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I. R. Krichevskii, N. E. Khazanova, and L. R. Linshits

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Abstract

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I. R. Krichevskii, N. E. Khazanova, and L. R. Linshits

DIFFUSION IN THE CRITICAL REGION OF TERNARY SOLUTIONS

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The rate of diffusion in solutions is determined by the gradients of the chemical potentials ([1]). At the critical point of a binary solution, the derivative of the chemical potential of a component with respect to composition is equal to zero ([2]). Therefore, at the critical point of a binary solution, the gradient of the chemical potential of a component is equal to zero for a component concentration gradient different from zero.

The cessation of diffusion toward the critical region of a binary solution, first predicted by D. P. Konovalov, has only recently received experimental confirmation ([3,4]). This fact of the practically complete cessation of diffusion in the critical region, very interesting from the theoretical standpoint, acquires great importance for practice, since it imparts a special character to the kinetics of processes occurring in this region ([4]).

At the critical point of a ternary solution, none of the derivatives of the chemical potentials of the components with respect to composition, in contrast to binary systems, becomes zero ([2]). Therefore, in the general case, the rate of diffusion of the components of a ternary solution near the critical point will not fall to a very small value. However, if the solution is dilute with respect to the third component, then, to a high degree of approximation, the theory of binary systems may be applied to the principal components. Then in such systems near the critical point the rate of diffusion of the two principal components will remain close to zero, since the derivatives of the chemical potentials of the components with respect to composition at the critical point will differ very little from zero (the less, the smaller the addition of the third component). The derivative of the chemical potential of the third component, however, will be different from zero, and its diffusion should proceed at a finite rate.

The use of such a phenomenon would make it possible to enrich with the third component (or to purify from the third component), if it were forced to diffuse through some line of separation at a relatively much greater rate than the principal components would diffuse. The use of such a phenomenon would also make it possible to carry out selective heterogeneous chemical reactions that would proceed according to chemical kinetics for the third component, whereas

for the two principal components these reactions can proceed only according to diffusion or mixed kinetics ([4]). Therefore, investigation of the rate of diffusion of components in the critical region of such ternary mixtures is of great interest.

The task of the present investigation was limited to solving the basic question—to determine unambiguously whether, owing to molecular diffusion in the critical region, a noticeable enrichment of the solution occurs by the third component, which plays the role of a small addition to a binary system.

The investigation of diffusion in ternary solutions was, for a number of reasons, carried out using the system triethylamine—water with the addition of a small amount of butylamine. The investigation was performed by the capillary method. For

capillaries about 2 mm in diameter and about 40 mm long were used. The experiments were carried out over 50-90 hours. Thermostating was maintained with an accuracy of $\pm 0.05°$. The experimental procedure was the same as in the study of diffusion in the critical region of ternary systems ([3], [4]).

The minimum amount of butylamine added was limited by the accuracy of the van Slyke analysis method used. The design of the apparatus and the analytical method, developed for application to the present case*, made it possible to determine a butylamine content of the order of 1 mg, present in approximately 10 ml of liquid, with a relative error of 3-5 wt.%.

The study of diffusion in the three-component mixture was carried out for solutions in which the same ratio of butylamine to triethylamine was always maintained (~ 1 : 14). Determinations were performed at one temperature, 18° (the critical temperature of the ternary mixture studied was 21.8°).

In order to obtain clearer results (taking into account the limited sensitivity of the analytical method for butylamine), a large concentration gradient of the diffusing component was chosen for the study. The difference in the concentrations of the initial solutions in the beaker and in the capillary was of the order of 0.2 g/cm^3 for triethylamine and of the order of 0.013 g/cm^3 for butylamine.

Table 2

Diffusion coefficient of triethylamine $D_{(but)}$ in the ternary mixture at 18°

Initial concentration in the capillary, g/cm^3	Final concentration in the capillary, g/cm^3	Duration, h	$D \cdot 10^{-7}$, cm^2/sec
Triethylamine concentration in the beaker 36.3 wt.%	**Triethylamine concentration in the beaker 36.3 wt.%**	**Triethylamine concentration in the beaker 36.3 wt.%**	**Triethylamine concentration in the beaker 36.3 wt.%**

Initial concentration in the capillary, g/cm^3	Final concentration in the capillary, g/cm^3	Duration, h	$D \cdot 10^{-7}$, cm^2/sec
0.157	0.166	45.25	2.3
0.157	0.164	45.25	1.4
0.169	0.180	45.9	5.2
0.169	0.182	45.9	3.7
0.169	0.184	69.9	4.7
0.158	0.178	95.3	5.3
0.158	0.169	71.4	2.2
0.158	0.169	71.4	2.2
		Average . . .	3.4 ± 0.4
Triethylamine concentration in the beaker 19.3 wt.%	**Triethylamine concentration in the beaker 19.3 wt.%**	**Triethylamine concentration in the beaker 19.3 wt.%**	**Triethylamine concentration in the beaker 19.3 wt.%**
0.000	0.0302	65.5	15.9
0.000	0.0326	65.5	18.4
0.000	0.0370	69.1	18.6
0.000	0.0379	69.1	19.7
		Average . . .	18.1 ± 0.5

From the data given in Tables 1 and 2 it is evident that the diffusion coefficient of butylamine, both in the critical region and in dilute solutions, has the same order of magnitude. The somewhat larger value of D_{but} in dilute solutions is explained by their lower viscosity as compared with concentrated solutions. Thus, the diffusion rate of butylamine, present as a small additive to the binary mixture triethylamine–water, does not cease in the critical region, in contrast to triethylamine (Table 2), whose diffusion rate in this region decreases sharply. In the same dilute solutions the diffusion coefficient of triethylamine has the same order of magnitude as the diffusion coefficient of butylamine. It is interesting to note that D for triethylamine in dilute

* The analytical method will be described in a separate communication.

solutions–both ternary and binary ones[4]–has close values.

In agreement with theoretical premises, enrichment of the system with butylamine was obtained. The ratio of butylamine to triethylamine in the diffusing flux is about $1 : 6$, whereas in the initial solution it was $1 : 14$.

Table 1

Diffusion coefficient of butylamine (D_{but}) in a ternary mixture at 18°

Concentration in the capillary, g/cm^3	Concentration in the capillary, g/cm^3	Duration, hours	$D \cdot 10^{-5}$, cm^2/sec
initial Concentration of triethylamine in the beaker 36.3, in the capillary 17.6 wt. %	final Concentration of triethylamine in the beaker 36.3, in the capillary 17.6 wt. %	Concentration of triethylamine in the beaker 36.3, in the capillary 17.6 wt. %	Concentration of triethylamine in the beaker 36.3, in the capillary 17.6 wt. %
0,0115	0,0140	45,25	0,17
0,0114	0,0130	45,9	0,14
0,0114	0,0130	45,9	0,14
0,0114	0,0137	69,9	0,19
0,0114	0,0127	69,9	0,06
0,0108	0,0130	95,3	0,12
0,0108	0,0136	71,4	0,25
0,0108	0,0131	71,4	0,17
		Average . . .	$0,16 \pm 0,01$
Concentration of triethylamine in the beaker 19.3 wt. %, in the capillary 0.0	Concentration of triethylamine in the beaker 19.3 wt. %, in the capillary 0.0	Concentration of triethylamine in the beaker 19.3 wt. %, in the capillary 0.0	Concentration of triethylamine in the beaker 19.3 wt. %, in the capillary 0.0
0,0000	0,0055	65,5	0,50
0,0000	0,0037	65,5	0,23
0,0000	0,00405	69,1	0,41
0,0000	0,00343	69,1	0,29
		Average . . .	$0,35 \pm 0,04$

Thus, the first study carried out of the diffusion rate in the critical region of ternary solutions has shown, in agreement with theory, the possibility of enriching a solution with a third component by means of its molecular diffusion.

State Scientific-Research
and Design Institute of the Nitrogen Industry

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REFERENCES

[1] L. Onsager, R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).
[2] D. V. Gibbs, *Thermodynamic Works*, Moscow–Leningrad, 1950.
[3] I. R. Krichevskii, N. E. Khazanova, L. R. Linshits, *DAN*, **99**, 113 (1954).
[4] I. R. Krichevskii, Yu. V. Tsekhanskaya, *ZhFKh*, **30**, 2315 (1956).

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