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A METHOD OF SIMULTANEOUS MEASUREMENT OF THE SORET AND DIFFUSION COEFFICIENTS OF LIQUID SOLUTIONS

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A method is developed for the simultaneous measurement of the Soret and diffusion coefficients under the conditions of a quasiisothermal process of damping of concentration disturbances in the measurement cell. Measurement results are presented for aqueous solutions of potassium chloride and sodium sulfate.

The principal methods of measuring the Soret coefficient, which characterizes the amount of thermodiffusional separation, presume the use of thermodiffusion columns or so-called convectionless cells. Optical methods are usually used to measure the concentration gradient in the cells. The latter do not introduce disturbances, permit one to reduce the size of the cell, and shorten the time of one test to several hours [1].

Finding the Soret coefficient from the conditions of a steady-state process is hindered by the fact that the optical signal is determined by the temperature and concentration fields simultaneously. In this case the contribution of the temperature field considerably exceeds the contribution of the concentration field. Therefore, measurement of the concentration difference is performed with considerable errors. The absence of precise information about the temperature dependence of the index of refraction of the mixture results in additional errors. Nonsteady methods, based on an analysis of the process of establishment of the concentration field under the action of an applied temperature difference, have the same drawbacks.

The accuracy in measuring the concentration gradients can be increased if the experiments are conducted under isothermal conditions. In this case the initial concentration difference is also created through thermodiffusion, but after the stationary regime is established the temperature at the boundaries of the measurement cell is made the same. Thanks to this, the time of relaxation of temperature disturbances is two orders of magnitude less

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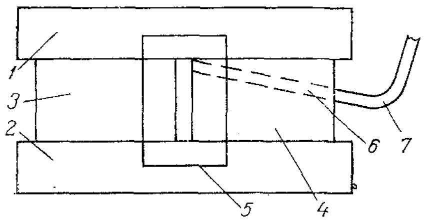

Fig. 1. Diagram of the measuring cell.

than the time of relaxation of concentration disturbances and the diffusion process takes place mainly under isothermal conditions. The first calculation of the Soret coefficient from interferograms obtained under isothermal conditions was evidently made in [2]. The variation of the concentration field with time was not taken into account in that report, however.

It is known [3, 4] that one of the main sources of error in experiments on measuring the Soret coefficient is gravitational convection due to a slight inclination of the cell, nonisothermicity of the heat exchangers, or convective instability of the equilibrium of the liquid. Therefore, in the present work we used a Korshing cell, the advantages of which from the point of view of the suppression of free convection were shown earlier [5].

The measurement cell (Fig. 1) consisted of a narrow rectangular cavity 1 mm wide, 4.45 mm high, and 77 mm long. The cavity was bounded above and below by heat exchangers (heater 1 and cooler 2) made of sheet copper 3 mm thick. With thicker heat exchangers the time of establishment of a stationary temperature regime was increased unjustifiably, while a decrease in the thickness resulted in disruption of isothermicity. The temperatures of the cooler and heater were kept constant with two constant-temperature water baths. When necessary, both heat exchangers could be connected rapidly (in 90 sec) to the same constant-temperature bath. The side boundaries 3 and 4 of the cell were made of Plexiglas. The cell was bounded on the ends with glass plates 5 with a thickness of 0.3 mm. The channels 6 and tubes 7 served to fill the cell with the liquid being investigated. To reduce heat transfer to the external medium and improve the conditions of thermal regulation the model was thermally insulated with a layer of wadding 3-5 cm thick.

The temperatures of the cooler and heater were measured with thermocouples, the signals from which were fed to a potentiometer of type R-306 with an R-325 microvolt–nanoammeter as the null galvanometer. The hot junctions of the thermocouples were soldered to the surface of the heat exchangers while the cold junctions were immersed in a Dewar vessel filled with crushed ice and water. The average concentration of the solution was determined from the index of refraction measured on an RPL-2 refractometer before and after each test. The concentration field in the cell was investigated on a real-time holographic interferometer. For this the model was mounted horizontally in the working space of the interferometer.

At the start of each test the cell was filled with the investigated liquid and a uniform vertical temperature gradient was created in it. Thermodiffusional separation of the mixture took place under the action of this gradient, and after a certain time a stationary height distribution of concentration was established. The time of establishment was determined experimentally for each solution and was 2-5 h. A further increase in this time no longer affected the final results. After the stationary regime was established both heat exchangers were connected to the constant-temperature bath with the lower temperature and the entire model was reduced to an isothermal state. The time t_1 of establishment of the isothermal state was determined mainly by the construction of the model, particularly by the heat capacities of the cooler and heater. In the experiments which were conducted it was 90 sec. The state was considered to be isothermal if the maximum temperature difference in the cell did not exceed 0.05°K. Under these conditions the contribution of the temperature field to the interference pattern was negligibly small.

Interference patterns corresponding to the isothermal diffusion process were photographed with an interval of 2-5 min. The interference bands on such photographs were lines of equal concentration. The transition from one band to another corresponded to a change in concentration by $(5.8\text{-}6.2)\cdot 10^{-3}\%$, depending on the solution. The temperature drop on the measurement cell at the start of a test was chosen so that the majority of the interferograms contained no less than 30-70 bands. The interferograms were interpreted on an instrumental microscope. The interpretation error did not exceed 0.25 band.

If the process of diffusion took place only under isothermal conditions, then the amplitude of the first spatial harmonic of the concentration disturbance would die out with time in accordance with the exponential law

$$a(t)=\frac{4\Delta c}{\pi^2}\exp(-\delta t), \tag{1}$$

where $\Delta c=Sc_0(1-c_0)\Delta T$; $\delta=\pi^2D/h^2$. The instant the heat exchangers are connected to the same constant-temperature bath is taken as the start of time reckoning.

In reality, the diffusion took place under nonisothermal conditions at $t < t_1$. Therefore, to estimate the error of Eq. (1), the diffusion and heat-conduction equations were solved jointly by numerical methods. The thermodiffusion term was taken into account in the diffusion equation. The time variation of the temperature at the cell boundaries corresponded to the conditions under which the tests were run.

The numerical solution showed that allowance for thermodiffusion fluxes results in a correction not exceeding 2% of $a(t)$. Thus, Eq. (1) proved to be quite suitable for the analysis of experimental results. We note that the contribution of thermodiffusion fluxes to the last spatial harmonics increases rapidly. Therefore, to calculate the Soret and diffusion coefficients it is most advisable to use just the first spatial harmonic, for which the diffusion $\tau = 1/\delta$ is much longer than the time t_1 of the transition to an isothermal regime.

The experimentally found height distribution of concentration was subjected to a harmonic analysis. From the time dependence of the amplitude of the first harmonic we found its value at the initial time and its damping decrement δ. These data were used to calculate the Soret coefficient and the diffusion coefficient in accordance with Eq. (1).

The results of the analysis of the interferograms showed that for the time interval $t_1 < t < 0.15\tau$ the value of the concentration gradient ∇c at the center of the cell remains the same as at the time $t = 0$ to within 1%, while the temperature disturbances have already been able to die out to the degree that they make no contribution to the interference pattern. (This conclusion was confirmed by the numerical solution.) Thus, if one measures the value of ∇c corresponding to this time interval, then one can obtain a second means of determining the Soret coefficient. Such a method was used in [2]. (Unfortunately, information about t_1 and τ are absent from [2], which prevents one from evaluating the possibilities of the installation used.) This method was also used in the majority of the tests in the present work. Because of the dependence of the time interval corresponding to the optimum conditions of measurement of ∇c on the diffusion coefficient, the size of this interval was varied from 30 to 200 sec.

The Soret and diffusion coefficients of aqueous solutions of potassium chloride and sodium sulfate were measured in the experiment. For KCl solutions there are rather detailed data on both the Soret coefficient and the diffusion coefficient. Therefore, the tests with KCl solutions were run mainly to check the experimental procedure. The values of the Soret coefficient of Na_2SO_4 solutions are eight to nine times larger than those of aqueous solutions of many other salts. This made it possible to do the measurements with small temperature drops between the cooler and heater (2-3°K) and investigate the temperature dependence of both kinetic coefficients.

The measurement results are presented in Table 1. The values of the Soret coefficients obtained by the two different means — from the damping of concentration disturbances (S_1) and from the concentration gradient at the center of the cell (S_2) — coincide within the error limits. The maximum difference between S_1 and S_2 for an Na_2SO_4 solution does not exceed 2%. The value of S_2 for KCl with a weight concentration of 13.7% evidently contains a small systematic error.

The results on the Soret coefficient for KCl solutions coincide with Longsworth's data [6] to within 2-4%. Tanner's results [7] are 30% lower. This is evidently explained by the existence of convective motions in Tanner's tests. (The Soret coefficient decreased while the diffusion coefficient increased with an increase in the Reynolds number.) The disagreement in the results of the second and third tests (Table 1) is explained by the temperature dependence of the Soret coefficient. In this connection we note that the diffusion coeffi-

TABLE 1. Soret Coefficients and Diffusion Coefficients of Aqueous Solutions of Potassium Chloride and Sodium Sulfate

Test number	Dissolved substance	c_0, wt.%	ΔT, °K	T_1, °K	$S_1 \cdot 10^3$, °K^{-1}	$S_2 \cdot 10^3$, °K^{-1}	$D \cdot 10^9$, m^2/sec
1	KCl	7,13	20,0	292,1	0,69	0,70	1,48
2		13,7	13,2	292,0	0,76	0,83	1,70
3			19,4	292,0	0,99	1,06	1,69
4	Na_2SO_4	15,7	1,12	297,6	8,81	8,70	0,62
5			2,01	297,2	9,23	9,11	0,59
6			2,43	296,3	8,62	8,51	0,65
7			3,26	296,3	8,46	8,35	0,65
8			4,33	296,4	8,77	8,66	0,61
9			4,71	295,6	9,26	9,13	0,56
10			2,06	282,1	8,21	8,05	0.41
11			3,09	283,8	8,27	—	0,40
12			3,01	289,4	8,78	8,68	0,49
13			2,86	299,9	9,22	9,28	0.57
14			2,86	301,8	9,26	9,45	0,64

cient is measured under the conditions when the temperature of the cell equals the temperature T_1 of the cooler. Thermodiffusional separation takes place under nonisothermal conditions. Therefore, the Soret coefficients must pertain not to the temperature T_1 but to the mean value, equal to $T_1 + \Delta T/2$.

The diffusion coefficients of a KCl solution with a concentration of 13.7% found in the present work coincide with the data of [8]. For a concentration of 7.13% the value of D proved to be 7% lower than the results presented in [8]. The reason for such disagreement still remains unclear.

In tests Nos. 4-9 the Soret coefficient of a sodium sulfate solution was measured with a constant mean temperature of about 298°K and different temperature drops ΔT was discovered. This indicates the absence of convective motions in the measurement cell. The presence of convection would inevitably have resulted in a decrease in S with an increase in ΔT. The temperature dependence of the Soret coefficient proved to be weak for this solution. It grew by only 13% with an increase in the mean temperature from 283°K to 303°K. The results of the measurements of the Soret coefficient of an Na_2SO_4 solution coincide with the data presented in [1]. The increase in the diffusion coefficient with an increase in temperature detected in the present work is characteristic for aqueous solutions of a majority of salts. The absence of information on the diffusion coefficient of this solution in the literature prevents us from making a comparison with the data of other authors.

An analysis of the results obtained shows that the proposed method makes it possible to simultaneously measure the Soret coefficient and the diffusion coefficient liquid solutions with an error not exceeding an average of 2-6%. The use of a measuring cell 3-5 mm high shortens the time of one test to 4-8 h.

NOTATION

S, Soret coefficient; D, diffusion coefficient; c, concentration in mass fractions; c_0, mean value of concentration; Δc, difference in concentrations at cell boundaries at the initial time; T_1, temperature of cooler; ΔT, temperature difference under the action of which the mixture separates; t, time; t_1, time of establishment of an isothermal state in the cell; h, cell height; a, amplitude of the first spatial harmonic of the concentration disturbance; δ, damping decrement of the first harmonic; τ, damping time of the concentration disturbance; S_1, Soret coefficient determined from the process of damping of a concentration disturbance; S_2, Soret coefficient obtained by measuring the concentration gradient at the center of the cell.

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NONSTEADY THERMODIFFUSIONAL SEPARATION OF BINARY MIXTURES UNDER SAMPLING CONDITIONS

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An accurate solution is obtained for the nonlinear nonsteady problem of the thermodiffusional separation of two-component mixtures in sampling conditions.

The process of thermodiffusional separation of binary mixtures, taking account of sampling, is described by the system of equations [1]

$$\frac{\partial c}{\partial \tau}=\frac{\partial}{\partial \xi}\left[\frac{\partial c}{\partial \xi}-2bc(1-c)-2\varkappa c\right],\quad c(\xi,\ 0)=c_0 \tag{1}$$

with the appropriate boundary conditions at the ends of the column. In particular, if the column is closed at one end ($\xi = 1$), while the other is connected to an infinite reservoir ($\xi = 0$), these conditions take the form

$$c(0,\ \tau)=c_0,\quad \left[\frac{\partial c}{\partial \xi}-2bc(1-c)\right]_{\xi=1}=0. \tag{2}$$

Here and above, the following dimensionless parameters are used

$$\tau=\frac{Kt}{L^2\mu},\quad \xi=\frac{z}{L},\quad b=\frac{HL}{2K},\quad \varkappa=\frac{\sigma L}{2K}. \tag{3}$$

An important characteristic of separating equipment is the concentration difference at the ends of the columns

$$\Delta c=c(1,\ \tau)-c_0, \tag{4}$$

i.e., it is necessary to know the explicit dependence $c(1, \tau)$. The steady value $c(1, \infty)$ of this quantity is known [2]; it is found from the following transcendental equation

$$\underset{\tau\to\infty}{c(1,\ \tau)}=c(1,\ \infty)=c_0\,\frac{1+\dfrac{b+\varkappa}{\sqrt{p_0}}\operatorname{th}\sqrt{p_0}}{1+\dfrac{2bc_0+\varkappa-b}{\sqrt{p_0}}\operatorname{th}\sqrt{p_0}}, \tag{5}$$

$$p_0=(\varkappa+b)^2-4b\varkappa c(1,\ \infty)>0. \tag{6}$$

Although the nonsteady thermodiffusional separation of two-component mixtures forms the subject of an extensive literature (see [1], for example), the solution has been obtained either without taking account of sampling ($\varkappa=0$) or in a linear approximation $c(1-c) \simeq$ const c. At the same time, methods of linearizing the generalized nonlinear boundary prob-

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