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Thermal Diffusion Measurements of Symmetric Tetraalkylammonium Bromides in Water

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The Soret coefficients for 0.01 M aqueous solutions of R_4NBr (R=H, Me, Et, *n*-Pr, *n*-Bu, *n*-Pen, *n*-Hex, and *n*-Hep) were measured by the Snowdon-Turner conductimetric method with accuracy within ±0.1%, and were found to be −0.13, −4.18, −7.16, −9.05, −9.61, −9.47, −8.65, and −7.34, respectively in 10^{-3} K^{-1}, at the mean temperature 25 °C. They show a maximum at the carbon number 4 or 5 in R, whereas the diffusion coefficients show a minimum at the same carbon number in an exactly inverse manner. The apparatus and procedure are described.

The peculiar property of tetraalkylammonium salts, *viz.* they are easily soluble in water despite the fact that they consist of ammonium type ions entirely substituted by hydrophobic alkyl chains, has attracted attention. Measurements on molar volumes,1) activity coefficients,2) specific conductivities,3) viscosity *B*-coefficients,4) NMR chemical shifts,5) and apparent energies of activation6) have been reported by many workers, the results being interpreted in terms of "hydrophobic bond,"7) which emphasizes the water structure around the tetraalkylammonium ions. However, studies on the diffusion (ordinary and thermal) of tetraalkylammonium salts do not seem have been carried out. One of us (T. I.) predicted that tetraalkylammonium salts would show very large Soret coefficients in water,8) and gave proper estimates which were found to be of the right order of magnitude by experiments using "combined thermocell" technique.9,10) However, the technique provides essentially the Soret coefficients relative to an appropriately selectred reference, *e.g.*, LiCl, which shows a negligiblly small Soret effect. It is desirable to carry out direct, accurate determination of the Soret coefficients of tetraalkylammonium salts.

Experimental

Cell Assembly. Measurements were carried out according to the Snowdon-Turner conductimetric method11,12) with minor revision. The cell (Fig. 1) consists of a rectangular cylindrical hole (10 mm ϕ, 10 mm height) drilled at a corner of 100×100 mm^2, 10 mm thick "Acrylite" (poly(methyl methacrylate)) plate, the remaining flat area being used as an apron on which a well calibrated level can be placed for levelling the cell. Platinized platinum disk electrodes, 20 mm ϕ, 0.5 mm thick (P_1 and P_2) are stuck watertight on either side of the top and bottom of the cell cylinder with a small amount of silicone paste ("Black Silicone" sealant, Tōre Chem. Ind. Co. Ltd.) which was drawn circularly along the peripheral region within 1 mm from the ends of the cylinder using a special applicator (Fig. 2) cut out from polyethylene plate, 1 mm thick. The silicone sealing is convenient and very effective for its adaptability and sufficient elasticity as well as for repelling water.

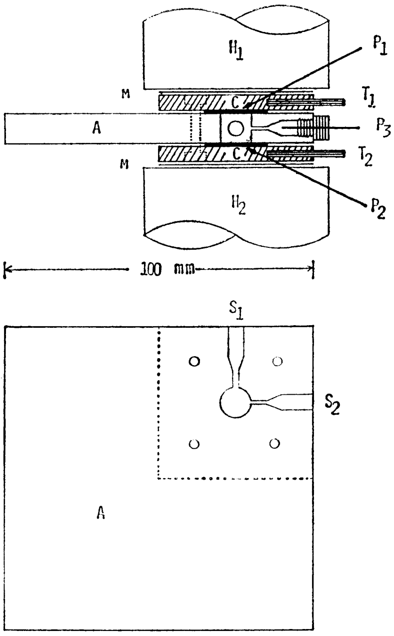

Fig. 1. Cell assemblies. A: Acrylite cylinder and apron. C: Heat conducting Cu-plate. M: Mica sheet. H_1 and H_2: Heat reservoirs. T_1 and T_2: Thermister probes. S_1 and S_2: Side holes. P_1 and P_2: Pt-disc electrodes. P_3: Pt-needle electrode.

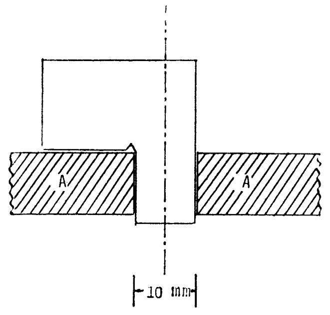

Fig. 2. Polyethylene applicator for pasting sealants.

The cell cylinder is equipped with two capillaries, 2 mm ϕ, both at right angle to the cylindrical cell wall at the half level, extending horizontally through the cell and opening directly outside to the neighboring sides of the square cell at S_1 and S_2. The cell is filled through the 2 mm ϕ capillary *via* S_1 which is closed with a 5 mm ϕ teflon screw plug through which a pinhole (0.5 mm ϕ) is bored to allow for thermal expansion of the solution. The opening S_2 is closed by a 5 mm ϕ teflon screw plug through which a platinized platinum needle electrode P_3 (0.5 mm ϕ) is threaded, extending through the 2 mm ϕ hole to the point near the innermost, narrowed part of the capillary (0.2 mm ϕ) which communicates with the cell cylinder. The Acrylite cell cylinder, with the platinum disk electrode P_1 and P_2 stuck on either side, is sandwiched between two platinum plated copper plates (5 mm thick and 50×50 mm^2 area) which serve as a conductor for heat as well as electricity. They are fixed tightly together evenly with polycarbonate bolts and nuts at the four corners (Fig. 1). The cell assembly is further sandwiched between two heat reservoirs, H_1 and H_2, *via* mica sheet for electric insulation. The temperature of the heat reservoirs was maintained constant within ±0.01 °C by circulation of thermostated water at 20 °C on the lower reservoir H_2 and at 30 °C on the upper H_1 to keep the mean temperature at 25 °C with thermo-circulators (CTE-2 and CTR-120,Komatsu Electronics Co. Ltd.).

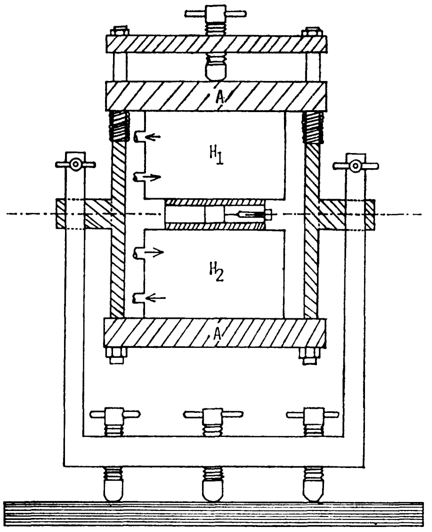

Fig. 3. Rotary cradle. H_1 and H_2: Heat reservoirs.

The entire system, including cell and heat reservoirs, was built in a stout rotary cradle supported on a massive iron rack provided with tripod screw for levelling (Fig. 3). This was placed in a large, foamy polystyrene box (30 mm thick wall) for thermal insulation from the exterior, empty space being stuffed loosely with cotton. Air conditioning of the laboratory around 25 °C (±1 °C) is desirable.

The temperature of the platinum disk electrode was assumed to be the same as that of the central region of the heat conducting copper plate in contact with it, the latter being measured with a well-calibrated precision thermister thermometer (T-005A, Takara Instrument Co. Ltd.) to an accuracy ±0.005 °C, where the thermister probe of 3.1 mm ϕ was mounted in a hole 3.2 mm ϕ and 25 mm deep reaching the center of the heat conducting plate.

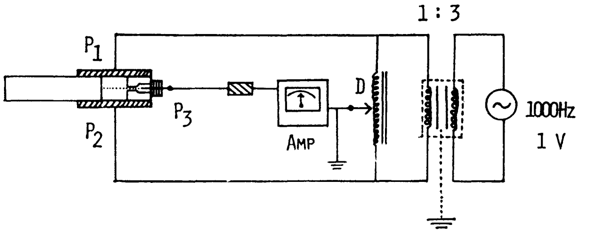

Fig. 4. Electric circuit. P_1, P_2, and P_3: Pt-electrodes. D: Decade ratio transformer. Amp: AC-amplifier as a detector.

Bridge Circuit. A block diagram of the bridge is shown in Fig. 4. Our aim was to find directly the ratio of resistances (impedances) Z_l and Z_u of the lower and upper halves of an electrolyte solution in the cell cylinder with respect to the central electrode P_3 by using a transformer bridge. A decade ratio transformer ("Decatran", DT-1145, Electroscientific Industries Ltd. U. S. A.) was used, with which we can read the resistance ratio, x, where $x=Z_u/(Z_l+Z_u)$, to the 5th figure below the decimal point, visually to the 6th. The sensitivity of this order is sufficient for the limited accuracy of the temperature control within ±0.01 °C. Audiofrequency of 1 kHz and 1 V was supplied by an oscillator (VP-722, Matsushita Communication Ind. Co. Ltd.) driven by a battery source, but was dropped down to (1/3) V through a matching transformer before being applied across the top and bottom electrodes of the cell. By this arrangement the Joulean heat that evolves in the solution can be nearly swept away by the steady heat flow caused by the temperature gradient of 10 °C per cm between the two heat reservoirs. A highly sensitive AC amplifier 4402-AV-13C of Yokogawa-Hewlet-Packard (120 dB with sensitivity of 1 μV) was used as a zero indicator for the balancing of the bridge by means of an impedance matching preamplifier.

Sample Solutions. In the series of symmetric tetraalkylammonium bromides, R_4NBr (R=H, Me, Et, *n*-Pr, *n*-Bu, *n*-Pen, *n*-Hex, and *n*-Hep), the first six compounds were obtained from Wakō Pure Chem. Ind. Ltd., and the last two from Eastman Kodak Co. These chemicals were recrystallized from ethanol and used to make 0.01 M (1 M=1 mol dm^{-3}) solutions with conductance water, the concentration being determined by volumetric or potentiometric titration as regards bromide ions. Before use, all the solutions were subjected to partial deareation by boiling for about 10 s under reflux, followed by rapid cooling, thus avoiding the formation of minute bubbles on the surface of the platinum electrode on the hot side, which spoil the experiments, when temperature difference is imposed across the cell.

Conditioning of the Cell and Measurement. Thorough washing of the cell inside with running fresh water is essential. *Ca.* 10 L of partially deareated hot water (70—90 °C) was allowed to enter the cell cylinder by means of a siphon *via* the side hole S_1 and to run out of the second side hole S_2 over a period of *ca.* 10 h, while leaving both platinum electrodes at the short circuit. The cell cylinder was then rinsed several times with the sample solution with a syringe and left to stand overnight with the solution in it so that it might soak through all the corners inside the cell cylinder including the two side holes. The solution was renewed and the cell assembly was warmed up for measurement, fixed on the cradle, first in the reverse position, the top at 20 °C and the bottom at 30 °C (mean 25 °C) for 1 h to make the solution uniform throughout by the violent convective flow caused by an inverse temperature gradient. The cradle was then turned to the normal position, this instant being regarded as the time zero. The measurement was started after the levelling of the assembly had been roughly made within the first 10 s and completely within 5 min. Incomplete levelling causes a convective flow in the cell, spoiling the measurements. The bridge balance reading, x, read on the Dekatran were made every 5 min in the early stage and every hour in the latest stage. The duration of a run varied from 6 h for the fastest diffusing solute to 12 h for the slowest. Essential points for measurements are as follows: Thorough rinsing and soaking of the cell, strict control of temperature, correct levelling of the system, correct setting of the cell assembly, and deareation of solutions.

Analytical Method. *General Description*: Let R_l and R_u denote the resistance of the lower and upper, respectively, halves of the solution in the cell cylinder with respect to the center-tap electrode P_3 at time t after a temperature difference ΔT has been applied across the cell. With use of $Y(t)$, a function of time t, defined by

$$Y(t) = \frac{R_l - R_u}{R_l + R_u} \tag{1}$$

Agar and Turner[11] derived the following equation for the determination of the Soret coefficient σ:

$$Y(t) - Y(0) = \frac{8b_{01}\sigma\Delta T}{\pi^3} F\left(\frac{t}{\theta}\right) \tag{2}$$

$$F\left(\frac{t}{\theta}\right) = \frac{\pi^3}{32} - \sum_{n=1}^{\infty} \frac{1}{n^3} \sin\left(\frac{n\pi}{2}\right) \exp\left(-\frac{n^2 t}{\theta}\right) \tag{3}$$

where $Y(0)$ is the Y value at time $t=0$. θ denotes the characteristic time constant defined by

$$\theta = \frac{a^2}{\pi^2 D} \tag{4}$$

where a is the cell height, D the diffusion coefficient at the mean temperature. σ is the Soret coefficient at the mean temperature defined by $\sigma = -(\partial \ln m/\partial T)_p$ in the steady state, where m is the molality. b_{01} is defined by

$$b_{01} = -\left(1 + \frac{\partial \ln \varLambda}{\partial \ln c}\right)_{T,P} \tag{5}$$

where $\varLambda$ is the equivalent conductivity at concentration c at constant temperature T and pressure P.

When an appropriate value of θ is found, we can obtain σ readily from the slope of the $Y(t)$-F plot. However, it is difficult to find the exact value of θ from the values of a and D measured independently, since, owing to the elasticity of the silicone sealants, fluctuation in a values may result depending on the pressure put on the cell assembly when sandwiched between two heat reservoirs H_1 and H_2 and the value of D is scarcely known experimentally for tetraalkylammonium salts except n-Bu_4NBr.[13] Though D might be estimated from conductance data, it would be inaccurate. Consequently, we adopted an alternative method of finding a suitable, effective value of the characteristic time constant, θ_{eff}.

Determination of θ_{eff}: Since in the same run ΔT is kept constant (10 °C), we have

$$Y(t) - Y(0) = \alpha F\left(\frac{t}{\theta}\right) \tag{6}$$

where α is a constant. When Eq. 6 is satisfied, the following function which involves four observational points Y_1, Y_2, Y_3, and Y_4 at respective times t_1, t_2, t_3, and t_4,

$$\begin{aligned} G(\theta) &= \frac{Y_1 - Y_2}{Y_3 - Y_4} - \frac{F\left(\frac{t_1}{\theta}\right) - F\left(\frac{t_2}{\theta}\right)}{F\left(\frac{t_3}{\theta}\right) - F\left(\frac{t_4}{\theta}\right)} \\ &= \frac{x_1 - x_2}{x_3 - x_4} - \frac{F\left(\frac{t_1}{\theta}\right) - F\left(\frac{t_2}{\theta}\right)}{F\left(\frac{t_3}{\theta}\right) - F\left(\frac{t_4}{\theta}\right)} \end{aligned} \tag{7}$$

should be equal to zero (the Decatran reading x_i may be used instead of Y_i). Solving Eq. 7 we can find the value of θ that fits the experimental results, θ_{eff}. Calculation was performed by using a minicomputor TI-59 Texas Instrument. The results are given in Table 1. By means of this effective value θ_{eff}, we obtained a linear relation between $Y(t)$ and F with a correlation coefficient exceeding 0.9999, which is sufficient if we consider that the temperature control was accurate within ±0.01 °C.

In case of NH_4Br, however, θ_{eff} could not be obtained by this method, since NH_4Br shows a very slight Soret effect,[10] giving a small value of Y, and making $G(\theta)$ practically indefinite. The value of θ for NH_4Br was calculated from the diffusion coefficient D and the cell height a in a similar way as described below.

Results and Discussion

The results for aqueous 0.01 M solutions of R_4NBr are shown in Figs. 5-a and 5-b, where $Y(t)$ is plotted against t and F. The linearity of the Y-F relation is good. The Soret coefficients obtained from the slope in the $Y(t)$-F diagram and given in Table 1 are plotted in Fig. 6 against the carbon number of the alkyl chains of the tetraalkylammonium bromides in terms of the molar heats of transfer Q^* ($Q^* = -2RT^2B\sigma$ for uni-univalent electrolytes, where R is the gas constant and B is defined by $B = [1 + (\partial \ln \gamma_\pm/\partial \ln m)]_{T,P}$, $\gamma_\pm$ being the mean activity coefficient.). All the results for 0.01 M aqueous solutions, except for n-Hep_4NBr whose concentration was 0.000978 M owing to its limited solubility, are given at the mean temperature 25 °C, where a possible shift was within ±0.03 °C during 6—12 h of the measurements (Table 1). Q^* shows a maximum around the carbon number 4—5 of the alkyl chain of R_4NBr. The present Soret coefficients of 0.01 M tetraalkyl-

Table 1. Soret coefficients and heats of transfer for 0.01 M tetraalkylammonium bromides at the mean temperature 25 °C

Bromide	$-b_{01}$[a]	B[b]	θ_{eff} / s	$10^9 D_{eff}$[c] / $m^2\,s^{-1}$	$10^9 D_{calcd}$[d] / $m^2\,s^{-1}$	$-10^3\sigma$ / K^{-1}	Q^* / kJ mol^{-1}	$-10^3\sigma_{calcd}$[e] / K^{-1}
H_4NBr	0.966	0.955	—	—	1.926	0.13	0.18	−0.28
Me_4NBr	0.962	0.953	6400	1.37	1.438	4.18	5.89	5.78
Et_4NBr	0.956	0.945	8360	1.05	1.148	7.16	10.00	9.65
n-Pr_4NBr	0.950	0.941	10120	0.870	0.898	9.05	12.6	13.4
n-Bu_4NBr	0.945	0.934	11600	0.761[f]	0.761[f]	9.61	13.3	16.3
n-Pen_4wBr	0.939[g]	0.929[g]	11850	0.744	0.705	9.47	13.0	18.5
n-Hex_4NBr	0.934[g]	0.923[g]	10600	0.828	—	8.65	11.8	—
n-Hep_4NBr	0.928[g]	0.917[g]	7400	1.19	—	7.34[h]	9.95[h]	—

a) Ref. 3, graphical determination. b) Ref. 2, graphical determination. c) Values for 0.01 M R_4NBr families were obtained by means of Eq. 4 from θ_{eff} found by experiment for the respective bromide using the effective cell height, a_{eff}, determined from the best fit value of θ_{eff} for the cell of n-Bu_4NBr using the literature value of D for 0.01 M n-Bu_4NBr (Ref. 13). d) Calculated by the Nernst-Hartley equation. e) Theoretical prediction.[8] f) Ref. 13. g) Extrapolation of the bromide series. h) The value for 0.000978 M.

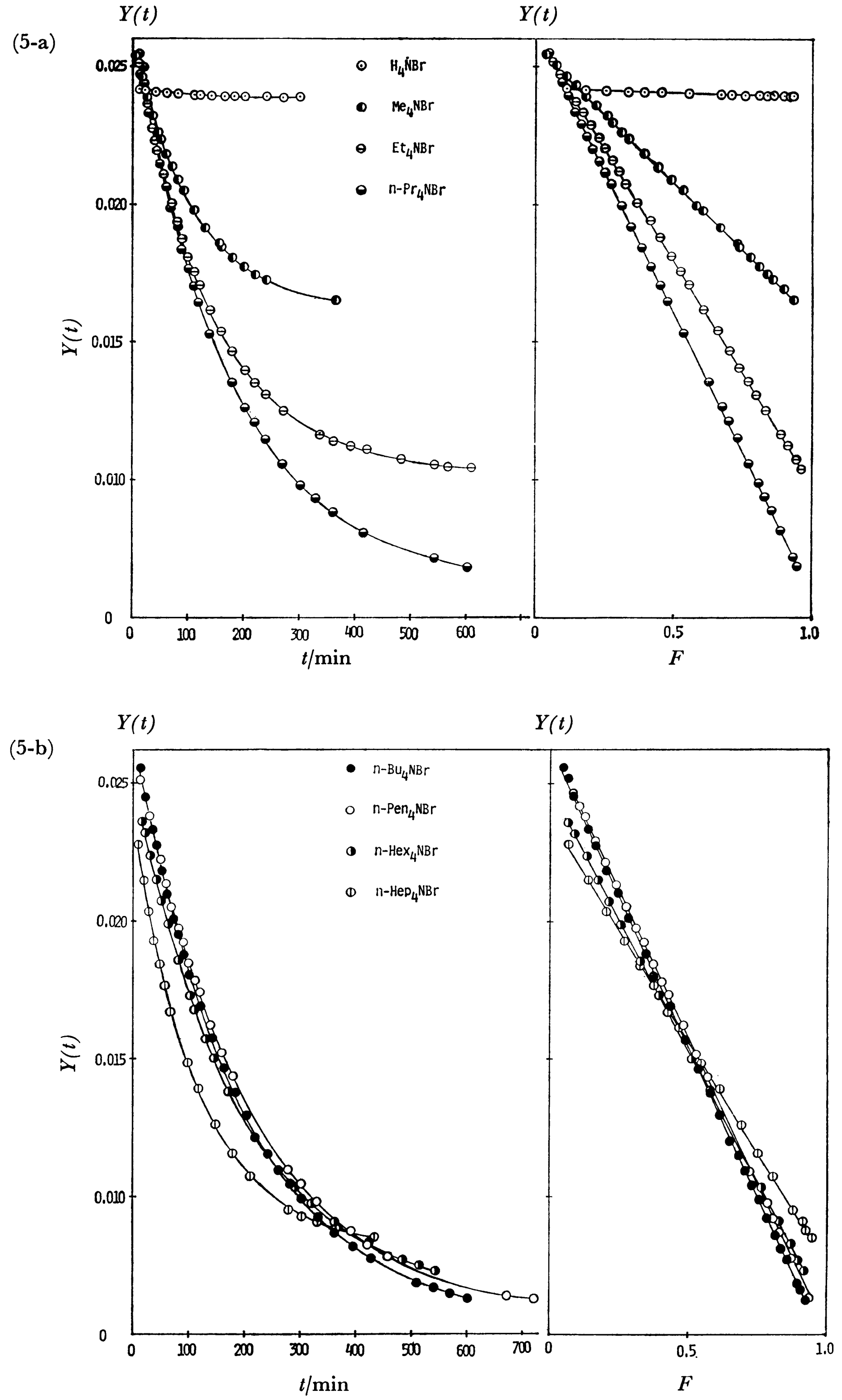

Fig. 5. (5-a and 5-b). $Y(t)$ plots *vs.* time and F.
⊙, H_4NBr; ◐, Me_4NBr; ⊖, Et_4NBr; ◒, *n*-Pr_4NBr; ●, *n*-Bu_4NBr; ○, *n*-Pen_4NBr; ◑, *n*-Hex_4NBr; ⦶, *n*-Hep_4NBr.

ammonium bromides are somewhat lower than those observed by Snowdon and Turner[12)] by a similar method. One of us (T. I.) estimated theoretically the Soret coefficients of 0.01 M aqueous solutions of a series of R_4NBr, in the range $R=H-R=n\text{-}C_5H_{11}$, from the initial thermoelectric powers of thermocells of 0.01 M solutions of R_4NBr families by taking 144 JK^{-1} mol^{-1} for the molar transported entropy of the bromide ions.[8)] The calculated values of the Soret coefficients σ (Table 1) are much greater than those observed, not showing any maximum but appearing to approach asymptotically a certain limit with increase in the carbon number of

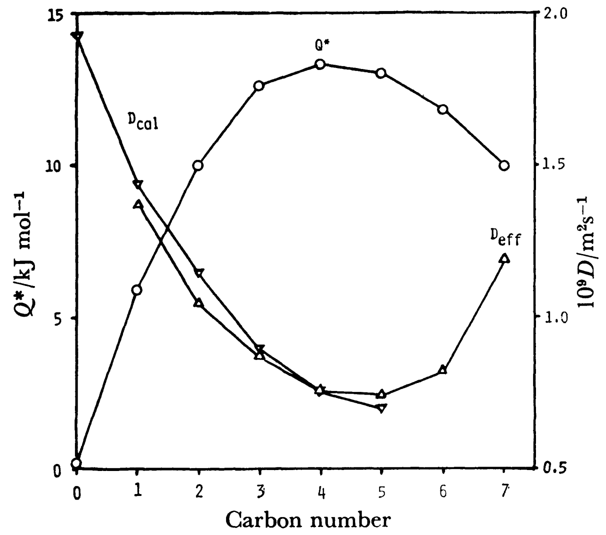

Fig. 6. Dependence of the heat of transfer or of the diffusion coefficient on the carbon number of the alkyl chain of R_4NBr.
○, Q^*; △, D_{eff}; ▽, D_{cal}.

the alkyl chain. This indicates that there is a limitation for calculation of the Soret coefficients from the initial thermoelectric power and the transported entropy, as in the case of the bromide ions where hydrophobic hydration becomes predominant, particularly in R_4NBr families with alkyl chain of higher carbon numbers beyond 4.

The diffusion coefficient, D, of the R_4NBr series has been determined experimentally only for n-Bu_4NBr.[13] For the other bromides, we could get rough estimates of D by (i) using θ_{eff} for the solution in question and the effective value of the cell height, a_{eff}, determined from the θ_{eff} for a reference solution such as Na_2SO_4 or n-Bu_4NBr, whose diffusion coefficient is known (D_{eff} in Table 1), and (ii) calculating the ionic equivalent conductance with use of the Nernst-Hartley equation,[14] (D_{calcd}). If we take into consideration the fact that D_{eff} and D_{calcd} were obtained from entirely different sources, the two diffusion coefficients are in fairly good agreement. We see that the D values pass minimum around the carbon number 4—5 of the alkyl chain, in an inverse tendency of Q^* showing maximum around the same carbon number (Fig. 6). This might be explained as a result of competition between two opposite tendencies: the enhancement of the water structure (hydrophobic bond formation) around the alkyl chain moieties of the tetraalkylammonium ion with increasing chain length, and the decrease in the number of completely dissociated free ions with increasing chain length owing to the reinforced ion-pairing effect[2,15] caused by the enhanced water structure around the ions.

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