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EFFECT OF ACOUSTIC OSCILLATIONS ON THE DIFFUSION PROCESS

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MOST physico-chemical processes occurring in a liquid, a solid, or on the interface between them are accompanied by directed motion of ions and molecules, i.e., by diffusion. Diffusion transport of particles in a liquid is very slow compared, say, with convective transport of matter. Therefore, to prevent the distorting action of different types of currents in the observation of diffusion from a liquid to a liquid, a thin porous partition of organic material is usually placed between the two; the properties of the partition should, according to the original idea, not disturb the general diffusion picture.

However, if the membrane has appreciable thickness and low porosity, and if the transport of dissolved substances in liquid media located on both sides of the membrane is accelerated in some manner, then the diffusion resistance of such a partition becomes appreciable. The diffusion rate will then depend both on the properties of the diffusing substance and on the diffusion permeability of the membrane. An increase in the membrane thickness leads to the case of diffusion into a semi-infinite solid through one interface. The existence of convective displacements of the liquid medium causes formation of a hydrodynamic boundary layer on the liquid-solid interfaces, and this introduces a certain singularity in the character of the diffusion of substances from one medium to another [44].

Introduction of acoustic oscillations into such many-layer diffusion systems can lead to a change in the variation of some of the processes occurring in it. Usually the transfer of matter is accelerated thereby. In order to know the causes of the acceleration, it is necessary to ascertain in what part of the system the changes originate, and how they occur. During the last three decades extensive but far from complete experimental material has been accumulated on the action of ultrasonic oscillations on transport processes; this makes it possible to draw a rather clear picture of the acceleration of diffusion processes in an acoustic field. The factors capable of influencing the diffusion process in an acoustic field include the following secondary effects, which occur in the sounded medium: cavitation, heating of the medium, and acoustic macro- and micro-currents. As a result of ultrasonic cavitation and heating of the medium in the acoustic field, the kinetic energy of the diffusing molecules can increase and the diffusion process can therefore be accelerated. Acoustic currents, and especially microcurrents produced on the phase separation boundary, are capable of intensely accelerating the mass transfer in the ultrasonic field near the solid surface.

1. DIFFUSION IN FREE LIQUID

The diffusion transport of matter in a liquid is the result of a continuous transfer of molecules and ions from one position of equilibrium to the other, and constitutes a process wherein dynamic equilibrium is established in the entire medium. The rate of diffusion, as well as the viscosity of the medium and the mobility of the ions, depends on the number of transitions j of the molecules (ions) in the liquid. It is known that the number of transitions j can be represented by the Arrhenius formula [42]

$$j = j_0 e^{-\frac{q}{kT}}, \tag{1}$$

where q is the activation energy, k Boltzmann's constant, $j_0 = 2\nu_0 k_1$, ν_0 the frequency of the natural oscillations of the particles relative to the equilibrium position, and k_1 a proportionality factor which takes into account the number of molecules having an energy sufficient to execute the transition.

According to modern notions, the physical properties of a liquid are not all due to the molecular structure, and depend also on different types of inhomogeneities present in the liquid, such as molecular complexes or concentration and density fluctuations. Such inhomogeneities, interacting with one another, are in dynamic equilibrium with the medium and cause the liquid to become quasicrystalline. Equation (1) can be applied to such media, too, provided the quantities contained in it characterize not the molecules of the medium but the inhomogeneities themselves.

If we start from the ideal picture of diffusion in a liquid (absence of convective, thermal, density, and acoustic currents), then the transport process can be accelerated in the presence of ultrasonic oscillations in the medium (i.e., rapidly alternating variations of density, velocity, and pressure) only if the diffusion coefficient or in the viscosity is changed by increasing the number of transitions and the number of charge carriers (in electrolytes), or by destroying the structural quasicrystalline inhomogeneities of the liquid. The diffusion and viscosity coefficients, and also the mobility of the ions, are complicated functions of the pressure. In the linear approximation, the action of an alternating sound pressure, when aver-

aged over the time, can yield either a zero effect, when each half-cycle cancels the preceding one, or a summary effect different from zero, when the action of each half-cycle has the same sign. The coefficient of diffusion of matter and the ion mobility are proportional to the number of transitions j, and the viscosity of the liquid is inversely proportional to this quantity [1]. At present it cannot be stated whether the viscosity of a liquid changes or whether it remains constant in the ultrasonic field, owing to the difficulty of setting up experiments of this type. In addition, there are no data on the effect of acoustic oscillations on the unperturbed process of diffusion from a liquid into a liquid (change in the diffusion coefficient), owing to the fundamental difficulty of carrying out such measurements, since it is impossible to eliminate completely the convective motions of the liquid. Therefore attempts were made to obtain information on the change or constancy of the number of transitions j in an ultrasonic field by indirect means, say from data on the action of acoustic oscillations on the electric conductivity of a liquid medium.

The electric conductivity of a liquid depends on the number of carriers and on their mobility. To assess the variation of these quantities in an ultrasonic field it is necessary to consider limiting cases. One of them is to measure the conductivity of an electrolyte in which the concentration of the dissolved substance is large, and consequently the number of carriers is also large. One usually neglects the increase in the number of carriers as the result of the action of the ultrasound, compared with their total number, and account is taken of the change in the ion mobility.

The behavior of the electric conductivity of electrolytes in an acoustic field was observed in [2-4]. However, the results obtained in the two first investigations cannot be used for our analysis, since the electric conductivity was determined with direct current, i.e., a slow drift of ions [2], or else the electric conductivity was measured only after sounding the liquids [3]. The electric conductivity of a 0.01 N solution of electrolyte in alternating current was measured only in [4], where it was established that, within the limits of experimental error (1%), ultrasound of frequency 800 kHz and intensity 1—2.5 W/cm^2 does not change the conductivity and consequently also the mobility of the ions in the solution.

Another limiting case of measurement of electric conductivity in an ultrasonic field involves the use of a liquid (say an organic dielectric) containing a very small number of carriers. Recognizing that in this case the mobility of the electrolyte ions in the ultrasound field does not change, we can establish in such measurements the ability of acoustic oscillations of producing an additional number of carriers. Unfortunately, the determination of the electric conductivity of a liquid dielectric (hexane, toluene, carbon tetrachloride, etc.) in an ultrasonic field has been likewise carried out only in the presence of a constant potential difference between the measuring electrodes [5,6]. This circumstance does not make it possible to ascertain whether the number of carriers increases or decreases, since directional convective displacements of the liquid medium, resulting from the presence of a propagating ultrasound wave, are superimposed on the measured effect.

Experimental data pointing to the absence of a change in the electric conductivity and consequently in the number of transitions j in the ultrasonic field [4] can be supported by theoretical premises. Transport theory leads to the conclusion that it is impossible to change the number of transitions j of molecules by means of electric oscillations [1]. Indeed, an estimate of the terms of a series expansion of Eq. (1), in which j_0, q, and T are functions of the pressure p, shows [1] that the increase in the number of transitions due to the periodic variation of the pressure in the medium is smaller by three orders of magnitude than the number of transitions in the absence of ultrasound $j_p = 0$.

Thus, no change in the number of carriers and in the number of particle transitions from one equilibrium position to another is observed in an ultrasonic field. This conclusion agrees with a quantitative estimate [7] from which it follows that the energy of the ultrasonic waves is negligibly small compared with the energy of the thermal motion of the molecules, and consequently, the vibrational displacement, velocity, and acceleration of the particles and the alternating sound pressure do not add noticeably to the random motion of the molecules during the process of molecular diffusion.

The number of carriers and the number of transitions of the molecules in the liquid are not the only parameters that can change in the field of ultrasonic waves. According to present concepts, liquids have a near-order structure (quasicrystallinity), and solutions of electrolytes have in addition solvation and association aggregates. If it is assumed that both can be destroyed by ultrasound as a result of resonance phenomena, then one must expect an increase in the mobility and in the number of active particles as a result of the decrease in the effective cross section of their interaction.

The supporting premise for considerations of this type, which were advanced in [8] and [9], is the existence of anomalous absorption of acoustic oscillations in solutions of electrolytes [10]. There is still no published experimental confirmation of the connection between the absorption of ultrasound waves and the acceleration of diffusion processes in an ultrasound field, although some authors attempt to use this, without justification, to explain experiments on the intensification of the diffusion process by acoustic oscillations in large-porosity media [11].

The idea of such "acoustic diffusion" presupposes

agreement of the frequency of the external exciting perturbation with the natural frequency of the structure inhomogeneity, which can become distorted as a result of this agreement. The natural frequency of the oscillations of the statistical inhomogeneities of the quasi-crystalline type in liquids is of the order of 10^{11} Hz,[8], greatly exceeding the elastic-oscillation frequencies used in practice. The same can be said concerning the associates of homogeneous molecules that are in dynamic equilibrium with the surrounding medium, whose natural frequency can be estimated[12] and has an order of magnitude 10^9 Hz. It must be noted that the dissociation of the molecules into ions in the acoustic field produces in electrolytes regions of maximal absorption of ultrasound in the frequency range 10^5 Hz and higher, a process accompanied by hydration. This is equivalent to shifting the equilibrium of the chemical association-dissociation reaction in the direction of dissociation[10], i.e., to a change in the concentration pH of the hydrogen ions in the solution. There are published reports that no change in the pH of electrolyte solutions takes place upon irradiation with ultrasound[43] and also after prolonged exposure to sound[13-15].

Thus, it can be assumed that the process of matter transport in liquids under ideal conditions, when there are no convective motions of the medium at all, cannot be accelerated by acoustic oscillations at the ultrasound frequencies and intensities used in practice at the present. Similar conclusions concerning the absence of a "specific" action (i.e., action not due to secondary effects) of ultrasound on the diffusion process, is reached by authors of a number of experimental papers[16-19]. These experiments revealed acceleration of the diffusion process in electrolytes under the influence of ultrasonic oscillations, in spite of the fact that the latter cannot change the diffusion properties of the liquid medium.

2. DIFFUSION IN HETEROGENEOUS SYSTEMS

a) Role of the Parameters of the Sound Field

A distinguishing feature of real diffusion systems used in practice is the presence in them of liquid-solid interfaces, the latter being permeable to the liquid as a result of the existence of micro- or macropores in it. Under ordinary conditions, natural convective flows exist in the liquid phase of such heterogeneous systems; these are due to temperature or density gradients. Liquid motion vanishes only near the solid surface, as a result of which a thin stagnant diffusion layer of thickness δ is produced[32]. A certain loss in the concentration of the dissolved substance at any point of the volume of the solution (except this layer) can therefore be always replenished by natural convection. The transport of matter in the diffusion layer and in the pores of the solid is due essentially to molecular diffusion, which is much slower than the convective motion of the medium.

The action of ultrasonic oscillations on the diffusion process in heterogeneous systems can thus become manifest in a change of the conditions under which matter is transported both within the volume of the solution and in the diffusion layer, as well as in the solid porous medium. It will always depend, obviously, on the parameters of the diffusion system and of the sound field. The propagation of ultrasound waves in the liquid is always accompanied by convective motion of the medium, by acoustic wind similar to the forced convection produced in the liquid by oozing of a solution. The established diffusion equilibrium can consequently be changed by stirring the liquid or by applying sound to it. As a result, the thickness of the boundary diffusion layer decreases, and the transport velocity of the matter through this layer (equal to $\beta_c = D_{liq}/\delta$, where D_{liq} is the diffusion coefficient in the liquid[31] increases.

The effect of stationarily-produced currents around a membrane in the absence of sound was mentioned many times in the literature and was compared with the effect of acoustic oscillations. Flow around a membrane has resulted under certain conditions in the same value of the diffusion rate obtained in ultrasonic field[18]. Under other conditions it resulted in rates on the order of 50–85% of this value[13-16,22,25]. Even an increase in the intensity of stirring the solution, to values at which no further acceleration of the diffusion process can be observed, will not make it possible to attain the same acceleration as obtained by ultrasound in the absence of stirring[30]. In addition, elimination of the sound wind by introducing a film impermeable to sound near the interface changes very little the effect of the acoustic oscillations on the process[46]. These facts obviously indicate that the microscopic flows of the sound fields play a negligible role in the acceleration of the diffusion by ultrasound.

One might think that the radiation pressure of the sound wave, which is closely related to the acoustic wind, has likewise no effect on the process of diffusion in the ultrasound field. In[29] (in a study of the diffusion of sodium oxalate through a membrane) and in[22] (in the study of the diffusion of SCN^- ions in frog muscles) it is indicated that radiation pressure accounts for 15% of the total effect of acceleration of the process. However, the effect of radiation pressure on the diffusion of oxalate and SCN^- ions was determined by the authors of[22] and[29] by reversing the diffusion direction relative to the direction of ultrasound propagation. It was assumed here that a change takes place in the direction of the action of the radiation. Such a conclusion, however, cannot be drawn by starting from the experiments of Hertz and Mende[41], since the radiation pressure on the inter-

face between two liquids is directed into the medium in which the speed of sound is higher, and does not depend on the liquid from which the ultrasonic wave propagates through the interface. One must therefore assume that the 15–16% increase in the amount of matter diffusing in an ultrasonic field is due to sound wind [46], whereas radiation pressure has no influence whatever on the diffusion transfer of matter.

Propagation of ultrasound waves in a real medium is accompanied by a loss of energy, which is transformed into heat and increases the temperature of the system and can accelerate the heterogeneous and diffusion processes. In ordinary aqueous solutions, the absorption of sound is small and incapable of changing greatly the rate of the free diffusion process in the liquid, which depends on the temperature like $\sqrt{T}$. In the presence of a membrane, it is necessary to take into account the heating of the solid in the ultrasound field. The permeability of porous bodies is more sensitive to changes of the temperature, since it depends on the latter exponentially. However, owing to the very small thicknesses of the organic partitions customarily used, local heating of the membrane as a result of absorption of ultrasound is in practice very small and does not exceed 1–2°C [19,16]. In many papers [22,24,25,18] it is also noted that heating of the membrane has little effect on the acceleration of the diffusion process in an ultrasonic field. To the contrary, diffusion in a semi-infinite medium was accelerated by acoustic oscillations of high frequency (2 MHz) and intensity (0.3 W/cm^2) as a result of local heating of a gelatin sample by 25% [46], although the temperature of the sample did not increase by more than 2°C. This fact indicates that gelatin-like media have a very high sensitivity to small changes in the temperature, which lead to a noticeable increase in the diffusion permeability of the gel.

Valuable information concerning the role of the individual components of the sound field could be obtained from the form of the true dependence of the acceleration of the process on the intensity of the acoustic oscillations. However, the behavior of such a dependence is masked by the character of the evolution of the diffusion process in any particular heterogeneous medium. A change in the relative increment of the concentration of the diffusing substance* $\Delta C/C_s$ with increasing intensity I in an ultrasonic field of frequency 830 kHz [25], during the diffusion of sodium oxalate for t = 15 min through a thin cellophane membrane, is shown in Fig. 1 (curve 1). Note the characteristic saturation of a solution of copper sulfate in a semi-infinite medium (25% of gelatin gel),

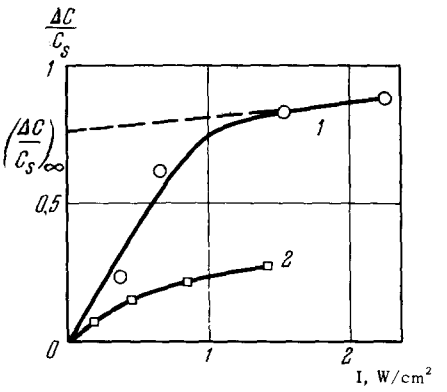

FIG. 1.

characterized by curve 2 of Fig. 1, which is plotted on the basis of [45,50] for a time t = 4 min and for a distance S = 0.03 cm from the phase separation boundary. We see that in this case the curve exhibits no saturation and expresses the dependence of $\Delta C/C_S$ on I. The change in the relative concentration C/C_e of potassium ions in a surrounding solution, after 10 min of diffusion through a human erythrocyte membrane 200 Å thick is shown in Fig. 2 (curve 1) as a function of the intensity I of the ultrasound (frequency 1 MHz). We observe here an exponential dependence of the increment of the potassium ions in the solution on the sound intensity. The relative ultrasonic effect $\Delta D/D_m$ of the increase of the diffusion coefficient rises linearly with increasing sound intensity (Fig. 3) in the case of diffusion of copper sulfate through a thick ceramic partition (plotted on the basis of the data of [52]; the given in-

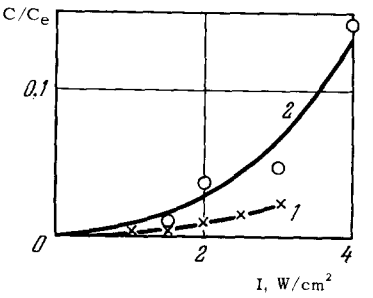

FIG. 2.

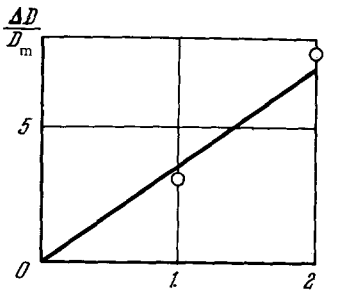

FIG. 3.

*The quantity $\Delta C/C_s$ is called the relative ultrasonic effect, where $\Delta C = C_{ac} - C_s$, C_{ac} – concentration of substance diffused in the ultrasonic field, and C_s is the same in the absence of sound.

tensities I are for the continuous regime). The differences in the action of the ultrasound on the diffusion process, occurring when its intensity changes, are thus determined by the form of the heterogeneous diffusion system and do not explain the role of the basic parameters of the sound field in the acceleration of the diffusion transfer of matter by the acoustic oscillations.

Owing to the existence of phase boundaries in the heterogeneous diffusion system (unlike in the free liquid), it is necessary to discuss the primary ultrasonic-field factors that can influence the diffusion process. These may be the following: 1) relative normal and tangential vibrational displacement, velocity, and acceleration of the liquid particles (relative to the phase separation boundary), 2) alternating sound pressure and its gradient, 3) cavitation. On the basis of qualitative [20,30] and quantitative experiments [46], the acceleration of the diffusion process in solid media, in which the pore dimensions are too small to permit vibrational motion of the liquid inside the pores, does not depend on the frequency in the wide range from hundreds of Hz to 9 MHz. Consequently, for such diffusion systems, we can discard all the frequency-dependent factors such as displacement, acceleration, alternating sound pressure gradient, and cavitation. The fact that the diffusion is not affected by the latter parameter is confirmed, furthermore, by the fact that diffusion transfer of matter is accelerated by ultrasound of different frequency under pulsed conditions [11,19,30], when the occurrence and development of cavitation is impossible. Figure 4 shows the dependence [19] of the amount P_{NaCl} of table salt diffusing from a 5% solution through a cellophane membrane in an ultrasonic field (frequency 1 MHz) on the duration of the sound pulse τ_p. The diffusion time was t = 5 min at a sound intensity I = 0.2 W/cm^2. The quantity τ_p/T_r in the figure (where T_r denotes the pulse repetition frequency) is the fraction of the radiated power in the pulsed mode relative to the power in the continuous mode, and the product $\tau_p I/T_r$ will thus characterize the time-averaged sound intensity in the pulsed mode. Therefore the knee on the curve of Fig. 4 is observed at an average intensity 0.03 W/cm^2 in the

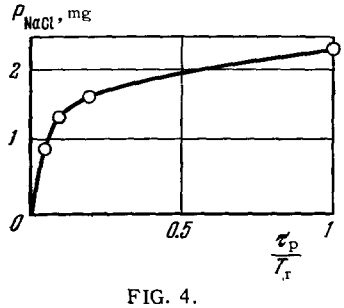

FIG. 4.

medium, i.e., in the absence of cavitation, whereas the knee on Fig. 1 (curve 1) is observed at 0.7 W/cm^2 [26,27]. This indicates only that the diffusion processes are kinetically similar in both cases. Consequently, cavitation in a liquid medium and on the interface, under the conditions of the experiments described in the literature, can not cause the acceleration of the diffusion by ultrasound [18].

As regards the role of the alternating sound pressure in the acceleration of diffusion in microporous organic media whose compressibilities do not differ from the compressibility of the liquids, its magnitude, just as in the case of diffusion in homogeneous systems, is insufficient to change the coefficient of the molecular diffusion, as was indicated earlier. Finally, the normal component of the oscillation velocity of the liquid particles relative to the boundary surface of the microporous medium is zero, and the tangential component is generally speaking different from zero, and therefore can be responsible for the acceleration of the diffusion process in the ultrasonic field, as will be shown below, although the localization of the material-transfer acceleration takes place in the antinode of the alternating pressure of the standing sound wave [46].

When the diffusion is accelerated in large-pore media, vibrational motion of the liquid can set in relative to the walls of the pores. In addition, if porous ceramic materials are used, it is necessary to take into account the significant difference between the compressibilities of the solid and liquid phases. Therefore we cannot discard in this case the normal components of the relative vibrational displacement, velocity, and acceleration, as we did above for the microporous media. However, owing to the lack of any experimental data showing how the sound-field factors under consideration affect the diffusion process in large-pore heterogeneous systems, we cannot give preference to any of them. Nonetheless, as will be shown later, one must classify as such the alternating sound pressure and its gradient, which lead, owing to the small compressibility of the solid and to the appreciable diameter of the channels, to the occurrence of vibrational motion of the liquid inside the pores relative to the pore walls, i.e., to a periodic tangential displacement of the liquid and solid. In the case when the gradient of the alternating sound pressure takes part in the creation of the relative displacements, we can expect the diffusion process to be accelerated in the large-pore medium with increasing frequency of the ultrasonic oscillations. The major role played by the relative tangential motion of the liquid for microporous and large-pore media indicates that the boundary layer of the liquid is particularly significant in the acceleration of the diffusion process in heterogeneous systems under the influence of ultrasound.

b) Acoustic Microcurrents

The propagation of a sound wave in an infinite free liquid medium is always accompanied by the action of volume viscosity forces. These forces, called volume sources, lead to the occurrence of potential motion of the medium in the form of sound wind. When the liquid particle oscillations have a non-zero tangential velocity component relative to a solid placed in the liquid, an important role is played on the liquid-solid boundary by the shear viscosity forces, called surface sources [53]. Within distances on the order of several viscous wavelengths from the phase separation boundary, the surface sources are capable of producing circulatory motion of the medium, constituting acoustic microcurrents [54].

From the solution of the Navier-Stokes hydrodynamic equations, expressions were derived for the velocity of the microcurrents in the case of a flat surface [54] or a surface with small curvature [47], a cylinder [37, 38, 55, 56], and a sphere [57]. Regardless of the form of the solid surface, the velocity of the microcurrents was in all cases proportional to the square of the tangential vibrational velocity of the liquid particles, but a difference was established between the configurations of the currents and the character of the variation of the current velocity on approaching the solid surface. A theoretical description was also presented of the microcurrents produced near a membrane which is locally excited by ultrasonic oscillations normal to its surface [58]. Tangential periodic displacements of the liquid relative to the diaphragm exist in this case as a result of flexural oscillations of the diaphragm.

The occurrence of acoustic microcurrents on the phase separation boundaries in an ultrasonic field lead to an essential decrease in the thickness of the boundary hydrodynamic layer [86] and consequently the thickness of the diffusion layer. Questions involved in the use of the theory of acoustic microcurrents to explain the acceleration of chemical heterogeneous reactions were discussed on this basis [59] and satisfactory agreement was obtained between theory and experiment [58, 87].

The results of the theory of acoustic microcurrents are applicable only when the oscillation amplitude A of the liquid particles in the sound wave is much smaller than the dimension of the solid obstacle, and also smaller than the length of the viscous wave or the thickness of the acoustic boundary layer $\delta_0 = (2\nu/\omega)^{1/2}$, where ν is the kinematic viscosity and ω is the cyclic frequency. Failure to satisfy the condition $A \ll (2\nu/\omega)^{1/2}$ or $Re = U_0 A/\nu \ll 1$ (where U_0 is the vibrational velocity of the particles and Re is the Reynolds number) leads to an appreciable increase in the velocity of the microcurrents U_{ac} [60] and to a change in their form and direction [61, 62]. However, the shear viscosity is in all cases the main cause of the generation of acoustic microcirculations in the presence of periodic motions of the medium. Consequently, if the diffusion process is accelerated in real systems under the influence of ultrasonic oscillations as a result of acoustic microcurrents, then this diffusion is a phenomenon of second order of smallness, since it is the result of the fact that the medium in which the sound wave propagates is neither ideal nor homogeneous.

c) Diffusion through Porous Partitions

Unlike diffusion in a free liquid, the process of diffusion transport of matter through membranes proceeds in the presence of a solid medium, which, on the one hand produces boundary layers, in which the liquid has low mobility and larger kinematic viscosity than in free volume, and on the other hand it eliminates the convective transport of matter in the diffusion direction. In studying the diffusion in an acoustic field, use was made of different natural [18-20, 22-23], cellular [21, 24], and artificial thin membranes [13-16, 19, 25] having different diffusion permeabilities, and also thick porous partitions [11].

Experiments on diffusion penetration of different salts through membranes under laboratory conditions are carried out as a rule by using a porous diaphragm to separate two specified volumes of liquids, in one of which the liquid is free of the diffusing substance. Since the process of particle transfer proceeds relatively slowly and, furthermore, macroscopic flows always exist on both sides of the partition, owing to natural convection [32], it can be assumed that in the case of a short diffusion time the concentration of the electrolyte ions on one side of the membrane is constant in the entire volume (except the boundary layer), and that on the other side the concentration of the diffusing matter is practically close to zero. It can therefore be assumed that a source and a sink of matter with approximately constant concentration gradient exist on the two sides of the partition, making it possible to describe the process of diffusion through a membrane under the indicated conditions in terms of diffusion resistance [31].

The coefficient of permeability of the diaphragm was introduced as the ratio $\theta = D_m/d$, where d is the thickness of the membrane and D_m the coefficient of diffusion of the ions inside the membrane. The reciprocal of θ is the diffusion resistance of the partition. In similar fashion one defines the diffusion resistance of the boundary layer. Then, in analogy with [31], the total diffusion resistance of the membrane is

$$\frac{1}{\beta} = \frac{1}{\theta} - \frac{2\delta}{D_{liq}}, \qquad (2)$$

where β is the constant of the rate of diffusion through the partition, D_{liq} is the coefficient of diffusion of the ions in the liquid, and δ is the thickness of the boundary diffusion layer [32].

Table I.

No.	Diffusing substance	Temperature, °C	Type of membrane	Membrane thickness, μ	Average pore radius, mμ	θ, cm/sec	Ultrasound: Frequency, kHz	Ultrasound: Intensity, W/cm²	$\frac{\Delta C}{C_s}$
1	$Na_2C_2O_4$	18	Cellophane	26	2	$3.5\cdot10^{-4}$	830	2.3	2.63
2	$Na_2C_2O_3$	20	Gelatin 5%	150	10	$0.95\cdot10^{-4}$	1200	6	3.3
3	$Na_2C_2O_4$	18	Frog skin	30	—	$0.6\cdot10^{-4}$	830	2.3	0.77
4	$Na_2C_2O_4$	18	Parchment	60	25	$0.45\cdot10^{-4}$	830	2.3	0.68
5	$CuSO_4$	15	Steer's bladder	1000	20	$0.6\cdot10^{-5}$	10,5	0.5	19
6	$CuSO_4$	20	Porous ceramic	5000	1000	$0.3\cdot10^{-5}$	13—22	1.0	31
7	KCl	25	Porous ceramic	1200	300	$1.2\cdot10^{-5}$	350	1.0	—

The quantity D_{liq} characterizes the molecular diffusion of matter in the liquid and, as shown above, cannot change under the influence of acoustic oscillations. The diffusion coefficient in the membrane D_m is a linear function of the total porosity W of the membrane [38], the variation of which is possible only in connection with an increase in the swelling of the membrane material in the field of the ultrasonic waves. Such an assumption was advanced in [19]. However, it was not experimentally confirmed in experiments with gelatin gel [50]. In addition, a number of investigators have noted that the permeability of the employed membranes remains unchanged after irradiation with ultrasound [16,20,22,24] or else changes insignificantly as a result of the heating in the ultrasonic field [18]. After prolonged and intense sounding, the permeability of the membranes may become irreversibly changed [16,18] as a result of the destruction of the organic base of the partition.

Table I lists the calculated and published data on the membranes used in [11,13-15,22,23]. We see that application of high-frequency acoustic oscillations (Nos. 1, 2, 3, and 4) to the diffusion process leads to a synchronous variation of the ultrasonic relative effect of increase of the concentration $\Delta C/C_S$ of the diffusing substances during one hour and of the permeability of the membrane θ when different types of partitions are used.

The comparison leads, on the one hand, to the conclusion that the permeability of the membrane θ is not responsible for the change in the diffusion through thin partitions in an ultrasonic field, and indicates on the other hand that the thickness of the diffusion layer δ decreases under the influence of the acoustic oscillations. Indeed, let us assume that the sound causes an increase in the permeability θ, which becomes equal to θ_{ac} at a fixed thickness δ of the diffusion layer or, conversely, it causes a decrease in the thickness δ of the diffusion layer to a value Δ_{ac}, the permeability θ remaining constant) The quantity Δ_{ac} is the total thickness of the diffusion layer under the joint action of the sound and the natural convection and is equal to

$$\Delta_{ac} = \frac{\delta\delta_{ac}}{\delta_{ac}+\delta}, \qquad (2a)$$

where δ_{ac} is the thickness of the boundary diffusion layer when ultrasonic oscillations are applied. We then get from (2) and (2a) after simple transformations

$$\left(\frac{\Delta C}{C_s}\right)_1 \approx \frac{\Delta\beta}{\beta} = \frac{\frac{\theta_{ac}}{\theta}-1}{\frac{2\delta\theta_{ac}}{D_{liq}}+1}, \qquad (3)$$

$$\left(\frac{\Delta C}{C_s}\right)_2 \approx \frac{\Delta\beta}{\beta} = \frac{\frac{\delta}{\Delta_{ac}}-1}{\frac{D_{liq}}{2\theta\Delta_{ac}}+1}, \qquad (4)$$

where $\Delta\beta = \beta - \beta_1$, β_1 is the diffusion-rate constant in the acoustic field. It can be noted that with decreasing permeability θ, the value of the relative ultrasonic effect $\Delta C/C_S$ increases in (3) and decreases in (4). The data of Table I for thin membranes (Nos. 1, 2, 3, 4) agree only with (4). In addition, there are experiments which confirm directly that ultrasound acts on the boundary diffusion layer. Indeed, in osmotic penetration of water through a dialysis (semipermeable) thin membrane into a saturated $CuSO_4$ solution, when there is no boundary diffusion layer, no noticeable acceleration of the process is produced by acoustic oscillations (570 kHz, 2.2 W/cm²) [17]. Consequently, the action of ultrasonic field on the diffusion of the electrolytes through thin membranes is connected with a decrease in the thickness of the diffusion layer on the liquid-membrane separation boundary. With increasing sound intensity, the sound reduces the thickness of the diffusion layer to such a degree that the inequality $\delta_{ac} \ll \delta$ sets in, hence $\Delta_{ac} \approx \delta_{ac}$. We then get from (4) that $(\Delta C/C_S)_\infty \approx 2\theta\delta/D_{liq}$. From this we can estimate the thickness of the diffusion layer δ in the absence of acoustic oscillations. From Fig. 1 we get $(\Delta C/C_S)_\infty \approx 0.8$ (dashed), giving $\theta = 3.5 \times 10^{-4}$ cm/sec (see Table I) and $\delta \approx 0.025$ cm when $D_{liq} = 10^{-5}$ cm²/sec. The thickness of the boundary diffusion layer under conditions of natural convection is $\delta \approx 0.03$ cm [32], i.e., in good agreement with the value obtained by us.

The conclusion that ultrasound acts on the diffusion layer was drawn in [18,21,13-15,23-25] on the basis of direct or indirect experimental data. However, the situation changes when thick membranes are used (see Table I, Nos. 5 and 6). Compared with thin membranes, the permeability θ of thick partitions is very small, i.e., the diffusion resistance of the membrane exceeds by one order of magnitude the resistance of the diffusion boundary layer. Since the dimensions of the ions of copper sulfite and of sodium sulfite and oxalate do not exceed 3—4 Å, the substitution of one set of particles by another cannot lead to a strong change in the permeability θ. In addition, there is no essential difference in the overall porosity ($W \approx 45\%$) and in the diameter of the pores of thick partitions as compared with thin ones, for example a cellophane membrane ($W \approx 55\%$). Therefore the small value of θ for thick partitions is due to the thick membrane, the thickness of which is quite appreciable, as can be seen from Table I. Consequently, a decrease in the thickness of the boundary diffusion layer in an acoustic field cannot lead to a noticeable change in the diffusion through thick membranes.

Nontheless, ultrasonic oscillations produce in this case a sharp increase in the relative ultrasonic effect $\Delta C/C_S$, compared with the results obtained with thin partitions. With decreasing permeability coefficient θ of the thick membranes (Table I, Nos. 5 and 6), the value of $\Delta C/C_S$ increases, from which follows agreement with (3) and with (4) as in the case of thin membranes. Consequently, during the process of diffusion through the thick partitions, when the mass-transport rate is limited by the permeability of the membrane, the accelerated mass transport is due to the change in the permeability coefficient θ of the diaphragm in the acoustic field.

The latter may be connected with the presence of larger pores in thick membranes. It is seen from the table, that replacement of one diffusing substance by another and a change-over to low-frequency ultrasonic oscillations does not change the value of $\Delta C/C_S$ noticeably (Table I, Nos. 4 and 5). For membranes with an average pore radius 2 mμ, a transition from a thin diaphragm (Table I, No. 1) to a thick one (cellophane of thickness 1000 μ) eliminates completely the effect due to the action of ultrasonic oscillations of frequency 175–800 kHz [16]. The use of thick membranes with larger pore dimensions greatly increases the ultrasonic effect $\Delta C/C_S$ (Table I, Nos. 5 and 6), although the permeabilities of these diaphragms do not differ essentially from the permeability of other membranes, given in Table I.

The observed acceleration of the diffusion through a ceramic porous partition is explained in [9,11] from the point of view of the destruction of the quasi-crystalline inhomogeneities of the liquid medium by the acoustic oscillations, and the resonant interaction between the sound and the pores of the ceramics. This opinion is based on the consideration that acceleration occurs only in the case of pulsed (broadband) irradiation of the diffusion system; continuous sounding does not lead to a noticeable action on the process in question. The authors chose a continuous sound intensity (10^{-3} W/cm^2) much lower than the threshold of the intensity at which the effect of acoustic oscillations on heterogeneous processes can be observed. Therefore the absence of acceleration of the diffusion through the porous ceramic under continuous sounding cannot be regarded as experimentally established.

The author of the present review believes that a more realistic cause of the large ultrasonic effect $\Delta C/C_S$ in acceleration of diffusion through thick large-pore membranes is the increase in the diffusion permeability of the diaphragm as a result of the occurrence of acoustic microcurrents in its pores. The formation of such currents is possible in principle in the presence of a periodic displacement of the liquid particles filling the cavities of the diaphragm relative to the surface of their walls, especially at the edges and at the bends of the pores themselves.

The relative periodic oscillations of the liquid inside the porous ceramic actually take place, since it was observed in [33,34] that an alternating electrokinetic potential is produced in 0.001 N solution of KCl in an ultrasonic field when a porous ceramic partition (Table I, No. 7) filled with the same liquid is introduced between the electrodes. A similar phenomenon was described by Nikitin [35], who observed an electrokinetic potential on some organic membranes, and pointed out its acoustic-electrochemical nature.

Calculation of the absolute value of the alternating electrokinetic potential from the stationary Helmholtz-Smoluchowski flow potential for porous bodies [36]*, using a value $p_0 = 1.77$ atm for the amplitude of the ultrasonic-wave pressure, leads to a potential which exceeds by 2.5 times the experimentally observed potential [33]. The larger value of the calculated potential is due to the fact that the pressure difference Δp applied to the opposite ends of the capillaries of the porous membrane is not equal to the maximum value of the acoustic pressure p_0. It is necessary to take into account the acoustic properties of the membranes (Table II), for example their reflecting ability,

*The Helmholtz-Smoluchowski potential has, under the condition $r \gg \delta'$, the form

$$E = \frac{\zeta \varepsilon \Delta p}{84.77 \cdot 10^7 \varepsilon \varkappa},$$

where ξ is the potential of the electric double layer, ϵ is the dielectric constant, Δp is the pressure difference on opposite sides of the capillary, κ is the specific conductivity of the liquid, r is the radius of the pores, and δ' is the thickness of the electric double layer.

and in addition, the fact that the diaphragm thickness d is comparable with the wavelength λ in its material, so that the pressure drop on the partition will be.

$$\Delta p = 2p_0 D_p \sin\frac{\pi d}{\lambda}, \quad (5)$$

where D_p is the coefficient of sound transmission through the porous diaphragm.

Table II lists the values of D_p for the membranes under consideration, and also the resonance frequencies f_p at which the diaphragms are perfectly transparent to the sound waves, i.e., when the transmission coefficient becomes equal to unity ($D_p = 1$).

For the porous ceramic (Tables I and II, No. 7) used in [33,34] we have $D_p = 0.5$, d = 0.12 cm, and $\lambda = 0.735$ cm. On the basis of (5) we get $\Delta p = p_0/2.4$, i.e., the actual pressure differential on the two sides of the membrane is approximately 2.5 times smaller than the amplitude of the sound pressure, thus eliminating the disparity indicated above. Consequently, we can assume that the Helmholtz-Smoluchowski equation describes well the acoustic-electrokinetic potential produced in a porous diaphragm. Therefore, to determine the vibrational velocity U_v of the liquid particles on the axes of the capillaries of a porous diaphragm, we can use the Poiseuille law [36]

$$U_v = \frac{\Delta p r^2}{4\pi d v}, \quad (6)$$

under the condition that the radius of the capillary r is smaller than or comparable with the length of the viscous wave λ' [39], i.e., $r \leq \lambda'/\pi$, where $\lambda' = \sqrt{4\pi\nu/f}$, and f is the frequency of the external action. The limiting frequencies $f = f_{p'}$ below which Eq. (6) is applicable, are listed in Table II for all the types of membrane indicated above.

For the porous ceramic No. 7, at a sound intensity of 1 W/cm^2 ($p_0 = 1.77$ atm) we have on the basis of (6) $U_v = 4.36 \times 10^{-2}$ cm/sec. Since in real membranes the capillaries are arbitrarily bent, and their edges have a noticeable radius of curvature, it can be assumed that inside the pores we get periodic flow over the cylindrical or spherical surface, the amplitude A of the oscillations of the current, being much smaller than the radius of curvature r_0 of the inhomogeneities of the bends inside the capillary surfaces. Therefore, the velocity of the conductive microcurrents inside the membrane and at its edges can be expressed by the following equation [37,38]

$$v_{ac} = \frac{3}{4\pi}\frac{U_v^2}{f r_0}. \quad (7)$$

Assuming the radius of curvature r_0 to be comparable in order of magnitude with the radius r of the capillary of the porous membrane, we obtain on the basis of Table I $v_{ac} = 5 \times 10^{-5}$ cm/sec for diaphragm No. 7. Since the permeability coefficient θ characterizes the rate of transfer of the dissolved substance through the membrane, it is obvious that $\theta_{ac} \approx v_{ac}$ and for the same ceramic No. 7 in an ultrasonic field, the permeability will be $\theta_{ac} = 5 \times 10^{-5}$ cm/sec. In the absence of external action, the permeability coefficient of the membrane, as seen from Table I, is $\theta = 1.2 \times 10^{-5}$ cm/sec, i.e., approximately one-fifth as large. Thus, we can assume that the acoustic oscillations actually can increase the permeability of thick large-pore membranes by accelerating the transport of diffusing substance through generation of convective microcurrents in their pores.

One can note from (6) and (7) that the velocity v_{ac} of the microcurrents, and consequently, the membrane permeability θ_{ac}, depends strongly on the radius of the membrane pores (proportional to r^3) and relatively little on its thickness d. Therefore, on going over from thick membranes to thin ones, the effect of increasing the permeability of the porous partition in the ultrasonic field should decrease rapidly. Calculation of the velocity v_{ac} of the microcurrents in the pores of the least permeable parchment membrane (Table I, No. 4) yields $\theta_{ac} = v_{ac} = 4 \times 10^{-6}$ cm/sec, i.e., one-tenth as large as the permeability θ in the absence of acoustic oscillations.

The change of the diffusion permeability of diaphragms in an acoustic field should probably occur at the pressure node of the standing sound wave, i.e., in the region of the largest value of the sound-pressure gradient dp/dx. This is indeed the case [34] for the alternating electrokinetic potential of the membrane, whereas no such information is available in the literature for the permeability of porous partitions. Nonetheless, this circumstance cannot cause us to assume that the permeability of the large-pore membranes is increased not by the gradient of the sound pressure but by the vibrational displacement of the particles in the sound field, whose amplitude maxima coincide in the space where the wave propagates. Passage of the sound wave cannot cause vibrational displacements of the liquid particles relative to the walls of the membrane pores in capillaries with radii $r \leq \lambda'/\pi$, as indicated above. It can be concluded from Table II that the vibrational displacement of the liquid cannot occur in the pores of all the diaphragms listed there. The relative displacement of the media can occur only as a result of the forcing of the liquid through the capillaries of the membranes by the pressure difference Δp applied to their ends on the two sides of the diaphragm.

It follows from (5), (6), and (7) that when the thickness of the porous diaphragm is commensurate with the wavelength, the gradient $\Delta p/d$ of the alternating sound pressure over the thickness, varies periodically with the frequency f of the external action, like $\sin(\pi d/\lambda) = \sin(\pi f d/C_a)$. Therefore the velocity v_{ac} of the acoustic microcurrents inside the pores, and consequently also the permeability θ_{ac} of large-pore membranes, should vary with fre-

Table II.

No.	Type of membrane	Density, g/cm³	Young's modulus, dyn/cm²	D_p	f_r, MHz	f_r, MHz
1	Cellophane	1.07	$4 \cdot 10^{10}$	1	39	400
2	Gelatin 5%	1.0	$2 \cdot 10^{10}$	1	4.7	200
3	Frog skin	~1.1	10^{10}	—	32	—
4	Parchment	1.15	$3 \cdot 10^{10}$	1	13	50
5	Steer's bladder	1.2	$3 \cdot 10^{10}$	1	0.8	68
6	Porous ceramic	1.3	$7 \cdot 10^{10}$	0.95	0.25	0.3
7	Porous ceramic	1.3	$8.6 \cdot 10^{10}$	0.5	1	0.6

quency like $(1/f)\sin^2(\pi fd/C_a)$. In the low-frequency ultrasound band, when $d \ll \lambda$, we have $\sin^2(\pi fd/C_a) \approx (\pi fd/C_a)^2$, and the permeability θ increases linearly with the frequency.

We must also discuss one more circumstance that becomes important when the diffusion permeability of thick large-pore ceramic membranes changes in an acoustic field. The compressibility $Q = 1/\rho C_a^2$ (C_a speed of sound in the medium) of water, organic substances, and polymers is of the same order of magnitude, whereas solids, particularly a ceramic membrane, have a compressibilities that are smaller by an approximate factor of 10. Therefore the relative vibrational displacement of the liquid inside the pore, under the influence of the ultrasound oscillations, will consist of periodic forcing of the liquid through the pores of the ceramic in accordance with the Poiseuille law, and a relative periodic motion which results from the difference in the coefficients of the volume expansion of the liquid and of the membrane core. In the latter case the minimum of the displacement should lie in the midplane, and the maxima should be on both sides of the membrane. Consequently, we can expect the relative vibrational velocity of the liquid particles to increase over the thickness of the ceramic partition, from the center to its peripheral surfaces, in analogy with the behavior of the alternating electrokinetic potential of flow in an ultrasonic field, observed in [34].

In connection with everything stated above, we can expect in an ultrasonic field an appreciable acceleration of diffusion transport of moisture inside air-porous bodies during the course of drying of material, if the moisture is in the capillaries in the form of vapor. The large difference in the compressibility of moisture-saturated air and the solid leads to the occurrence of sufficiently large vibrational motion of the air relative to the walls of the pores. The latter causes the large increase in the transport of moisture inside the capillary-porous body under the influence of the acoustic oscillations. The radius of the pores at which such an accelerating action of the ultrasound is possible, can be calculated from formulas (6) and (7) for concrete materials and experimental conditions.

d) Diffusion in Bounded Bodies in the Form of Plates and Cylinders

In the study of diffusion through membranes, one usually disregards the time required to fill the membrane with the diffusing substance, since it is small compared with the duration of the entire experiment or else, the membrane is first saturated with the solution of the electrolyte under the experimental conditions. If a body free of any ions and having finite dimensions is dropped in an electrolyte solution having a constant concentration C_0, then the diffusing substance gradually penetrates into the body. The presence of a source of matter in the form of a time-constant initial concentration C_0 is not offset in this case by a sink, which is missing from such a diffusion system, so that diffusion in a bounded body, unlike a membrane, cannot be regarded in terms of diffusion resistances. Therefore, for bodies in the shape of plates or cylinders one determines the total amount of matter $\overline{C}$ entering into the plate during the time t by solving the diffusion equation [51]. Assuming that the rate of transport of the matter depends only on the coefficient of internal diffusion D_m [29], we get

$$\frac{\overline{C}}{C_0} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} e^{-\frac{D_m(2n+1)^2\pi^2 t}{4h}}, \qquad (8)$$

where h is the thickness of the plate and n = 0, 1, 2, ...

At relative large diffusion time t, it is sufficient to take into account the first term of the expansion in (8) with n = 0.

The dependence of $\log(\overline{C}/C_0 - 1)$ on the time t (Fig. 5, curve 1) was obtained in [29] for the diffusion of a solution of NaSCN with concentration C = 0.1% (Temperature 20°C) in the sartorial muscle of a frog, which has a plate- like form. A similar curve was obtained for the gastrocnemius muscle which is of cylindrical form. It follows from (8) that the slope of the linear portion of curve 1 of Fig. 5 determines the coefficient of internal diffusion, which for both muscles is $D_m = 0.6 \times 10^{-5}$ cm²/sec, i.e., approximately smaller by 1.5 times than the coefficient of

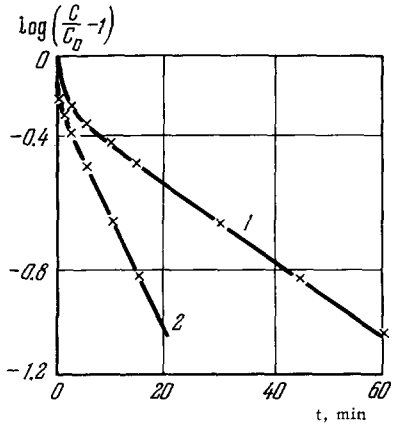

FIG. 5.

diffusion of the SCN^- ions in the free liquids [29]. The action of ultrasonic oscillations of frequency 800 kHz (2.5 W/cm^2) (Fig. 5, curve 2) caused the internal diffusion coefficient to increase (change in the slope of the linear section) by approximately four times ($D_m^{ac} \approx 2.4 \times 10^{-5}$ cm^2/sec [29]), i.e., it makes it larger than the coefficient of diffusion in a free stagnant liquid. This fact indicates that the change in the diffusion coefficient D_m in an ultrasonic field is connected with the occurrence of acoustic microcurrents inside the muscle.

The frog muscle consists of individual fibers, interconnected by a friable connective tissue. The average radius of the muscle fiber is approximately 10—15μ [40], so that it can be assumed that the radius of the pores of the friable connective tissue is approximately 0.5—1 μ. Free diffusion can occur between such a porous internal region of the muscle and the surrounding medium. Consequently, in analogy with thick large-pore membranes, the increase in the internal-diffusion coefficient D_m under the influence of the ultrasonic oscillations can occur in this case as a result of microcurrents produced inside the pores of the connective tissue of the muscle. From (5), (6), and (7) we get for the diffusion coefficient inside the muscle under the influence of sound

$$D_m^{ac} = v_m \frac{h}{2} = \frac{3p_0^2 D_p^2 r_0^3}{16\pi^3 \nu^2 C_a} \frac{\sin\left(\frac{\pi h}{\lambda}\right)}{\frac{\pi h}{\lambda}}. \quad (9)$$

Putting $r_0 = 0.5$ μ, $h = 0.05$ cm we get for $D_p = 1$, $C_a = 1.55 \times 10^{-5}$ cm/sec and an intensity 2.5 W/cm^2 from Eq. (9), $D_m^{ac} \approx 2.8 \times 10^{-4}$ cm^2/sec, which in our case is an acceptable value for the diffusion coefficient in the muscle in the presence of a sound field, since D_m^{ac} depends on the third power of the radius r_0 of the capillaries, i.e., on their volume. The absence of published data on the dimensions of pores and on the general porosity of frogs' muscles does not make it possible to carry out more accurate calculations on the basis of formula (9).

Actually the assumption that the rate of the process depends on the coefficient of internal diffusion D_m in the muscle, advanced in [29], is valid only after the lapse of a certain time following the start of the diffusion, for at the first instant the course of the process is determined by the conditions for the transport of matter in the liquid medium (slope of the initial section of the curve 1 in Fig. 5). Under the influence of ultrasound, these conditions change (slope of the initial section of curve 2 of Fig. 5) as the result of the increase in the concentration gradient on the phase separation boundary, changing by the same token the subsequent evolution of the transport of matter in the ultrasonic field.

As seen above, the concentration gradient is increased in the ultrasonic field because of the decreased thickness of the diffusion boundary layer. Therefore the solution in the form (8) is not fully applicable to the results of [29], and it is consequently necessary to describe the diffusion process under the influence of ultrasound by solving the diffusion equation for a medium consisting of a bounded solid surrounded by a thin layer of a stagnant liquid. Unfortunately, there are no published reports of investigations of the effect of ultrasound on diffusion in bodies of limited dimensions with microporous structure, for which it can be assumed that the diffusion coefficient D_m in the ultrasonic field remains constant.

e) Diffusion in Semi-infinite Medium

If one of the interfaces of a membrane is allowed to go to infinity, we have a semi-infinite diffusion system. To determine the diffusion in such a system one determines the amount of matter penetrating into the solid phase. Diffusion in an extensive medium, just as in a bounded body, is governed not by two interfaces, but only one, unlike the transport of matter through a membrane. In analogy with diffusion in a bounded body, the diffusion in a semi-infinite medium cannot be described with the aid of diffusion resistances. It is therefore necessary to use a solution of the general problem of nonstationary diffusion in a semi-infinite medium, as a function of the experimental conditions, resorting to various simplifications.

If the solid medium in which diffusion takes place is not a large-pore formation, then, just as in the case of membranes, it can be assumed that the internal diffusion coefficient D_m does not change in the acoustic field, and that the effect of the action depends only on the change in the diffusion conditions in the liquid. Therefore, as the result of the action of ultrasonic oscillations of frequency 20 kHz on the diffusion of a $CuSO_4$ in 0.65% agar-agar gel [23,24] and 5% gelatin gel [30], the thickness of the boundary diffusion layer decreases and the rate of the diffusion process in such microporous medium increases by 2—3 times. This follows from the fact that when the

diffusion system consisting of the electrolyte solution and the gel is replaced by a system consisting of an electrolyte-impregnated gel and a gel, the effect of acceleration of diffusion vanishes [23-24,30,50]. Consequently, on the one hand, ultrasound does not change the internal coefficient of diffusion of the extended microporous medium, and, on the other hand, just as in the case of thin membranes, it acts on the boundary diffusion layer existing at the phase separation boundary.

For a complicated medium consisting of two semi-infinite spaces separated by a layer of thickness δ, the concentration C_2 of matter diffusing from the liquid medium into the solid is given [5] by solving the diffusion equation in the form

$$C_2 = \frac{2C_0}{1+\sqrt{\frac{D_m}{D_{liq}}}} \sum_{n=0}^{\infty} \alpha^n \operatorname{erf} c \frac{(2n+1)\delta + \sqrt{\frac{D_{liq}}{D_m}} S_p}{2\sqrt{D_{liq} t}},$$

where

$$\alpha = \frac{1-\sqrt{\frac{D_{liq}}{D_m}}}{1+\sqrt{\frac{D_{liq}}{D_m}}},$$

n is an integer, S_p is the distance from the interface into the solid, erfc is 1 – erf, and erf is the error function. It is assumed here that the initial concentration C_0 is maintained constant in the entire volume of the solution during the course of the experiment as a result of natural convection of the liquid.

The effect of ultrasonic oscillations of intensity I leads to a decrease in the thickness of the boundary diffusion layer [50], which for n = 0 is equal to

$$\delta = 2\sqrt{D_1 t} \operatorname{erf} c^* \left[\frac{C_2\left(1+\sqrt{\frac{D_2}{D_1}}\right)}{2C_0}\right] - \sqrt{\frac{D_1}{D_2}} S_p, \qquad (10)$$

where erfc* is the function dependence that is inverse to erfc.

On the basis of (10) we can calculate and plot the relative change in the concentration, $\Delta C/C_S$, at a distance from the interface $S_p = 0.03$ cm for a time t = 4 min as a function of the sound intensity I (Fig. 1, curve 2) when electrolyte diffuses into a semi-infinite sample of gelatin gel. The synchronous behavior of the values of $\Delta C/C_S$ with increasing ultrasound intensity, shown in Fig. 1 (Curves 1 and 2), indicates that the change in the diffusion permeability in the sound field has the same cause for diffusion in a semi-infinite medium and for diffusion through thin microporous membranes.

3. DIFFUSION IN BIOLOGICAL MEDIA

a) Single Cells

The use of ultrasonic oscillations in biology and medicine has led to a large number of scientific papers devoted to the effect of sound on different biological objects [64]. In particular, the possibility of accelerating in an ultrasound field the penetration of solutions of different substances into single cells, live or dead tissues, muscles and organs, etc. has been discussed many times. In view of some distinguishing features and the complexity of the structure of biological systems, no clear concept has yet been developed concerning the activating action of ultrasonic radiation of low intensity, when no irreversible damage is produced in the sounded object.

A single biological cell is a certain closed microvolume which maintains exchange of matter with a surrounding medium. The content of each cell is separated from this medium by a thin ultraporous partition, which consists of a porous wall approximately 150 Å thick, providing the mechanical strength of the cell, and a biological membrane 60—80 Å thick, which regulates the exchange of matter between the protoplasm of the cell and the outer medium. The cell wall is riddled by pores having a diameter of several millimicrons, whereas the biological membrane, situated on the inside of the wall, has no pores at all, if we disregard the gap of 5—6 Å in the pale of the lipoid molecules forming the biological membrane [65]. The protoplasm of the cell consists of a colloid solution, which is formed in the vacuoles, where almost the entire liquid is in a bound state. Consequently, the rate of diffusion transport of matter in an individual cell will be determined both by the permeability of the biological membrane and by the diffusivity of the liquid inside the cell.

There exists an opinion [65] that the principal role in the selective permeability of the cell is played by the protoplasm as a system of complex coacervates, capable of accumulating large amounts of potassium ions, which are there in an adsorption-bound state. Such a protoplasm can form structured liquids or pseudogels having a structural viscosity and thixotropic properties [66,67]. Any external mechanical action can destroy the gel-like structure of the cell protoplasm, releasing, on the one hand, the potassium ions bound by the complex coacervates, and on the other, decreasing the viscosity of the medium and consequently the coefficient of diffusion in it.

The action of ultrasonic oscillations on the thixotropic liquids and gels was observed long ago [66]. Colloid liquids in a sonic field decrease their viscosity [68,70] without destruction of the polymer particles, and gels go over reversibly into sols [67], losing temporarily their structure properties. Irradiation of a gel consisting of 6—7% gelatin (photographic emulsion from which silver bromide has been removed), impregnated with 5% solution of potassium dichromate, with ultrasound of frequency 800 kHz, leads to acceleration of formation of the Liesegand rings [69]. The thixotropic action of ultrasound produces in this case, obviously, an increase in the diffusion coefficient of the electrolyte ions in the gelatin, and consequently in the rate of the periodic reaction.

For a physico-chemical periodic process, the

number of strata K depends on the diffusion coefficient D_g of the components of the reaction in the medium [71]:

$$K = K_0 D_g = K_0 D_0 e^{-\frac{Q_{br}}{kN_0 T}}, \quad (11)$$

where K_0 is a constant, D_0 the coefficient of diffusion of ions in water, Q_{br} the energy necessary to break the structural bonds of the gel lattice (activation energy), k is Boltzmann's constant, and N_0 is the number of gelatin molecules per cm^3.

The binding energy of the structural-dispersion long-range forces in the gel lattice is $Q_{disp} \approx 10^{-13}$ erg/bond [72,73]. The number of molecules in 6% gelatin gel is $N_0 = 2.14 \times 10^{15}$ per cm^3. Assuming that at least two transverse bonds are produced for one molecule, we have $N_c = 4.3 \times 10^{15}$ cm^{-3} bonds, and the average energy density necessary to break the most probable structural bonds is $Q_0 = Q_{disp} N_c = 4.3 \times 10^2$ erg/cm^3.

However, the structural bonds have a statistical character, and therefore the distribution of the molecule interaction energies obeys the normal law. Consequently, the long-range Van der Waals attraction forces will be reduced in part by the action of the external force at energies lower than Q_0. Then the energy necessary to resolve the structure of the gel can be expressed in the form

$$Q_{br} = Q_0 \left(1 - \operatorname{erf} \frac{Q_0}{Q_x}\right), \quad (12)$$

where $\operatorname{erf}(Q_0/Q_x)$ is the error integral, Q_x is the energy of the external action. For ultrasonic oscillations $Q_x = I/C_a$ and $Q_0 = I_0/C_a$, hence $I_0 = 6.5$ W/cm^3. Starting from (11) and (12), we can describe the process of formation of Liesegang rings in the case of prior irradiation of the medium with ultrasound of intensity I. The relative variation $\Delta K/K$ of the number of Liesegang rings with the intensity of preliminary man-minute sounding, shown in Fig. 6, is plotted from the data of [69]. Equations (11) and (12) describe the curve of Fig. 6 very well, the slope of the line $\varphi_0 = Q/kN_cT$, in the coordinates $\ln(\Delta K/K_0 + 1)$ and $\operatorname{erf} I_0/I$, turns out $\varphi_0 = 3.2$. An estimate of this coefficient for $T = 293°$, $k = 1.38 \times 10^{-16}$ erg/deg, and the values obtained above for N_c and Q_0 yields $\varphi_0 = 3.8$, showing that the initial premises assumed to explain the thixotropic action of acoustic oscillations are correct.

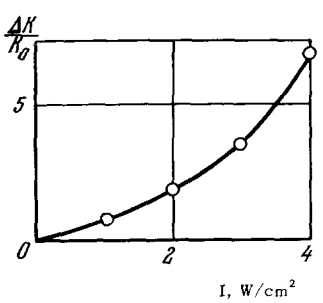

FIG. 6.

Thus, the energy of ultrasound of medium intensity is perfectly sufficient to destroy the structural state of certain colloidal systems obtained from low-concentration solutions of high-organic compounds. With increasing gelatin content, the average breaking energy Q_0 will be increased by the increase in the number of the bonds in the gel lattice, so that destruction of the structure by acoustic oscillations becomes so small, that its action has practically no effect on the state of the medium. Therefore concentrated gel-like structures in a macrovolume do not exhibit any thixotropy when the beaker is shaken by hand in the usual manner, whereas weakly-concentrated gels and colloidal solutions readily go over into cells when the beaker is slightly tapped [67]. The coacervates of the cell protoplasm, which have similar properties and which are contained in the microvolume of the cell, do not change their state when the biological tissue is shaken, but when a single cell is periodically massaged with a microprobe, the structured state of the plasma coacervate is destroyed [67]. Therefore placing a biological cell in an ultrasonic field unavoidably leads to a transition of the protoplasm from a gel into a sol [79], freeing the previously adsorbed bound ions.

In red human blood cells, such ions are potassium ions, with a concentration $C_d = 90$ mg-mole/1. Erythrocytes in a saline physiological solution retain this ion concentration for a long time, but application of ultrasound of frequency 1 MHz lowered reversibly, giving up potassium cations to the solution. Figure 2 (curve 1) shows the dependence of the relative change of the concentration of potassium ions, C/C_e, in a surrounding solution on the intensity of the sound in the medium [25]. We see that the behavior of the quantity C/C_e, where C is the concentration of the potassium ions in the solution, with increasing intensity of the sound I, is analogous to the same dependence in the case of formation of Liesegang rings (see Fig. 6). It is apparently therefore necessary to assume that the structural properties of the cell plasma can be described by the exponential factor of (11), where the error integral will express the statistical distribution of the energy of resolving the structural bonds of the coacervate of the cell protoplasm for the continuum of the erythrocytes of a blood serum. When $I_0 = 3$ W/cm^2 ($E_0 = 2 \times 10^2$ erg/cm^3), curve 1 of Fig. 2 agrees with Eq. (11) very well, the slope of the straight line, plotted in coordinates $\ln(C/C_e)$ and $\operatorname{erf} I_0/I$, turns out to be equal to 3.5. Thus, ultrasonic oscillations can produce reversible thixotropic damage of the plasma coacervate of the cell, and lead to release of potassium ions from the absorption bond with the protein molecules of the protoplasm and to a transfer of these ions to the plasma water, with subsequent release into the solu-

tion via diffusion through the membrane and through the wall of the erythrocyte.

However, the coacervate cell theory does not have a comprehensive experimental verification, especially when it comes to the ability of the cell to accumulate a large number of certain ions. Although the long-existing theory of the semi-permeable cell membrane has been recently [65] placed under doubts, nonetheless it is not excluded that the role of the electrobiological partition in the active transport of potassium ions inside the cell is fundamental, and perhaps even exclusive [74]. According to this theory, the biological membrane located on the inside of the cell wall has electric properties such that the potassium ions can pass in only one direction, operating like an electric membrane pump. The cell wall behaves like a passive microporous partition, which is permeable for all ions. Under the action of acoustic oscillations, as established above, the permeability of such a diaphragm remains unchanged. Consequently, from the point of view of the membrane theory, the decrease in the internal concentration of the potassium ions in human erythrocytes when irradiated with ultrasound should be connected with the change in the semi-permeability properties of the biological membrane.

In the experiments described above, in which the diffusion through live and dead organic diaphragms was accelerated, the diaphragms were not placed under experimental conditions such as to be able to establish the ability of acoustic oscillations to change the maximum of their semipermeability. However, the fact that microporous membranes do not change in an ultrasonic field gives grounds for assuming that their property of selective transmission of ions remains the same when exposed to sound. This is indicated by experiments carried out with a dialysis membrane [17], constituting an osmotic cell in conjunction with a colloidal solution, saturated with ions from copper sulfate, on one of its sides. The action of the sound waves (frequency 570 kHz) of intensity 2.2 W/cm^2 does not affect the osmotic transfer of the liquid in such a semipermeable system, and consequently does not change the unidirectional diffusion of the copper and SO_4^- ions in opposite directions.

If we assume the transfer mechanism proposed in [74] for the potassium ions in single live cells, then the pump action of the biological membrane is determined not only by its electric charge, as is the case for semipermeable partitions, but also by the presence of the adenosinetriphosphoric acid, which is capable of producing on the outer side of the cell membrane, together with the potassium ion, a neutral molecule that penetrates freely inside the erythrocyte. Coming in contact with the cell plasma, this molecule releases the potassium ion into the content of the cell and, joining the sodium ion, immediately metabolizes to a neutral molecule, which is already capable of diffusing to the outer side of the membrane.

Adenosine-triphosphoric acid (ATP) should be situated on the inside surface of the cell membrane in order to produce a total cation flux - either absorption of potassium or expulsion of the sodium.

Exposure of a blood cell to acoustic oscillations can disturb the equilibrium on the inner surface of the biological membrane of the erythrocyte, for example as a result of the occurrence of microcurrents inside the cell following the destruction of the structure bonds of the cell protoplasm. A number of investigators observed under a microscope a rapid motion of the cell plasma in an ultrasonic field [66]. Human erythrocyte is a single cell of cylindrical form with 7 μ diameter and 1 μ height, with an elastic wall, capable of flexural oscillations when the blood cell is in an ultrasonic field [75]. For different types of single cells, the first mode of the oscillations is observed when the sound frequency is several dozen kHz. Resonant oscillations at higher modes can occur more readily than at lower ones. For a cylinder with a vibrating wall, the velocity of the acoustic microcurrents at the internal and external surfaces of the wall is given by [47]

$$v_{ac}=\frac{3nU_c^2}{4\omega d_c}, \qquad (13)$$

where n = 1, 2, 3, ... is an integer characterizing the number of the mode of the flexural oscillations of the wall, d_c is the cylinder diameter, and U_c is the vibrational velocity of the cylinder wall.

We can obtain an approximate estimate of the velocity of the acoustic microcurrents for the erythrocyte. From the formulas obtained in [75] it follows that the fundamental resonant frequency for the human erythrocyte is approximately 100 kHz. Then at a frequency 1 MHz there will be excited the tenth mode of the flexural oscillations of the wall, i.e., n = 10. Further, assuming that the amplitude of the vibrational velocity of the wall is close to the vibrational velocity in the sound wave, we obtain at an intensity I = 1 W/cm^2, for human erythrocyte a microcurrent velocity of approximately $v_{ac} \approx 0.3$ cm/sec.

The flow of such currents on the outer surface of the erythrocyte can lead to removal from the surface layer of the cell wall of the colloidal particles responsible for the physico-chemical state of this layer causing a decrease in the ζ-potential of the erythrocytes of rats [76,77]. The microcurrents produced inside the cell will apparently be capable of changing the physico-chemical state of the internal surface layer of the erythrocyte, removing from this surface layer the molecules of the adenosinetriphosphoric acid, and increasing by the same token the diffusion penetrability of the biological membrane of the human erythrocyte for the potassium ions [25]. Both processes are reversible, since the molecules and the colloidal particles return, in the course of time, to the previous position after the end of the sounding.

b) Diffusion in Biological Tissue

Vegetable and animal organic structures are complex cell formations, representing from the physical point of view an aggregate of a number of closed microvolumes. The diffusion resistance of biological tissue will thus consist of the diffusion resistances of the cell wall, the boundary layer, and the cell protoplasm, multiplied by the number of cells through which the diffusion transport of matter takes place.

When ultrasound oscillations act on this process, the diffusion resistances of the protoplasm and of the boundary layer decrease greatly as a result of the occurrence of acoustic microcurrents in the cells. The existence of the microcurrents in the cells of sounded biological tissue is a well-known experimental fact [66], although in this case the shell of each cell is not free in the sense of the mechanical bonds with the neighboring cells. Therefore, in this case there can occur resonant oscillations only at the free elements of the cell wall, located between the junctions with the neighboring cells. It must be noted, however, that in order for microcurrents to be produced inside the cell it is not necessary, generally speaking, to have resonance of its elastic elements, and it is sufficient to have forced flexural oscillations of the wall, but in this case the velocity v_{ac} of the microcurrents will be much lower than that obtained above for a single resonating cell such as the erythrocyte.

As to the diffusion resistance of cell walls, it can remain unchanged in an ultrasonic field, as was shown above for microporous partitions, and consequently the total diffusion permeability of biological tissue under the action of sound will be limited by the sum of permeabilities of the cell walls. Consequently, the dependence of the ultrasonic effect on the intensity of the sound should be described by curve 1 of Fig. 1, as was indeed observed, for example, for the acceleration of the diffusion of a solution of KH_2PO_4 and radioactive iodine through the cornea into a dog's eye fluid under the influence of acoustic oscillations of frequency 800 kHz [78,80] at intensities up to 1.5 W/cm^2.

At such ultrasound intensities, no damage is observed in the cell shells of the eye tissue. Acceleration of the diffusion of radioactive phosphorus P^{32} in the same experimental conditions, but at intensities up to 4 W/cm^2 [63] leads to an increased dependence of the relative change $P^{32}_{ac}/P^{32} = C/C_e$ of the concentration of the radioactive phosphorus in the eye fluid with increasing sound intensity I (Fig. 2, curve 2). No damage to the eye tissue was observed for ultrasound intensities 0.2—1 W/cm^2, whereas at I = 1—4 W/cm^2 deep damage to the cell walls of the cornea was observed. Consequently, the acceleration of the process by acoustic oscillations, obtained under such conditions, is not an acceleration of the diffusion process, since it is accompanied by irreversible changes in the biological tissue, in analogy with hemolysis of erythrocytes in an ultrasonic field [81], in which the emergence of the potassium ions from the damaged red blood bodies into the solution takes place.

Damage of organic tissue by ultrasound results from the occurrence of cavitation or else mechanical resonances [82] in the biological structures and is an example of the deep polymerizing action of ultrasonic oscillations on the high molecular organic compounds, accompanied by destruction of the latter [85]. In this sense a thixotropic action of acoustic oscillations occupies an intermediate position, since it is also accompanied by damage of the biological medium, but has a reversible character. Therefore, in considering the influence of ultrasound on biological systems, it is very important to known the threshold intensities at which a transition is observed for a given object, from one character of action to the other.

The most sensitive to the action of the ultrasound is the cell plasma, giving rise to different subtle effects in biological cells placed in weak acoustic fields [25,76,77,83,84]. With increasing intensity, the sound is capable of acting both on the cell nucleus, on the chloroplasts, and on the chloroplasts in buckwheat [79], and at high intensities it can break the cell wall and lead to irreversible changes of the biological structure.

CONCLUSION

Acoustic oscillations have such a low energy, that they are unable to change noticeably the kinetic energy of the molecules and by the same token the diffusion coefficient in the medium. Therefore the acceleration of diffusion processes in an ultrasonic field is a second-order phenomenon, taking place only in the presence of liquid-solid interfaces, and is connected with the increasing role of viscosity on approaching the solid surface. An important factor here is the existence of a relative tangential vibrational displacement of the particles of the medium and the solid boundary, which is transformed into unidirectional motion of liquid, replacing by the same token the molecular transport of the diffusing particles by convecting transport when the acoustic field is applied.

A large number of papers devoted to the action of ultrasound on diffusion-heterogeneous processes has made it possible to consider three aspects of the problem: the diffusion through microporous media, through large-pore media, and in biological systems. However, most experimental investigations were made by specialists in the field of biology and medicine, so as to stimulate the viability of numerous living organisms, and also because of the desire to use acoustic oscillations for healing and therapeutic

purposes. Therefore, not sufficient attention was paid in the experiments to the physical conditions of the experimental setup and its description and to the elimination of extraneous factors during the choice of the procedure. The main attempt of these investigations was to establish the presence or absence of action of ultrasound on the diffusion process. In most cases the investigators did not pay attention to the diffusion properties of the materials used in the experiments, thereby greatly lowering the value of many of the investigations.

As a result, individual aspects of the acceleration of diffusion processes in an ultrasonic field remain far from clear. The invariance of the number of molecular transitions has not been finally proved, making it necessary to measure the electric conductivity of the liquid and its viscosity in an ultrasonic field. Few studies were devoted to the acceleration of diffusion in large-pore media, for which it is necessary to measure simultaneously the elektrokinetic potential of the membrane and its diffusion permeability in an ultrasonic field. There was no research done at all on the role of the pore dimensions, the sound frequency, the compressibility of the membrane material. No observations were made of the acoustic microcurrents in pores, and the dependence of the velocity of the microflow on these quantities has not been determined.

In biological media, it is of undisputed interest to study the acceleration of diffusion and exchange of matter in connection with the thixotropic action of ultrasonic energy and the associated problems of the effect of acoustic oscillations on live organisms.

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