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EFFECT OF ULTRAVIOLET RADIATION ON EVAPORATION OF SUSPENDED ALCOHOL DROPLETS

The influence of 390-nm ultraviolet radiation on the droplet evaporation under various pressures in the atmosphere of dry nitrogen has been studied for a series of homologous alcohols (n-propanol, n-butanol, n-pentanol, n-heptanol, n-octanol, and n-decanol). The alcohol evaporation rates under and without irradiation are calculated. A significant increase in the evaporation rate under low-power radiation is found for higher alcohols, and this growth is shown to be not associated with the heating of a droplet. The obtained results are analyzed by comparing them with experimental data on the slow neutron scattering.

Keywords: evaporation of alcohols, irradiation, suspended droplet method, neutron scattering.

1. Introduction

An important direction of modern researches is the study of the influence of radiation on the thermodynamic behavior of condensed media, in particular, on the evaporation processes which are used for the fabrication of medical preparations, drugs, and dry foodstuffs from solutions. There are both theoretical and experimental works devoted to this issue [1–3]. However, the mechanism of radiation influence on the processes running in liquids and liquid systems is not clarified at length, so that the further researches are required. This work aimed at studying the effect of ultra-violet radiation on the evaporation rate of droplets of various alcohols in the atmosphere of a background gas (dry nitrogen) at pressures of 10, 30, 50, 100, and 200 mm Hg.

The examined substances (n-propanol, n-butanol, n-pentanol, n-heptanol, n-octanol, and n-decanol) form a homologous series of alcohols. The topicality of studying the alcohols is explained by a variety of their application regions, e.g., as a fuel, in the manufacture of synthetic detergents, solvents, perfumery and cosmetics, in the food and pharmaceutical industries, and so forth [4]. At the same time, the scientific literature mainly contains the results of theoretical and experimental researches concerning the properties of lower alcohols, whereas the structural and dynamic characteristics of higher alcohols still remain little studied [5]. Therefore, in our opinion, it is expedient to consider the behavior of alcohols in the homologous series during their evaporation, because the addition of every CH_2 group changes the structure of researched substances, their absorption spectra, and the diffusion coefficient of alcohol molecules, which may affect the evaporation rate of alcohols under the influence of radiation.

2. Experimental Part

Measurements were carried out in a hermetic chamber with a thermostat. A droplet of one of the alcohols to study was suspended on a special suspension (the p–n transition of a chip transistor). The latter simultaneously played the role of temperature sensor with an error of droplet temperature measurement of 0.03 K in the interval of 278–313 K. The required values of the pressure and the temperature of a surrounding gas (nitrogen) were maintained in the working chamber. A laser light-emitting diode 0.1 W in power was mounted at a distance of 2.5 cm from the droplet. It generated light with a wavelength of 390 nm and served as a radiation source. In such a manner, both the droplet and its gas-vapor environment were irradiated. During the evaporation, the droplet and a scale ruler were periodically photographed in equal time intervals with the help of an attached web-camera. The photos were automatically registered in a computer. Then, using the method of graphic integration, the surface area of the droplet was determined at every time moment. Afterward, from the dependence of the droplet surface area S on the time t in the course of droplet evaporation, the corresponding evaporation rate dS/dt was calculated [6]. The detailed information on the experimental installation and procedure can be found in work [7].

In work [1], the results of experimental research concerning the influence of optical radiation with various wavelengths (390, 565, and 625 nm) on the evaporation rate of droplets of a number of liquids in the dry nitrogen atmosphere in a wide range of pressure were reported. A considerable growth of the evaporation rate under the action of radiation was revealed for water (up to 25%), nitrobenzene (up to 40%), and iodobenzene (up to 60%) droplets, provided their constant temperature in the course of evaporation. It was also found that the influence of irradiation on the evaporation rate of the substances belonging to the benzene series was the largest at pressures much lower than the atmospheric one. In addition, the irradiation with a wavelength of 390 nm turned out the most effective. Therefore, on the basis of the data presented in work [1], we selected pressures of 10, 30, 50, 100, and 200 mm Hg for studying the influence of radiation on the process of evaporation of alcohol droplets. Moreover, the researches were performed using ultraviolet radiation with a wavelength of 390 nm.

3. Experimental Results

At the first stage of our researches, we used the installation in a series of experiments to study the evaporation of suspended droplets of alcohols in the wide range of pressures from 10 mm Hg to the atmospheric one without droplet irradiation. The evaporation rates of ethyl and methyl alcohol droplets were too high even at the atmospheric pressure and grew as the environment pressure decreased. This fact did not allow us to make a required number of photos during the droplet evaporation for the reliable treatment of experimental data. Therefore, the experiments on the droplet evaporation at various external pressures were performed only for alcohols from propanol to decanol.

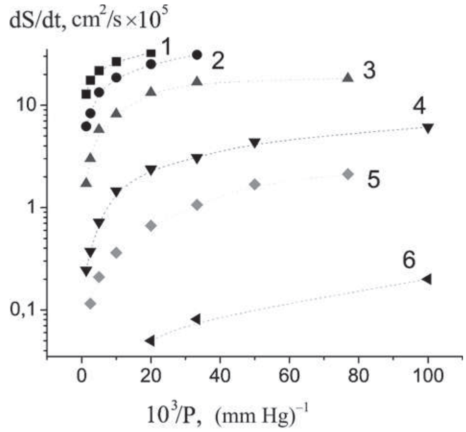

Fig. 1. Dependences of the alcohol droplet evaporation rates on the inverse external pressure for n-propanol (*1*), n-butanol (*2*), n-pentanol (*3*), n-heptanol (*4*), n-octanol (*5*), and n-decanol (6)

The time dependences of the droplet area at a constant pressure are linear for all alcohols. This means that the derivative dS/dt can be used to determine the evaporation rate of alcohol droplets. It is necessary to pay attention to that the temperatures of the droplet and the gas environment throughout the experiment practically did not change, so that the evaporation at a constant pressure occurred in a quasistationary regime. For the sake of comparison between the evaporation kinetics for the alcohols in the examined series, the dependences of the evaporation rates on the inverse environment pressure are depicted for some of them in Fig. 1. One can see that, as the molar masses of alcohols increase, the evaporation rates of their droplets decrease provided that the external pressure is constant. A similar behavior was observed within the whole range of experimental pressures.

When the pressure decreased, the effect of alcohol droplet cooling at the evaporation became more and more pronounced. For example, the temperature of n-butanol droplets decreased from 453 to 303 K, when the pressure was varied from the atmospheric

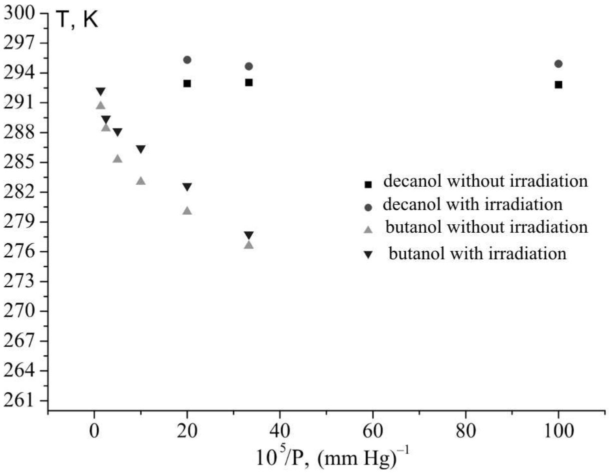

Fig. 2. Dependences of the butanol and decanol droplet temperatures on the inverse external pressure obtained under droplet irradiation and without it

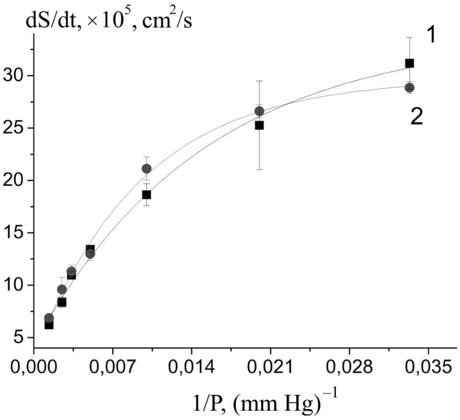

Fig. 3. Dependences of the n-butanol evaporation rate in dry nitrogen on the inverse external pressure in the dark regime (*1*) and under light irradiation with a wavelength of 390 nm

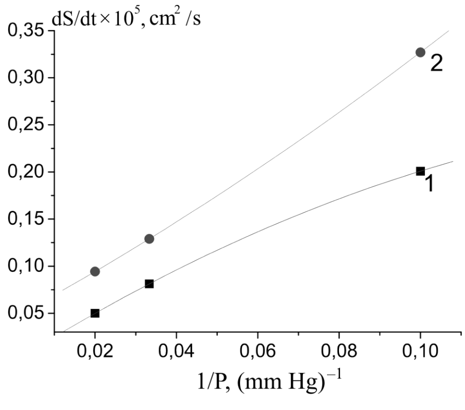

Fig. 4. The same as in Fig. 3, but for n-decanol

one to 30 mm Hg. Moreover, the droplet temperature during the evaporation substantially grew when changing from lower alcohols to higher ones (Fig. 2).

To study the influence of radiation on the evaporation rate of alcohols, a low-power light-emitting diode (P = 0,1 W) was used, which produced radiation with the wavelength λ = 390 nm. In Fig. 3, the dependences of the evaporation rate dS/dt on the inverse pressure are shown for a low-molecular alcohol (n-butanol), which were measured in two regimes: dark (without irradiation) and with irradiation. In both cases, the temperature of the surrounding gas was 293 K. One can see that the evaporation rate of n-butanol droplets almost did not change within the experimental error. Small differences between both regimes are explained by the insignificant heating of n-butanol droplets (not exceeding 3–4 K) owing to irradiation and the experimental error itself. The same situation was observed for other low-molecular alcohols (n-propanol, n-butanol, and isoamyl alcohol) as well. Hence, the change in the evaporation rates of the indicated alcohols under the influence of radiation was not detected.

Similar dependences on the environmental pressure were obtained for other alcohols in the examined homologous series. In the experiments with n-pentanol, the growth of the evaporation rate by 31% under the action of radiation was observed at a pressure of 100 mm Hg. At a pressure of 50 mm Hg, the difference was smaller (8%). The growth of the evaporation rate under the influence of radiation was also observed for other high-molecular alcohols, but no such variation took place for low-molecular alcohols. Irradiation was the most efficient for decanol (Fig. 4), for which the evaporation rate increased by 85% at a pressure of 50 mm Hg.

In Table 1, the relative variations of the evaporation rate under the action of radiation, $\Delta V/V$, where $\Delta V = V_{h\nu} - V$, are quoted for all studied alcohols at various environmental pressures. From whence, one can see a substantial growth of the evaporation rates of alcohol droplets under the droplet irradiation at a wavelength of 390 nm, as compared with the dark regime.

4. Analysis of Obtained Results

As follows from the results of our experiments, the influence of radiation on the evaporation rate of alco-

Table 1. **Relative growth of the droplet evaporation rate under irradiation for various alcohols and pressures**

Alcohol	10 mm Hg	30 mm Hg	50 mm Hg	100 mm Hg	200 mm Hg
Propanol, %		1	2	3	3
Butanol, %		1	5	13	3
Pentanol, %		4	8	31	4
Heptanol, %	12	27	37	56	17
Octanol, %	27	24	35	45	48
Decanol, %	62	58	85		

hol droplets becomes appreciable for alcohols starting from pentanol, whereas the low-molecular members of this series do not manifest such behavior. On the basis of the obtained data, it is possible to predict that ethanol and methanol should not practically change their evaporation rates at irradiation, although, as was mentioned, experimental measurements for those alcohols are rather difficult.

An evident reason for the obtained growth in the evaporation rate of alcohols may be, first of all, the heating of examined alcohol droplets under the action of radiation in the course of evaporation. However, the additional researches concerning the heating effect on the evaporation rate of alcohol droplets were carried out, and their results demonstrated that the growth of the droplet temperature by 1–3 K (which took place at the droplet irradiation) induced the increase in the evaporation rates of the studied alcohols only by 3–7%. Such value cannot explain the effect observed at the droplet irradiation (see Table 1).

The growth of the alcohol evaporation rates under the influence of radiation can also be explained by the effect similar to the photoeffect, but for alcohols [8]. However, the researches carried out for the dependence of the evaporated substance flux on the irradiation light wavelength testify that this effect is most likely not crucial. Therefore, we consider that the increase of the evaporation rate of alcohols with the growth of their number in the homologous series can be explained by the known simultaneous enhancement of the role of collective motions of molecules in alcohols. A unique method that allows the collective and one-particle motions in the liquid to be resolved and their quantitative ratio to be estimated is the scattering of slow neutrons in the examined liquids [9]. Therefore, in order to explain the growth of the evaporation rate of alcohol droplets owing to the increase in the collective contribution to the general motion of alcohol molecules, we compared the obtained experimental results with the available data on quasielastic scattering of neutrons in the alcohols under study.

The decreases in the evaporation rates of alcohol droplets with the growth of the alcohol molecular mass are connected, first of all, with a reduction of the diffusion coefficient along the alcohol series. Therefore, it seemed to be expedient to compare the obtained experimental data with the self-diffusion coefficients calculated according to the data of the quasielastic scattering of slow neutrons in the studied alcohols [9]. In Table 2, D is the self-diffusion coefficient of alcohol molecules, D_k the collective contribution to the self-diffusion coefficient, and D_0 the one-particle contribution, so that $D = D_k + D_0$. As is seen from Table 2, when the effective length of the alcohol molecule increases, the total diffusion coefficient D decreases, although the collective contribution grows. This fact testifies that alcohols are not isostructural liquids. As the alcohol number grows, the alcohol structure becomes denser.

In Fig. 5, the dependence of the ratio between the collective contribution in the self-diffusion coefficient of an alcohol molecule and the total value of this coefficient on the number of hydrogen atoms N in the molecule is plotted. The collective contribution to the total self-diffusion coefficient grows with N. However, the variation of this quantity is different for lower and higher alcohols. Since the evaporation rate of alcohol droplets is governed to a great extent by the diffusion coefficient, such characteristic variations in the diffusion coefficients for alcohols belonging to the homologous series can turn out useful at studying the evaporation processes for the liquids concerned. Really, if

Table 2. **Diffusion coefficients of alcohol molecules obtained in neutron scattering experiments**

Alcohol	Chemical formula	Number of hydrogen atoms	D, 10^{-9} m^2/s	D_k, 10^{-9} m^2/s	D_0, 10^{-9} m^2/s	$D/D_k \times 100\%$
Methanol	CH_3OH	4	1.65	0.09	1.57	5.23
Ethanol	CH_3CH_2OH	6	1.59	0.18	1.42	11
Propanol	$CH_3(CH_2)_2OH$	8	1.41	0.22	1.19	15.8
Butanol	$CH_3(CH_2)_3OH$	10	1.24	0.24	1.01	19
Heptanol	$CH_3(CH_2)_6OH$	16	0.96	0.22	0.73	23.4
Octanol	$CH_3(CH_2)_7OH$	18	0.92	0.27	0.66	29.2
Nonanol	$CH_3(CH_2)_8OH$	20	0.88	0.31	0.58	34.6
Decanol	$CH_3(CH_2)_9OH$	22	0.78	0.36	0.42	46.1

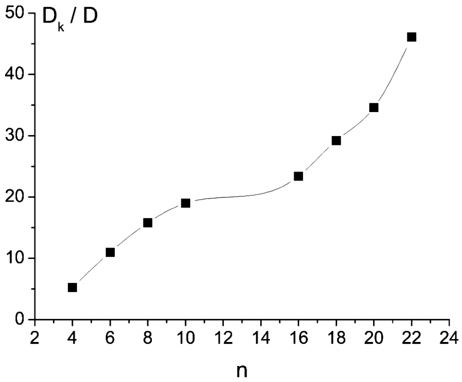

Fig. 5. Dependence of the relative fraction of the collective contribution to the self-diffusion coefficient of alcohols on the ordinal alcohol number

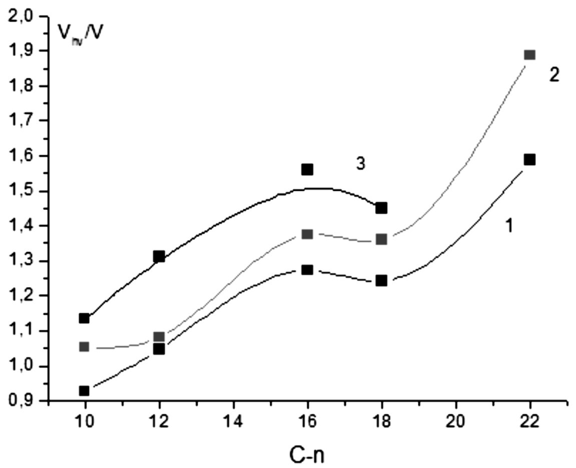

Fig. 6. Dependences of the alcohol droplet evaporation rate change owing to irradiation with 390-nm light on the number of hydrogen atoms in an alcohol molecule for environmental pressures of 30 (*1*), 50 (*2*), and 100 mm Hg (*3*)

we compare the dependences of the ratio between the evaporation rates at the droplet irradiation with 390-nm light and in the dark regime on the ordinal number of the alcohol, which were obtained at pressure values of 30, 50, 100, and 200 mm Hg (Fig. 6), with the same dependence for the relative value of collective contribution to the diffusion coefficient (Fig. 5), their similar characters become evident.

Hence, the analysis of experimental results gives us grounds to consider that radiation affects, first of all, the collective motions of molecules in the liquid, and this effect is better observed in the case of substances with low evaporation rates, because the collective motions play a more significant role in diffusion processes under those conditions. The reduction of the evaporation rate of alcohol droplets with the growth of the alcohol molecular mass is associated, first of all, with a decrease in the total diffusion coefficient in the alcohol series. Similar conclusions can be made from the analysis of the results of computer simulation [10].

In our opinion, the substantial growth of the evaporation rate for high-molecular alcohols under the influence of radiation is primarily connected with structural changes, namely, with the growth in the number of solvated complexes for larger alcohol numbers, which is testified by the increase of the collective contribution to the self-diffusion coefficient of alcohols. In low-molecular alcohols, one-particle motions prevail. Therefore, single alcohol molecules do not absorb light quanta. For the alcohols, in which the role of collective motions is considerable, the transmission of the energy of ultra-violet radiation quanta by alcohol molecules becomes, most likely, possible owing to the existence of a considerable number of complex formations in the liquid structure. In such a manner, when obtaining the additional energy under the influence of radiation, some alcohol molecules leave the liquid surface at a rate a little higher than under ordinary evaporation conditions. As a result, the evaporation rate of droplets increases, especially at lower pressures, because the concentration of gas molecules in the gas-vapor medium strongly decreases. A similar mechanism of energy transfer is observed at the resonance radiation emission or absorption of γ-quanta by atomic nuclei when no energy is spent on the nuclear recoil.

5. Conclusions

As was shown in the experiments on the quasielastic scattering of slow neutrons in alcohols, the collective contribution of a molecular motion to the alcohol self-diffusion coefficient grows and has a little different character for lower alcohols up to pentanol than for higher alcohols. This fact manifested itself in our experiments on the influence of radiation on the evaporation rates of alcohols.

1. Irradiation of droplets of higher alcohols (from n-pentanol to n-decanol) with 390-nm light results in an appreciable growth of the evaporation rate (up to 85%, depending on the alcohol number). No influence of radiation on the droplet evaporation rate was found for low-molecular alcohols.

2. Monitoring the droplet temperature in the course of the experiment showed that droplets of all studied alcohols were heated up insignificantly during the radiation-induced evaporation, so that the corresponding acceleration of the evaporation rate of high-molecular alcohols cannot be substantial.

3. First of all, radiation influences the collective motions of molecules in the liquid, and this effect grows as the evaporation rate diminishes.

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ДОСЛІДЖЕННЯ ВПЛИВУ ОПРОМІНЕННЯ
НА ПРОЦЕС ВИПАРОВУВАННЯ ПІДВІШЕНИХ
КРАПЛИН СПИРТІВ

Р е з ю м е

Досліджено вплив ультрафіолетового випромінювання з довжиною хвилі 390 нм на процес випаровування краплин ряду спиртів (а саме, n-пропанолу, n-бутанолу, n-пентанолу, n-гептанолу, n-октанолу та n-деканолу) для тисків 10, 30, 50, 100 та 200 мм рт. ст. в атмосфері сухого азоту, обчислено значення швидкості випаровування спиртів під опроміненням та за його відсутності. Виявлено значне зростання швидкості випаровування під дією малопотужного випромінювання для краплин вищих спиртів, починаючи з n-пентанолу, причому ці процеси не пов'язані з нагріванням краплин. Одержані результати проаналізовано на основі порівняння з експериментальними даними по розсіянню повільних нейтронів спиртами.