SOVIET PHYSICS JETP VOLUME 29, NUMBER 1 JULY, 1969

EFFECTS OF STRATIFICATION OF BINARY LIQUID SOLUTIONS UNDER THE INFLUENCE OF RADIATION

L. K. LYTKIN, A. F. PISAREV, A. P. SUMBAEV and S. F. CHALKIN

Joint Institute for Nuclear Research

Submitted July 3, 1968

Zh. Eksp. Teor. Fiz. 56, 73–77 (January, 1969)

An experimental study was made of the influence of γ radiation on the rate of stratification of two-component liquid solutions in a supersaturated state. It is established that radiation accelerates the decomposition of solutions such as nitrobenzene in hexane and water in triethylamine. Supersaturation of the solution was attained by rapidly dropping the pressure over the surface or by pulsed application of a field.

1. INTRODUCTION

ONE of the authors and Biryukov[1] considered theoretically the possibility of stratifying a two-component liquid solution which is in a metastable state by using ions. The physical basis for this effect consists in the fact that if one of the components of a boundary homogeneous solution has a large static dielectric constant, then an increased density of this component is produced around the extraneous ion. The contraction of the molecules into a microcomplex around the ion is the result of the forces exerted on the molecules by the inhomogeneous electric field of the ion. At the instant when the solution becomes supersaturated, these charged complexes become nuclei on which excess matter with increased dielectric constant is deposited from the solution.

In the cited paper, the effect of stratification of the solution on ions was considered from the point of view of its use to develop a controllable liquid track chamber. It seems that after a particle passes through the solution, the aforementioned complexes are produced on the residual ions in the medium, and then grow rapidly to a visible dimension at the instant when the solution is forcibly transformed from the saturated state into a supersaturated one.

In the present investigation, we verified qualitatively the effect of stratification of binary liquid solutions on ions produced by γ radiation. We used in the experiments solutions of methyl alcohol in hexane, nitrobenzene in hexane, water in triethylamine, and carbon dioxide in benzene. In the first two cases, short-duration supersaturation was attained by rapidly dropping the pressure over the solution or by applying a high-voltage pulsed field. In the experiment with the solution of water in triethylamine, the supersaturation was produced by pulsed heating. Finally, in the experiment with benzene saturated with CO_2 the supersaturation was produced, as in the first case, by dropping the pressure.

2. CHANGE OF PRESSURE, TEMPERATURE, AND ELECTRIC FIELD CORRESPONDING TO THE INITIAL LIMIT OF THE SENSITIVITY OF THE SOLUTION TO STRATIFICATION ON IONS

A. Effect of pressure. In accordance with[1], the pressure drop that ensures stratification of a solution on ions can be determined from the formula

$$\Delta P = \frac{3}{2}\frac{MC}{\rho RT}\left(\frac{4\pi\sigma^4}{(ze)^2}\frac{\varepsilon\varepsilon_2}{\varepsilon_2-\varepsilon}\right)^{1/3}\frac{\lambda}{T\Delta V}\frac{dT}{dC}. \tag{1}$$

Here $\Delta P = P_0 - P_c$ is the difference of the pressures over the solution before and after supersaturation, C is the molar concentration of the solution, M and P are the molecular weight and the density of the dissolved substance, T is the saturation temperature, σ is the surface tension on the boundary between the drop released from the solution and the remaining part of the solution, λ and ΔV are the heat and change of volume of the dissolution, dT/dC is the derivative taken along the stratification curve at the saturation point, ϵ and ϵ_2 are respectively the dielectric constants of the drop and of the solution, and ze is the charge of the ion.

For the solution of nitrobenzene in hexane used in the present investigation, with concentrations 0.2 and 0.3, the values of ΔP calculated from formula (1) lie in the range 25–30 atm.

B. Effect of heating. Solutions having a lower critical stratification temperature can be supersaturated by pulsed heating[1]. The magnitude of the superheating ΔT, corresponding to the initial limit of the sensitivity of the solution to stratification of ions, is obtained from the formula

$$\Delta T = \frac{3}{2}\frac{MC}{\rho RT}\frac{1}{\partial C/\partial T}\left(\frac{4\pi\sigma^4}{(ze)^2}\frac{\varepsilon\varepsilon_2}{\varepsilon_2-\varepsilon}\right)^{1/3}. \tag{2}$$

We have used here the same notation as in expression (1). For the indicated solution of water in triethylamine, the value of ΔT obtained in accordance with this formula is approximately 1°.

C. Action of electric field. In accordance with the general theory of solubility of substances, the saturation of a solution depends on the electric field in its volume. In general form, this dependence is complicated and will be presented, together with the derivation, in a separate paper. Here we present only the result of an approximate calculation for a solution of nitrobenzene in hexane with weight concentration 0.2. It follows from the theory that an increase of the field intensity in a saturated solution by 200 kV/cm leads to its supersaturation by 0.5%. To reach the initial limit of sensitivity of the solution to stratification and ions, the required field is

$$E \sim 4.5 \cdot 10^5 z^{-1/3} \text{ V/cm.} \tag{3}$$

3. EXPERIMENTAL VERIFICATION OF THE INFLUENCE OF γ RADIATION ON THE STRATIFICATION OF A SOLUTION

The effect of stratification of solutions was observed in all the experiments with the aid of a photomultiplier that registered the scattering or absorption of the light passing through the solution. The measure of the influence of the γ radiation on the stratification process was the change of the rise time τ of the pulse from the photomultiplier. This method, in our opinion is the most sensitive. In fact, the rate of stratification of a solution, at specified conditions, is determined by the intensity of generation of stratification centers, on which the excess dissolved matter is deposited. Without irradiating the solution, such nuclei are produced on microfluctuations of the concentration, and in the case of the irradiation also on the ions. Therefore the formation time τ, which depends on the rate of accumulation of the light scattering in absorbing droplets in the volume of the solution, should be different for irradiated and non-irradiated solutions.

In addition to the photomultiplier and the oscilloscope used to measure the temporal characteristics of the pulse, the setup contained a thermostatic bath, pressure and temperature pickups, a cell with the investigated solution, and an illuminator producing a stable parallel light beam. The setup was equipped also with a system of gas-bypass valves, a pulsed heater, and a generator of high-voltage pulses. The source of the γ quanta was a cell with Co^{60}, rated 60 mg equivalent of radium in the first three experiments and 0.45 mg equivalent of radium in the last experiment. The distance between the source and the cell with the solution was 40 cm. The cell was thermostatically controlled in a bath near the supersaturation point, accurate to $\pm 0.05°$. The cell was illuminated continuously. The start of the oscilloscope was synchronized with the instant of the start of supersaturation of the solution.

A. Experiment with pressure. In the case of slow application of a pressure of 25—30 atm, the stratification point of the solution of nitrobenzene in hexane shifts by 0.4°. On the other hand, when this pressure is removed suddenly, the change of the stratification temperature was 0.7°, of which 0.4° was due to the effect of removing the pressure and 0.3° to the adiabatic expansion of the solution.

The pressure in the investigated cell, with a value of 15 cm^3, was produced with the aid of a gas that was separated from the solution by a moving bellows. It was found in these experiments that when the solution is irradiated with γ quanta, the rise time of the pulse is about one-third shorter than without irradiation. The absolute value of τ was $\sim 10^{-3}$ sec. It is appropriate to note here that the effective stratification of the solution following pulsed removal of the pressure is very clearly observed also visually. The dimensions of the drop released from the solution, determined in a separate experiment, was 6 μ.

A second experiment using pressure was performed, as already mentioned, with a solution of carbon dioxide in benzene. When this solution is supersaturated, crystalline solvates are precipitated. We propose to use this circumstance in the experiment.

Carbon dioxide gas was fed to a cell filled with benzene at a pressure of 12 atm, and the entire solution was cooled to a temperature $-4°$ C. When the pressure was dropped to 1 atm, the system was supersaturated and supercooled by 9°. In this situation, two processes could occur: formation of crystalline solvates, and degassing of the liquid by formation of bubbles. It was expected that strong supercooling of the benzene would greatly increase its viscosity and prevent direct bubble degassing, and that the process of formation of solvate crystals would be predominant. Assuming that the electric polarizability of the solvate molecules is higher than in the solution from which they are formed, it was expected, in accordance with the theoretical predictions, that the nucleation of the solvate crystals would occur predominantly on the ions produced by the γ radiation. Actually, however, it turned out that when the pressure was dropped intense boiling of the benzene took place, and the effect of crystal solvate formation was lost against the background of the upward-floating bubbles. To suppress the boiling it is apparently necessary to compress the solution beforehand at high pressure, thereby eliminating the micronucleation of the bubbles.

B. Experiment with heating. The experiment was performed with a solution of water in triethylamine with molar concentration 0.4. Such a binary liquid system has, as is well known, a lower critical stratification temperature near 18—19°. When the solution is heated above this temperature, it breaks up into two liquid phases.

In the experiment, a glass cell with the solution was thermostatically controlled at a temperature 1° below the stratification point. The solution was heated by a current pulse passing through a calibrated nichrome coil wound on the cell. The time of heating the solution above the stratification point was 0.5—1 sec. In this experiment, only a weak correlation was observed between the rate of stratification of the solution and the irradiation.

C. Experiment with electric field. In accordance with formula (3), the fields necessary for the stratification of the solution are close to the breakdown fields. Therefore particular attention was paid in the experiment to running off the edges of the electrodes and to their thorough polishing. The cell contained two such electrodes, completely immersed in a solution of nitrobenzene in hexane with weight concentration 0.2. The interelectrode gap was 0.2 cm, and the field intensity in it was about 200 kV/cm. The field was produced in pulses of duration $\sim 10^{-3}$ sec and of frequency once every 10 minutes. The solution in the cell was thermostated at 0.1—0.01° above the stratification point.

In the experiment with transmitted light, it was found that in the absence of irradiation of the solution the pulse rise time was 4×10^{-4} sec, but for light scattered through an angle of 24° it amounted to 2.5×10^{-5} sec. These times do not include the lifetime of the solution in the metastable state, i.e., the time between the instant of supersaturation of the solution and the start of the appearance of the pulse on the photomultiplier. This time was not measured in the experiment.

The great difference between the rise times of the pulse front was connected with the induced change of the sensitivity of the apparatus when the photomultiplier was shifted from the directly-passing beam to the scattered beam. In the latter case, the sensitivity of the recording apparatus was set to be several orders of magnitude higher than for the transmitted light. Therefore the process of stratification of the solution in these two experiments was observed at different stages of its development.

It was established that irradiation of the solution with γ quanta leads to a decrease of the pulse rise time by approximately a factor of 1.5. From a comparison of this result from the data of an experiment in which the pressure was varied we see that the stratification of the solution following application of an electric field is more intense than when the pressure is dropped. This circumstance is apparently connected with possibly somewhat different experimental conditions, and also with the fact that a high-voltage electric field increases partly the concentration of the ions produced in the solution by the γ quanta.

It is appropriate to mention here the clearly pronounced glow of the solution, observed when the field intensity in it reached 300—400 kV/cm.

4. BRIEF CONCLUSIONS

The main results obtained in the present investigation can be formulated as follows:

1. The ions produced by γ quanta in a metastable solution accelerate its stratification.
2. The drops produced upon stratification of the solution have a dimension of several microns.
3. The most convenient methods of increasing pulsewise the sensitivity of the solution to stratification on ions are methods connected with variation of the pressure or of the electric field.
4. The data obtained in this investigation can serve as a basis for further searches for ways of developing a controlled liquid track chamber.

In conclusion, the authors consider it their duty to thank V. M. Sheshunov, T. N. Antonov, and N. I. Chernov for help with the work.

---

[1] A. F. Pisarev, V. A. Biryukov, Zh. Eksp. Teor. Fiz. **54**, 469 (1968) [Sov. Phys.-JETP **27**, 255 (1968)].

Transl. by J. G. Adashko