DETERMINATION OF THE SORET COEFFICIENT
IN A THERMAL-DIFFUSION COLUMN OPERATING
IN THE SAMPLING MODE

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UDC 621.039.3

The Soret coefficient for an ethanol—water mixture near the azeotropic point is determined in a continuously operating thermal-diffusion column.

At the present time two methods are generally used for determination of the Soret coefficient in a thermal-diffusion column: separating a binary mixture in a state of established equilibrium [1-6], or employing the kinetic curve describing the transient process in the initial stage of separation [7-13], with the column operating in the nonsampling mode in either case. Both these methods have shortcomings. In the first method the Soret coefficient is determined with a formula in which the desired value is highly dependent on the accuracy of measuring the operating gap, which appears in the formula raised to the fourth power. In the second method errors occur due to inaccuracy in constructing the tangent to the zero point of the kinetic curve if de Groot's method [14] is used, and while the method of the present authors [11, 12] avoids this difficulty, it, like the first method, requires precision measurement of concentration shifts on the initial segment of the kinetic curve in those cases where one of the components is present in a low concentration.

Both difficulties can be avoided to a significant degree by a method based on separation in a thermal-diffusion column operating under conditions of continuous sampling of the separated mixture.

Only two previous studies [15, 26] have used this method. Powers and Wilke [15] performed experiments in a plane column with central supply using an ethanol—water mixture with initial ethanol concentrations of 33 and 40% by mass. To reconcile their experimental data with theory the authors were compelled to introduce semiempirical correction coefficients which, in their opinion, considered the effects of sampling on hydrodynamics within the column. The data obtained on the Soret coefficient with this approach were in satisfactory agreement with the experiments of [16, 17]. Heines et al. [26] studied the operation of a continuously functioning column with central supply using a mixture of n-heptane and benzol in the concentration range which allows use of formulas obtained under the condition $c(1 - c) = const$.

The experiments were performed in four cylindrical columns and gave Soret coefficient values quite close to those obtained in a cell without convection.

In performing the experiments described below it was necessary, first, to determine whether the introduction of correction coefficients as proposed in [15] is justified; second, to verify the results predicted in theory for the case where sampling does not occur at the column center; and finally, to obtain data on the Soret coefficient for an ethanol—water mixture near the azeotropic point, i.e., in a practically unstudied region of obvious practical interest.

A schematic diagram of the column with supply in the intermediate section is shown in Fig. 1a. For the portion of the column above the supply point the flow in the positive z direction is described by

$$j' = Hc'(1 - c') - K \frac{dc'}{dz} + \sigma_e c', \tag{1}$$

while for the portion below the feed point

$$j'' = Hc''(1 - c'') - K \frac{dc''}{dz} - \sigma_i c''. \tag{2}$$
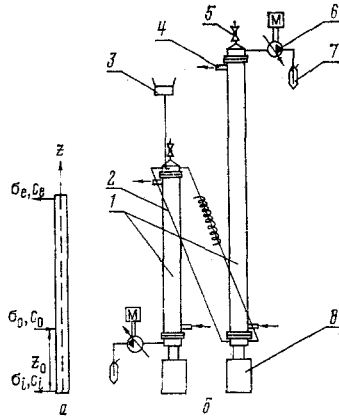

Fig. 1. Schematic diagram of experimental apparatus: a) column with supply lead; b) thermal-diffusion apparatus [1] thermal-diffusion columns; 2) circulation device; 3) supply reservoir; 4) connecting pipes for supply and withdrawal of cooled water; 5) needle valve; 6) automatic sampler with regulated flow; 7) fraction collector; 8) vapor generator].

Since we consider the steady state ($\mathrm{div}\,\vec{j} = 0$), instead of Eqs. (1), (2) transforming to dimensionless variables we obtain

$$\frac{d^2c'}{dy^2} - \frac{dc'(1-c')}{dy} - \varkappa_e\,\frac{dc'}{dy} = 0,$$

$$\frac{d^2c''}{dy^2} - \frac{dc''(1-c'')}{dy} + \varkappa_i\,\frac{dc''}{dy} = 0. \tag{3}$$

System (3) must satisfy the boundary conditions

$$j'|_{y=y_e} = \sigma_e c'|_{y=y_e} = \sigma_e c_e, \tag{4}$$

$$j''|_{y=0} = -\sigma_i c''|_{y=0} = -\sigma_i c_i, \tag{5}$$

$$c'|_{y=y_0} = c''|_{y=y_0} \tag{6}$$

and the conservation conditions

$$\sigma_0 c_0 = \sigma_e c_e + \sigma_i c_i, \quad \sigma_0 = \sigma_e + \sigma_i$$

or

$$\varkappa_0 c_0 = \varkappa_e c_e + \varkappa_i c_i, \quad \varkappa_0 = \varkappa_e + \varkappa_i. \tag{7}$$

Unfortunately, it is impossible to solve system (3) with conditions (4)–(7) in quadratures, so that we use the linearization of the term $c(1-c)$ proposed in [18]

$$c(1-c) \approx a + bc, \quad a = c_i c_e, \quad b = 1 - c_i - c_e. \tag{8}$$

Then instead of Eqs. (3)–(5), we obtain

$$\frac{d^2c'}{dy^2} - (b+\varkappa_e)\frac{dc'}{dy} = 0, \quad \frac{d^2c''}{dy^2} - (b-\varkappa_i)\frac{dc''}{dy} = 0, \tag{9}$$

$$\left(\frac{dc'}{dy} - bc'\right)_{y=y_e} = a, \tag{10}$$

$$\left(\frac{dc''}{dy} - bc''\right)_{y=0} = a. \tag{11}$$

The solution of Eq. (9) with conditions (6), (7), (10), and (11) has the form

$$a + bc_e = \varkappa_0(a + bc_0)(\varkappa_e + b)[\varkappa_i - b\exp[(b-\varkappa_i)y_0]]\{\varkappa_i(\varkappa_i - b) \times$$
$$\times [\varkappa_e + b\exp[-(b+\varkappa_e)(y_e - y_0)]] +$$
$$+ \varkappa_e(\varkappa_e + b)[\varkappa_i - b\exp[(b-\varkappa_i)y_0]]\}^{-1}, \tag{12}$$

TABLE 1. Experimental and Calculated Data for Determination of Soret Coefficient in an Ethanol−Water Mixture at $\overline{T} = 310°K$

Sampling 10^4, g/sec		Concentration, mass fraction of ethanol		a	b	$H \cdot 10^4$, g/sec	$-s \cdot 10^3$, deg^{-1}
upper	lower	upper	lower				
4,6	4,68	0,959	0,928	0,890	−0,887	1,35	3,0
3,71	3,77	0,964	0,926	0,890	−0,890	1,45	3,2
1,75	1,80	0,983	0,885	0,970	−0,868	1,41	3,1

$$a + bc_i = \varkappa_0 (a + bc_0)(\varkappa_i - b)\{\varkappa_e + b \exp[-(b + \varkappa_e)(y_e - y_0)]\} \times$$
$$\times \{\varkappa_i(\varkappa_i - b)[\varkappa_e + b \exp[-(b + \varkappa_e)(y_e - y_0)]] +$$
$$+ \varkappa_e(\varkappa_e + b)[\varkappa_i - b \exp[(b - \varkappa_i) y_0]]\}^{-1}. \tag{13}$$

We can find special cases of Eqs. (12), (13). Thus, for $a = 0$, $b = 1$ we have $c \ll 1$; for $a = 1$, $b = -1$ we have $1 - c \ll 1$; for $b = 0$, $c(1 - c) \approx$ const.

From Eqs. (12), (13) we find

$$k \equiv \frac{a + bc_e}{a + bc_i} = \frac{(\varkappa_e + b)\{\varkappa_i - b \exp[(b - \varkappa_i) y_0]\}}{(\varkappa_i - b)\{\varkappa_e + b \exp[-(b + \varkappa_e)(y_e - y_0)]\}}. \tag{14}$$

For sufficiently large samples the exponential terms in square brackets may be neglected and instead of Eq. (14) we obtain

$$k = \frac{\varkappa_i(\varkappa_e + b)}{\varkappa_e(\varkappa_i - b)}; \tag{15}$$

hence, with the notation used here

$$H = \frac{\sigma_i \sigma_e (k - 1)}{b(\sigma_i + k\sigma_e)}. \tag{16}$$

As is evident from Eq. (15), at high σ the position of the supply point has almost no effect on the separation result, and Eq. (16) makes it possible to calculate the Soret coefficient.

Equation (16) was verified in a UTDL-4 device [22], developed at the Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR (ITMO AN BSSR). Its basic components are shown in Fig. 1b. Two columns are connected by a thermosyphon circuit 2. Supply comes from reservoir 2 into the upper part of the small column corresponding to point z_0 in Fig. 1a.

Fraction sampling is effected by continuously operating samplers 6 and collectors 7. The hot heat-transfer agent is vapor of 94% ethyl alcohol with which vapor generators 8 are filled. A pressure of 0.1 gage atm is maintained automatically in the vapor generators, corresponding to a vapor temperature of 81°C [19]. Cooling is performed by cold water through pipes 4. Temperature was measured by thermocouples on the inner surface of the outer column and was equal to 13°C in all experiments. With a separation slit perimeter of 15.7 cm the columns differed slightly in operating gap. The 350-mm-high (short) column had a 0.258-mm gap and the 700-mm-high (tall) column had a 0.266-mm gap. In the calculations a mean (weighted over length) gap value of $2.6 \cdot 10^{-4}$ m was taken with consideration of expansion of the inner cylinder due to heating. The temperature difference between the column working surfaces was determined by calculation with the known heat-transfer coefficient determined in [20], 1850 W/m² · deg, the known thermophysical properties of the separated mixture and column walls, and the thicknesses of the inner cylinder walls. The small column was made of type 45 steel with $\lambda = 47.4$ W/m · deg with inner cylinder wall thickness of $7.7 \cdot 10^{-3}$ m, while the inner cylinder of the large column was made of Kh18N9T steel with wall thickness of $4.5 \cdot 10^{-3}$ m and $\lambda = 16.2$ W/m · deg. Using the data of [21], the thermal conductivity of 94% by mass ethyl alcohol at the mean gap temperature of 36°C was taken as 0.171 W/m · deg. As a result, for the small column we have $\Delta T = 46.4°C$, while for the large column, $\Delta T = 44.2°C$. Subsequent calculations used a mean weighted (over length) value of $\Delta T = 45°C$ and $\overline{T} \approx 35°C$ for both columns. The values of a and b were found with Eq. (8). Experimental results are presented in Table 1. Ethanol concentration was measured by an RPL-2 refractometer to an accuracy of $\pm 0.2\%$.

The Soret coefficient was calculated from the H value found by Eq. (16) with the formula

$$s = \frac{720 H \eta}{g\rho^2 \beta \delta^3 (\Delta T)^2 B}. \tag{17}$$

The values of the physical characteristics in Eq. (17) were taken at $\overline{T} = 36°C$ for a concentration $c_0 = 0.94$, in consideration of the relatively small concentration change. The viscosity of the mixture studied was $\eta = 1.03 \cdot 10^{-3}$ Nsec/m², $\rho = 795$ kg/m³, $\beta = 0.96 \cdot 10^{-3}$ deg⁻¹ [21].

To determine the effect of sampling on the parameter H and to eliminate systematic errors the experiments were performed without dismantling the column, using one and the same mixture and control and analysis methods. Therefore, in determining the Soret coefficient it is necessary to consider only relative error, which is significantly lower than absolute error. In our case its value was less than 4%, which indicates that the theory describes the separation process in the sampling regime with completely satisfactory accuracy, and the introduction of any correction coefficients for the parameter H is not necessary.

On the basis of the data presented in Table 1 it is possible to determine how well the conditions which permit use of Eqs. (16), (17) were satisfied in the experiments. The dimensionless sampling γ in all cases was greater than unity. As for the quantity y_e, using a value on the order of 10^{-9} m²/sec for the diffusion coefficient, we obtain $y_e \approx 50$ and $y_0 = \frac{1}{3} y_e \approx 16$. It is obvious that with these $\varkappa$ and y_e values the assumptions on which Eq. (16) is based are completely applicable.

We note that the only available data on the Soret coefficient in the concentration range on the order of 0.9 is that of Von Halle [23], obtained at $c_0 = 0.9$ and $s = 0.6 \cdot 10^{-3}$ deg⁻¹ and the data of Tikhachek, presented in the same study, for $c_0 = 0.94$, which gave a value $s = -1.7 \cdot 10^{-3}$ deg⁻¹.

Von Halle performed his experiments in a horizontal thermal-diffusion column in which two flows moving in opposite directions were separated by a permeable membrane. When one considers that the theory of such a column is based on a number of assumptions which have not yet been reliably confirmed, one can not consider the Soret coefficient data obtained with the column reliable. In Tikhachek's experiments, performed in a cell divided by a glass diaphragm (T = 298°K), in calculating the Soret coefficient the temperature difference between the diaphragm surfaces was not used and was replaced by the temperature difference between the hot and cold volumes. Alexander [24] has demonstrated that this must lead to significant reduction in Soret coefficient values. Korsching and Wirtz [25] did perform a study of azeotropic mixture separation in a thermal-diffusion column operating in the sampleless regime, but it was only of a qualitative character, and as noted in [23], cannot be used to evaluate the Soret coefficient, since a stationary state was not achieved.

NOTATION

c, concentration; σ, sampling; $H = g\rho^2 s\beta\delta^3(\Delta T)^2 B/\eta$; $\gamma = \sigma/H$; $y = Hz/K$; $y_e = y|_{z=L}$; $y_0 = y|_{z=z_0}$; δ, gap width; L, total column height; ΔT, temperature difference between working surfaces; B, gap perimeter; s, Soret coefficient; ρ, η, D, and β, density, coefficients of dynamic viscosity, diffusion, and volume expansion, respectively; $K = g^2\rho^3\beta^2\delta^7(\Delta T)^2 B/\eta^2 D$. Indices: e, upper; i, lower column end; 0, supply point.

LITERATURE CITED

1. I. Prigogine, L. de Brouckere, and R. Buess, Physica, 18, 915 (1952).
2. K. Alexander and U. Krecker, Kernenergie, 1, 437 (1958).
3. D. J. Trevoy and H. G. Drickamer, J. Chem. Phys., 17, 1120 (1949).
4. F. H. Horne and R. J. Bearman, J. Chem. Phys., 37, 2857 (1962).
5. C. J. Grownover and J. E. Powers, AIChE J., 8, 166 (1962).
6. G. J. Langhammer, Chim. Phys., 54, 885 (1957).
7. I. Prigogine, L. de Brouckere, and R. Amand, Physica, 16, 577 (1950).
8. I. Prigogine, L. de Brouckere, and R. Amand, Physica, 16, 851 (1950).
9. K. Alexander, Z. Phys. Chem., 203, 203 (1954).
10. H. F. John and H. E. Bent, J. Phys. Chem., 60, 1524 (1956).
11. G. D. Rabinovich, Inzh.-Fiz. Zh., 26, No. 3 (1974).
12. G. D. Rabinovich and M. A. Bukhtilova, Inzh.-Fiz. Zh., 26, No. 4 (1974).
13. G. D. Rabinovich and V. P. Ivakhnik, Inzh.-Fiz. Zh., 28, No. 5 (1975).
14. S. R. de Groot, Physica, 9, 801 (1942).
15. J. E. Powers and C. R. Wilke, AIChE J., 3, 213 (1957).
16. P. F. Velden, H. G. P. Voort, and C. J. Gorter, Physica, 12, 151 (1946).
17. J. Cabicar and V. Zatka, Chem. Listy, 48, 348 (1954).
18. K. Johns and W. Ferry, Isotope Separation by Thermodiffusion [Russian translation], Moscow (1947).
19. V. N. Stabnikov and S. E. Kharin, Theoretical Bases of Distillation and Rectification of Spirits [in Russian], Dishchepromizdat, Moscow (1951).

20. G. D. Rabinovich and V. P. Ivakhnik, Inzh.-Fiz. Zh., 26, No. 2, 314 (1974).
21. Handbook of Chemistry [in Russian], Goskhimizdat, Moscow (1952).
22. V. P. Ivakhnik, V. I. Shaplyko, and G. D. Rabinovich, Teor. Osn. Khim. Tekhnol., 8, No. 4 (1974).
23. E. Von Halle, AEC Res. Dev. Rep., K-1420 (1959).
24. K. F. Alexander, Z. Phys. Chem., 195, 175 (1950).
25. H. Korsching, K. Wirtz, and L. W. Masch, Ber. Dtsch. Chem. Ges., 73B, 249 (1940).
26. T. S. Heines, O. A. Larsen, and J. J. Martin, Ind. Eng. Chem., 49, 1911 (1957).

STRUCTURE OF UNIDIMENSIONAL TEMPERATURE STRESSES

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Using the structural approach, the temperature stresses are examined in a semiinfinite rod, insulated on the lateral faces and rigidly fixed at the end. A comparative analysis is made for three heat-transfer models.

Shashkov and Abramenko [1] proposed a new, original method for describing physical phenomena. The problems of unidimensional heat conduction were examined for three heat-transfer models using the structural approach. The structural description does not require the solution of the initial determining equations. Within the scope of Laplace representations, it makes it possible to very graphically trace the formation of the physical fields and to isolate the observed coordinates.

The present work uses the structural method to describe the temperature stresses in a semiinfinite elastic rod insulated on the lateral surfaces and rigidly fixed at the end. Stresses develop in the rod as a result of the heat flux going into the fixed end. The heat transfer is described by the classic Fourier equation, by the hyperbolic equation based on the modified relationship of Vernotte−Lykov between the heat flux and the temperature gradient, and by the linearized Nunziato heat-conduction equation, which takes the thermal "memory" effects into account. A comparative structural analysis is subsequently made.

The thermoelastic state of a thin isotropic rod is described by the equation

$$\frac{\partial \sigma_{xx}(x, t)}{\partial x} = \rho \frac{\partial^2 u(x, t)}{\partial t^2} \tag{1}$$

and the relationship

$$\sigma_{xx}(x, t) = E\left(\frac{\partial u(x, t)}{\partial x} - \alpha_t T(x, t)\right). \tag{2}$$

Eliminating σ_{xx} stresses from (1) and (2), we obtain

$$\frac{\partial^2 u(x, t)}{\partial x^2} - \frac{1}{c_0^2} \frac{\partial^2 u(x, t)}{\partial t^2} = \alpha_t \frac{\partial T(x, t)}{\partial x}, \tag{3}$$

where $c_0 = (E/\rho)^{1/2}$ is the velocity of elastic vibrations in the rod.

The initial and the boundary conditions for the displacements have the form

$$u(x, 0) = \frac{\partial u(x, t)}{\partial t}\bigg|_{t=0} = 0, \tag{4}$$

$$u(0, t) = 0; \lim_{x \to \infty} u(x, t) < \infty. \tag{5}$$

I. Let us show the structure of temperature stresses in a rod when the heat-transfer process is described by the classic heat-conduction equation. The temperature field is found from Fourier equation