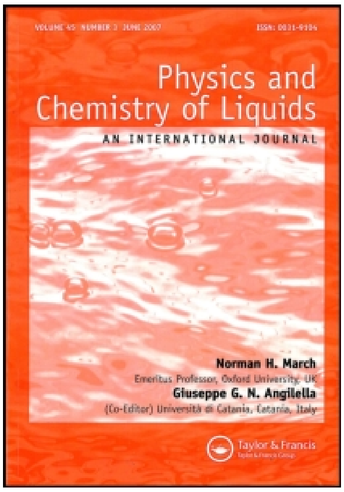

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Investigation of Liquid Eutectic Near Its Crystallization Point in a Centrifuge

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The significant separation effect of a H_2O–H_3PO_4 eutectic mixture near its crystallization temperature has been observed. The fairly large cluster size and its weak temperature dependence seems to be a serious argument in favor of chemical nature of clustering in the considered solution. Therefore it is not a preference of a eutectic mixture.

INTRODUCTION

The hypothesis of a segregation tendency in a liquid eutectic mixture near its crystallization point has been considered in the literature for a long time.[1,2] Experimental evidence of partial ordering in a liquid metal eutectic based on X-ray and neutron diffraction measurements has been published recently.[3,4]

At the eutectic point two different processes are taking place simultaneously: separation of a homogeneous mixture and crystallization of these separated components. Therefore, two different origins of inhomogenity exist near the eutectic point: concentration fluctuations and structural fluctuations respectively. It is difficult to imagine the crystallization of a homogeneous eutectic mixture into a macroscopically inhomogeneous eutectic alloy without fluctuations of composition. The structural fluctuations, or partial ordering, in eutectic mixtures are similar to those observed in pure liquids[5] or azeotropic mixture[6] near the crystallization temperature.

Very often eutectic crystallization is followed by the formation of new chemical compounds in a solid state, such as intermetallic in metal alloys, or hydrogen-bounded networks (or hydrates) in water solutions.[7] Then the third origin of inhomogenity takes place near the eutectic point: fluctuations of chemical ordering.

The significant separation effect in liquid eutectics in a centrifugal field observed in Refs. (8, 9) is the direct experimental evidence of eutectic inhomogenity. A cluster size of 3000 atoms was estimated from the rate of separation for Pb-Sn eutectic just above the freezing temperature.[8]

The present communication deals with an optical study of the concentration distribution of a eutectic mixture when it was centrifuged.

EXPERIMENTAL

For the optical investigation of the separation phenomenon a H_2O-H_3PO_4 eutectic system was chosen (Figure 1).[10] This mixture is optically transparent and has the eutectic point in a temperature range convenient for investiga-

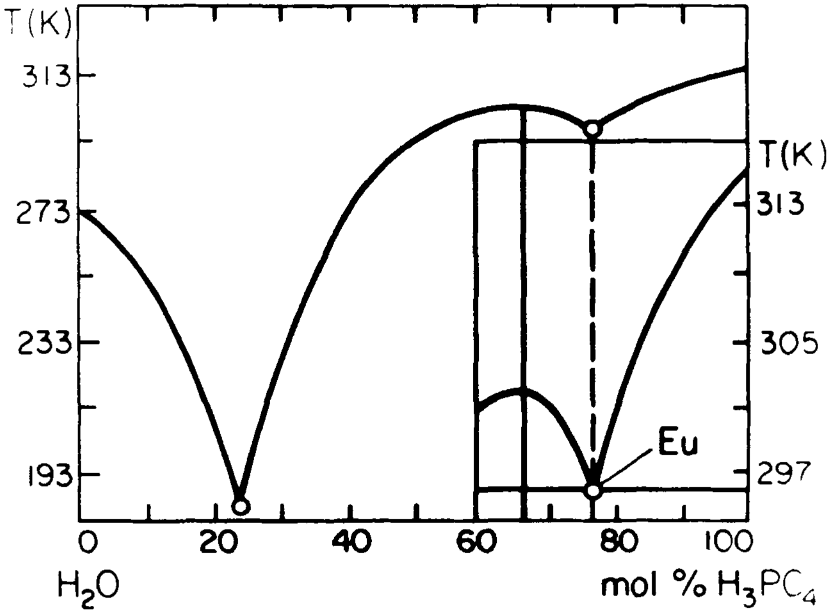

FIGURE 1 The phase diagram of H_2O-H_3PO_4 mixtures. The chosen for investigation eutectic mixture is composed of hydrate $H_2O \times 2H_3PO_4$ and pure H_3PO_4. This part of the diagram is shown in detail in the right lower quarter of the picture. The figures for the eutectiv point are $T_{eut} = 296.6$ K and the composition 76.97% mol H_3PO_4 (or 94.7% wt H_3PO_4).[10]

tion. The samples of the H_2O–H_3PO_4 mixture were prepared from doubly distilled water and ortho-phosphoric acid H_3PO_4 (Merck, 98% cryst GR-analytically pure) in a glove box with dry atmosphere by weighing with an accuracy of 0.1%. All of the samples had a eutectic composition within an error of about 0.2% in weight concentration. Also the melting point of every sample was checked several times and its average value compared with data from the literature.[10] The phase diagram, as well as the physical properties of the investigated mixture, are known fairly well. The assential fact for our experiment is that the temperature of eutectic crystallization depends comparatively weakly on pressure, unlike most organic eutectics ($dP/dT \sim 100$ atm/K);[11] due to the small height of the sample cell the pressure difference within the sample was negligible.

A Beckman Model E optical centrifuge was used. The refractive index gradient dn/dx along the sample cell was measured by schlieren technique as a function of the coordinate x in the cell (Figure 2) during a long time (more than 40 hours) until the picture became stable. The cell was inserted in a massive rotor, and temperature control with an accuracy of ±0.1 K was provided for a long time period. The absolute temperature accuracy provided by a calibrated thermistor was about 0.5 K, so the approach to the eutectic

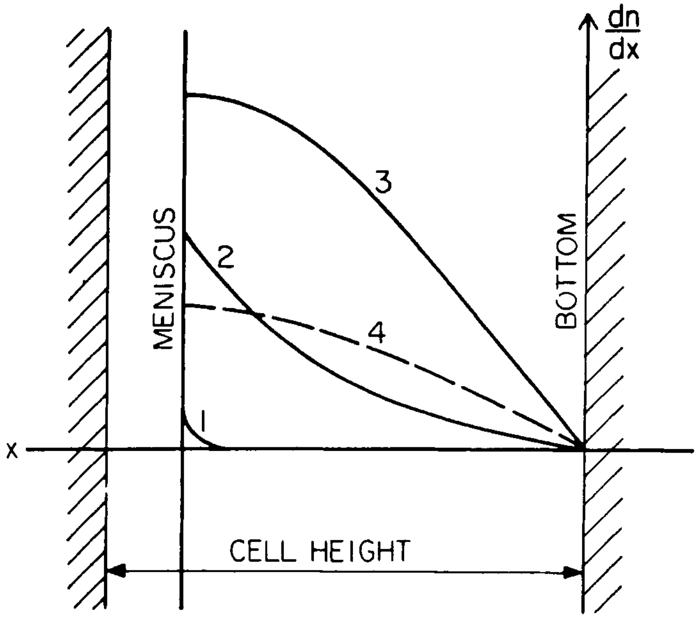

FIGURE 2 Schlieren photo patterns of the refractive index gradient dn/dx as a function of coordinate x along the cell with H_2O–H_3PO_4 eutectic mixture samples and its time evolution: ——— $T = 298.1$ K. --- $T = 307.9$ K. 1-after 10 hours. 2-after 24 hours. 3-after 45 hours. 4-after 24 hours.

point was limited by this accuracy range. The investigation was carried out at a rotation speed of $\omega = 3200$ r.p.m. that corresponded to an effective acceleration of $\omega^2 x \simeq 750$ g (the length of the cell in the radial direction was 0.91 cm and the spinning radius 6.7 cm).

RESULTS AND INTERPRETATIONS

The results of two series of measurements at $T_1 = 298.1$ K and $T_2 = 307.9$ K can be compared (Figures 2 and 3). The Lorentz–Lorenz formula was assumed valid in order to perform density or concentrations calculations from the experimental results.

In Figure 2, one can see a significant sedimentation effect depending on time. After the equilibrium has been reached, the density distribution in the cell became stable and very inhomogeneous. The equilibration time was

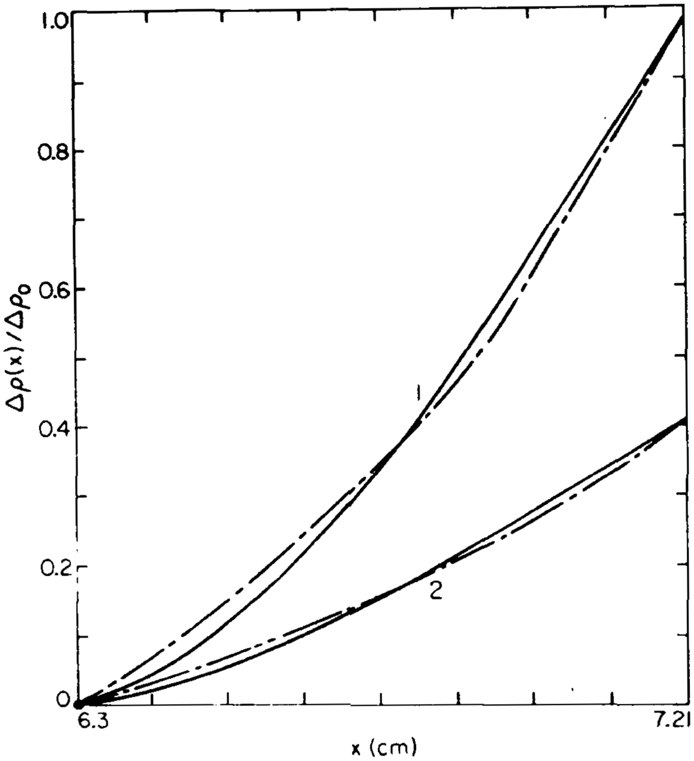

FIGURE 3 Equilibrium density distribution of a H_2O–H_3PO_4 eutective mixture for two temperature: 1-T = 298.1 K. 2-T = 307.9 K. ——— experimental result. --- calculations according to Eq. (1).

temperature dependent. Thus, we observe a separation of components as a result of centrifuging that is dependent on the distance from the crystallization point; the closer to the eutectic point, the larger the separation effect.

We have discussed above the possible origins of a eutectic inhomogenity before crystallization. Regardless of the physical origin of the separation effect, in order to explain our experimental results we have to assume the existence of some sort of clusters. These clusters might be structural complexes like hydrates or intermetallic structures in compound containing systems, as well as concentration or structural fluctuations.[12]

In order to estimate the cluster size one assumes that a eutectic mixture consists of clusters of volume V_i for both components. If V_i is equal to a molecular volume V_m, there is a mixture with a complete molecular mixing. Assuming the Boltzman's distribution for the clusters in a centrifugal field and using the material conservation equation, one can obtain the formula for a relative density distribution of a binary mixture in the experimental cell:

$$\frac{\Delta\rho(x)}{\Delta\rho} = \frac{\rho(x) - \rho_1}{\rho_2 - \rho_1}$$

$$= Z_1\alpha(1 - \exp 2Z_2)[1 - \exp(-2\alpha Z_1)]$$

$$\times \frac{\left[1 - \exp\left(-2\alpha Z_1 \frac{x^2 - x_1^2}{x_2^2 - x_1^2}\right)\right] + Z_2\left[1 - \exp\left(2Z_2 \cdot \frac{x^2 - x_1^2}{x_2^2 - x_1^2}\right)\right]}{(1 - \exp 2Z_2)(Z_1\alpha + Z_2)}$$

and

$$\alpha = \frac{\rho_0 - \rho_1}{\rho_2 - \rho_1}, \quad Z_i = \frac{n_i V_m}{2V_0}, \quad V_0 = \frac{2kT}{\omega^2(\rho_2 - \rho_0)(x_2^2 - x_1^2)} \tag{1}$$

Here ρ_i, ρ_0 are the densities of the components and the binary mixtures respectively ($i = 1, 2$), n_i is the number of particles associated in a cluster volume V_i.

If we do not assume any association of particles ($n_i = 1$), the potential energy under our experimental conditions will be much smaller than the kinetic energy:

$$\tfrac{1}{2}V_m\omega^2(\rho_2 - \rho_0)(x_2^2 - x_1^2) \ll kT \tag{2}$$

This means there is no separation in the system at all. Since we definitely observed the significant separation effect, we have to assume $n_i \gg 1$. Our calculations also show that for the best fitting of formula (1) to the experimental data in Figure 3, the equal cluster volumes ($n_1 = n_2 = n$) should be assumed. Then to estimate the cluster size n from (1) it is sufficient to use the

TABLE I

TK	α	$V_0 \times 10^{-18}$ cm^3	$n \times 10^4$	R Å
298.1	0.580	0.85	1.67	95
307.9	0.592	0.87	1	80

Results of the cluster sizes calculations from the experimental density distribution for two temperatures.

experimental value of the density difference $\Delta\rho(x)$ in any point x of the experimental cell. The results of calculations for two temperatures are represented in Table I. As may be seen from Table I, in spite of a large difference in the density distribution for two temperatures (see Figure 3), the calculated cluster sizes are pretty close. The number of particles in a cluster does not vary too much with temperature and $n \simeq 10^4$ particles. Corresponding radii are $R = 95$ Å for $T = 298.1$ K and $R = 80$ Å for $T = 307.9$ K. This weak temperature dependence seems to be a serious argument in favor of the chemical nature of clustering.

Using the calculated values of the cluster sizes the relative density distribution described by Eq. (1) has been fitted to the experimental curves (Figure 3). Even though the oversimplified assumptions are used in deriving the formula (1), it is possible to see from Figure 3 how well the Eq. (1) fits the experimental density distribution.

Since the optical measurements also provide us the possibility of studying the kinetics of sedimentation, one can estimate the relaxation time from the experimental data. Irrespectively of the inhomogenity origin it is possible to consider the relaxation process as the diffusion of clusters in a centrifugal field. The diffusion coefficient of the Brownian particles (clusters) is defined by[13]

$$D = \frac{kT}{6\pi\eta R},$$

where R is the cluster radius and η is the kinematic viscosity of the medium. Then the relaxation time observed will be of the order

$$t \sim \frac{l^2}{D} \sim \frac{6\pi\eta l^2}{kT} R, \tag{3}$$

where l is the cell height.

Thus, the relaxation time is proportional to the cluster radius. The estimation of the equilibration time from (3) for the investigated cutectic H_2O–H_3PO_4 is $t \sim 100$ hours which adequately fits the experimental figure of 40–50 hours.

CONCLUSIONS

The main goal of our research is to clarify whether the eutectic solution is the strongly fluctuating system which properties completely are defined by these fluctuations in the sufficient vicinity of the eutectic point; or this solution is just the liquid with the rather long living structural clusters of some nature (chemical compound clusters or heterophase fluctuations). In the first case, the eutectic solution properties should be universal close enough for the crystallization point. In the second case, these properties strongly depend on a solution nature.

The results show up that the structural clusters occur in the vicinity of the eutectic point in the considered solution. The fairly large cluster size and its weak temperature dependence seems to be a serious argument in favor of chemical nature of clustering in the solution. It might be that the water solutions have their own specific features in accordance with Ref. 14, but also it could be connected with more basic properties in accordance with Ref. 15.

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