

Order parameter in the vicinity of the double critical point of stratification

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The results have been presented of an investigation of the conductivity and IR absorption spectra of the propanol-water solution with a NaCl impurity having a double critical point of stratification. By making use of the conductivity measurement results, the phase diagrams have been restored with respect to each component of the solution. It has been shown that, in describing phase equilibria in multicomponent systems, the difference of the concentration of any component, including an impurity, as well as the difference of the conductivity and near-IR absorption in coexisting phases, may be chosen as the order parameter.

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INTRODUCTION

In describing phase transitions the most complex objects are multicomponent fluid systems. The complexity of the description is due to both the great number of required independent variables and the existence of several multiphase stratification regions in such systems, i.e., the existence of several critical points being able to merge with each other [1–5].

The universal character of regularities observed in phase transition processes allows critical phenomena of different natures to be regarded as isomorphous [6]. The term isomorphism means identical functional dependences of thermodynamic quantities on the order parameter and the temperature [7]. A proper choice of the order parameter enables one to obtain a simple description of extremely fluctuating systems in the framework of the scaling-invariant theory. In the case of one- and two-component systems it is natural to introduce the difference of the concentrations of identical components in coexisting phases as an order parameter. Such a choice is completely unambiguous. In three-component solutions the conservation of isomorphism is conditioned by the constancy of the third component [7,8]. This condition is difficult to observe in experiments. In the case of the investigation of multicomponent solutions the situation is essentially complex, and a matter of unambiguous choice of the order parameter remains open.

EXPERIMENTAL DETAILS

Measurements of temperature and concentration dependences of the conductivity and IR-absorption spectra were carried out in both one- and two-phase regions. When investigating conductivity, we used a cell with two pairs of platinum electrodes on its top and bottom parts. Readings from the electrodes were equalized by the calibration in a sodium chloride aqueous solution. The conductivity was determined by the bridge method at a frequency of 1 kHz. The measurement's accuracy amounted to 0.03%, while the accuracy of the thermostating was 0.02 K.

An installation with light detectors connected in the compensating circuit [9] was used when studying absorption spectra. The installation had been designed on the basis of an ordinary monochromator. A hermetically sealable quartz cell with a thickness of about 1 mm was filled up with the solution under investigation. The cell was thermostatted with an accuracy of no worse than 0.2 K. The absorption measurement accuracy was 0.5%.

A propanol-water-NaCl solution has been chosen as the object of the investigation. In this solution at an external pressure equal to atmospheric, one can observe the double critical point (DCP) with the following state parameters [6]: the basic component concentration $X = X_0 = 0.15$ m.f. propanol in water (m.f. denotes mole fraction), the salt concentration $C = C_0 = 5.383$ mass % and the temperature $T = T_0 = 45.1^\circ\text{C}$. Solutions on propanol subjected to additional redistillation, doubly distilled water, and NaCl salt of chemically pure grade, were prepared. The accuracy of the preparation of the solutions was no worse than 0.01%.

DISCUSSION OF THE OBTAINED RESULTS

The three-dimensional phase diagram of a binary solution with the closed stratification region on the X, P coordinates is a dome-shaped surface, the vertex of which coincides with the DCP. As a rule, three-component solutions are used to obtain double critical points. For such solutions the stratification dome on the X, P coordinates is badly deformed, the location of the DCP on the coexistence surface had not been determined previously and, as a rule, it does not coincide with the vertex of the stratification dome [6]. A propanol-water-NaCl solution relates to such a system.

The coexistence surface of the ideal binary solution can be described by the following relations [6]:

$$\Delta X \sim [(T_u - T)(T - T_1)]^{\beta_T}, \quad (1)$$

$$\Delta X \sim (P - P_0)^{\beta_P}, \quad (2)$$

$$T - T_0 \sim (P - P_0)^{\beta_0}, \quad (3)$$

where ΔX is the difference of concentrations of coexisting phases; β_T, β_P are critical exponents of the order parameter; β_0 is the critical exponent describing the dependences of the upper (T_u) and lower (T_l) critical temperatures on pressure.

For a solution in which the double critical point has been obtained by introduction of the third component at fixed external pressure, Eqs. (2) and (3) can be written as

$$\Delta X \sim (C - C_0)^{\beta_P}, \quad (4)$$

$$(T - T_0) \sim (C - C_0)^{\beta_0}. \quad (5)$$

When making use of Eq. (4) and (5) it should be taken into account that there is a difference in principle between the change in pressure and the introduction of the impurity. In the case of stratification in a binary system resulting from the change in external pressure, only intermolecular interactions between solution molecules are changed, and the connecting lines are parallel to the concentration axis. The influence of the impurity on a binary system is revealed in two ways. When changing the concentration of the impurity, not only is the intermolecular interactions between basic components changed but also the composition. When a binary solution contains an impurity, the connecting lines may be parallel to the concentration axis only in the case of the third component having equal solubilities in both phases (fairly rare case). In the presence of the impurity component, the expressions (1), (4), and (5) take the form

$$\Delta X = A[(T - T_0)^2 - \Delta T^2]^\beta, \quad (6)$$

where ΔX is the difference of the basic solution concentrations in coexisting phases and ΔT is the difference of the upper and lower stratification critical point temperatures. The power of 2 in this equation shows parabolicity of the dependences of the stratification critical temperatures on pressure or concentration of the impurity component, i.e., it shows that the exponent $\beta_0 = 0.5$. This value, found from the theoretical premises, has been repeatedly confirmed experimentally [6, 8–14]. It is to be

noted that proper application of Eq. (6) is possible only in the case of changing the composition of basic components with the chemical potential of the impurity component being held constant. The correctness of the relations (1) and (6) for this instance has been confirmed in Ref. [6] for the cross sections along connecting lines obtained experimentally. In this case the slopes of the connecting lines have been indirectly presumed to be constant when changing the temperature of the solution.

Let us suppose that Eq. (6) is valid for three- and multicomponent solutions and let us write this supposition in the form

$$X_i = \pm A_i[(T - T_0)^2 - \Delta T^2]^\beta + F(T), \quad (7)$$

$$X_i = \pm B_i(C - C_0)^{\beta_P} + V(T), \quad (8)$$

where X_i is the concentration of the i th component in the stratified phases; the functions $F(T)$ and $V(T)$ are necessary for taking into account the asymmetry of the stratification curve, i.e., the position of the "straight" diameter. An experimental check of Eq. (7) is complicated by the necessity to determine concentrations of each solution component; therefore, in primary processing of experimental results, the conductivity and IR absorption of the solution have been used instead of the component concentrations in coexisting phases. For both temperature and concentration dependences, a change in conductivity (IR absorption) is accompanied by a change in the component concentrations of the system in corresponding phases. In this case there is an unambiguous correspondence between the solution component concentrations and conductivity (IR absorption). It allows one to presume the values σ and α to be proportional to the order parameter as well as to be able to describe its behavior in the framework of the statistical "scaling" law. Taking into account the merging of phase transitions [1,6] for σ (or α) we have the following expression:

$$\sigma = \pm A[(T_u - T)(T - T_l)]^{\beta_T} + B + CT + DT^2, \quad (9)$$

where β_T is the critical exponent, A the scaling factor,

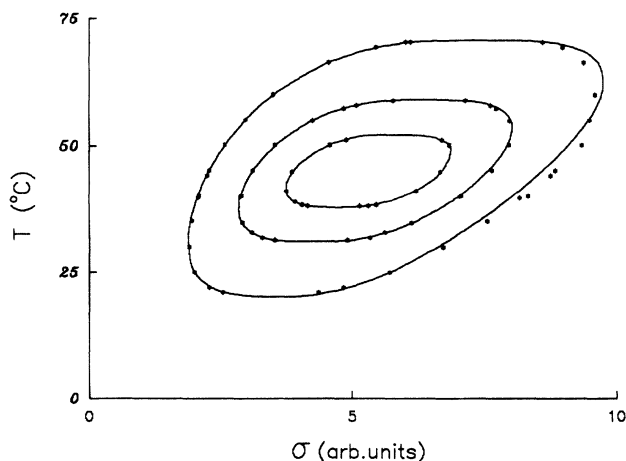


FIG. 1. Dependences of the conductivity of coexisting phases on the temperature and width of the stratification region.

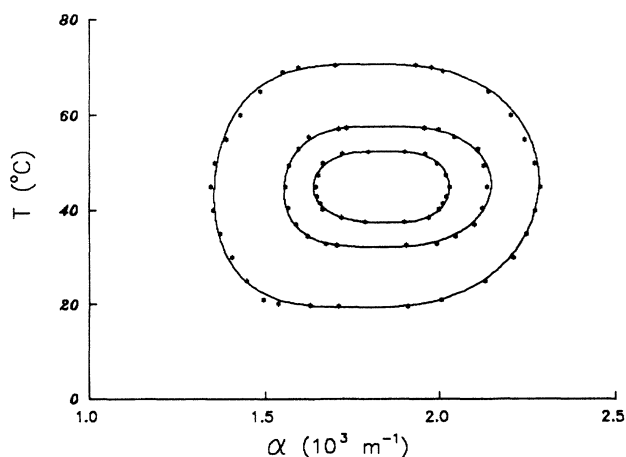


FIG. 2. Dependences of the IR absorption factor α on the temperature and width of the stratification region.

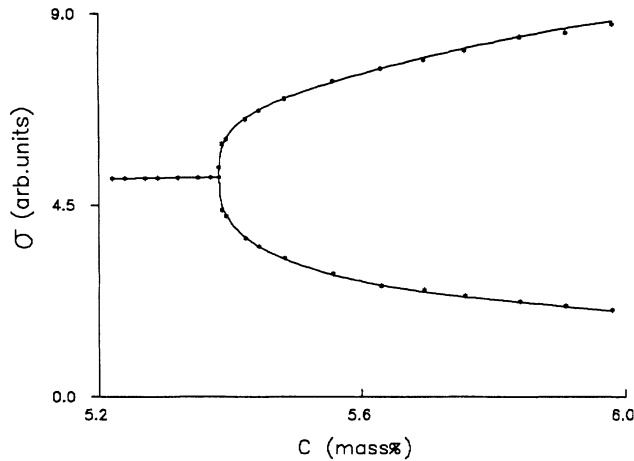


FIG. 3. Dependences of the conductivity of coexisting phases on the impurity concentration at fixed temperature 45.1 °C.

and B , C , and D are factors describing the asymmetry of the stratification curve and the location of the "straight" diameter.

In an analogous way, for a change in the impurity concentration at the fixed temperature,

$$\sigma = \pm A_1(C - C_0)^{\beta_C} + B_1 + C_1T + D_1T^2. \quad (10)$$

Figures 1 and 2 show the temperature dependences of the solution conductivity σ and IR absorption factor α in heterogeneous regions at various values of the impurity concentration C . The plots of $\sigma(T)$ and $\alpha(T)$ form a closed region, the difference of σ and α in coexisting phases being maximal at $T = T_0$ and tending to zero at T_u and T_l . In Figs. 3 and 4 the plots of σ and α have been presented depending on the impurity concentration at fixed temperature. The IR absorption measurements have been carried out at the wavelength of 6900 cm^{-1} , which corresponds to the absorption band maximum.

The measurement results processed by formulas (9) and (10) have been shown in the corresponding figures by

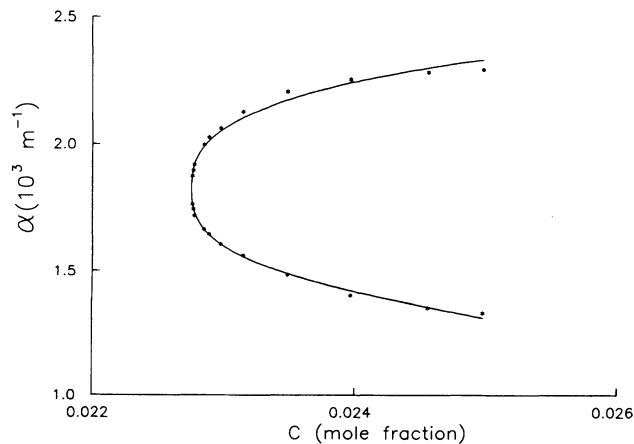


FIG. 4. Dependences of the IR absorption factor α on the impurity concentration at fixed temperature 45.1 °C.

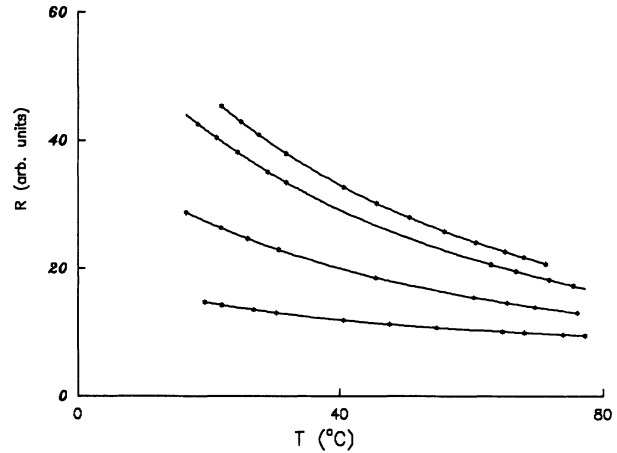


FIG. 5. Dependences of the solution resistance along the stratification line at different impurity concentrations. The curves 1–4 correspond to 0.05, 0.1, 0.2, 0.3 m.f. propanol in water.

solid lines. The values of the conductivity exponents ($\beta_T = 0.33 \pm 0.03$ and $\beta_C = 0.33 \pm 0.03$) and IR absorption ($\beta_T = 0.33 \pm 0.03$ and $\beta_C = 0.35 \pm 0.03$) are in accordance with the theoretical ones and the results of direct measurements [6]. A better confirmation of the formula (7) requires determination of concentrations of each component in the coexisting phases. When calculating the solution component concentrations, the data on conductivity are used. The high accuracy of the data has allowed us to restore the distribution of all components in the coexisting phases. To calculate phase diagrams from the measurements of conductivity and stratification temperature, additional investigations of the conductivity along the line of stratification of solutions with uncritical content of basic components were carried out (the propanol content varied from 0.05 to 0.3 m.f.). Some of the dependences are presented in Fig. 5. Restored diagrams have been shown in Figs. 6 and 7. A good description of the experimental data, which is achieved by making use

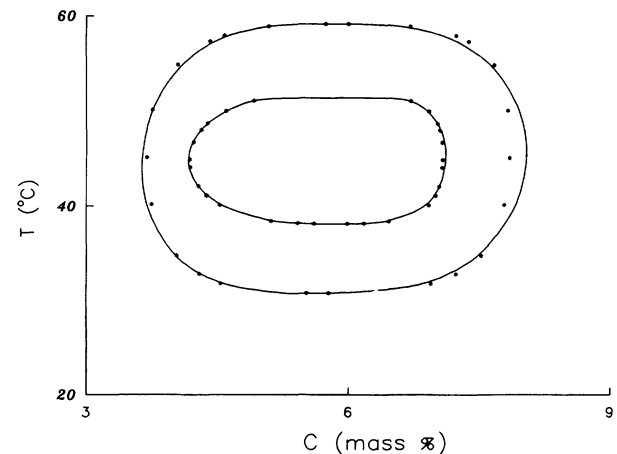


FIG. 6. Temperature dependences of the concentrations C in layers at different widths of the stratification region.

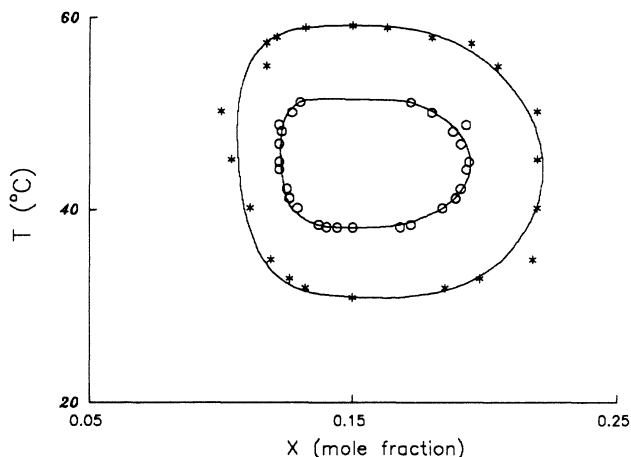


FIG. 7. Temperature dependences of the alcohol concentrations in layers at different widths of the stratification region.

of the formulas presented, allows one to conclude that an isomorphous description of the phase diagram of a multicomponent solution is achieved when choosing the difference of concentrations of any component in coexisting phases of the solution as an order parameter.

Finally it is to be noted that the correctness of the relations (7) and (8) leads to one more conclusion. Let us transform (7) into the following form:

$$\Delta X_1 / A_1 = \Delta X_2 / A_2 = \Delta X_3 / A_3, \quad (11)$$

which contains no temperature dependence. Relation (11) shows a linear dependence of concentrations of the coexisting phases on each other, or, in other words, the constancy of the slope of all connecting lines passing

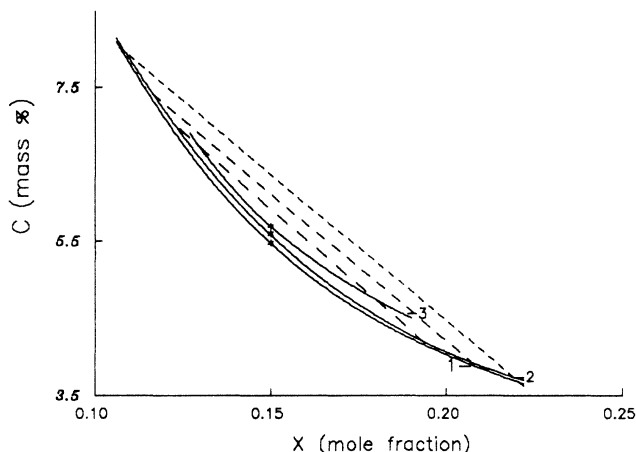


FIG. 8. Phase diagrams of the solution at fixed temperatures 1 40°C, 2 45°C, and 3 50°C. Dashed lines correspond to the connecting lines.

some specified point independent of the temperature of solution (Fig. 8).

CONCLUSIONS

In stratified multicomponent solutions the difference of the concentrations of any solution component (including impurity) as well as intensive solution properties such as conductivity and IR absorption may be chosen as the order parameter. Critical exponents of the order parameter with respect to the temperature, pressure, and concentration of the impurity are equal to each other. The direction of connecting lines passing a concrete point of the solution phase diagram is not changed while changing the temperature.

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