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DIFFUSION OF SIMPLE IONS IN LYOTROPIC LIQUID CRYSTALS AND ORDINARY GELS IN RELATION TO THEIR STRUCTURES

Norio WATANABE, Misako MUKAI, and Bun-ichi TAMAMUSHI
Nezu Chemical Institute, Musashi University,
1-26 Toyotama-kami, Nerimaku, Tokyo 176

The diffusion velocities of simple ions: K^+ Cl^- into two types (lamellar and hexagonal) of lyotropic liquid crystals involved in the system: sodium dodecyl sulphate (SDS) + n-hexanol + water were measured. The results showed that the diffusion velocities into the lamellar type liquid crystals were greater than those into the hexagonal ones. The diffusion velocities for both types of liquid crystals were however found smaller than those into ordinary colloidal gels. The effect of added ions on the flow properties of the above two types of liquid crystals was examined and found different according to the difference in their ordered structures.

The lyotropic liquid crystals under present studies are considered to be ordered gels in wider sense.[1)] It is therefore interesting to study their properties in comparison with those of ordinary gels.

We first established the phase diagram of the system: SDS + n-hexanol + water at 25°C which is given in Fig. 1, where L_1: normal micellar solution, L_2: microemulsion, 2L: emulsion or two-layers liquid mixture, LC: liquid crystals and L + LC: liquid crystal in equilibrium with micellar solution or microemulsion. In this system, flow properties and diffusion velocities were measured in the phase regions of L + LC. The samples taken for measurements are denoted by letters: A,B, C,D,E,F and G in the diagram. The samples were put in the centrifugal force of 3000 r.p.m. for 60 min, the distance between central axis and samples being 8.0 cm, to separate them into two phases (upper solution and lower liquid crystal), whose

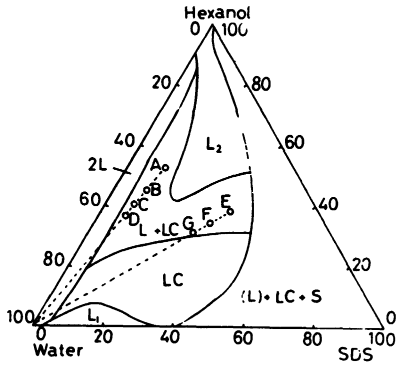

Fig. 1 Phase diagram of SDS/n-hexanol/water at 25°C.

point	phase	SDS (wt%)	water (wt%)	hexanol* (wt%)
A	L	3.2	16.2	80.6
	LC	15.3	61.4	23.3
B	L	4.6	11.6	83.8
	LC	13.5	66.6	19.9
C	L	3.6	10.0	86.4
	LC	11.7	66.7	21.6
D	L	2.7	8.5	88.8
	LC	10.1	72.7	17.2
E	L	31.1	18.5	50.4
	LC	48.0	28.9	23.1
F	L	28.9	23.4	47.7
	LC	40.5	34.3	25.2
G	L	28.1	25.5	46.4
	LC	34.2	39.4	26.4

* hexanol(%) = 100 - SDS(%) - water(%)

Table 1 Chemical composition for the upper (L) and lower (LC) phase.

chemical compositions were determined by Karl-Fischer reagents for water content and by Epton's method for SDS. The results are indicated in Table 1. The structure of liquid crystal for A ∼ D was found lamellar, while that for E ∼ G was hexagonal from their characteristic figures appeared in polarization microscopic pictures.[2)]

We measured diffusion velocities of K^+ Cl^- into liquid crystalline phases of A and E. The results were compared with the diffusion velocity of the same ions into agar-agar gel applied as an example of ordinary gels. In this experiment, test tubes of the same size (2.8 cm diameter) were filled with gels of the same volume (20 cm^3), and then the same volume of the KCl-solution of a definite concentration (4 ∼ 28 mM) was gently put on each of the above gels. After keeping these samples about 20 hr in a thermostat of 25°C, a definite volume of the upper solution was taken out and its Cl-ion concentration was determined. The ratio of the initial and final Cl-ion concentrations: C_t/C_o was calculated. The results are indicated in Table 2. It is here remarked that the diffusion velocities of simple ions in liquid crystals of hexagonal structure are smaller than those in liquid crystals of lamellar structure, the diffusion time being between 19 hr to 22 hr in both cases.

We then measured the flow properties of liquid crystalline phases by Couette-type auto viscometer for samples (A $\sim$ G) and it was found that all samples showed non-Newtonian and generally plastic flows of the Bingham type. The apparent viscosities decreased with the increase of the water content in series: A → D and also in series: E → G. However, the apparent viscosities for liquid crystals of

Table 2.

composition	diffusion time (hr)	initial concentration of KCl : C_o (mM)	C_t/C_o
A	19.5	5,1	0.91
	21.6	4.4	0.90
		6.2	0.90
		7,8	0.89
E	18.7	5.6	0.95
		9.5	0.96
	20.5	6.4	0.93
		8.0	0.94
		17.4	0.98
2 wt% agar agar gel	16.1	28	0.80
	21.5	28	0.76

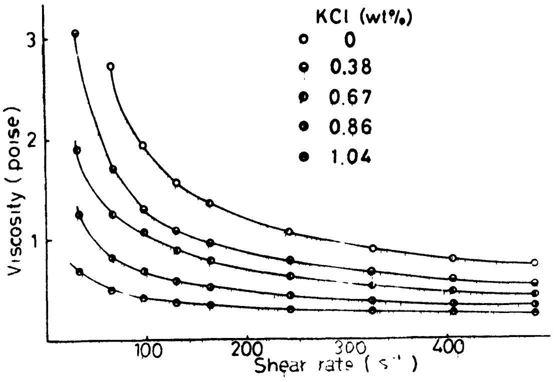

Fig. 2. Apparent viscosity vs. shear rate of liquid crystalline phase of A point added KCl.

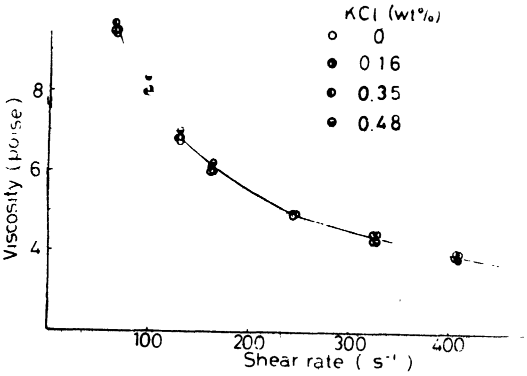

Fig. 3. Apparent viscosity vs. shear rate of liquid crystalline phase of E point added KCl.

hexagonal structure (E ~ G) were generally found greater than those of lamellar structure (A ~ D). We further observed the effect of simple ions: K^+ Cl^-, on the viscosities of two liquid crystal samples corresponding to A and E, which were prepared by using KCl-solution of various concentrations instead of pure water. The behavior of the sample corresponding to A containing KCl was different from that of the sample corresponding to E, as shown in Figs. 2 and 3, respectively, which represent the relation between apparent viscosity and shear rate. As in Fig. 2, the apparent viscosity of the liquid crystalline phase of A (lamellar structure) decreases gradually by the addition of KCl, and finally, above 1.3 wt%, the liquid crystalline phase disappears.[3] On the contrary, as in Fig. 3, the apparent viscosity of the liquid crystalline phase of E (hexagonal structure) containing KCl remains almost constant independent of KCl-concentrations.

The difference found in diffusion velocities for liquid crystals of lamellar and hexagonal structures is corresponding to the difference in apparent viscosities measured in the shear rate range of 100 ~ 500 sec^{-1} of these two types of liquid crystals. It is suggested that water existing in liquid crystalline phase of E (hexagonal structure) is more strongly bound than that in A (lamellar structure). The diffusion velocities in those liquid crystalline phases are however smaller than that in agar-agar gel as indicated in Table 2. This indicates that the water in liquid crystalline phases (lamellar or hexagonal structure) is in more bound state in comparison with that in ordinary gels. This may be due to the reason that ordinary gels like agar-agar gel have in general disordered net work structures, while lyotropic liquid crystals have more or less ordered structures.

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