ANALYSIS OF THERMODIFFUSION IN LIQUIDS

A. I. Narbekov and A. G. Usmanov

UDC 532.72:536.22

The results are presented on an experimental study concerning thermodiffusion in aqueous solutions and in liquid organic mixtures within a wide range of initial concentration and at various temperatures.

Thermodiffusion is of great interest as a method of separating substances. Partition is effected in so-called thermogravitational columns. From studies made on thermodiffusion columns one may conclude that the problem of increasing the partition rate is basically solved by way of minor design changes. The mechanism of the partition process has not yet been explored sufficiently well and, therefore, the thermodiffusion method could not be thoroughly evaluated.

Acquiring an accurate concept about thermodiffusive partition is also of interest for the purpose of developing a general theory of thermodiffusion in liquids. The theories known so far describe the process qualitatively only and do not offer any reliable means for calculating the characteristic partition process parameters, namely the Soret coefficient and the thermal diffusivity, under nonisothermal conditions.

In order to describe the thermodiffusive partition process, it is necessary to establish the concentration and temperature distributions in the partitioned mixture as functions of time. Such an analysis is performed more conveniently in a thermodiffusion apparatus operating in the heat-conduction mode, i.e., by the static method. This method was used in our study.

Various groups of aqueous solutions and of mixtures with different physicochemical properties and behavior were chosen for this analysis of the thermodiffusion process: water–potassium chloride, water–potassium bromide (initial concentrations in the $c_{2i} = 0.2$-1.0 M range); water–glucose, water–saccharose ($c_{2i} = 1$-5% weight); water–ethyl alcohol, water–propyl alcohol ($c_{2i} = 5$-95% weight); heptane–octane, and isooctane–octane ($c_{2i} = 10$-90% weight).

The temperature difference $\Delta T = T_2 - T_1$ across the layer of mixture to be partitioned was 15°C for the aqueous solutions of salts, 10°C for the aqueous solutions of saccharides, and 5°C for the other mixtures. The mean temperature was $T_m = (T_2 + T_1)/2 = 293$°K.

In addition, water–isopropyl alcohol and heptane–benzene mixtures ($c_{2i} = 50\%$ weight) were tested at $T_m = 288$ and 293°K, $\Delta T = 2.5$-15°C.

Thermodiffusive partition of these mixtures was performed in a special beaker which had been described in [1]. It will be noted that the thickness of the liquid layer in this beaker was $h = 5.00$ mm.

Concentration changes in the layer were determined continuously by the interferometer method. The optical instrumentation and the procedure for processing the test data are shown in [2, 3]. The change in concentration Δc from its original value at any point in the layer of mixture was calculated by the formula

$$\Delta c = \frac{k\lambda}{l\,\frac{dn}{dc}}. \tag{1}$$

The derivative of the refractive index, as a function of the concentration, with respect to concentration was found by measuring n on an IRF-23 refractometer.

S. M. Kirov Chemical Engineering Institute, Kazan'. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 21, No. 2, pp. 334-340, August, 1971. Original article submitted October 9, 1970.

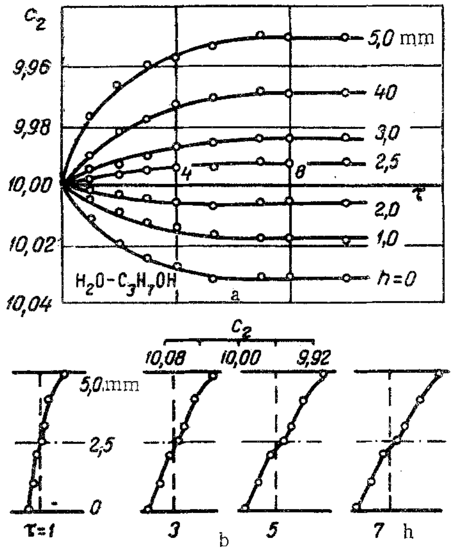

Fig. 1

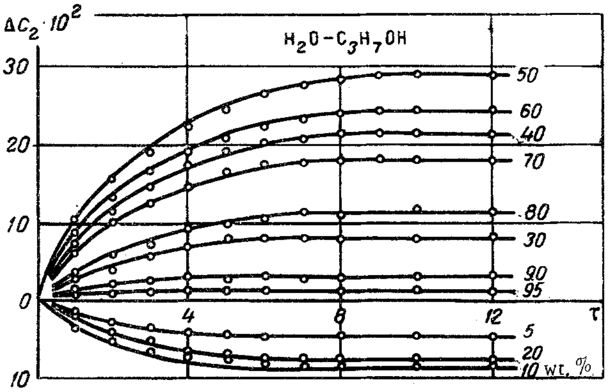

Fig. 2

Fig. 1. Concentration distribution during thermodiffusion in a horizontal layer of aqueous propyl alcohol solution: c_2, wt. %; τ, h.

Fig. 2. Change in the concentration difference between hot and cold surface in a beaker, as a function of test time: τ, h.

In this way it was possible to track the changes in the concentration field during thermodiffusive partition. As an example, a graph is shown in Fig. 1a which represents the change in concentration with time at different heights of a 10% aqueous propyl alcohol layer. It is to be noted that the error in measuring concentrations from interferograms did not exceed ±1.2%.

It can be seen from Fig. 1a that the change in concentration at the upper (hot) and at the lower (cold) surface in the beaker is asymmetrical with respect to the initial concentration. For the aqueous solutions of KCl, KBr, $C_6H_{12}O_6$, and $C_{12}H_{22}O_{11}$ as well as for the $C_7H_{16}-C_8H_{18}$, $C_7H_{16}-C_6H_6$, and $iC_8H_{18}-C_8H_{18}$ mixtures this asymmetry is slight. It becomes significant in the aqueous solutions of C_2H_5OH, C_3H_7OH, and iC_3H_7OH.

The asymmetry in the partition of aqueous alcohol solutions is particularly pronounced during the initial stage of the process, but remains still considerable even after steady state has been approached; for example, in a 10% aqueous C_3H_7OH solution the concentration of propyl alcohol changes by 0.034% at the lower surface and by 0.05% at the upper surface.

The equation of thermodiffusion, according to the solutions obtained by various authors [4, 5, 6], yields symmetrical changes in concentration at the hot and at the cold surface. A more rigorous solution by Bobrova and Rabinovich [7] indicates some asymmetry and, according to it, this change in concentration should be greater where the component with a concentration $c < 0.5$ precipitates. This conclusion has been confirmed in our experiments. It must be noted here that the magnitude as well as the orientation of asymmetry depend on the nature of the mixture. Our test data indicate that the asymmetry in aqueous solutions of salts and alcohols is much greater than according to the Bobrova–Rabinovich solution to the thermodiffusion equation. This can be explained by the fact that Bobrova and Rabinovich do not take into account the dependence of the Soret coefficient on the concentration – a dependence which, as will be shown here, is strong for certain groups of mixtures.

The concentration distribution over the layer height is shown in Fig. 1b after various periods of time. The earlier noted asymmetry increases also by some shift of the constant-concentration level with respect to the median line.

The change in the concentration difference $\Delta c = \Delta c^{up} - \Delta c^{low}$ with time characterizes the actual partition kinetics. Kinetics curves have been plotted for all the mixtures under study. The data on the partition kinetics of the water–propyl alcohol mixture are shown in Fig. 2. The effect of concentration on the partition progress will now be analyzed when the data on the Soret coefficient are examined.

TABLE 1. Results of Thermodiffusive Partition as Functions of c_i, ΔT, and T_m

Name of mixture	c_{2i}	T_1, °K	T_m, °K	ΔT, °C	$\Delta c \cdot 10^2$	$\frac{dn}{dc} \cdot 10^4$	$S^T \cdot 10^3$, deg^{-1}
H_2O—KCl	0,2M	285,5	293,0	15,0	0,37	100,6	1,18
	0,6				0,83	100,5	0,92
	1,0				1,52	100,4	1,01
H_2O—KBr	0,2	285,5	293,0	15,0	0,43	143,0	1,38
	0,6				1,10	142,0	1,22
	1,0				2,12	140,0	1,39
H_2O—$C_6H_{12}O_6$	1,0% вес	288,0	293,0	10,0	0,6	14,5	0,61
	3,0				1,6	14,6	0,63
	5,0				3,1	14,8	0,66
H_2O—$C_{12}H_{22}O_{11}$	1,0	288,0	293,0	10,0	0,8	14,45	0,81
	3,0				2,4	14,63	0,87
	5,0				4,5	14,84	0,95
H_2O—C_2H_5OH	5,0	290,5	293,0	5,0	9,8	6,65	—4,18
	10,0				17,2	7,10	—3,92
	20,0				19,8	7,18	—2,48
	30,0				22,0	5,50	2,07
	40,0				48,2	3,79	4,02
	50,0				56,2	2,60	4,48
	60,0				50,2	1,69	4,25
	70,0				37,5	0,80	3,54
	80,0				20,0	0,11	2,47
	90,0				5,5	1,61	1,20
	95,0				1,3	2,89	0,53
	10,0	288,0	293,0	10,0	33,7	7,10	—3,72
	20,0				45,3	7,18	—2,83
	30,0				48,5	5,50	2,31
H_2O—C_3H_7OH	5,0	290,5	293,0	5,0	4,5	9,20	—1,96
	10,0				8,2	9,25	—1,85
	20,0				7,6	7,75	—1,01
	30,0				7,8	6,20	0,78
	40,0				21,4	5,60	1,81
	50,0				30,0	5,05	2,32
	60,0				24,4	4,45	2,04
	70,0				17,6	3,70	1,72
	80,0				11,2	3,10	1,37
	90,0				2,6	2,00	0,58
	95,0				0,6	1,20	0,26
	10,0	288,0	293,0	10,0	14,0	9,25	—1,56
	20,0				15,0	7,75	—0,94
	30,0				15,1	6,20	0,72
H_2O—iC_3H_7OH	50,0	286,75	288,0	2,5	8,7	4,05	1,39
		285,5		5,0	16,6		1,33
		283,0		10,0	32,0		1,28
		290,5	293,0	5,0	20,8	3,95	1,66
		288,0		10,0	38,7		1,55
		285,5		15,0	56,2		1,50
C_7H_{16}—C_8H_{18}	10,0	290,5	293,0	5,0	7,2	1,20	1,53
	30,0				19,0	0,90	1,68
	50,0				23,3	1,00	1,86
	70,0				22,8	0,90	2,02
	90,0				10,2	0,90	2,19
	10,0	288,0	293,0	10,0	14,1	1,20	1,56
	90,0				20,5	0,90	2,28
iC_8H_{18}—C_8H_{18}	10,0	290,5	293,0	5,0	4,3	0,75	0,95
	30,0				10,7	0,65	1,02
	50,0				13,5	0,60	1,08
iC_8H_{18}—C_8H_{18}	70,0				11,6	0,55	1,12
	90,0				5,3	0,50	1,17
	10,0	288,0	293,0	10,0	8,8	0,75	0,98
	90,0				10,9	0,50	1,21
C_7H_{16}—C_6H_6	50,0	286,75	288,0	2,5	6,5	11,53	—1,04
		285,5		5,0	13,6		—1,09
		283,0		10,0	28,8		—1,15
		290,5	293,0	5,0	14,2	10,10	—1,13
		288,0		10,0	30,5		—1,22
		285,5		15,0	47,2		—1,26

It is to be noted that a thermodiffusion experiment requires much time, since usually all process characteristics are determined only after steady state has been reached. If an exact general equation were available for the change in concentration as a function of time, then the desired parameters could be found also from the transient portion of the $\Delta c = f(\tau)$ curve and the test time could thus be reduced considerably.

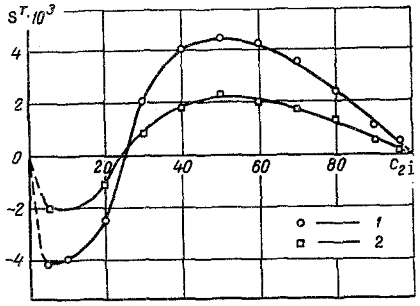

Fig. 3. Soret coefficient as a function of the initial concentration, for aqueous solutions of ethyl and propyl alcohols: $H_2O-C_2H_5OH$ (1) and $H_2O-C_3H_7OH$ (2).

A comparison of such equations obtained by various authors with the experimental $\Delta c = f(\tau)$ curves shows that, in most cases, the former do not reflect the real character of concentration changes with time. This, in effect, considerably reduces the importance of methods of calculating the Soret coefficient S^T and the diffusivity D from tests performed under transient conditions [5, 7]. Regardless of the lengthy test time, the calculation of S^T and D from steady-state data seems more reliable.

The Soret coefficient is calculated from the concentration difference at the end of the partition process. For aqueous salt solutions we have the equation

$$S^T = -\frac{1}{m} \cdot \frac{(\Delta m)^{s.s}}{\Delta T}. \tag{2}$$

For the other aqueous solutions and for the mixtures of organic liquids we have

$$S^T = -\frac{1}{c_1 c_2} \cdot \frac{(\Delta c_2)^{s.s}}{\Delta T}. \tag{2'}$$

In our case the error in calculations of the Soret coefficient according to Eqs. (2) and (2') was within ±2.6%.

The values of S^T as a function of the initial concentration in the mixture are shown in Table 1 and in Fig. 3. The value of S^T is taken to be positive if during partition the heavy component moves toward the cold surface. The S^T versus concentration characteristic is peculiar for each group of mixtures.

A great deal of test data pertaining to aqueous solutions of KCl and KBr is available in [8]. All measurements were made there at concentrations above 1.0 M, however, and in this range S^T is a linear function of m. Our measurements made at concentrations 0.2, 0.6, and 1.0 M have shown that, as m decreases, the coefficient S^T first decreases too; it becomes minimum at approximately 0.5 M, and then continues to increase. A similar relation between S^T and m is peculiar to diffusion processes in electrolyte solutions [9].

The Soret coefficient for aqueous saccharide solutions increases with concentration. Naturally, the behavior of aqueous solutions is much simpler than that of electrolytes.

Most interesting is the S^T versus concentration characteristic of water–alcohol solutions (Fig. 3). At low concentrations the Soret coefficient is negative, as indicated by the movement of the lighter component toward the cold surface in the beaker. At alcohol concentrations in the 24-26% range the Soret coefficient becomes zero (the partition process ceases). At a 50% concentration the Soret coefficient attains its maximum value; within this range of concentrations it is the heavier component which moves toward the cold surface. Such a behavior can be explained by the peculiarities of intermolecular interaction within these mixtures [10].

In Table 1 also results are presented of measurements of the Soret coefficient at various temperature differences and different mean temperatures. As the mean temperature is raised, the absolute value of the Soret coefficient increases. The effect of the temperature difference on the Soret coefficient varies depending on how the concentration difference changes with the temperature difference.

Thus, the Soret coefficient depends largely on the concentration. A change in the mean temperature and in the temperature difference has also a definite effect on the Soret coefficient. The results presented here concerning the dependence of the Soret coefficient on the concentration and the temperature as well as the data on the process kinetics and the concentration distribution in a layer of mixture provide a full picture about thermodiffusive partition in liquids and they may be of use for refining the theory.

NOTATION

λ	is the wavelength of light used in tests;
n	is the refractive index;
k	is the number of interference bands;
l	is the path length of the light beam through layer;
c_1, c_2	are the concentration of the first and second component, respectively;
T	is the temperature;
m	is the molarity
D	is the diffusivity;
S^T	is the Soret coefficient;
τ	is the time.

LITERATURE CITED

1. A. I. Narbekov and A. G. Usmanov, Trudy Kazan Khim. Tekh. Inst. im. S. M. Kirova, No. 39, 3 (1968).
2. A. I. Narbekov and A. G. Usmanov, in: Heat and Mass Transfer [in Russian], Vol. 7, Nauka i Tekhnika, Minsk (1968).
3. A. I. Narbekov, P. A. Norden, and A. G. Usmanov, Inzh.-Fiz. Zh., 16, 136 (1969).
4. J. Bierlein, J. Chem. Phys., 23, 10 (1955).
5. T. Mizushina and R. Ito, Chem. Engin. Japan, 25, 34 (1961).
6. V. P. Zhuravleva, Inzh.-Fiz. Zh., 6, 73 (1963).
7. G. I. Bobrova and G. D. Rabinovich, in: Problems in Transient Heat and Mass Transfer [in Russian], Nauka i Tekhnika, Minsk (1965).
8. C. Tanner, Trans. Faraday Soc., 23, 75 (1927); 49, 611 (1953).
9. R. Robinson and R. Stokes, Electrolytic Solutions [Russian translation], IL (1963).
10. G. P. Roshchina, in: Critical Phenomena and Fluctuations in Solutions [in Russian], Izd. AN SSSR (1960).