SOVIET PHYSICS JETP VOLUME 30, NUMBER 2 FEBRUARY, 1970

EFFECT OF EXTERNAL FIELDS ON THE THERMODYNAMIC PROPERTIES OF SOLUTIONS AND SURFACE TENSION

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Submitted February 12, 1969

Zh. Eksp. Teor. Fiz. **57**, 529–533 (August, 1969)

It is shown that an external electric field can transform an exothermal (endothermal) solution into an endothermal (exothermal) one. The effect of electric and magnetic fields on the coefficient of surface tension is investigated; it is found that both its magnitude and sign may change.

THE properties of binary solutions in an external electric field E close to the critical point have been studied by Voronel' and Giterman.[1] It has been shown that the relative change in critical values brought about by the electric field is very small. Thus, for example, the relative change in the critical temperature is $\Delta T_c/T_c \approx 3 \times 10^{-6}$ for a field $E \approx 50$ kV/cm. In the present paper, we shall show that in liquid dielectrics and their solutions, an external electric field of a given value can not only lead to a relative change in the characteristic quantities (for example, the osmotic pressure and the latent heat of transition) that is approximately 100 times greater than in[1] but also cause qualitative changes: if the solution in the absence of the field was endothermal (exothermal), then the presence of the electric field can make the solution exothermal) (endothermal).

Further, we shall investigate the effect of external electric and magnetic fields on the surface tension of weak solutions of electrolytes and solids (semiconductors and metals) with current carriers of both signs. By a method similar to that used by Onsager and Samarus[2] (see also the book by Landau and Lifshitz[3]), we shall show that the presence of external fields can not only increase significantly the coefficient of surface tension α, such that $\Delta\alpha(E, H)/\alpha_0 \gtrsim 1$ (the index zero indicates the value in the absence of external fields), but also lead to a change in the sign of α.

The latter result becomes understandable if we take into account the fact that non-parallel electric E and magnetic H fields in a bounded medium can lead to an increase or decrease in the concentration of current carriers (ions in the case of solutions, electrons and holes in crystals) at the boundary of the medium. However, as has been shown,[2,3] an increase (decrease) in the concentration of carriers associated with the presence of a boundary of the medium should lead to a decrease (increase) in the coefficient of surface tension. We note that if we consider the boundaries of a solution at the medium in which the dielectric constant is greater than the dielectric constant of the solution, then the results of[2,3] lead to a decrease in the coefficient of surface tension, while it is not difficult to furnish conditions under which the surface tension changes sign.

In the present article, we shall not investigate the oscillations of the liquid or crystalline plates associated with the dependence of the coefficient of surface tension on external fields, as this goes beyond the framework of this article.

1. THERMODYNAMIC PROPERTIES OF SOLUTIONS IN EXTERNAL FIELDS

Without taking up model representations, we can (see, for example,[4]) write down the dielectric constant of a solution of concentration c_n in the form

$$\varepsilon = \varepsilon_N(1 + bc_n), \tag{1}$$

where b is a number of the order of unity, which is positive (negative) if the dielectric constant of the solute ϵ_n is larger (smaller) than the dielectric constant of the solvent ϵ_N; in (1) and everywhere below, it is assumed that $c_n \ll 1$. It is also possible without model representations[4] to write down the chemical potential of the i-th type of particles in an electric field:

$$\zeta_i = \zeta_{i0} - \frac{v}{8\pi}\frac{\partial\varepsilon}{\partial c_{ni}}E^2 \tag{2}$$

(v is the volume per particle). Using (1) and (2), we can, in the usual way, find the heat of solution of a single molecule in the electric field:

$$Q_E = Q_0 + \Delta Q_E = T\frac{\partial \ln \tilde{c}_n}{\partial \ln T} + \frac{b}{8\pi}\varepsilon_N v E^2$$

($\tilde{c}_n$ is the concentration of the saturated solution, T the temperature in energy units).

The value of ΔQ_E can be either positive (for $\epsilon_n > \epsilon_N$) or negative (for $\epsilon_n < \epsilon_N$); $|\Delta Q_E|$ can be larger than $|Q_0|$. Thus, for a solution of nicotine in water or water in nicotine, in the temperature range 100–140°C, the value of $Q_0 = 0$,[5] while $\Delta Q_E < 0$ in the first and $\Delta Q_E > 0$ in the second case. For a solution of SO_2 in water at a temperature of 90–95°C, $Q_0 > 0$,[5] while $\Delta Q_E < 0$, and even for fields of the order of 50 kV/cm the solution changes from exothermal to endothermal.

We proceed to quantitative effects. Using (1) and (2), we find the correction to the osmotic pressure P_{osm}:

$$\frac{\Delta P_{\text{осм}}}{P_{\text{осм}}} = \frac{b}{8\pi}\frac{\varepsilon_N E^2}{T},$$

In dimethoxyethane[6] at room temperatures and for fields of the order of 50 kV/cm, this quantity reaches 10^{-3}, and up to 0.1 in prebreakdown fields (about 300 kV/cm). This correction does not depend on the difference in concentrations and can be both positive and negative. Precisely the same correction exists in Raoult's law, while in Henry's law the concentration depends on the field in exponential fashion:

$$c \backsim \exp\left(\frac{b}{8\pi}\frac{\varepsilon_N v E^2}{T}\right).$$

(We note that the electric field does not change the effect of two soluble materials on their solubility.)

We shall also point out one effect which is not connected with the binarity of the solution and which is related to the phase transition (which is considered in[1]), that, is, to the effect of the electric field on the heat of transition. Calculation shows that the relative change in the heat of transition q is equal to

$$\frac{\Delta q}{q_0} = \frac{\varepsilon_2 - \varepsilon_1}{8\pi}\frac{E^2}{q_0 p}$$

($\epsilon_{1,2}$ is the dielectric constant in the two phases). For ethyl alcohol at fields of the order of 50 kV/cm, this quantity reaches 1.5×10^{-4}, while in prebreakdown it is close to unity.

2. SURFACE TENSION OF WEAK SOLUTIONS OF ELECTROLYTES IN EXTERNAL FIELDS

In the calculation of the change in the surface tension in external fields, we shall start out from the relation[2,3]

$$\frac{\Delta\alpha}{\alpha_0} = -\frac{T}{S\alpha_0}\sum_i (N_i - N_{i\infty})\, d\ln c_i, \tag{3}$$

where $N_{i\infty} = SLn_{i\infty}$ is the number of ions of the i-th type of the dissolved substance, which corresponds to the distribution of ions with concentration equal to the concentration of an unbounded solution, per area S of the surface of the liquid of depth L; N_i is the number of ions of the i-th type in the medium of depth L and surface area S. If we direct the z axis normal to the liquid boundary, then

$$N_i - N_{i\infty} = S\left[\int_0^L n_i(x)\,dx - n_{i\infty}L\right]. \tag{4}$$

Thus the problem reduces to finding the function $n_i(x)$ connected with the presence of the boundary of the liquid and brought about by the external fields. We consider two cases.

A. Nonparallel electric and magnetic fields. From the expression for the flux of particles in the direction of the liquid boundary

$$j_{\pm x} = -D_\pm \frac{dn_i}{dx} \pm \mu_\pm E_x n_i + \mu_{1\pm} n_i [\mathbf{EH}]_x = 0$$

we find

$$n_i(x) = C_i \exp\left\{\frac{e[\mathbf{EH}]_x x}{Tc}(\mu_+ + \mu_-)\right\} = C_i \exp\left(\beta\frac{x}{L}\right) \tag{5}$$

where $\mu_\pm$, $\mu_\pm$, $D_\pm$ are the mobility, Hall mobility and the diffusion coefficient for ions of different charge sign, c is the speed of light, n_i the concentration of the ions. It is assumed that $\mu_1 H \approx \mu^2 H/c \approx \mu(\Omega\tau)$. Taking into account the fact that[5] $\mu_\pm \approx 1$ absolute unit, it is easy to see that in real circumstances, $\beta \ll 1$ and, with accuracy up to β^2 we have $C_i = n_{i\infty}$. Then, substituting (4) and (5) in (3), we find

$$\frac{\Delta\alpha}{\alpha_0} = -\frac{e}{\alpha_0} n_{i\infty} [\mathbf{Eh}]_x [(\Omega\tau)_+ + (\Omega\tau)_-] L^2,$$
$$\mathbf{H} = \mathbf{h}H.$$

As is seen, by changing the directions of the fields, we can change the sign of $\Delta\alpha$. The value of $\Delta\alpha/\alpha_0$ reaches unity at $L \approx 1$ cm, $\alpha_0 \approx 10^2$ erg/cm², $c_i \approx 10^{-2}$, $E \approx 30$ V/cm and $H \approx 10^3$ Oe. (Estimates show that for these conditions, the joulean heating is still small and the change in temperature can be neglected.)

We shall show that for inhomogeneity of temperature in the direction of the x axis, a similar calculation leads to the expression

$$\frac{\Delta\alpha}{\alpha_0} \approx \frac{n_{i\infty} T L \delta}{\alpha_0}\left[L\frac{d\ln T}{dx}\right],$$

where δ is of the order of unity.

B. Strong electric field. When a sufficiently strong current flows through the solution of an electrolyte, the magnetic field of the current leads to a compression of the ions in a direction perpendicular to the direction of the current, i.e., to the pinch effect. Under real conditions, only a weak pinch effect is possible, when the change of the ionic distribution is still small. Using the results of Stephanovich[7], we find that

$$n_i = n_{i\infty}[1 - (x/L)^2 (I/I_c)^2],$$

where I is the current density and

$$I_c = \frac{n_{i\infty} c}{L}\sqrt{\frac{T}{\pi n_{i\infty}}}.$$

We then find, according to (3) and (4),

$$\frac{\Delta\alpha}{\alpha_0} = \frac{n_{i\infty} T L}{\alpha_0}\left(\frac{I}{I_c}\right)^2 > 0.$$

For the values of α and $n_{i\infty}$ given above and $T \approx 4 \times 10^{-14}$ erg, we have $\Delta\alpha/\alpha_0 \gtrsim 1$ for $(I/I_c)^2 \gtrsim 10^{-2}$, which is entirely attainable.

We have limited ourselves in this section to the case of ions of two types. The results are not changed upon increasing the number of types of ions.

3. SURFACE TENSION OF CRYSTALS IN THE PRESENCE OF EXTERNAL FIELDS

In the case of a metal or semiconductor with current carriers of both signs, external fields can lead to an excess or a deficiency of electrons and holes at the boundary of the crystal if the surface recombination is sufficiently small. We shall consider just such a case. (In the case of current carriers of the same sign, the corrections to the coefficient of surface tension do not exceed 10^{-6}. We limit ourselves to the case of equal concentrations of electrons and holes, since in improper crystals the effects are smaller although still completely observable. In improper crystals, the method of calculation is the same but the formulas are more involved.) By the method used in[2,3], we find that (ζ is the chemical potential of the particles)

$$d\alpha = -2S^{-1}\sum_i (N_i - N_{i\infty})\, d\zeta.$$

As in Sec. 2, the problem reduces to finding $n_i(x)$. Calculation shows that the pinch effect cannot lead to a noticeable change in the coefficient of surface tension. For nonparallel electric and magnetic fields, in contrast to the case of a liquid, one must take into account the recombination in the volume, and the quantity characterizing the change in concentration is not β but $\beta L_D/L$, where $L_D = \sqrt{D}\,\tau^*$ is the diffusion length, τ^* the lifetime of the excess carriers.

For $\beta L_D/L > 1$, which is the case of $IH > c\xi n L_D^{-1}$, we have

$$\Delta\alpha / \alpha_0 \approx \zeta nL / \alpha_0;$$

for $\beta L_D/L < 1$, it will be

$$\Delta\alpha / \alpha_0 = IHL_D^2 / c\alpha_0.$$

Estimates show that the value $\Delta\alpha/\alpha_0 \approx 1$ is attainable in semiconductors for $L \approx 0.1$ cm $< L_D$ and $n \approx 10^{18}$ cm^{-3} (which is reached, for example, in germanium upon irradiation) for $IH > 10^3$A-Oe/cm^2. In metals, the condition $IH > c\xi n/L_D$ is unattainable and the largest values of $\Delta\alpha/\alpha_0$ do not exceed 0.2.

[1] A. V. Voronel' and M. Sh. Giterman, Zh. Eksp. Teor. Fiz. 55, 2459 (1968) [Sov.-Phys.-JETP 28, 1310 (1969)].

[2] L. Onsager and N. T. Samarus, J. Chem. Phys. 2, 528 (1934).

[3] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics) Nauka, 1964).

[4] L. D. Landau and E. M. Lifshitz, Elektrodinamika sploshnykh sred (Electrodynamics of Continuous Media) (Fizmatgiz, 1959).

[5] Spravochnik Khimika (Handbook of Chemistry) 3, Gostekhizdat, 1962).

[6] G. V. Hormont, Angewandte Chemie, 79, 1029 (1967).

[7] A. E. Stefanovich, Fiz. Tverd. Tela 9, 2035 1967) [Sov. Phys.-Solid State 9, 1598 (1968)].

Translated by R. T. Beyer
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