DETERMINATION OF MASS-TRANSFER COEFFICIENTS

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The convectionless partition of two organic mixtures is examined and the Soret coefficients as well as the concentrative diffusivity are determined. The values obtained for these coefficients and the trends of their variation confirm the appropriateness of purifying a substance by means of thermal diffusion.

This article is an extension of article [1]. For the design of a thermodiffusion apparatus one must know the values of the Soret coefficients and of the concentrative diffusivity for the partitioned mixture, determined under conditions approaching those of the actual partition process; one must also know how these coefficients vary over a wide range of concentrations which may be covered during the partition process, especially when thermal diffusion is used for cleaning purposes and for obtaining substances of standard-grade purity. It is important to know how the transfer coefficients vary over concentrations from 5% down of the heavier and of the lighter components; whether these coefficients do not become reduced to infinitesimal levels, which would mean that thermal diffusion is not a practically feasible method of purification.

Using an earlier development method, the authors have determined the diffusivity and the Soret coefficients for CCl_4 + benzene and CCl_4 + hexane mixtures over a wide range of concentrations: 5-95% (weight) of the heavier component.

The tests were performed on an apparatus shown in Fig. 1 and constructed so as to form a horizontal gap between the end surfaces of two thermostatically controlled steel cylinders 1 and 2. The cylinder end surfaces were carefully ground and chrome plated. The gap was 10 mm high and the diameter of its circular cross section was 50 mm. Between these cylinders was placed a metallic disk 3 whose upper and lower surface were precisely parallel. Tightness between the disk and the cylinders was ensured by Teflon seals 4. In order to vary the temperature vertically only and to prevent lateral heat leakage into the disk, a thick Teflon washer 5 was pressed on to separate the active liquid from the metal side walls. Inside each cylinder there had been milled out cavities through which the thermostatic water could circulate. The apparatus was suitable for performing experiments under convectionless conditions in the layer of test liquid. In order to make this possible, the upper cylinder was heated and the lower cylinder was cooled, while the entire apparatus (more precisely: the disk bolted to both cylinders) was adjusted to a level position within 0.08 mm/m. The temperature of the active surfaces in the apparatus was measured with copper–constantan thermocouples accurately within ±0.1°C at five points along the diameter on each side of the gap. The temperature of the hot surface was maintained at 50°C, the temperature of the cold surface was maintained at 20°C. The temperature of the active surface was, within the measurement error, the same at all test points.

Specimens were sampled precisely from the center of each surface. For this purpose, a receptacle at each cylinder was connected to the active space by way of a center hole 1 mm in diameter through that cylinder, while the active space at the time of sampling was connected to a reference container with mixture at the initial concentration level. After each sampling, the apparatus was completely emptied and then refilled for the next test with mixture at the initial concentration level.

The specimens were analyzed in an IPF-22 instrument. The values of the Soret coefficient and of the concentrative diffusivity shown in Fig. 2 have been calculated from the test data on concentration changes

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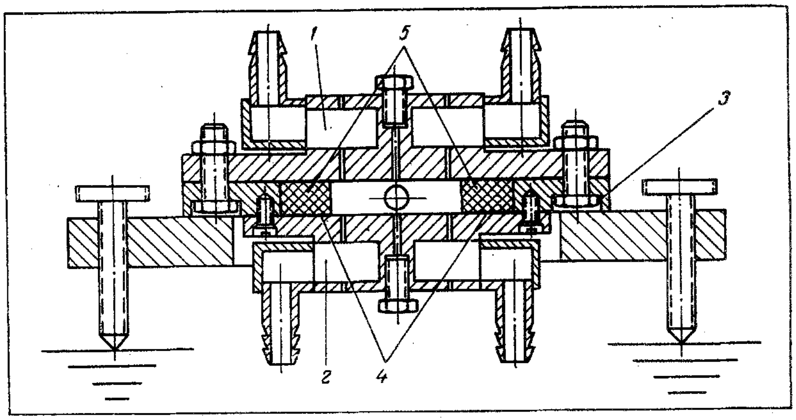

Fig. 1. Schematic diagram of the convectionless apparatus for determining the Soret coefficients and the concentrative diffusivity.

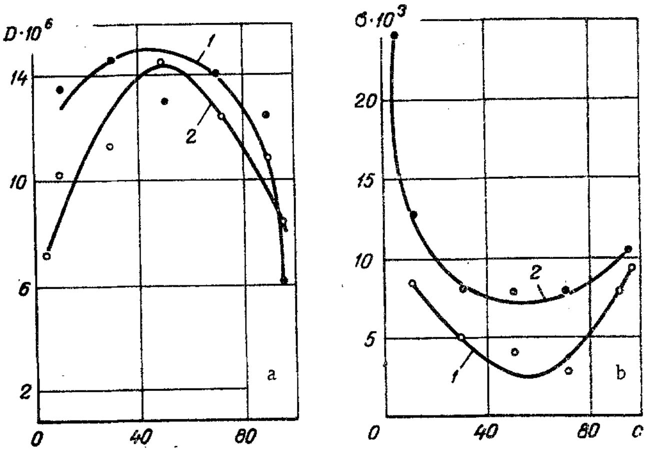

Fig. 2. a) Concentrative diffusivity; b) Soret coefficient, as functions of the concentration of the heavier component in: 1) benzene + CCl_4 mixture; 2) hexane + CCl_4 mixture.

at the cold and at the hot surface of the apparatus, according to the following formulas derived in [1]:

$$\sigma_{z=0} = \frac{2}{\Delta T} \frac{\overset{*}{c}_{01}}{1 - \frac{8}{\pi^2} \exp(-\pi^2 \mathrm{Fo}_m)}, \tag{1}$$

$$D_{z=0} = -\frac{l^2}{\pi^2 \tau_1} \ln\left[\frac{\overset{*}{c}_{02}}{\overset{*}{c}_{01}} - \sqrt{\left(\frac{\overset{*}{c}_{02}}{\overset{*}{c}_{01}}\right)^2 - \frac{\pi^2}{4}\left(\frac{\overset{*}{c}_{02}}{\overset{*}{c}_{01}} - 1\right)}\right], \tag{2}$$

where

$$\overset{*}{c}_{01} = \frac{c - c_0}{c_0 (1 - c_0)}. \tag{3}$$

The values in Fig. 2 represent the arithmetic averages between those at the hot surface and those at the cold surface of the apparatus. From these data for the test mixtures one can see clearly that, as the concentration of the heavier or of the lighter component decreases, the Soret coefficient becomes much higher. While for 5% (weight) of carbon tetrachloride in the hexane + CCl_4 mixture the Soret coefficient is equal to $24 \cdot 10^{-3}$ deg^{-1}, for the 50:50 mixture it is equal to only $7 \cdot 10^{-3}$ deg^{-1}, i.e., the rate of the partition process increases as the concentration of the heavier component in the mixture becomes lower. The same is observed also when the concentration of the lighter component decreases, which means that impure substances whose Soret coefficient varies in such a manner will be effectively purified in thermal diffusion columns.

As the numerical values of the coefficients, they agree with the data in [2], but, unfortunately, only a narrower range of concentrations were studied there.

NOTATION

σ	is the Soret coefficient, $\deg^{-1}$;
ΔT	is the temperature difference, °C;
c_0	is the initial concentration (weight fraction) of a mixture;
c	is the concentration (weight fraction) of a mixture;
Fo_m	is the Fourier number of mass transfer;
τ_1	is the initial time interval from which on the coefficients are calculated;
c_{01}^*, c_{02}^*	are the concentrations corresponding to time τ_1 and $\tau_2 = 2\tau_1$, respectively;
D	is the concentrative diffusivity, cm^2/sec;
l	is the height of column (apparatus), cm.

LITERATURE CITED

1. G. I. Bobrova and G. D. Rabinovich, in: Transient Heat- and Mass-Transfer Processes [in Russian], Minsk (1965).
2. E. Von Halle, AEC Research and Development Report, K-1420 (1959).