Short Communications

Refractometric Determination of Diffusion Constants in the Critical Region of Partly Miscible Liquids

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Owing to the convenient critical temperature of about 30° the system chosen for starting off diffusion measurements was ethyl alcohol-succinonitrile. The diffusion constant approaches zero at the critical point.

The sample of about 50 mm³ liquid mixture was contained in a hollow, vertical 60° prism of about 10 mm in height. An astigmatic optical system was employed which showed directly on a photographic diagram the refractive indices of the liquids at different levels inside the prism, and thereby the composition of the liquid. The system has been described earlier^{1,2}.

Before being sealed off the prism was filled with a liquid mixture of roughly critical composition. By agitating the prism at a temperature above the critical point (where the components are entirely miscible) a certain gradient of composition was obtained, the liquid at the bottom being richer in the denser component than at the top.

The prism was then lowered into the thermostat³, which was set just above the critical temperature. When the thermostat was then regulated to temperatures just below the critical, two phases developed. Both these phases will have constant composition as indicated by vertical lines on the diagram. When now the thermostat was again raised to a temperature above the critical, a diffusion commenced at the former surface between the two phases. The vertical composition lines on the diagram

Fig. 1. Schematic drawing of photographically obtained diagram. Line AB shows the composition of the liquid at different levels inside the prism at the beginning of the experiment. The sigmoid curve FG is formed due to the diffusion when the temperature is raised to a selected temperature above the critical.

will thereby be connected by a sigmoid curve. Fig. 1 shows in principle the photographically obtained diagram, while Fig. 2 shows an actual photograph. The inclination of the tangent at the sigmoid curve's inflexion point was determined from the photographs, as were also the compositions of the two phases of constant compositions (C_1 and C_2).

The composition was calculated to be the following function of the time and of the vertical coordinate z in the prism. z equals zero at the transition between the

Fig. 2. Photographically obtained diagram. This belongs to a second system now under investigation, i. e., triethylamine water. The straight lines are for orientation of the curve on the photographic plate, and are horizontal and vertical. The distance between the two vertical lines corresponds to a difference in refractive index of the sample of about 0.015. The total length of the curve corresponds to 17 mm vertically in the prism.

two phases, and the time t equals zero at the beginning of the diffusion. D is the diffusion constant to be determined.

$$C = \frac{C_2 - C_1}{\sqrt{\pi}} \int_0^{z/2\sqrt{Dt}} e^{-x^2} dx + \frac{1}{2} (C_2 + C_1)$$

$$\text{This gives for } z = 0 \quad \frac{\partial C(0)}{\partial z} = \frac{C_2 - C_1}{2\sqrt{\pi Dt}} \quad (1)$$

On the photographs we regard Z as ordinate, k_v as vertical magnification, X as abscissa, and k_h as horizontal proportional factor. Linearity was previously found to exist between the refractive index and X . Assuming linearity between the composition and the refractive index, we then get:

$$\frac{\partial c}{\partial z} = \frac{k_v}{k_h} \quad \lim \frac{\delta X}{\delta Z} = \frac{k_v}{k_h} \frac{1}{\text{tg} \theta}$$

On the other hand, when we assume that

$$C_2 - C_1 = \frac{\Delta X}{k_h}, \text{ eqn. 1. gives } \frac{k_v}{\text{tg} \theta} = \frac{\Delta X}{2\sqrt{\pi Dt}}$$

from which it will be seen that $\text{tg} \theta$ is a function of time of the type: $\text{tg} \theta = bt$

$$\text{This gives } D = \frac{k_v^2 \cdot b^2}{4\pi} \Delta X^2$$

From a series of photographs $\text{tg} \theta$ was measured as a function of time and the factor b determined by the method of least squares.

The method employed presupposes equal diffusion constants for all compositions in the range between C_1 and C_2 . The results seem to indicate that the presupposition is reasonably correct. In fact, when carrying out the measurements the difference between C_1 and C_2 has been kept rather on the low side (less than 5 %) and the compositions between C_1 and C_2 correspond to the very flat top of the coexistence curve.

The method requires the concentrations C_1 and C_2 to be constant during the individual series at the selected temperatures. The series had therefore to be terminated when the vertical lines C_1 and C_2 were disturbed due to diffusion. Actually the individual series has to be broken long before the vertical lines C_1 and C_2 on the photograph seem visually to be destroyed.

Fig. 3. $\text{tg}^2 \theta$ as function of time, for the two representative series 0.070° above T_c , $C_1 - C_2 = 4.6\%$ (solid dots) and 0.036° above T_c , $C_1 - C_2 = 4.9\%$ (open circles).

Fig. 4. Diffusion constant as function of temperature. The solid dots and the open circles belong to two different series. The deviation of the one open circle may be due to the thermostat working imperfectly.

In Fig. 4 the diffusion constants are plotted against the temperature distance from the critical point. The points belong to two different series with different prisms and samples used for filling up the prisms. Minor impurities in the samples are certainly different in the two series. Moreover, certain reactions seem to take place inside the prism. This is shown by the fact that the critical temperature has not been constant the whole time, but has decreased from day to day so that it had to be checked at all individual diffusion measurements at the selected temperatures.

In Fig. 4 the diffusion constant does not extrapolate exactly to zero at the critical temperature. However, no conclusions can be drawn from this, especially as the exact determination of the critical temperature has been a difficult undertaking, and the temperature regarded as critical may have been one or two millidegrees below the actual temperature.

The diffusion constant seems to approach zero by lowering the temperature down to the critical by 0.37 cm^2 per day and $^{\circ}\text{C}$.

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The Ultraviolet Absorption Spectra of Some Aroyl Compounds Derived from Phloroglucinol

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The electronic absorption spectra of 2-hydroxy-4,6-dimethoxybenzaldehyde (Fig. 1; max. $294 \text{ m}\mu$, $\log \epsilon = 4.31$; infl. $330 \text{ m}\mu$, $\log \epsilon = 3.58$), 2-hydroxy-4,6-dimethoxyacetophenone (Fig. 2; max. $288 \text{ m}\mu$, $\log \epsilon = 4.24$; infl. $320 \text{ m}\mu$, $\log \epsilon = 3.60$) and 2-hydroxy- ω ,4,6-trimethoxyacetophenone (Fig. 3; max. $288 \text{ m}\mu$, $\log \epsilon = 4.31$; infl. $323 \text{ m}\mu$, $\log \epsilon = 3.62$) in 95 % ethanolic solution show a close resemblance to each other and to the spectra of flavanones^{1,2} and 2-benzylcoumaran-3-ones¹ that have the group

in common and are unsubstituted in the isolated phenyl group. It is, therefore, to be concluded that this type of spectrum represents the absorptional properties of the aroyl group in question when coplanar or nearly coplanar.

Methylation of the two acetophenones mentioned leads to a quite different type