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EFFECT OF ELECTRIC FIELDS ON STRATIFICATION OF SOLUTIONS ON IONS

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The effect of an electric field on supersaturation and stratification of a binary liquid solution on ions is considered. It is shown that in strong electric fields exceeding a certain value an ionic component, which possesses a large dielectric constant, is liberated from the solution. This conclusion qualitatively agrees with the results of an experiment performed for a solution of nitrobenzene in hexane irradiated by γ-quanta. The present investigation may serve as a basis for further studies of the behavior of solutions in electric fields with the aim of elucidating means of designing controlled liquid track chambers.

INTRODUCTION

PREVIOUSLY published papers[1-3] have discussed the possibility of developing a new type of track chamber by using the effect of stratification of binary liquid solutions under the influence of a pulsed pressure or temperature. It is shown theoretically in these papers that the ions produced by the particle in the solution become active centers of its stratification upon supersaturation. Microscopic centers for the formation of the new phase are produced on these ions and subsequently grow to visible dimensions. In order to verify this conclusion qualitatively, a special experiment was performed with a solution of nitrobenzene in hexane, irradiated with γ quanta from a cobalt source. It was established experimentally[4] that a definite relation exists between the density of the ions produced in the solution and the rate of the stratification of this solution. In the same experiment it was also noted that a high-voltage pulsed electric field has a noticeable influence on the degree of supersaturation of the solution and on the rate of its precipitation on the ions. This circumstance, in our opinion, is very interesting, for if the stratification effect is to be used in practice for particle registration, control of this process with the aid of an electric field may turn out to be the simplest. The possibility of such a prospect has induced us to carry out a theoretical analysis of supersaturation, produced by the influence of an external electric field, of a solution and its stratification on an ion. We present below the results of this analysis and of their experimental verification.

2. INFLUENCE OF ELECTRIC FIELDS ON THE SOLUTION CONCENTRATION

It follows from the general premises of non-equilibrium thermodynamics[5] that application of an electric field on a solution changes its thermodynamic potentials. One of the reactions of the solution to the change of these potentials is the change of the solution concentration. Let us determine the magnitude of this change.

The Gibbs thermodynamic potential for a solution placed in an electric field on intensity E is equal to[5]

$$\Phi = U + PV - TS - W, \quad W = \frac{\varepsilon E^2}{4\pi} V, \tag{1}$$

where U is the internal energy of the solution, S its entropy, P the external pressure, T the absolute temperature, E the intensity of the electric field in the solution, ϵ the dielectric constant of the solution, and V the specific volume of the solution. The independent variables in this potential are P, T, and E. At the first-order phase transition point—the stratification point—equilibrium should obtain between the old and new phases. In terms of thermodynamics, this should mean equality of the total differentials of the thermodynamic potentials of the two co-existing phases[6], i.e.,

$$d\Phi_1 = d\Phi_2. \tag{2}$$

Calculating the differentials of each of the terms in the right side of (1) we get

$$\begin{aligned}
dU &= \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT \\
&= \left[-T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T\right] dP + \left[C_P - P\left(\frac{\partial V}{\partial T}\right)_P\right] dT, \\
d(PV) &= \left(\frac{\partial (PV)}{\partial P}\right)_T dP + \left(\frac{\partial (PV)}{\partial T}\right)_P dT \\
&= \left[V + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP + P\left(\frac{\partial V}{\partial T}\right)_P dT, \\
d(TS) &= \left(\frac{\partial (TS)}{\partial P}\right)_T dP + \left(\frac{\partial (TS)}{\partial T}\right)_P dT = T\left(\frac{\partial V}{\partial T}\right)_P dP + C_P dT + S dT, \\
dW &= \left(\frac{\partial W}{\partial T}\right)_{P,E} dT + \left(\frac{\partial W}{\partial P}\right)_{T,E} dP + \left(\frac{\partial W}{\partial E}\right)_{T,P} dE \\
&= \left[\frac{E^2}{4\pi} V \left(\frac{\partial \varepsilon}{\partial T}\right)_{P,E} + \frac{\varepsilon E^2}{4\pi}\left(\frac{\partial V}{\partial T}\right)_{P,E}\right] dT \\
&+ \left[\frac{E^2}{4\pi} V \left(\frac{\partial \varepsilon}{\partial P}\right)_{T,E} + \frac{\varepsilon E^2}{4\pi}\left(\frac{\partial V}{\partial P}\right)_{T,E}\right] dP \\
&+ \left[\frac{\varepsilon E}{2\pi} V + \frac{\varepsilon E^2}{4\pi}\left(\frac{\partial V}{\partial E}\right)_{T,P}\right] dE.
\end{aligned}$$

Substituting now these expressions in (2), we get

$$\begin{aligned}
\Delta\Big\{\Big[V - \frac{E^2}{4\pi}\Big(V\frac{\partial \varepsilon}{\partial P} + \varepsilon\frac{\partial V}{\partial P}\Big)\Big] dP - \Big[\frac{E^2}{4\pi}\Big(V\frac{\partial \varepsilon}{\partial T} + \varepsilon\frac{\partial V}{\partial T}\Big) + S\Big] dT \\
- \Big[\frac{\varepsilon E}{2\pi} V + \frac{\varepsilon E^2}{4\pi}\Big(\frac{\partial V}{\partial E}\Big)\Big] dE\Big\} = 0.
\end{aligned} \tag{3}$$

The symbol Δ denotes the difference between the quantities pertaining to the new and the old phases, for example, $\Delta V = V_2 - V_1$, where V_2 and V_1 are the specific volumes of the new and old phases, respectively.

We consider next the case when the external pressure in the system remains unchanged, i.e., $dP = 0$. It can be shown by numerical calculations that for weakly-polar liquid solutions (these are the only ones of interest to us) the electrostriction change of the volume is $\partial V/\partial E \approx 0$. Taking this approximation into account, we can rewrite (3) in the form

$$\Delta\left\{\left[\frac{E^2}{4\pi}\left(V\frac{\partial\varepsilon}{\partial T}+\varepsilon\frac{\partial V}{\partial T}\right)+S\right]dT+\frac{\varepsilon E}{2\pi}VdE\right\}=0. \tag{4}$$

This equation is the starting point for the determination of the shift δT of the stratification temperature of the solution when an electric field is applied to it. It follows from (4) that

$$\delta T=-\frac{A}{2\pi}\int_0^E\frac{EdE}{BE^2/4\pi+q/T}=-\frac{A}{B}\ln\frac{BE^2/4\pi+q/T}{q/T},$$
$$A=\varepsilon_2V_2-\varepsilon_1V_1,\quad B=V_2\frac{\partial\varepsilon_2}{\partial T}-V_1\frac{\partial\varepsilon_1}{\partial T}+\varepsilon_2\frac{\partial V_2}{\partial T}-\varepsilon_1\frac{\partial V_1}{\partial T}. \tag{5}$$

We took into account here the fact that $S_2 - S_1 = q/T$, where q is the heat of stratification. The shift of the stratification temperature by δT is equivalent to supersaturation of the solution, which is equal to

$$\delta C=\frac{\partial C}{\partial T}\delta T, \tag{6}$$

where $\partial C/\partial T$ is the derivative along the stratification curve at the point C.

3. VALUE OF CRITICAL FIELD

The field corresponding to the upper limit of sensitivity of the solution to stratification on ions will be called the critical field. It follows from[2] that the critical supersaturation of the solution, at which the ions become centers of stratification, is equal to

$$\delta C_c=\frac{3}{2}\frac{MC}{\rho RT}\left(\frac{4\pi\sigma^4}{(Ze)^2}\frac{\varepsilon_1\varepsilon_2}{\varepsilon_2-\varepsilon_1}\right)^{1/3}, \tag{7}$$

where ρ is the density of the solution in the drop, M the molecular weight of the substance in the drop, Ze the charge of the ion, and σ the surface tension on the interface between the solution and the drop produced on the ion. Combining now relations (5)–(7) and solving the resultant expression with respect to E_c, we get

$$E_c=\left\{4\pi\frac{q}{T}\frac{1}{B}\left[\exp\left(-\frac{B}{A}\frac{1}{\partial C/\partial T}\delta C_c\right)-1\right]\right\}^{1/2}. \tag{8}$$

The absolute value of the argument of the exponential in (8) is much smaller than unity for all values of the parameters characterizing the stratifying solutions. Therefore the exponential term can be expanded in a power series, of which only the first two terms need be retained. Performing this operation and simple transformations, we obtain

$$E_c=\left\{-4\pi\frac{q}{T}\frac{1}{A}\frac{1}{\partial C/\partial T}\delta C_c\right\}^{1/2}. \tag{9}$$

The physical meaning of this equation is as follows: when the electric field intensity increases to a value E_c, nuclei of radius $r \geq r_c$ will grow on the ions in the solution; r_c is given by[2]

$$r_c=\left[\frac{(Ze)^2(\varepsilon_2-\varepsilon_1)}{4\pi\sigma\varepsilon_1\varepsilon_2}\right]^{1/3}.$$

On the other hand, with further increase of the field ($E > E_c$), all nuclei, no matter how small, will grow on the ions.

We do not consider here the growth kinetics of the nucleus, since this problem is solved in[3].

4. COMPARISON WITH EXPERIMENT. CONCLUSION

To verify the validity of (9) and consequently the possibility of controlling the stratification of the solution on ions by applying an external field, an experiment was performed with a solution of nitrobenzene in hexane (weight concentration 0.2). Near the stratification point, at a temperature $T = 288°K$, this solution is characterized by the following data: $M = 100$ g/mole, $\rho = 0.87$ g/cm^3, $\epsilon_1 = 2$, $\epsilon_2 = 5$, $\sigma = 0.5$ dyne/cm, $q/T = -0.24$ cal/g-deg, $V_1 = 1.36$ cm^3/g, $V_2 = 1.16$ cm^3/g, $\partial C/\partial T = 0.03$ deg^{-1}. Substituting these data in (19), we get

$$E_c \approx 400\,Z^{-1/3}\,[\text{kV/cm}] \tag{10}$$

where Z takes on the values 1, 2, 3, ... and is a multiple of the ion charge. At $Z = 1$ we get $E_c = 400$ kV/cm, and at $Z = 2$ we get $E_c = 320$ kv/cm. We see that the critical value of this field is close in order of magnitude to the breakdown field. Therefore special attention was paid in the experiment to rounding off the edges of the electrode and to polishing the electrodes carefully. The cell with the solution contained two such electrodes, and the gap between them was 0.3 cm. The solution was thermostatically maintained at a temperature 0.01–0.05° above the stratification point.

In the experiments, the cell with the solution was irradiated with quanta from a cobalt source with intensity 0.45 mg-eq of radium. The distance between the cell and the source was 40 cm. The electric field applied to the solution was chosen to be lower than the breakdown value. At a pulse duration 10^{-3} sec, it turned out to be 200 kV/cm. On the other hand, in fields of 200–400 kV/cm, a strong glow of the solution was observed, definitely pointing to the presence of secondary processes connected with a partial electric discharge in the solution.

The effect of stratification of the solution was observed experimentally 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 in the rise time τ of the leading front of the pulse received from the photomultiplier. This method is in our opinion the most sensitive since the solution stratification rate at a given supersaturation is determined by the intensity of generation of the stratification centers on which the excess of the dissolved matter is separated. If the solution is not irradiated, such nuclei should occur on microscopic fluctuations of the concentration, and in case of irradiation they should also occur on ions. Consequently, the rise time τ, which depends on the rate of accumulation of light scattering and absorbing droplets in the volume of the solution, should be different for irradiated and non-irradiated solutions.

The experiment has demonstrated that irradiation of the solution with γ quanta in the absence of an electric field causes no stratification. On the other hand, application of a field pulse with intensity ~200 kV/cm and duration 10^{-3} sec always causes stratification, with and without irradiation. However, the solution stratification rate is approximately 1.5 times larger with irradiation than without irradiation. This fact was unambiguously confirmed both with transmitted and scattered light beams. This result can be explained by assuming that the ions produced by the gamma quanta accelerate the drop-generation process in the supersaturated solution.

The field used in the experiment was lower than the calculated field. This quantitative difference is apparently connected with three circumstances. First, in the calculation of E_c by means of formula (9) approximate data were used for q/T and σ, which might have led to a certain overestimate of the critical field. Second, the ions in the solution could be partially multiplied under the influence of the high-voltage field, and form charged complexes with a total charge $Z > 1$. This phenomenon, in accordance with expression (10), could decrease the value of E_c. Finally, third, the field applied to the solution could change the dynamics of the ion-recombination process, in particular, slow this process down. This could result in an increase of the ion density in the solution, and consequently in the formation of microcomplexes with charge $Z > 1$. In other words, this phenomenon, as well as the multiplication of charges under the influence of the fields, is likewise capable of lowering the critical value of the field.

Additional investigations of these phenomena is of undisputed interest, since it can lead to the development of a new liquid particle track detector controlled by an electric field.

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