Bull. Chem. Soc. Jpn., 57, 349—354 (1984)

Exponential Distribution of Aqueous 1-1 Electrolytes Due to Convective Thermal Diffusion in Vertical Columns

Naokata TAKEYAMA* and Kimie NAKASHIMA
Department of Industrial Chemistry, Faculty of Science and Engineering, Saga University, Saga 840
(Received July 11, 1983)

Using titanium columns of 10 cm length and glass columns of different lengths, the vertical exponential distribution of the concentration of aqueous 1-1 electrolytes in each column has been ascertained at the steady state of convective thermal diffusion. The value of $(a^4/L)\ln q$ is found to be characteristic of individual solutes, and possibly proportional to the thermal diffusion coefficients, where q is the quotient of the steady concentration of a solute at the bottom of column to that at the top, L is the effective column length, and a is the working column space. This fact has been also shown by jointed glass columns with and without top vessel, capable of multistep sampling from the top to the bottom through intermediate jointed parts along columns. The rate constants in processes to the steady state have been examined to be proportional to the square of temperature difference applied, and to decrease with increasing L. Although the enhancement of downward enrichment of solutes has been observed by attaching a large top vessel to the column top, the rate constants decrease inevitably and significantly thereby.

The thermal diffusion in liquid systems has been studied by measuring the Soret effect in a nonconvective cell,[1] and by using the Clusius-Dickel column settled vertically to utilize effectively natural convection induced by a temperature gradient applied horizontally.[2,3] The former is mainly directed to the determination of the Soret coefficient of solutes, while the latter is being examined to be applied to the separation of mixtures. Regarding aqueous ionic solutions, however, in spite of valuable efforts by several authors,[4-8] the basic principle of convective thermal diffusion in the column method is still unsolved in many respects. At present, various applications of the column method are being attempted by the present authors to seek a clue to effective utilization of thermal energy in a lower grade, concerning aqueous electrolytes.[9]

From a fundamental viewpoint, the thermal diffusion coefficient of aqueous electrolytes provides important information on the dissolved state of ions through the reduction rule in heats of transfer in connection with water structure-making and breaking properties of ions.[10] In the course of these applicative and basic studies, it grows as an important subject whether the thermal diffusion coefficient may be obtained by the column method in comparison with the Soret cell method established well.

Toward the subject, this paper describes basic experimental results by the column method to show the validity of exponential distribution of aqueous electrolytes along vertical columns, single and jointed, in a sedimentation-like way. From the exponential distribution of a solute at the steady state of convective thermal diffusion, a constant quantity having the dimension of volume, characteristic of the solute, may be obtained independently of column size to show a direct connection with the thermal diffusion coefficient from the Soret coefficient, in spite of large discrepancy in experimental conditions.

Experimental

Titanium Columns (Ti-I and Ti-II). Two columns made of titanium, Ti-I and Ti-II, were prepared by courtesy of the Nippon Kōgyo Co. and the Nikko Engineering Co., having a similar structure to that in Fig. 1 of a glass column. The outermost cylindrical wall was made by a poly (vinyl chloride) pipe equipped with two branches for circulation of cooling water, in which Ti made double annular part was fixed by sealing with poly(vinyl chloride) paste. The innermost Ti tube (1.00 mm thickness and 6.00 mm ϕ) and the outer Ti tube (1.00 mm thickness and 10.0 mm ϕ) were set to form the co-annular cylindrical space having 1.00 mm spacing for Ti-I and 0.97 mm for Ti-II,[11] in 10.0 cm length between the top and bottom reservoirs of 3.4 and 5.4 cm^3, respectively. Warm water at T_h°C was circulated into the innermost tube of column from a thermostatted bath. At the same time, colder water at T_c°C was circulated into the outermost space between the outer Ti tube and the outermost poly(vinyl chloride) pipe. Two by two branches were attached to the top and bottom reservoirs as an inlet of test solution and as an outlet of sample. As a reference column having 1.00mm spacing and 10.0cm length, Ti-I was selected. Both were individually used as single columns of total 10.5±0.2 cm^3 volume.

Glass Columns. The structure of a Pyrex glass column, in Fig. 1, was composed of co-annular triple walls having 1 mm thickness in an outlook of Liebig condenser. Three main parts were the innermost tube, into which warm water was circulated, the co-annular cylindrical space between the top and bottom reservoirs of 6 cm^3, of which

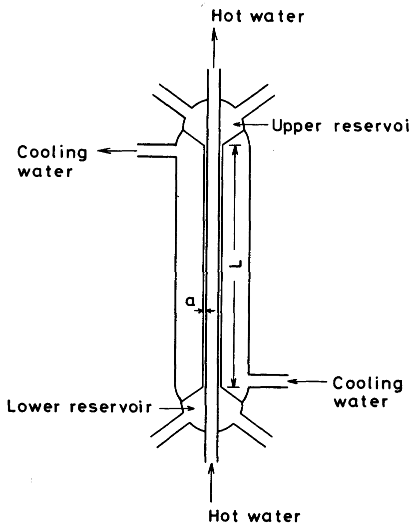

Fig. 1. Structure of a glass column. a; The spacing of working annular space, L: the effective length.

spacing a was kept at about 0.9 mm as constant as possible, and the outer space, in which cooling water was circulated. Two by two branches were attached to the top and bottom reservoirs for sampling outlets and for jointing branches. In some cases, a 500 cm^3 vessel was directly connected with one of two top branches to enhance downward enrichment of solutes. The working space was in the co-annular space of effective length L between the innermost (hotter) and outer (colder) walls. A unit column of L=10 cm was used to be jointed in series and in V-shape to lengthen total effective length as shown in Fig. 2, without and with top vessels. These jointed columns were very useful and effective for practical applications. In single column experiments, 4 glass columns of L=5.0, 10.0, 24.5, and 49.0 cm were used to examine the dependence of enrichment of solutes on the effective length. For the same purpose, jointed column experiments were successfully performed.

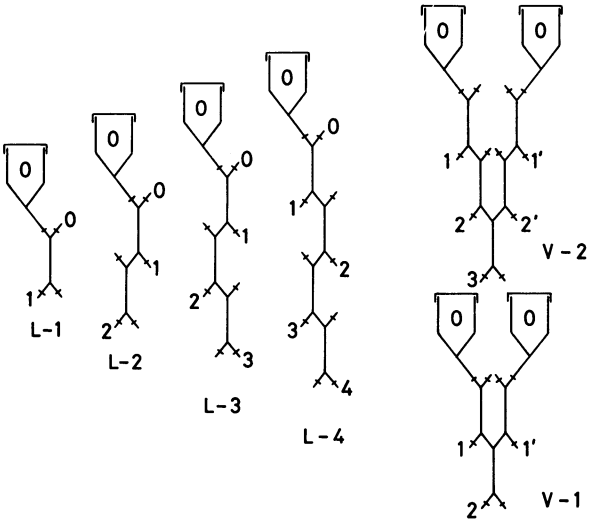

Fig. 2. Arrangement of jointed columns with and without top vessels.

The sampling outlets are denoted by 0, 1, ···, n for a column jointed linearly of n unit columns, and by 0, 1 and 1′, 2 and 2′, ···, n for a V-shape jointed column composed of $(2n-1)$ unit columns.

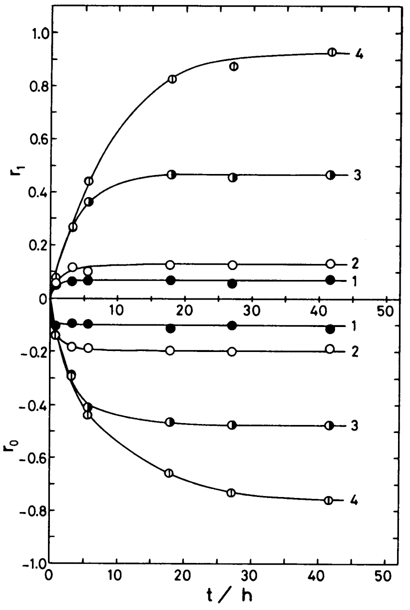

Fig. 3. Changes in the extents of dilution (r_0) at the top of column, and of enrichment (r_1) at the bottom with time, referring to 0.983 mol dm^{-3} HCl, at ΔT= 40.1, and T_m=54.0 °C.

Column length L: 5.0 cm for (1), 10.0 cm for (2), 24.5 cm for (3), and 49.0 cm for (4).

Sample Solutions. All of aqueous solutions were prepared from the purest available reagents using distilled and deionized water. Before and after a run of experiment, the concentration of a solute was volumetrically determined in each sample taken from the top and bottom outlets, including intermediate outlets in the case of jointed column experiments, shown in Fig. 2. Chemical analyses were performed according to the ordinary methods established well.

Procedure. A sample solution of the initial concentration C_i of an electrolyte was filled from the bottom inlet to the top of column using a leveler connected by a flexible tube with the inlet. After closing all stopcocks except one at the top, a run was started by circulating water at different temperatures from the bottom to the top. The top stopcock was closed after relaxation of thermal expansion of the solution filled. In a batch operation, test solutions were taken at a time t elapsed from the top outlet by a pipette, and then from the bottom outlet, after wasting a few drops to clean the part, by about 2 cm^3 in a dropping way. Such a sampling did not cause serious error. In a jointed column experiment, test solutions were taken from the top to the bottom through each intermediate outlet in order in a quite similar way.

When the concentration of the electrolyte under consideration was C_j at the j-th outlet, where j was numbered from the top j=0 to the bottom j=n as shown in Fig. 2, the result was expressed by the following relative deviation from the initial C_i at t:

$$r_j(t) = [C_j(t) - C_i]/C_i. \tag{1}$$

The duration of a run was changed in repetition of batch operations to be plotted $r_j(t)$ against t in a wide range. On a curve of $r_j(t)$ *versus* t, a time derivative $\mathrm{d}r_j(t)/\mathrm{d}t$ was evaluated by a graphical differentiation at t.[12] A linearity from plotting $\mathrm{d}r_j(t)/\mathrm{d}t$ against $r_j(t)$ showed

$$\mathrm{d}r_j(t)/\mathrm{d}t = A_j - k_j r_j(t), \tag{2.1}$$

which was characterized by constant A_j *and* k_j. The steady value $r_{j,\mathrm{st}}$ was graphically determined as an intercept on the abscissa of $r_j(t)$, given by

$$r_{j,\mathrm{st}} = A_j/k_j. \tag{2.2}$$

From Eqs. (2.1) and (2.2), the following equation was obtained:

$$\mathrm{d}r_j(t)/\mathrm{d}t = k_j[r_{j,\mathrm{st}} - r_j(t)], \tag{2.3}$$

or

$$r_j(t) = r_{j,\mathrm{st}}[1 - \exp(-k_j t)]. \tag{2.4}$$

Thus k_j was called the rate constant at the j-th outlet.

A set of experiments were specified by an average temperature difference $\Delta T = T_h - T_c$ applied and a mean temperature $T_m = (T_h + T_c)/2$ for the set of runs.

Results and Discussion

To clarify the nature of enrichment of solutes due to convective thermal diffusion in a vertical column, first of all, it is required to establish empirical relations from experimental results for the dependence of enrichment on column length and the working space. The subject is closely associated with the actual formulation of experimental results described below.

In the first place, the results from single column experiments are described, and then those by jointed columns without and with top vessels are reported.

Using 4 glass columns kept at $a \approx 0.9$ mm as constant as possible and having $L=5.0$, 10.0, 24.5, and 49.0 cm, the temporal changes of $r_j(t)$ for $j=0$ and 1 are studied to examine the dependence of $r_{j,\mathrm{st}}$ on L, referring to aqueous 1-1 electrolytes, 4 alkalis, 3 acids, and 2 neutral salts, at *ca.* 1 mol dm^{-3}. In Fig. 3, the curves of $r_j(t)$ *versus* t for 0.983 mol dm^{-3} HCl are shown. In all columns used, the positive values of r_1 increase with time to individual steady values of $r_{1,\mathrm{st}}$ to show the enrichment of HCl at the bottom of each column, while the negative values of r_0 decrease simultaneouly with time to individual steady values of $r_{0,\mathrm{st}}$ to show the dilution of HCl at the top of individual columns. Such behavior is common to the cases of other species. Qualitatively, the extents of enrichment and dilution increase with increasing L. More quantitatively, firstly $r_{1,\mathrm{st}}$ and $r_{0,\mathrm{st}}$ are plotted in Fig. 4 against L for various electrolytes. Although $r_{1,\mathrm{st}}$ increases with L almost linearly in all cases, $r_{0,\mathrm{st}}$ decreases upward-concavely with L. Next, each pair of curves for an electrolyte in Fig. 4 may be transformed into one plait line, almost straight, by introducing

$$\begin{aligned}\ln q &= \ln(C_{1,\mathrm{st}}/C_{0,\mathrm{st}}) \\ &= \ln[(r_{1,\mathrm{st}}+1)/(r_{0,\mathrm{st}}+1)], \qquad (3)\end{aligned}$$

as shown in Fig. 5, though the practical convenience of $r_{j,\mathrm{st}}$ is inevitably lost. The values of $\ln q$ are individually proportional to L in all cases. The proportional constant for an electrolyte, given by $(\ln q)/L$, expresses an enriching power of column, still dependent on a, within experimental errors, partly due to slight difference in a. The values of $(\ln q)/L$ are tabulated in Table 1 as glass columns for 9 electrolytes at *ca.* 1 mol dm^{-3} and at $\Delta T=38.2\pm0.8$ °C and $T_\mathrm{m}=55.1\pm0.8$ °C.

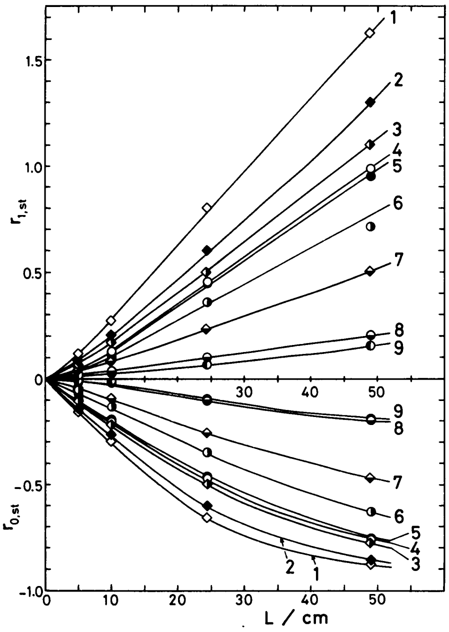

Fig. 4. Changes in the steady extents of dilution ($r_{0,\mathrm{st}}$) at the column top, and of enrichment ($r_{1,\mathrm{st}}$) at the bottom due to column length (L), at $\Delta T=38.2$, and $T_\mathrm{m}=55.1$ °C.
1: 0.226 M CsOH, 2: 1.080 M KOH, 3: 1.044 M NaOH, 4: 1.530 M HBr, 5: 0.983 M HCl, 6: 0.999 M HNO_3, 7: 1.112 M LiOH, 8: 1.038 M KCl, and 9: 1.054 M NaCl (1M=1 mol dm^{-3}).

In Table 1, the data of $(\ln q)/L$ by Ti-I and Ti-II are shown for 12 electrolytes at *ca.* 1 mol dm^{-3} and at $\Delta T=49.7\pm0.5$ °C and $T_\mathrm{m}=48.2\pm0.5$ °C. Moreover, for Ti-II and glass columns, the ratio of $(\ln q)/L$ to that of Ti-I is given in Table 1 to examine the constancy in the individual ratios by columns, because Ti-I is selected as a reference. The ratios are 1.14 ± 0.16 for Ti-II, and 1.91 ± 0.27 for glass columns as a whole, independently of the nature of electrolytes under consideration. According to the theoretical treatment of convective thermal diffusion in liquid mixtures,[2,3,13] the ratio may be mainly attributable to the difference in a in reference to a_0 of Ti-I as follows:

$$\frac{[(\ln q)/L]_{\text{for a column}}}{[(\ln q/L]_{\text{for Ti-I}}} = \left(\frac{a_0}{a}\right)^4 \qquad (4)$$

This is valid in a crude approximation, at this stage, that other conceivable factors from differences in temperature, concentration, and column material do not seriously influence the ratio. The values of a, however, may be determined by Eq.(4) in reference to a_0; $a=0.97\pm0.03$ mm for Ti-II, and 0.85 ± 0.03 mm for glass columns on an average. These are reasonable values. Regarding the importance of this result, the dependence of $\ln q$ on ΔT and on the initial concentration of electrolytes is examined by using Ti-I. Figures 6 and 7 show that the values of $\ln q$ are independent of ΔT and initial concentrations, irrespectively of the nature of electrolytes investigated. Hence, the validity of Eq. (4) may be admitted.

Now, for a single column, the enriching power per unit length multiplied by a^4, $(a^4/L)\ln q$, represents an intrinsic quantity characteristic of an aqueous electrolyte solution, at least referring to single solutions, independently of experimental conditions and the column size a and L. Although the physicochemical content of characteristic volume $(a^4/L)\ln q$ at the steady state of convective thermal diffusion should be experimentally and theoretically clarified, it may be directly proportional to $(\eta/\beta\rho g)D'$ at the present status of theoretical treatment,[2,3,13] where

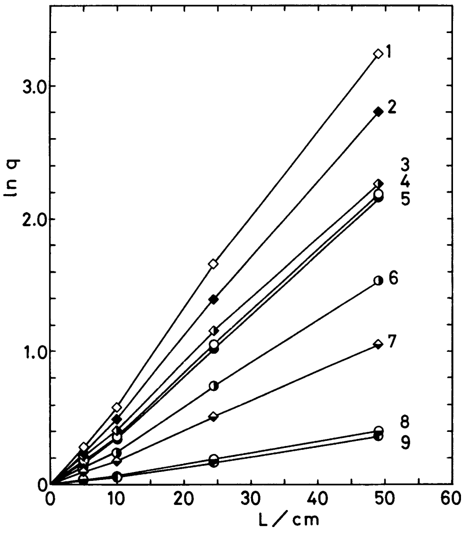

Fig. 5. Natural logarithms of the quotient of the steady concentration at the bottom to that at the top ($\ln q$) *vs.* column length (L). The data are the same as Fig. 4.

Table 1. The enriching powers per unit column length, (ln q)/L, for titanium and glass columns

Aqueous electrolyte	Titanium columns Ti-I[a)] (ln q)/L cm^{-1}	Titanium columns Ti-II (ln q)/L cm^{-1}	Ratio to Ti-I[c)]	Glass columns having different lengths[b)] (ln q)/L cm^{-1}	Ratio to Ti-I[c)]
CsOH				0.0618±0.0063	
KOH	0.0277	0.0315	1.14	0.0521±0.0057	1.88
NaOH	0.0220	0.0245	1.11	0.0430±0.0041	1.95
HBr	0.0194			0.0384±0.0041	1.98
HCl	0.0166			0.0379±0.0051	2.28
HNO_3				0.0273±0.0039	
LiOH	0.0117	0.0120	1.03	0.0195±0.0019	1.67
NaBr	0.0048	0.0050	1.04		
NaCl	0.0046	0.0050	1.09	0.0067±0.0006	1.46
KBr	0.0037	0.0055	1.49		
KCl	0.0034			0.0072±0.0015	2.12
NaI	0.0028	0.0030	1.07		
LiBr		0.0015			
LiCl	0.0004				
		Average	1.14		1.91
		Standard deviation	0.16		0.27

a) A reference column having 10.0 cm length and 1.00 mm spacing. b) L=5.0, 10.0, 24.5, and 49.0 cm, respectively. Refer to Fig. 5. c) The ratio of (ln q)/L in individual cases is taken to (ln q)/L for Ti-I column.

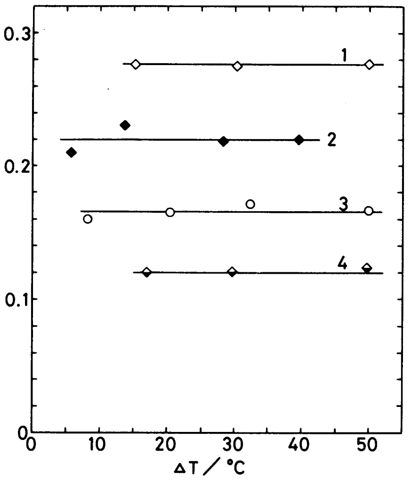

Fig. 6. ln q $vs.$ temperature difference applied (ΔT), by a titanium column Ti-I. 1: 0.830 M KOH, 2: 1.013 M NaOH, 3: 1.054 M HCl, and 4: 1.114 M LiOH.

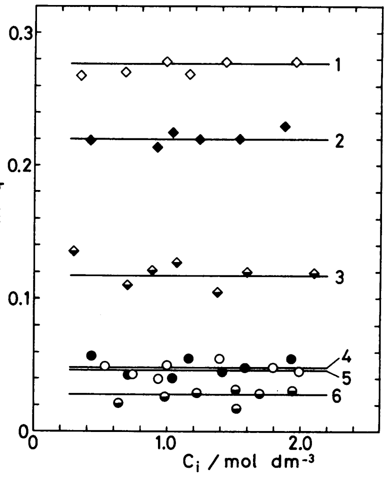

Fig. 7. ln q $vs.$ initial concentration (C_i), by Ti-I column, at ΔT=49.7, and T_m=47.5 °C.
1: for KOH, 2: for NaOH, 3: for LiOH, 4: for NaCl, 5: for NaBr, and 6: for NaI.

η is the viscosity, β the thermal expansion coefficient, ρ the density of a sample solution, g the acceleration of gravity, and D' the thermal diffusion coefficient of an aqueous electrolyte. These physical properties should be estimated at the mean temperature and at the experimental conditions. It remains to be solved, however, whether the above expression for the characteristic volume, $(a^4/L)\ln q$, is compatible with the insensitibity to the experimental conditions mentioned above. At present, unfortunately, we cannot directly examine the validity because of no available data. In comparison with the thermal diffusion coefficients of 14 electrolytes at 0.01 mol kg^{-1} and at the mean temperature 25 °C, which are calculated from the Soret coefficients measured by Snowdon and Turner,[14)] the values of $(a^4/L)\ln q$ in cm^3 are summarized in Table 2, obtained from the data in Table 1 by using the values of a estimated. The values for individual electrolytes are in good agreement with each other among columns used. Moreover, in spite of large discrepancies in experimental conditions, a parallelism between $(a^4/L)\ln q$ and D' may be seen, apart from a few inversions in order. This fact suggests $(f\eta/\beta\rho\, g)$ to be the order of magnitude of 10 cm s K by introducing a non-dimentional f. In this respect, it may be commented that for pure water at T_m=50 °C $(\eta/\beta\rho\, g)$ is 1.23×10^{-2} cm s K, thereby f is of the order of magnitude of 10^3.

Concerning the difference in column material between titanium and Pyrex glass, titanium is a good thermal conductor appropriate for the column material, especially best for aqueous alkaline and salt solu-

TABLE 2. THE VALUES OF $(a^4/L)\ln q$ MEASURED BY TITANIUM AND GLASS COLUMNS IN COMPARISON WITH THERMAL DIFFUSION COEFFICIENTS D' FROM SORET COEFFICIENTS AT 0.01 mol kg^{-1} AND 25 °C[a)]

Aqueous electrolyte	$(a^4/L)\ln q/10^{-7}$ cm^3			$D'/10^{-8}$ cm^2 s^{-1} K^{-1}
	Columns			
	Ti-I	Ti-II	Glass	
CsOH			32.3	40.7
KOH	27.7	27.9	27.2	36.5
NaOH	22.0	21.7	22.4	27.8
HBr	19.4		20.0	29.5
HCl	16.6		19.8	28.8
HNO_3			14.3	24.8
LiOH	11.7	10.6	10.2	19.5
NaBr	4.8	4.4		3.28
NaCl	4.6	4.4	3.5	3.15
KBr	3.7	4.9		2.78
KCl	3.4		3.8	2.69
NaI	2.8	2.7		0.878
LiBr		1.3		0.105
LiCl	0.4			0.027

a) From the date of Soret coefficients, observed by Snowdon and Turner[14)], D' may be calculated using the limiting diffusion coefficient in the Nernst-Hartley approximation.

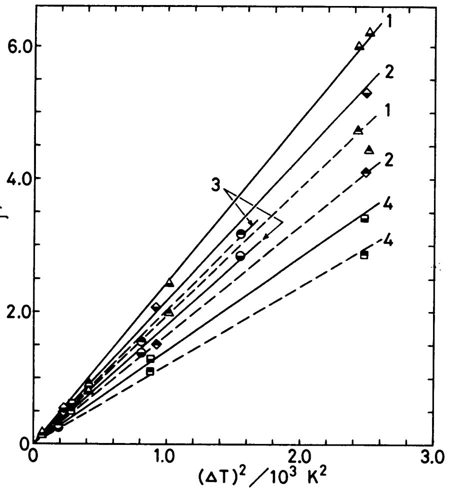

Fig. 8. Rate constants (k_j) *vs.* $(\Delta T)^2$, by Ti-I column. 1: 1.054 M HCl, 2: 0.830 M KOH, 3: 1.013 M NaOH, and 4: 1.114 M LiOH. k_0 at the top is denoted by broken lines, and k_1 at the bottom is by solid lines.

tions, capable of specifying $(\Delta T/a)$ for the gradient of temperature applied, while glass is a poorer one having the thermal conductivity comparable with that of aqueous solutions, and hence the effective temperature gradient may be $(1/3)(\Delta T/a)$, because in glass columns ΔT is applied to an aqueous layer in the working space of column between innermost and outer glass walls having the thickness comparable with a. Actually, the occurrence of convective thermal diffusion can be detected at $\Delta T \approx 1.5$ °C at the lowest in titanium columns, but at $\Delta T \approx 6$ °C at the lowest in glass columns.

The kinetic results by Ti-I are shown in Fig. 8. The rate constants k_0 at the top and k_1 at the bottom are proportional to $(\Delta T)^2$. This is true for glass columns, too, though the rate constants are smaller by 1/10 than those for Ti-I and Ti-II. Such a fact is consistent with the earlier theoretical prediction.[15)]

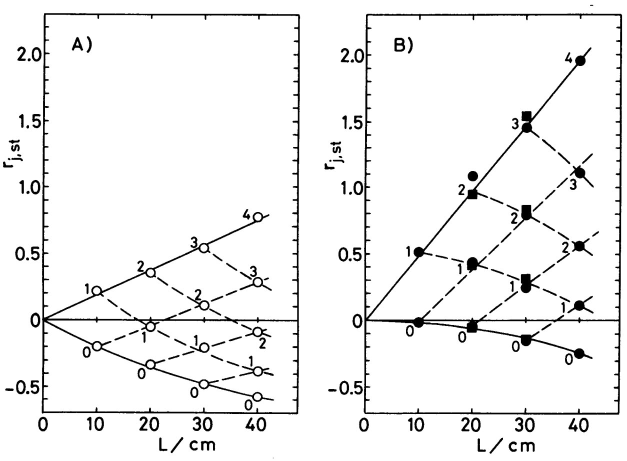

Fig. 9. Extents of variation in the steady concentration relative to the initial concentration ($r_{j,st}$) at the j-th outlet of jointed columns *vs.* total column length L, referring to 1.051 M HCl at ΔT= 49.8, and T_m=49.0 °C.
A): For the arrangements L-1, L-2, L-3, and L-4 without top vessel in Fig, 2, and B): for the same arrangements as in A) with top vessel (500 cm^3) denoted by solid circles and for V-shape arrangements V-1 and V-2 in Fig. 2 with two top vessels (each 500 cm^3) denoted by solid squares

In order to ascertain the relation of ln q proportional to L with jointed column experiments, the results for 1 mol dm^{-3} HCl are summarized in Fig. 9, in which $r_{j,st}$ in each jointed column of the number of jointed unit columns n=1 to 4 are plotted against total effective column length given by $L=10\times n$(cm) in A) referring to the cases without any top vessel, and B) for the cases with a top vessel (500 cm^3 volume) in the linear arrangements of L-1, L-2, L-3, and L-4 in Fig. 2, and also with two top vessels (each 500 cm^3) in the V-shape arrangements of V-1 and V-2 in Fig. 2.

In A) and B) in Fig. 9, curvilinear lattices are formed among the points of (L, $r_{j,\,st}$) in each jointed column. Connecting with the points of $r_{0,st}$ at the top in the cases of A), and in the top vessels for B), solid curves are drawn to show the changes in the extent of dilution. The extents of dilution in the top vessels in the cases of B) are lowered due to the presence of top vessels, while the extents of enrichment at the bottom are enhanced in each case in comparison with A). Such an enhancement of downward enrichment is clearly caused by the simple direct attachment of large vessels at the top of columns jointed. In the linear and V-shape arrangements of columns, L is taken as the effective height jointed column part except jointed parts and top vessels. Although the representation of $r_{j,st}$ is useful for the practical applicative purpose, the data in A) and B) are numerically examined in terms of ln q_j at the j-th outlet of jointed columns to compare with the results from single column experiments, where ln q_j has been defined by

$$\ln q_j = \ln[(r_{j,st}+1)/(r_{0,st}+1)] = \ln(C_{j,st}/C_{0,st}), \qquad (5)$$

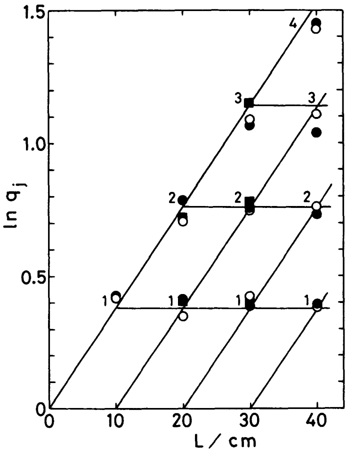

Fig. 10. Transformation of the data in Fig. 9, A) and B), into ln q_j for the j-th outlet of jointed columns against L.

in place of Eq. (3), for $j=1, 2, \cdots, n$, to investigate the vertical distribution of HCl from the top to the bottom through intermediate jointed parts. For jointed columns without any top vessel, the value of $(\ln q_j)/L_j$ is reduced to 0.0376 ± 0.0026 cm^{-1} averaged over 10 points, where L_j is the effective length from the top to the j-th outlet of an n-jointed column, $L_j=10\times j$(cm). For those with top vessels, it is 0.0380 ± 0.0024 cm^{-1} on average, in good agreement with the value mentioned above. As a whole, the average of $(\ln q_j)/L_j$ is 0.0379 ± 0.0025 cm^{-1} which is just equal to the value for HCl by single glass columns in Table 1. Using this average value, an inclined lattice is drawn in Fig. 10 by solid lines, in which the lattice points coincide satisfactorily with the observed points transformed from those in A) and B) in Fig. 9. Therefore, it may be mentioned that all of the points expressed by $r_{j,\mathrm{st}}$ converge finally on one point averaged over those.

Regarding rate constants k_j at the j-th outlet of jointed columns, the dependence of k_j on L is numerically shown in Table 3. First, in the cases of jointed columns without and with top vessels, all k_j in each column are nearly constant independently of j, but k_0 in the top vessel is much smaller than other k_j at lower outlets presumably due to the large volume of top vessel, though such a trend vanishes gradually with increasing total L. Second, k_j for jointed columns with top vessel is smaller than that in the cases without top vessel by about 1/10 to 1/5. These facts show that, although the time required for one-half each $r_{j,\mathrm{st}}$ to be attained are almost equal in a given total L except in top vessels, the rate constants decrease with increasing L, and the time required for each $r_{j,\mathrm{st}}$ are prolonged with it.

Table 3. Rate constants k_j of convective thermal diffusion for each outlet j numbered from the top to the bottom of jointed columns without and with a top vessel of 500 cm^3 operated at $\Delta T=50.0\pm0.2$ °C and $T_m=49\pm0.2$ °C, and at 1.0 mol dm^{-3} HCl

Total effective length L/cm	Number of outlet j	k/h^{-1} Without top vessel	k/h^{-1} With top vessel[a]
10.0	0	0.637	(0.01)
	1	0.605	0.130
20.0	0	0.537	(0.02)
	1	0.520	0.059
	2	0.540	0.053
30.0	0	0.260	(0.01)
	1	0.260	0.025
	2	0.265	0.022
	3	0.263	0.025
40.0	0	0.130	(0.02)
	1	0.102	0.015
	2	0.125	0.020
	3	0.102	0.022
	4	0.124	0.021

[a] The values of k_0 at the top vessel in each case are shown in parentheses.

References

1) J. Chanu, *Electrochim. Acta*, **22**, 1025(1977) and the references cited therein.

2) R. C. Jones and W. H. Furry, *Rev. Mod. Phys.*, **18**, 151 (1946) and the references cited therein.

3) Regarding the recent theoretical studies, see, for example, J. L Navarro, J. A. Madariaga, and J. M. Saviron, *J. Phys. Soc. Jpn*, **52**, 478 (1983) and the references cited therein.

4) K. Hirota, *Bull. Chem. Soc. Jpn.*, **16**, 232, 475 (1941); *J. Chem. Phys.*, **18**, 396 (1950).

5) L. J Gillespie and S. Breck, *J. Chem. Phys.*, **9**, 370 (1941)

6) G. Guthrie, J. N. Wilson, and V. Schomaker, *J. Chem. Phys.*, **17**, 310 (1949).

7) K. F Alexander, *Z. Phys. Chem. (Leipzig)*, **203**, 213 (1954).

8) F. S. Gaeta, *Phys. Rev.*, **182**, 289 (1969); F. S. Gaeta, G. Perna, G. Scala, and F. Bellucl, *J. Phys. Chem.*, **86**, 2967 (1982); D. G. Mlta, F. Bellucl, M. G. Cutull, and F. S. Gaeta, *ibid.*, **86**, 2975 (1982). We cannot reproduce the unfamiliar concentration dependence of the Soret coefficient of aqueous electrolytes by the column method, reported by them.

9) N. Takeyama and K. Nakashima, *Kagaku To Kogyo (Osaka)*, **51**, 427(1977); N. Takeyama, Jpn. Patent 1013221 (1980); N. Takeyama and K. Nakashima, Jpn. Patent 1096034 (1982); 1107716 (1982); 1111846 (1982); 1149780 (1983).

10) N. Takeyama and K. Nakashima, *J. Phys. Soc. Jpn.*, **52**, 2692; 2699 (1983).

11) The accuracy may be within ±0.02 mm.

12) In the initial period of time changes of $r_j(t)$, the values of $\mathrm{d}r_j(t)/\mathrm{d}t$ are slightly larger than the values extrapolated from the later phase subject to Eq.(2.1), presumably due to unsteady temperature distribution applied to columns. On the contrary, an induction effect has been discussed by G. D. Rabinovich, *Chem. Eng. Sci.*, **32**, 791 (1977).

13) The theoretical expression may be written as $(a^4/L)\ln q=(504\ \eta\ /\ \beta\rho\ g)D'$ in the present notation, which has been previously used by K. Hirota, in the second paper of Ref. 4), on the basis of the result by P. Debye, *Ann. Phys.*, **36**, 284 (1939).

14) P. N. Snowdon and J. C. R. Turner, *Trans. Faraday Soc.*, **56**, 1409 (1960).

15) J. W. Hiby and K. Wirtz, *Phys. Z.*, **41**, 77 (1940).