THERMODIFFUSION CONSTANT IN LIQUID ISOTOPIC MIXTURES OF CERTAIN BROMINATED HYDROCARBONS

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Using a nonstationary method values of the thermal diffusion constant in butyl, amyl, and heptyl bromide are determined.

Available literature offers very few studies concerned with experimental determination of the thermal diffusion constant in liquid isotopic mixtures [1-4]. Meanwhile, collection of data in this region is of great interest, since such data would provide excellent material for verification of theories concerned with transfer phenomena in liquids, as well as acting as criteria for determining the possibility of using thermal diffusion to separate isotopes in the liquid phase.

The limited amount of experimental material available in the literature may be explained by the absence of a reliable method for determination of the thermal-diffusion constant in thermal-diffusion columns, which in the present case are the only devices suitable for such experiments.

The article [5] proposes a new method of calculating thermal-diffusion constants, which we have employed to determine values for a series of brominated hydrocarbons.

The materials studied were "pure" grade tubyl, amyl, and heptyl bromides, all of which underwent additional purification. Since the literature offers no data on the temperature dependence of density and viscosity for these compounds, corresponding measurements were performed by standard methods directly in the laboratory. Results are offered in Table 1.

EXPERIMENTAL

The experiments were performed with a plane column of the type employed by the authors of [6, 7], with the following changes: spaces in the upper and lower portions of the column were eliminated; b) an input lead was installed in the center of one of the plates, connecting with an external supply reservoir to compensate for loss of mixture after removal of samples for analysis; c) heating was accomplished by a

TABLE 1. Density and Coefficient of Dynamic Viscosity in Butyl, Amyl, and Heptyl Bromide Versus Temperature*

T, °C	Butyl bromide		Amyl bromide		Heptyl bromide	
	$\rho \cdot 10^{-3}$, kg/m^3	$\eta \cdot 10^{3}$, nsec/m	$\rho \cdot 10^{-3}$, kg/m^3	$\eta \cdot 10^{3}$, nsec/m^2	$\rho \cdot 10^{-3}$, kg/m^3	$\eta \cdot 10^{3}$, nsec/m^2
15			1,223	0,854	1,146	1,400
20	1,276	0,638	1,217	0,803	1,140	1,293
30	1,261	0,572	1,205	0,713	1,130	1,113
40	1,247	0,519	1,192	0,638	1,119	0,970
50	1,233	0,472			1,109	0,856
50,1			1,180	0,575		
60	1,218	0,433	1,166	0,524	1,099	0,765
65			1,160	0,500		
81,4					1,088	0,609
93					1,065	0,548

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*These data like those of [10] are presented in the report of the Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR, for 1969.

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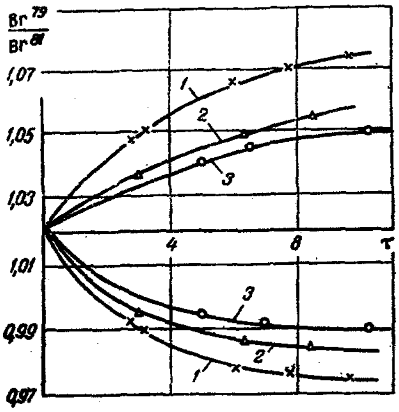

Fig. 1

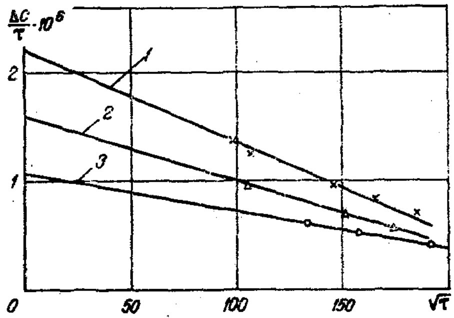

Fig. 2

Fig. 1. Changes in concentration of Br^{79} and Br^{81} at bottom and top of column versus time for: 1) butyl bromide; 2) amyl bromide; 3) heptyl bromide. τ, h.

Fig. 2. $\Delta c/\tau$ (sec^{-1}) versus $\sqrt{\tau}$ ($sec^{1/2}$) for: 1) butyl bromide; 2) amyl bromide; 3) heptyl bromide.

thermostat rather than an electrical heating element. The column consisted of four plates 230×14×10 mm, joined together with bolts. Between the two interior plates is mounted an annealed copper rectangular frame 163×80 mm, which forms the working volume of the column. After polishing, the working surfaces of the plates were nickel-plated chemically.

The required working gap between plates was obtained by installing hardened-steel precision washers between the mounting bolts.

The gap width was measured in the following manner; 16 pieces of lead 1×1×0.5 mm were placed in the working volume and the column was assembled, paying special attention to applying equal tension to all bolts; the column was then taken apart and the thickness of each lead spacer measured. After multiple repetition of this process, the mean deviation from the nominal gap thickness was determined. Since all measurements were of equal accuracy, the mean arithmetic value $\delta = 0.250 \pm 0.005$ mm was taken as the most probable value of the quantity measured. Thus, the working volume of the column comprised 3.3 cm^3.

Temperature measurements at each of the column working surfaces were made by copper — Constantan thermocouples (16 on each plate) with an accuracy of ±0.2°C. The hot and cold sources were applied as in Alexander's column [3] in the space between interior and exterior column walls. Heating was accomplished by thermostat and cooling by tap water.

The column was filled with the isotopic mixture through a lower valve from a polyethylene tube. Filling was performed slowly enough to avoid formation of cavities. After liquid appears at the two orifices at the top of the column the lower valve is closed, hot water is introduced from a preheated thermostat and cold water from the water supply line. After a 5-min period, which is needed to establish a stable temperature field, the upper orifices are hermetically sealed. Experimental time measurement commences from this moment. To ensure reliable results with each substance three experiments were performed under identical conditions. Replacement of the partially separated mixture by fresh mixture was performed by displacement through the upper valve, i.e., the same process used in filling was repeated, but with passage of a liquid volume five times as great as that of the column.

When changing to a new substance the column contents were completely emptied, the working volume was washed with ethyl ether, which is a good solvent for the substances studied, and the column was subjected to a vacuum with gentle heating. By using this method it was possible to perform all necessary experiments with one assembly of the column, which guaranteed both reproducibility and comparability of the results obtained.

To construct the separation, kinetic curve samples were taken from the top and bottom of the column at intervals of several hours. The volume of each sample did not exceed 0.015 cm^3. The total volume of all samples taken over the entire experiment was about 5% of the column volume, which should theoretically

TABLE 2. Experimental and Theoretical Data for Determination of Thermal-Diffusion Constant in Brominated Hydrocarbons

Theoretical and experimental values	Butyl bromide	Amyl bromide	Heptyl bromide
$D\cdot 10^9$, m^2/sec	2,42	1,89	1,16
$\eta\cdot 10^3$, $nsec/m^2$	0,505	0,619	0,936
$\rho\cdot 10^{-3}$ kg/m^3	1,243	1,189	1,116
$\beta\cdot 10^3$, deg^{-1}	1,12	1,00	0,90
T_1, °K	330	330	330
T_2, °K	302	302	302
Gr_δ	2900	1580	880
$\frac{\eta D}{\rho\beta}\cdot 10^{-13}$, $m^4 deg/sec^2$	8,73	9,80	10,75
$h\cdot 10^6$, sec^{-1} from Fig. 2	2,2	1,6	1,1
$n\cdot 10^9$. $sec^{-3/2}$ from Fig. 2	8,42	5,94	3,66
ω from Eq. (1)	0,272	0,246	0,196
α from Eq. (1)	0,038	0,033	0,031

reduce the amount of separation. However, control experiments in which first and second samples taken after equal time intervals were analyzed revealed that the experimental points lie on a single kinetic curve, and the deviation between them thus lies within the limits of measurement error.

The isotopic composition of the samples was determined with an MKh-1303 mass spectrometer using the standard method for analysis of liquid specimens. The analysis determined the ratio Br^{79}/Br^{81} from the most intense C_3H_7Br peak. This ratio was determined with an accuracy not less than 0.2%.

RESULTS AND DISCUSSION

Figure 1 shows the kinetic curves of the separation process which serve as the basis for subsequent processing of the experimental data.

Since the natural concentrations of the two bromine isotopes are almost equal, the following formulas presented in [5] are completely applicable:

$$\alpha\sqrt{D} = 1.17\frac{h^2\bar{T}\delta}{n\Delta T}, \quad \omega\sqrt{D} = 7.7\cdot 10^{-4}\frac{g\rho\beta\delta^3\Delta T h}{L\eta n}. \tag{1}$$

To determine the coefficients h and n the data of Fig. 1 are presented in coordinates $\Delta c/\tau - \sqrt{\tau}$ in Fig. 2, from which it is evident that the experimental data fit straight lines excellently.

Table 2 gives the necessary data concerning experimental conditions together with the other values needed for computation with Eq. (1).

Since there is no available data on the self-diffusion coefficient for the mixtures studied here, it was calculated with a modified Einstein formula,

$$D = \frac{RT}{2\pi\eta N_0}\left(\frac{N_0}{V_M}\right)^{\frac{1}{3}}, \tag{2}$$

which had been verified experimentally in [8]. Examination of data from that study permits the conclusion that for compounds containing hydrocarbon chains, deviations from Eq. (2) will be within the limits of ±5%. Values for density, dynamic viscosity, and coefficient of volume expansion were obtained by interpolation from Table 1.

The values of thermal-diffusion constant determined do show a tendency to decrease with decrease in relative mass difference, but a direct proportionality between their values was not established. This may be explained partially by the presence within the column of parasitic convection, which, in turn, might be caused by temperature nonuniformity on the two plate surfaces [9] produced by the low intensity of heat exchange in circulation of the thermostat hot water. Qualitatively, the effect of this factor may be estimated with the second formula of Eq. (1) by determining the value of the dimensionless volume ω which, as was shown in [5], considers not only the real volumes occurring in regions of convective flow rotation, but also some fictitious volume equivalent to the effect of parasitic convection, i.e.,

$$\omega = \omega_r + \omega_f. \tag{3}$$

From Table 2 it is evident that with change from butyl bromide to heptyl bromide the value of ω decreases.

This decrease may be the result of decrease of both terms in Eq. (3). The fictitious volume ω_f reflects the influence of parasitic convection, whose intensity, as was demonstrated in [9], depends on the parameter $\varkappa y_e$, which under unchanged heat-transfer conditions, temperature differences, and column dimensions, is directly proportional to the quantity $\eta D/\rho\beta$ presented in Table 2. With an increase in the number of carbon atoms this ratio shows some slight increase, which is equivalent to increase in ω_f. On the other hand, as was noted in [5], the value of ω_r also depends on the physical properties of the separated mixture, which affect the formation of convective flows in the column.

The more rapidly the opposed convective currents move, the more they interact with each other, promoting the formation of closed circulation contours over the column height, i.e., increasing ω_f.

It is known that in natural convection the criterion determining the flow hydrodynamics is the Grashof (Gr) number. As is evident from Table 2, this number decreases with increase in number of carbon atoms in the substance as the ratio 1 : 0.545 : 0.304, i.e., with growth in Gr one would expect more intense interaction of both convective flows and increase in the number of closed circulation contours within the column. Then, since the changes in Gr are quite significant, the decrease in ω_r with increase in mass should in all probability predominate over the increase in ω_f, leading finally to a decrease in the sum of these terms. Thus, the values of the thermal-diffusion constant obtained herein should be regarded as minimal.

NOTATION

α, thermal-diffusion constant; h, segment cut at ordinate axis (Fig. 2); n, tangent of slope of straight line in Fig. 2; $\bar{T} = 1/2\,(T_1 + T_2)$, T_1, T_2, temperatures of hot and cold column surfaces; $\Delta T = T_1 - T_2$; δ, gap; D, self-diffusion coefficient; $\omega = M/mL$; M, mass occupied by mixing fluids within column; $m = \rho B\delta$; B, column working parameters; L, column working length; ρ, density; η, dynamic viscosity; $\beta = -(1/\rho)\cdot(\partial\rho/\partial T)$; τ, time; Δc, concentration difference between column top and bottom; N_0, Avogadro's number; V_M, molar volume.

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