

EFFECT OF THE TEMPERATURE ON THE DIFFUSION
RATE OF CERTAIN SURFACE-ACTIVE SUBSTANCES
SOLUBLE IN WATER

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Results are shown of diffusivity measurements involving surface-active substances (OP pre-
parates) in aqueous solutions within the 293-363°K temperature range.

The use of soluble surface-active substances (surfactants) such as polyoxyethylene ethers of alkyl
—phenyls (OP preparates) is nowadays widespread in various sectors of the national economy. The posi-
tive result of using such surfactants in one or another technological process is that they reach their intended
destination, in many cases by molecular diffusion, just at the appropriate time. For instance, the deemul-
sification rate of petroleum depends largely on the diffusion rate of surfactants soluble in water [1, 2]. In
view of this, it would be of practical interest to study the diffusive characteristics of surfactants from all
possible aspects.

The temperature characteristics of the diffusivity are, in the case of an OP preparate, not very well
known yet. The object of this study will be to explore that problem. The diffusivity was measured by the
conventional method shown in [3], namely by determining the integral concentration of the already diffused
substance in capillaries which had been immersed in the solution of a given surfactant.

The diffusivity of a 2% OP-10 solution in distilled water is shown in Fig. 1a as a function of the tem-
perature. First, as the temperature rises, the diffusivity increases. According to theory, this increase
in the diffusivity of a dissolved substance under a rising temperature can be said to follow the relation

$$D = D_0 \frac{T}{T_0} \cdot \frac{\eta_0}{\eta}$$

The diffusivity has been calculated for temperatures up to 363°K, with the diffusivity of OP-10 at
293°K equal to D_0 , according to this formula. The results are indicated in Fig. 1a with a dashed line. Be-
ginning at 333°K, the test data diverge from theoretical values. Within the 353-358°K range the diffusivity
decreases appreciably. Inasmuch as 358°K is the turbidity point for a 2% OP-10 solution [4], this decrease
in diffusivity is apparently due to the dehydration of molecules and the sharp decrease in their solubility.

An analogous trend is noted in the case of grade OP-7 surfactant, except that the anomalous tempera-
ture range here shifts 8-10°K downward.

The $D = f(T)$ curve for a 1% OP-20 solution (Fig. 1b) agrees closely with the curve calculated accord-
ing to the given formula. Apparently, with a larger number of oxyethylene groups in an OP preparate, the
temperature range of anomalous diffusion continues shifting upward.

This anomaly in the temperature characteristic of diffusivity must be taken into account in practical
applications. For instance, the $D = \varphi(T)$ curve for OP-10 indicates that, in terms of accelerating the
transport of this deemulsifier to the interfaces in a petroleum emulsion, the optimum temperature at which
it should be added lies within the 333-343°K range. After a definite time of contact, the deemulsifier be-
gins to dislodge surface-active emulsifiers from the surface of droplets and to aid the coalescence pro-
cess [5]. The faster the deemulsifying surfactant diffuses and reaches the interface, the sooner will the

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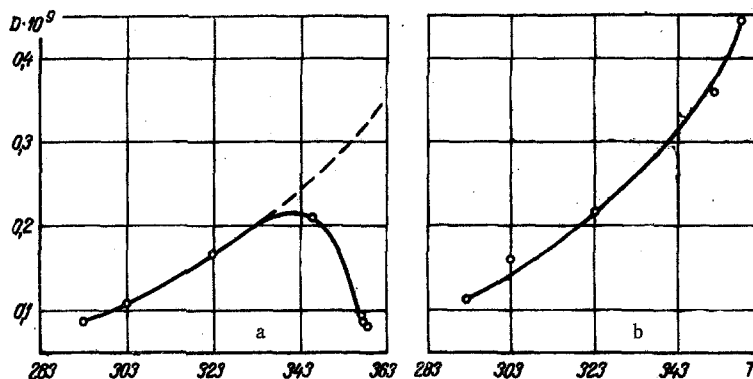


Fig. 1. Diffusivity (m^2/sec) as a function of the temperature ($^{\circ}K$), for (a) OP-10, (b) OP-20; the solid lines represent calculations, the dots represent test values.

natural emulsifiers be dislodged. At the instant when droplets begin to coalesce intensively, their surfaces are saturated both with surface-active emulsifiers constituting a structuromechanical barrier and with deemulsifiers. The total interface area decreases while droplets coalesce, causing the concentration of surfactants and emulsifiers to increase. Naturally, their concentration cannot be higher on the surface of every droplet than the overall saturation concentration. As the interface area decreases, therefore, part of the emulsifiers diffuses into the petroleum phase while part of the deemulsifiers diffuses into the water phase, i. e., into the droplet volume.

If the solubility and the diffusion rate of deemulsifiers are lower than those of natural emulsifiers in petroleum, then it is mainly the emulsifiers which will leave the surface of droplets and enter the bulk phase. Such a dislodgement of the stabilizers will further intensify when the deemulsifiers almost cease to diffuse into the droplet volume. This can be achieved by raising the temperature to 358 $^{\circ}K$ in the case of OP-10. According to the $D = \varphi(T)$ curve, the diffusivity decreases rapidly at this temperature and OP-10 molecules will settle mainly on the interfaces.

Since the surface activity of OP-10 does not decrease at this temperature, while the diffusion rate of emulsifiers soluble in petroleum increases with higher temperature, according to theory, hence such a reasonable adjustment of the operating temperature during dehydration of petroleum is equivalent to a more efficient deemulsification and contributes to lower deemulsifier consumption.

NOTATION

- D is the diffusivity;
 T is the temperature;
 η is the viscosity;
 D_0 is the diffusivity at temperature T_0 ;
 η_0 is the viscosity at temperature T_0 .

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