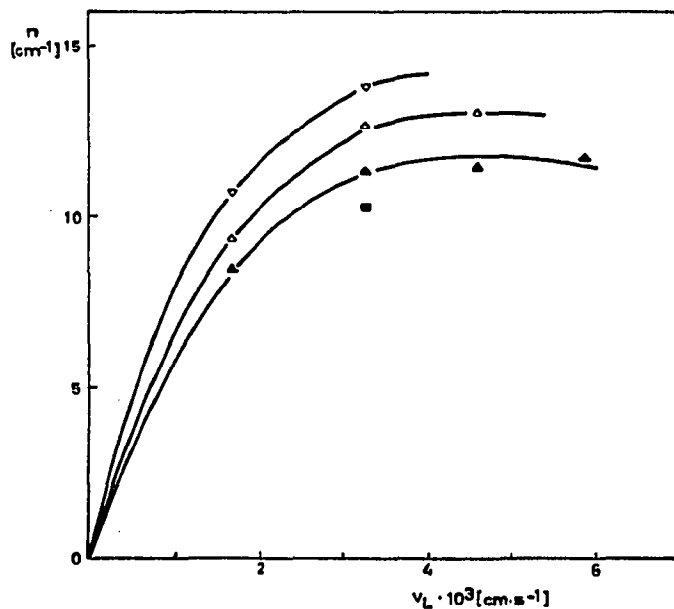


Fig. 10. Density of theoretical plates of the separation column calculated from values in Fig. 9. ∇ , $\Delta T = 10^\circ$; \triangle , $\Delta T = 15^\circ$; \blacktriangle , $\Delta T = 20^\circ$; \blacksquare , $\Delta T = 27^\circ$.

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