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EFFECT OF A SURFACE-ACTIVE SUBSTANCE ON NONEQUILIBRIUM PHENOMENA IN GAS-LIQUID SYSTEMS IN THE SUBCRITICAL REGION

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The process of the pressure drop in gas-liquid systems after adiabatic compression from various pressure levels higher than the saturation pressure is investigated. Experimental and theoretical investigations of the effect of a surface-active substance on nonequilibrium phenomena in gas-liquid systems are analyzed.

A large body of research on gas-liquid systems in subcritical regions [1-3] has revealed the presence of relaxational properties. In this case intense nucleation takes place in spite of the fact that the pressure in the gas-liquid medium is greater than the saturation pressure. It was shown in [4] based on experimental investigations that the presence of a surface-active substance (SAS) can lead to the creation of stable gas bubbles in water, and in [5] a hypothesis was proposed based on theoretical investigations that testifies to this fact for gas-liquid systems in subcritical regions, and relaxational properties of the media are explained on the basis of the hypothesis. This work, which continues investigations pioneered by Academician A. Kh. Mirzadzhanzade, presents the results of investigation of the effect of SAS on the behavior of gas-liquid systems in the subcritical region and an alternate explanation of the aforementioned phenomena is proposed.

Investigations of the gas-liquid system were carried out in a PVT bomb by the adiabatic compression (loading) method. The apparatus consisted of the following main parts: hydraulic press, PVT bomb, ultrathermostat, and measuring instruments. The main measuring unit consisted of a "Sapfir 22-DD" tensometer, a B5-49 dc power supply, an R-333 resistance box, and a recorder.

Experiments were carried out according to the following scheme:

- a gas-water mixture (with methane used as a gas) with a gas factor of 1 m^3/nm^3 and a volume gas content of 0.17 was prepared in a PVT bomb with continuous thermostabilization ($T = 303$ K); the mixture volume was 3 liters;
- the saturation pressure P_s of 3.2 MPa was determined by the volume method;
- the gas-liquid mixture was studied by the loading method; the loading proceeded ar a uniform rate of 0.017 MPa/sec from the level under consideration to 1.6 MPa, after which observations of pressure changes in the system were carried out.

In a similar manner we studied water-gas systems with SAS (sulfanol) additives with weight content $c = 0-0.4\%$. The level from which the loading started was varied over wide limits and was equal $P = (1.1-2.5)P_s$.

Changes in pressure P_T with time after loading gas-liquid systems from various levels is shown in Fig. 1, from which is evident that while the pressure drop equals 0.03 MPa when $P > 2P_s$, when $P < 2P_s$ the drop in the pressure increases and reaches 0.081 MPa at $P = 1.1P_s$. We should note also that the time of pressure relaxation after loading also increases with the initial loading level approaching the critical region.

In order to explain the results obtained the (P_T vs t) dependences were plotted in new coordinates [6] ($\ln((P_0 - P_\infty)/(P_T - P_\infty))$ vs t). The relaxation time can be determined from the slope angle α ($\tau = (\tan\alpha)^{-1}$).

The results plotted in the new coordinates are shown in Fig. 2a ($(P_0 - P_\infty)/(P_T - P_\infty) = P^*$). It is evident from the figure that while when $P < 1.7P_s$ (curve 1) the dependence is a broken line, when $P > 1.7P_s$ (curve 2) the dependence is a straight line, i.e., the model is changed from an exponential one to one described by a sum of

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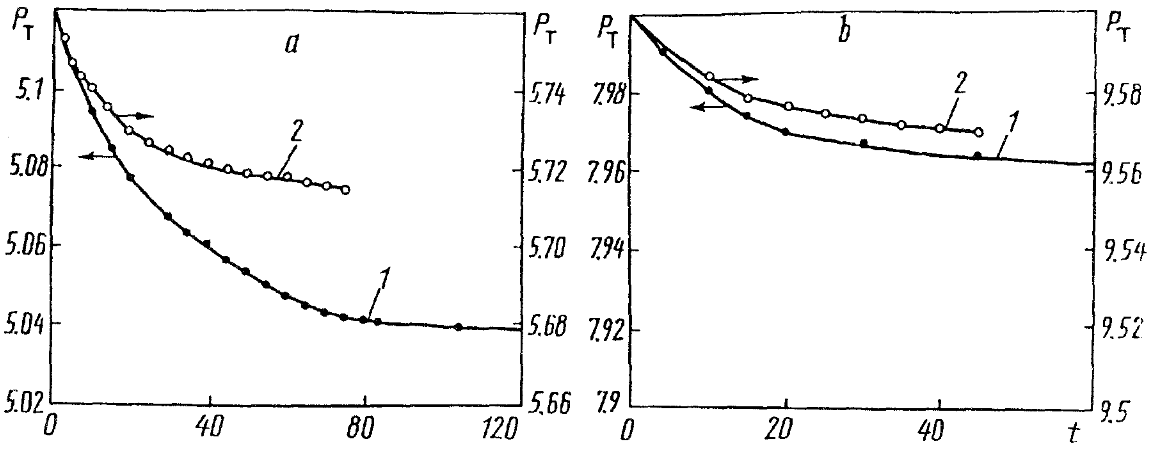

Fig. 1. Variation in pressure (MPa) with time (min) after loading of gas-liquid system without SAS additives from various initial pressure levels, P: a, 1) $P = 1.1P_s$, 2) $1.3P_s$; b, 1) $P = 2P_s$, 2) $2.5P_s$.

exponentials [7]. It should be noted that lines decline to the right when approaching the critical region, i.e., longer relaxation times.

The results obtained can be explained in the following manner. Although the physical reason and the mechanism of the subcritical origination of the gas phase volumes are not clearly understood so far, nevertheless, we, having in mind the results of the present and afore-enumerated works, will start from the established fact of the existence of gas micronuclei in the subcritical region. We will assume that uniformly distributed micronuclei with initial radii R_0 and number concentration N_0 dependent on the initial pressure P_{g0} and composition of the gas-liquid mixture are present in the initial liquid.

With increasing pressure in the gas-liquid mixture the system undergoes adiabatic compression. In this case, since the liquid is poorly compressible, the variation in the mixture volume takes place due to the presence of gas micronuclei. If the gas is poorly soluble then the nuclei pass from the initial state characterized by the parameters R_0, R_{g0}, and T_{g0}, into the state with R_e, P_{ge}, and T_{ge}, where

$$\frac{R_e}{R_0} = \left(\frac{P_{g0}}{P_{ge}}\right)^{1/3\gamma}, \quad \frac{T_{ge}}{T_{g0}} = \left(\frac{P_{ge}}{P_{g0}}\right)^{\frac{\gamma-1}{\gamma}}, \quad \frac{\rho_{ge}}{\rho_{g0}} = \left(\frac{P_{ge}}{P_{g0}}\right)^{1/\gamma}. \tag{1}$$

Being compressed, the nuclei release intensely the acquired heat (1) into the liquid as a result of the great temperature gradient of the gas on the interface and efficient removal of heat by the liquid. In the case of an isolated bubble the liquid takes the heat intensely without changing its temperature [8]. In contrast with [8], under the conditions of the present experiments it is necessary to take into account that as a result of the high compression of the gas ($\rho_{ge} \gg \rho_{g0}$) the temperature of the liquid in the vicinity of the surface differs from T_0 in accordance with Eq. (1).

Thus, increasing the potential energy of mutually attracting molecules of the liquid and gas upon compression leads to an increment in the internal energy of the gas-liquid medium. In turn, the excess internal energy goes into structural transformations in the mixture. Particles of the mixture change their mutual disposition under the transformations and transform the structure of the molecular complexes that condition the chemical transformations upon dissolution of the gas in the liquid. In this case, the structural transformations have a special feature that relates them to phenomena of heat and mass transfer: the transformations lead to a heat effect, which influences the thermal state of the mixture. The heat effect in the case of dissolution is subtle but can still be measured under laboratory conditions.

After a lapse of time equal to the characteristic time of structural rearrangement, the gas-liquid mixture is "unloaded." During the entire process the pressure falls slowly if no chemical transformations with additional heat liberation take place that could maintain or increase the pressure.

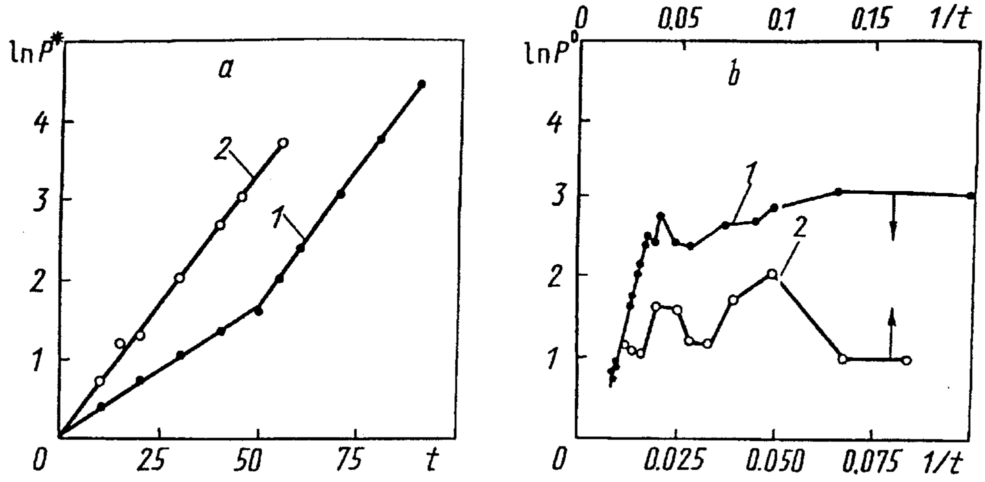

Fig. 2. Dependence of pressure on time plotted in semilog (a) and "diffusion" (b) coordinates for two levels of initial pressure: $P = 1.1P_s$ (1) and $2.5P_s$ (2). $1/t$, min^{-1}.

It is evident that the pressure drop will be enhanced if the initial pressure in the system is close to the saturation pressure when the volume content of gas micronuclei is greater.

It follows from the analysis presented that the pressure drop process can be divided into two stages: an initial one that takes place as a result of increasing gas temperature and redistribution of heat fluxes to the liquid and a final one resulting from the lack of diffusion equilibrium in the system and accompanied by its molecular and convective rearrangement. It is obvious that the second stage appears at pressures close to the saturation pressure when the volume content of micronuclei increases sharply.

We will try to describe the process of the structural rearrangement of the mixture by the following simplified model using the approach of Shtibina [9]. The gas flow through a unit area of liquid is

$$q = \frac{Dc\,(x\,,\,t)}{\partial x}\,. \tag{2}$$

Then after time t the gas mass transferred through area S equals

$$Q\,(x\,,\,t) = S\int_0^t q\,(x\,,\,t)\,dt\,. \tag{3}$$

At the same time, according to the equation of state, and in view of the fact that N_0 is rather large, the variation in the gas mass is determined as

$$\Delta M = Q = \frac{\rho_{\text{atm}}\,\Delta P_{\text{ext}} V}{P_{\text{atm}}}\,, \tag{4}$$

where $\Delta P_{\text{ext}} = P - P_{\text{atm}}$ is the jump in external pressure; P_{atm} is atmospheric pressure.

From Eqs. (2)-(4) we find the variation in the pressure with time due to diffusion

$$\frac{\partial P}{\partial t} = -\,D\,\frac{P_{\text{atm}}}{\rho_{\text{atm}}}\,\frac{S}{V}\,\frac{\partial c\,(x\,,\,t)}{\partial x}\,. \tag{5}$$

The gas flow entering Eq. (5) is determined from the diffusion equation, which in the case of boundary conditions

$$c\,(0\,,\,t) = c_0\,, \quad c\,(x\,,\,0) = c_1\,, \quad c\,(\infty\,,\,t) < \infty$$

is determined as follows:

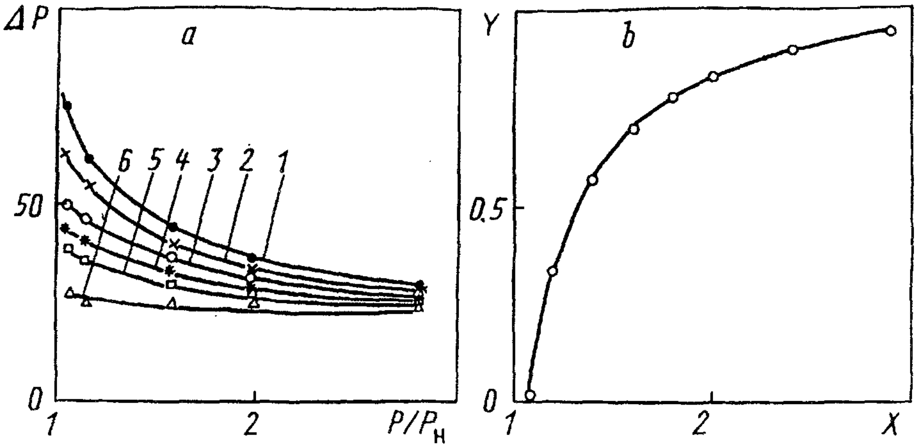

Fig. 3. Dependence of pressure drop (MPa) on level of initial pressure relative to saturation pressure at various weight-part concentrations c of SAS: 1) $c = 0$; 2) $c = 0.005\%$; 3) 0.01; 4) 0.025; 5) 0.04; 6) 0.4%.

$$q\Big|_{x=d} = \frac{D(c_1 - c_0)}{\sqrt{\pi D t}} \exp\left(-\frac{d^2}{4Dt}\right).$$

Then, in view of (5),

$$\frac{\partial P}{\partial t}\Bigg|_{x=d} = -\frac{S}{V}\frac{P_{\text{atm}}}{\rho}(c_1 - c_0)\sqrt{D/\pi}\,\frac{\exp\left(-\dfrac{d^2}{4Dt}\right)}{\sqrt{t}},$$

whence

$$\sqrt{t}\,\frac{\partial P}{\partial t}\Bigg|_{x=d} = A\exp\left(-\frac{d^2}{4Dt}\right), \tag{6}$$

where

$$A = -\frac{P_{\text{atm}}}{\rho}\frac{S}{V}(c_1 - c_0)\sqrt{D/\pi}\,.$$

Taking the logarithm, we finally obtain

$$\ln\left(\sqrt{t}\,\frac{\partial P}{\partial t}\Bigg|_{x=d}\right) = \ln A - \frac{d^2}{4Dt}, \tag{7}$$

i.e., dependence (6) in coordinates $(\ln(\sqrt{t}\,\partial P/\partial t),\ 1/t)$ is presented by a straight line with slope angle $d^2/4D$ [9].

A plot of the dependences obtained in the new "diffusion" coordinates is presented in Fig. 2b ($\sqrt{t}\,\partial P/\partial t = P^0$), from which is evident that while for levels of initial pressure close to the critical region ($P = (1.1-1.5)P_s$) the final portion of the (P_T vs t) dependence is rectified in the specified coordinates (see Fig. 2b, curve 1), for levels $P > 1.7P_s$ (Fig. 2b, curve 2) this does not happen, which substantiates our arguments.

In the second series of experiments, the entire set of investigations was carried out for a water-gas mixture with SAS additives.

It is evident from Fig. 3a that ΔP decreases with increasing SAS concentration and at $c = 0.4\%$ is virtually independent of the initial pressure level from which the system is loaded.

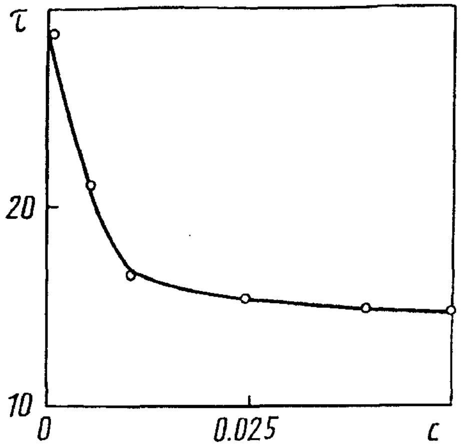

Fig. 4. Dependence of relaxation time (min) on weight-part concentration of SAS at $P = 1.1P_s$.

The method of asymptotic coordinates [10] was used to describe the results obtained. The new coordinates were determined in the following manner: $Y = (\Delta P^* - \Delta P_0^*)/(\Delta P_\infty^* - \Delta P_0^*)$; $X = P/P_s$, where $\Delta P_0^* = 1/\Delta P_0$, $\Delta P_T^* = 1/\Delta P_T$, $\Delta P_\infty^* = 1/\Delta P_\infty$. The results of processing are presented in Fig. 3b, from which is evident that the ΔP vs P/P_s dependence is identical for arbitrary SAS additives, i.e., in all cases the processes that take place are identical. Experimental results can be described by the following formula

$$Y = 1 - \exp\,[-\,1.9\,(x - 1.07)^{0.76}]\,.$$

with accuracy to 5%.

By an analogy with the described experiments with a water-gas mixture, the dependences (P_T vs T) obtained with SAS addition were also plotted in new coordinates ($\ln((P_0 - P_\infty)/(P_T - P_\infty))$ vs t); from the slopes of the initial portions of the curves the relaxation time was determined. It is evident from Fig. 4 that the relaxation time decreases with increasing SAS content, i.e., the decrease in the surface tension resulting from SAS addition is equivalent to increasing the rigidity of the system or, in other words, decreasing the compressibility of the system.

It should be noted that at high SAS concentrations the level of the initial pressure virtually does not affect the pressure drop and takes values equal to those obtained without SAS additives at $P > 2P_s$. In this case the diffusion stage is absent, whereas at lower SAS concentrations only a trend is observed towards decreasing the initial pressure level at which the diffusion part is absent.

Thus, the addition of SAS contributes to a decrease in nonequilibrium processes in gas-liquid systems in the subcritical region, which is likely connected with the screening action of SAS on gas inclusions. SAS film at the phase interface weakens heat transfer from the gas to the liquid, which leads to slowing down of the effect of structural rearrangement of the mixture. In addiiton, it is known that SAS decreases the elasticity of gas inclusions [11] and decreases their mean dimensions [12] (which also leads to a decrease in elasticity). All these factors slow down substantially the increase in the internal energy of the system during compression of the gas-liquid mixture.

Therefore, the hypothesis proposed in [5] according to which the relaxation properties of gas-liquid systems in the subcritical region are explained by the appearance of stable gas bubbles in the presence of SAS contradicts the obtained effect of decreasing, and, in the limiting case, removal of relaxational properties with the addition of SAS. In this case, it is better to speak not about bubble formation but rather about subcritical nucleation of the gas in the liquid. It should be noted that with addition of SAS the nuclei really become more stable [4], but at the same time they become less elastic (i.e., more "rigid") [11], which leads to the removal of nonequilibrium phenomena. In this case, as is noted in [5], the theory developed by Buevich becomes incorrect, due to violation of the condition adopted according to which the thickness of the SAS film is small compared with the bubble radius; the condition of mechanical equilibrium of the bubble also loses its meaning.

The following conclusions can be drawn on the basis of our investigations:

1. During the adiabatic compression of gas-liquid media in the subcritical region the subsequent drop in the pressure with time is characterized in the first stage by prevailing heat relaxation and by prevailing diffusion in the second stage.

2. SAS addition leads to the removal of relaxational properties of the systems specified.

The results obtained in the present work can be used in the field of oil production, where gas-liquid systems operating in the subcritical region are widely used [13, 14].

NOTATION

P_0, P_{T}, P_∞, initial, current, and final pressure after loading; P, initial pressure level from which loading proceeds; ΔP, pressure drop after loading; P_{s}, saturation pressure; P_{atm}, atmospheric pressure; P_{ext}, jump in external pressure; P_{g0}, P_{ge}, initial and final pressure in mixture; ΔP_0, ΔO_{T}, ΔP_∞, initial, current, and final drop in pressure; ρ_{a}, gas density reduced to atmospheric conditions; ρ, current value of gas density; ρ_{g0}, ρ_{ge}, initial and final density of mixture; T, temperature of environment; P_{g0}, T_{ge}, initial and final temperature of mixture; c, weight-part concentration of dispersed phase; t, time; τ, relaxation time; R_0, R_e, initial and final nucleus radii; d, diffusion interface layer thickness; S, area through which diffusion proceeds; D, diffusion coefficient; g, gas flow through entire contact area; ΔM, mass of gas; V, total volume of gas; γ, adiabatic exponent.

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