POLYMORPHISM, FORMATION OF HYDRATES OF OXYETHYLATED ALCOHOLS AND THEIR EQUILIBRIUM WITH MONOLAYERS

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

POLYMORPHISM, FORMATION OF HYDRATES OF OXYETHYLATED ALCOHOLS AND THEIR EQUILIBRIUM WITH MONOLAYERS

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Oxyethylated alcohols and other related oxyethylated aliphatic derivatives are of great interest as new surface-active substances. It has been shown that n-oxyethylated alcohols and, in particular, oxyethylated hexadecanol and octadecanol are good depressants of water evaporation ($^{1-3}$).

Fig. 1. Curves $F_e = f(t)$ for oxyethylated alcohols. For $C_{16}H_{33}OCH_2CH_2OH$, the numbers of the curves correspond to the numbers of the samples. For $C_{18}H_{37}OCH_2CH_2OH$—curve 4.

The dependence of the equilibrium two-dimensional pressure F_e on temperature t determines the temperature limits of stability of the condensed monolayer. We investigated $F_e = f(t)$ for oxyethylated n-hexadecanol $C_{16}H_{33}OCH_2CH_2OH$ and n-octadecanol $C_{18}H_{37}OCH_2CH_2OH$ with one oxyethyl group. Samples of $C_{16}H_{33}OCH_2CH_2OH$ of different degrees of purity and preparation conditions were studied. Sample No. 1 was less purified; sample No. 2 was more highly purified by additional recrystallization (this sample is described in work (^{3}) as No. 5). A sample* obtained from Dr. S. B. Ulkari was also studied, considered here as No. 3. The sample of $C_{18}H_{37}OCH_2CH_2OH$ is the same as that described in (^{3}) as No. 6, but additionally recrystallized. The studies were carried out on a new apparatus (^{4}).

Figure 1 shows the curves $F_e = f(t)$ for three samples of $C_{16}H_{33}OCH_2CH_2OH$ and for one sample of $C_{18}H_{37}OCH_2CH_2OH$. The melting temperature $t = T_3$ of the crystals (on water) proves to be higher than the usual melting temperature t_m of the same (anhydrous) crystals. The temperature point corresponding to the onset of a decrease or to a weakly expressed maximum, in the region of lower temperatures ($< T_3$), by analogy with the curves

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* Kindly provided to A. A. Trapeznikov during the Symposium on Reducing Water Evaporation, Pune, India, in December 1962.

for *n*-alcohols (5) was denoted T_2. It was assumed (6) that at this point a polymorphic transformation of the hydrated crystals of the oxyethylated alcohol occurs. The question of the polymorphism of oxyethylated alcohols apparently has not yet been considered in the literature.

The assumption concerning polymorphic transformations in crystals (both hydrated and dry) was tested by differential thermal analysis (DTA). Thin-walled bulbs at the ends of glass tubes were filled with: 1) anhydrous alcohol, 2) the same alcohol with a drop of water, and 3) nonpolar vaseline oil as the neutral comparison medium (amounts of substances 0.025–0.030 g). Two junctions from two differential copper-constantan thermocouples were placed in the vaseline oil; the other junctions were placed in the bulbs with dry and wetted alcohol. The ends of both differential thermocouples were connected through a reversing switch to a compensation microvoltammeter of type F-18, with a sensitivity of $1.5 \cdot 10^{-6}$ V/div. The three tubes were arranged 2 cm apart in an earthed box made of brass mesh (permeable to water) which damped fluctuations in the temperature of the water, and were placed in a water ultrathermostat, the temperature of which was raised at a rate of 0.5°/min. By successively switching both thermocouples to the voltmeter, changes in the temperatures in the samples of dry alcohol and alcohol with water were obtained in comparison with vaseline oil.

The differential heating and cooling curves referring to anhydrous and hydrated sample No. 2, $C_{16}H_{33}(OCH_2CH_2)OH$, are shown in Fig. 2. From comparison of the two heating curves it is seen that, in complete agreement with the conclusions from monolayers, for the alcohol with water the endothermic melting effect (the peak on the curve $\Delta t = f(t)$) lies at a temperature T_3 higher than for the anhydrous alcohol at the melting temperature. For sample No. 2 the increase in the melting temperature $+\Delta T_\mathrm{m} = T_3 - t_\mathrm{m}$ reaches $\sim 5.6°$; for sample No. 1, $+\Delta T_\mathrm{m} = 5°$. On the heating curves of both dry and hydrated crystals, second peaks of endothermic effects are visible, situated at lower temperatures, which we attribute to polymorphic transformations in the crystalline phase. In this case, for dry and hydrated crystals the positions of the peaks of this transformation prove to be the reverse of the positions of the melting peaks, i.e., the transformation peak in hydrated crystals lies at a lower temperature than the transformation peak of dry crystals by the amount $\Delta T_\mathrm{trans} = T_2 - t_\mathrm{trans}$. For sample No. 2, $\Delta T_\mathrm{trans} = -17°$.

Figure 3 shows the DTA curves for $C_{18}H_{37}OCH_2CH_2OH$. They are similar to the curves for $C_{16}H_{33}OCH_2CH_2OH$. The values of characteristic temperatures for different alcohols and methods of measurement are compared in Table 1. Ob-

Table 1

Fig. 2

Figure 2: Fig. 2

Substance	Medium	DTA: melting, heating temp., °C	DTA: melting, cooling temp., °C	DTA: polymorphic transformation, heating temp., °C	DTA: polymorphic transformation, cooling temp., °C	$F_e = f(t)$: melting, heating, °C	Capillary: melting, heating, °C
$C_{16}H_{33}OCH_2CH_2OH$ No. 1	Anhydrous	40.0*	38				39.0-40.4*
$C_{16}H_{33}OCH_2CH_2OH$ No. 1	Hydrated	45.0	42.6				
No. 2	Anhydrous	43.6	39.8	37.0	27.8		42.6-43.5
No. 2	Hydrated	49.2	46.6	19.7	14.6	48.8	
No. 3	Anhydrous						41.2-42.4*
No. 3	Hydrated					46-46.5*	
$C_{18}H_{37}OCH_2CH_2OH$	Anhydrous	51.0	48.0	39.0	31.6		49.0-50.0
$C_{18}H_{37}OCH_2CH_2OH$	Hydrated	57.3	54.5	23.5	13.7	56.0	

* Measurements were carried out 1-1.5 years after the samples had been prepared.

The results obtained mean that oxyethylated alcohols exhibit enantiotropic polymorphism, form hydrates, and this leads to an increase in the melting temperature and to a decrease in the temperature of the polymorphic transformation, i.e., to an expansion of the temperature interval of stability of the high-temperature modification and, correspondingly, to a decrease in the interval of stability of the low-temperature modification.

Fig. 2. Curves $\Delta t = f(t)$ by the DTA method for sample No. 2, $C_{16}H_{33}OCH_2CH_2OH$. *a*—for the hydrated alcohol, *b*—for the anhydrous alcohol (peaks at the phase-transition points are shaded).

Fig. 3. Curves $\Delta t = f(t)$ by the DTA method for $C_{18}H_{37}OCH_2CH_2OH$. *a*—for the anhydrous alcohol, *b*—for the hydrated alcohol; otherwise the same as in Fig. 2.

Fig. 3

Figure 3: Fig. 3

This phenomenon is completely similar to that found earlier for *n*-alcohols (5).

For anhydrous *n*-alcohols two modifications are known: α, the high-temperature modification, in which the molecules are oriented vertically and are presumed to be rotating, and β, the low-temperature modification, with tilted (at an angle of 55°), nonrotating molecules (7,8); however, a third has also been noted, as summarized in (9). For hydrated *n*-alcohols, two modifications have also been definitely established, which, by analogy with dry crystals, are consid-

were treated in a first approximation as the α- and β-modifications, but a third modification was also assumed to exist (4, 5). Recently, Australian investigators (10–12), in studying *n*-aliphatic alcohols C_{14}–C_{16}, confirmed the formation of hydrates and the broadening of the temperature interval of stability of the α-form. They suggested that in hydrated crystals the modification into which the α-form transforms on cooling is a pre-α-form, whereas the β-form should appear at still lower temperatures.

For oxyethylated alcohols, despite the lengthening of the chain of the normal alcohol by an additional $O(CH_2)_2$ group, the melting and polymorphic-transition temperatures of the anhydrous crystals are lower than those of the corresponding *n*-alcohols; at the same time, the stability interval of the α-form is wider. This apparently indicates a somewhat looser structure and a lower binding energy of the molecules in the crystal of the oxyethylated alcohol than in the crystal of the corresponding *n*-alcohol (evidently as a result of the incorporation of the ether oxygen). It is possible that this also accounts for the larger increase ΔT_{pl} under the influence of hydration in oxyethylated alcohols than in *n*-alcohols, since the addition of water binds the polar groups of neighboring and oppositely oriented molecules in the crystal and increases the stability of the lattice near the melting temperature.

It is seen from Fig. 1 that, in its general course, the curve $F_e = f(t)$ for sample No. 3 is analogous to the curves for samples Nos. 1 and 2. Certain differences are observed in the shape of the curve in the interval T_3–T_4, which does not show a distinct decrease at $t \simeq T_3 = 46$–$46.5°$ (with visible melting of crystallites on the water surface). The rise in the melting temperature $+\Delta T_{\text{pl}}$ of the crystals as a result of hydration is, for sample No. 3, somewhat smaller than for sample No. 2 and somewhat greater than for sample No. 1.

From the heating curves of DTA in Figs. 2 and 3 it is seen that the rise in Δt in many cases begins considerably before the peak itself and proceeds gradually. This indicates either gradually occurring premelting or, more probably, that the crystals contain, in addition to the principal modification, some other modification, melting or undergoing a polymorphic transformation at a lower temperature (lattice defects and impurities are also possible). This is also connected with the insufficient distinctness of the characteristic break points, for example, of the maximum F_e at T_2 on the curves $F_e = f(t)$.

In principle, from the DTA curves the thermal effects of phase transformations could be calculated from the areas. From comparison of the areas (and heights) of the peaks it follows that, for oxyethylated alcohols, the thermal effect of the polymorphic transformation (at $t = T_2$) is considerably smaller than the thermal effect of melting, and at the same time the thermal effect of melting of hydrated crystals is smaller than the thermal effect of melting of unhydrated crystals.

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Note: Figure translations are in progress. See original paper for figures.