Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: V. N. Matvienko , N. V. Pertsov & E. D. Shchukin (1979): Plasticizing of Naphthalene Single Crystals by Surface Active Organic Media, Molecular Crystals and Liquid Crystals, 51:1-2, 1-7

To link to this article: http://dx.doi.org/10.1080/00268947908084688

Mol. Cryst. Liq. Cryst., 1979, Vol. 51, pp. 1–8

Printed in Holland

Plasticizing of Naphthalene Single Crystals by Surface Active Organic Media

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(*Received March 22, 1978*)

The effect of surface active media on the flowrate of naphtalene single crystals was studied with the help of creep technique as a macroscopic reflection of dislocations movement. The results of creep tests are well described by an exponential dependence $\dot{\varepsilon} = \dot{\varepsilon}_0 \exp[-(U_0 - \gamma P)/KT]$.

According to this equation the activation energies U_0 and activation volumes γ were calculated for two basal glide systems and for 3 newly discovered non-basal systems. The type of glide system, its orientation and the presence of surface active media markedly affect γ. Surface active media considerably increase γ, sometimes twofold.

Organic molecular crystals are convenient materials for studies of the mechanical bahaviour of solids. They are usually transparent, very brittle, or, vice versa, very plastic. They can be readily cleaved, are chemically stable and fusible so that it is easy to convert them into perfect refined samples. The simplicity of their structure and binding between molecules (Van der Vaals bonds) permits the estimation of such macroscopic parameters as heat of sublimation, elasticity modulus,[1] surface energy[2] and others, and the comparison of the theoretical values with the experimental ones. These advantages of molecular crystals, as well as their excellent stability in the usual atmosphere (they are neither oxidized like metals nor adsorb water on the surface like most ionic crystals) make them a unique material for the investigation of the mechanisms and features of surface active media effects on the mechanical properties of organic compounds.

As a typical molecular crystal, naphtalene has been widely studied. Methods were reported for preparation of naphtalene samples and investigating them. Deformation and fracture of naphtalene has also been described, particularly as affected by surface active media.[3] We prepared naphtalene single crystals by the "cassette technique" developed in our laboratory by E. Sinevich[4] who improved the Bridgeman-Stockbard's method. The crystals were grown in a wide glass tube 32 mm in diameter and 110 mm long, filled by a paquet of thin (3 mm) glass tubes. All the crystals were grown from one nucleus and therefore had uniform crystallographic orientation whose scatter did not exceed 30′, and were of exclusively perfect structure (the dislocation density shown by air etching was 10^4 cm^{-2}). At the end of the growth process the cassette was disassembled, the tubes dissolved in dilute HF and the crystals cut into samples 30 mm long. Their orientation was determined from the position of the cleavage plane along which the crystal broke under the action of a heptane-wetted razor blade, and/or from the extinction angles in polarized light.[5] The samples were placed in special tube-like holders with the help of dental cement.

The creep tests involved either (1) deformation under constant stress, the flow rate recorded in the steady creep region at deformation not higher than a few per cent, or (2) step-like loading, each successive step followed by a delay to let the system reach stationary flow. Both methods gave similar results. The latter technique, however, yielded more data per sample. Therefore, the former technique was essentially used for control only.

We have found in special experiments that deformation of naphtalene single crystals of all the crystallographic orientations studied involved glide along certain planes. The type of the actual slip system depends on orientation of the crystal symmetry elements towards the axis of the sample, which coincided with the loading direction. For the sake of simplicity, in our experiments the glide direction imposed was the same as that of maximum shear stresses.

The crystal flow took place in the basal systems (001)[010] and (001)[110], which were found in the pioneer experiments by Kochendorfer and were studied since then in detail.[6] We have, however, observed the formerly unknown non-basal glide systems (100)[001], $(111)[1\bar{2}1]$, and $(\bar{1}11)[\bar{1}\bar{2}1]$, the first of which had been theoretically predicted by Williams.[7] Non-basal glide took place in those crystals where the basal plane was parallel to the axis of the sample so that glide along it was impossible. The glide in the (100)[001] system was observed when the *b* axis ([010] direction) was normal to the extension axis. Slight deviations of orientation from this position changed the place of the glide system so that χ_0 varied from 55° to 60°. The other two systems were observed when the *b* axis was parallel to the axis of the sample. Since both systems form approximately the same angle with the extension axis, they compete and often acted together.

We have found that the dependence of the steady creep rate of naphtalene single crystals on stress *P* (Figure 1) can be described by the well-known

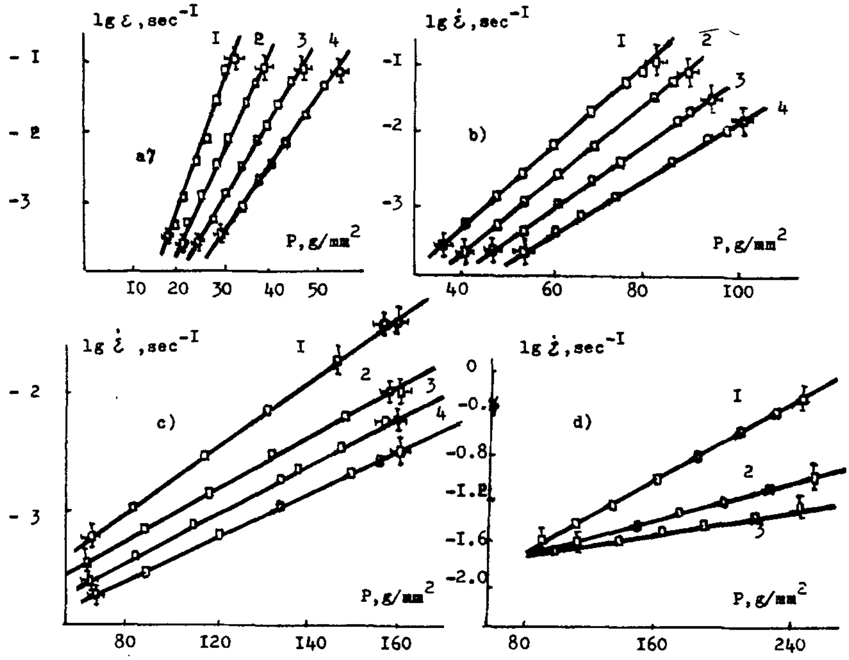

FIGURE 1 Creep rate of naphtalene single crystals vs. stress in different glide systems in air and in the presence of surface active media.

(a) (001) [010]
1—$\chi_0 = 45°$ in α-chlornaphtalene, 2—$\chi_0 = 45°$ in air
3—$\chi_0 = 25°$ in α-chlornaphtalene, 4—$\chi_0 = 25°$ in air
(b) (001) [110]
1—$\chi_0 = 68°$ *in α-chlornaphtalene*, 2—$\chi_0 = 68°$ in air
3—$\chi_0 = 40°$ in α-chlornaphtalene, 4—$\chi_0 = 40°$ in air
(c) (100) 001
1—$\chi_0 = 58°$ in α-chlornaphtalene, 2—$\chi_0 = 58°$ in air,
3—$\chi_0 = 60°$ in α-chlornaphtalene, 4—$\chi_0 = 60°$ in air
(d) (111) [1$\bar{2}$1] and ($\bar{1}$11) [$\bar{1}\bar{2}$1]
1—in benzene, 2—in α-chlornaphtalene, 3—in air.

Zhurkov's exponential equation:[8]

$$\dot{\varepsilon} = \dot{\varepsilon}_0 \exp\left(-\frac{U_0 - \gamma P}{KT}\right)$$

where U_0 is the activation energy of the process extrapolated to $P = 0$, γ is the structural factor, and the pre-exponential factor $\dot{\varepsilon}_0$ is constant for a given glide system, independent both of the orientation of the system towards the sample axis and of the load. As long as the temperature of the experiments could not be varied over a wide range, we had to estimate ε_0 from flow and fracture behaviour of the crystals. At first we determined the time till fracture τ, which is fairly well described by a correlation

$$\tau = \tau_0 \exp\left(\frac{U_0 - \gamma P}{KT}\right)$$

where U_0 and γ are the same as in the equation for the plastic flow rate. Then $\dot{\varepsilon}_0$ was estimated from the equation $\dot{\varepsilon}\tau = \dot{\varepsilon}_0\tau_0 = \text{const}$, where τ_0 was assumed to be 10^{-12} sec. The $\dot{\varepsilon}_0$ values thus obtained, as well as U_0 and γ are presented in Table I.

It follows from these data that the glide activation energy in the "easiest" system is the highest, considerably larger than the naphtalene sublimation energy (17 kcal/mol[9]). The lowest glide energy corresponds to the most "difficult" systems. This correlation between the flow parameters can not yet be explained, particularly since no data are available on the coefficients and activation energies of naphtalene self-diffusion in different directions. A possible explanation is that the dislocations are overcoming barriers due to non-conservative climb, which is more difficult the denser and "smoother" the glide plane.

Tensile tests with naphtalene single crystals have shown that in organic surface active media, which sharply reduce the surface energy of naphtalene, its flow rate considerably increased. The effect of the media depends on their chemical nature and on the orientation of the sample, on the glide system and on conditions of flow. The plasticizing effect of the environment also depends on time. Some media, like α-chlornaphtalene, increase the flow rate virtually at once, others, like benzene, do so only some time after they are deposited onto the crystal being extended (Figure 2). Fundamentally, the organic media close to naphtalene in polarity (nonpolar fatty hydrocarbons and aromatic hydrocarbons) have a pronounced plasticizing effect on naphtalene single crystals (Figure 1) increasing their flow rate by several orders

TABLE I

The parametres U_0 and $\dot{\varepsilon}_0$ as calculated from Eq. (1).

Glide system	(001)[010]	(001)[110]	(100)[001]	$(111)[1\bar{2}1]$; $(\bar{1}11)[\bar{1}\bar{2}1]$
$\dot{\varepsilon}_0$, sec^{-1}	5×10^{10}	8×10^{10}	3×10^{11}	5×10^{11}
U_0, kcal/mol	26.9	22.8	21.7	12.3
γ, $\text{cm}^3 \times 10^{-19}$	290.2 (45°)	55.9 (68°)	13.0	0.2

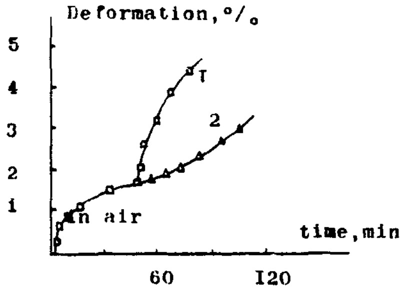

FIGURE 2 The plasticizing effect of surface active media after initial deformation in air. 1—α-chlornaphtalene, 2—benzene.

of magnitude. The plasticizing effect of the environment, which manifests itself in higher flow rate under constant stress or a lower stress producing the same strain rate as without environment, depends on several parameters. These are the nature of the medium, the system in which glide occurs, the orientation of the glide plane towards the axis of the sample, stress (and, respectively, flow rate) and temperature. We have shown, for instance, that the relative increase of single crystals flow in the presence of active media essentially depends on the orientation of the glide axis towards the extension axis. Each glide system displays its own maximum of the effect, which is reached at different orientations (Table II).

Studies on creep rate of crystals contacted with surface active media at different stresses have shown that neither the flow activation energy not the

TABLE II

Activation volumes (γ) for different orientations and for different surface active media decreasing the plastic flow stress. ($\gamma \times 10^{19}$)

Glide system		Air	α-chlornaphtalene	Vaseline oil	Benzene
(001)[010]	19°	159903	227313	230253	230253
	25°	211832	559465	471283	435031
	45°	290200	623152	593758	567304
	68°	186553	369384	300798	296879
(001)[110]	25°	37320	40563	39681	39192
	40°	43503	52321	48990	48990
	45°	50567	66626	63687	62707
	68°	55985	80441	74464	70545
(100)[001]	55°	9308	13130	9798	9798
	60°	11875	12639	12541	11757
	58°	13060	16166	14697	14697

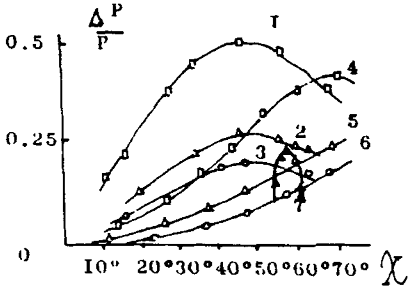

FIGURE 3 Reduction of the plastic flow stress by surface active media.

1—(001) [010] in α-chlornaphtalene
2—(001) [010] in benzene
3—(001) [010] in vaseline oil
4—(001) [110] in α-chlornaphtalene
5—(001) [110] in benzene
6—(001) [110] in vaseline oil
7—(100) [001] in benzene

pre-exponential factor depend on the presence of the medium (Figure 1). In semi-logarithmic coordinates all the data fit straight lines which can be extrapolated to one point at the Y axis. One more evidence that U_0 and $\dot{\varepsilon}_0$ are constant is provided by the temperature dependences of flow rate (Figure 4). Surface active media can considerably (sometimes twofold) increase the activation volume (Table I), possibly due to the decrease in the number of obstacles to dislocation movement in the area where the glide plane crosses the crystal surface or due to the decrease in the efficiency of the obstacles. Large organic molecules are unlikely to penetrate into the bulk of the crystal during the experimental period, and even if they do, they would only

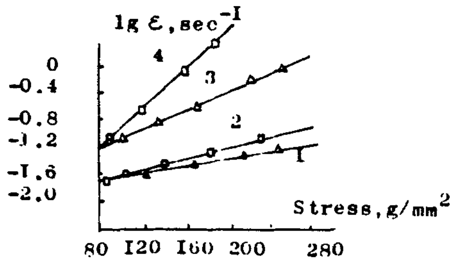

FIGURE 4 The temperature dependence of the creep of naphtalene single crystals in air and in surface active media in the glide systems (111) [1$\bar{2}$1] and ($\bar{1}$11) [$\bar{1}\bar{2}$1].

1—in air
2—in α-chlornaphtalene } 20°C

3—in air
4—in α-chlornaphtalene } 40°C

strengthen the crystal by alloying. The plasticizing effect must therefore be regarded as the surface effect of the active medium. We believe that this effect is consistent with our notions[10] on the facilitation of dislocation emergence at the surface due to reduction of surface energy and/or of the potential barrier of formation of an elementary step at the surface. Direct observations of dislocation movement in near-surface layers have shown that the distance covered by leading dislocations in naphtalene single crystals indented in surface active media increases considerably. The results of microscopic tests were in complete agreement with the observed influence of surface active environment on the creep of naphtalene single crystals.

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