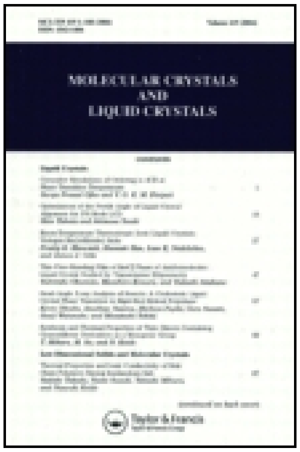

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On the Relation Between Mobility of Ions and Viscosity. The Walden's Rule

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The reproducibility of ionic mobility values obtained by means of different methods is shown. For nematic material 5CB the viscosity and mobility tensor components were compared. The applicability of Walden's rule is discussed.

1. INTRODUCTION

As evident from literature[1,2] even for nematic liquid crystals, ionic drift mobilities are subjected to considerable scatter of the data. To investigate the reasons of this scattering, ionic drift mobility in liquid crystalline materials: 5CB-pentyl-cyano-biphenyl and 8OCB-octyloxy-cyano-biphenyl have been determined by means of two principal methods:

- —Time of flight method. The details have been shown in previous papers.[3,4]
- —Isothermal current decay method.[5] The application of this method will be discussed in detail.

2. ISOTHERMAL CURRENT DECAY METHOD AND THE COMPARISON OF THE DATA

In the case of the evaluation of the drift mobility values from an isothermal decay of current three procedures have been used:

—the "initial decay" procedure,[6]

—fitting of experimental decay curves to the results of weak electrolyte theory,[7]
—fitting of experimental decay curves to the results of numerical integration of the Thomson-Thomson equations.[8]

For the "initial decay" procedure it was found that the formula used by Derfel[6] has to be corrected if reasonable data are going to be extracted. The reasons for the corrections are presented in Appendix 1.

The details of the applications of the two remaining procedures are shown in the previous paper.[9] For the nematic phase of 5CB and 80CB the fitting of the results of the experiments to weak electrolyte theory turned out to be better than the use of the Thomson-Thomson equations. However, for smectic A phase of 80CB the use of current-time relations obtained from the Thomson-Thomson equations produced, exclusively, the data in good agreement with the results of the time of flight method.

The comparison of the drift mobility data obtained for nonoriented 5CB by means of different methods is shown in Figure 1. The slight difference between the time of flight method and the remaining methods is due to the dilemma: should the time correction factor in the time of flight method be 1 or 0.78. Factor 0.78 was applied in Figure 1. Similar results for nonoriented 80CB are shown in Figure 2.

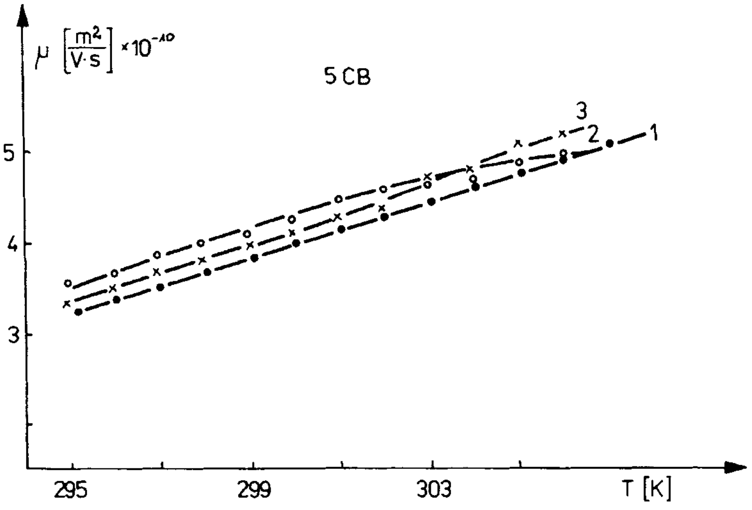

FIGURE 1. The comparison of the mobility values in 5CB obtained using different methods: ●— time of flight method /factor 0.8/, × — "initial slope," ○— fitting of experimental results to the theoretical ones.

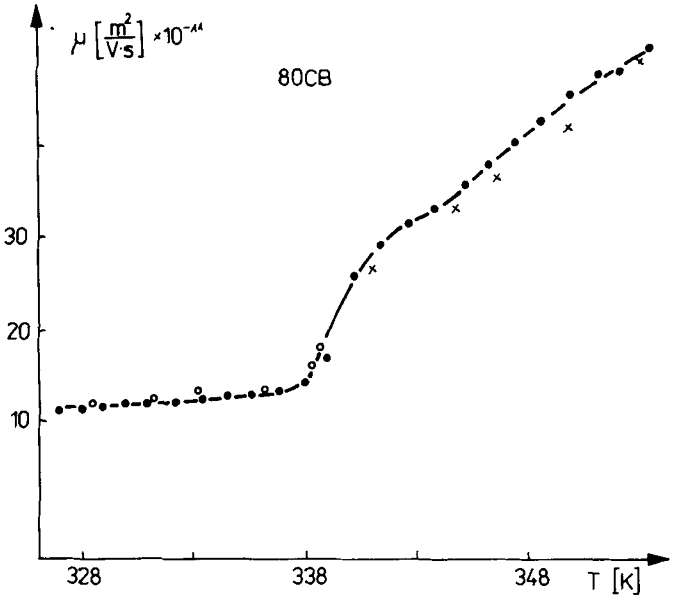

FIGURE 2. The comparison of the mobility values in 8OCB obtained by different methods: ●— time of flight of ions method, "fit" of the experimental current time curves to the theoretical ones obtained from: weak electrolyte theory —×— for nematic phase, the Thomson-Thomson theory —O— for smectic A phase.

In conclusion, one can argue that both methods are capable of producing reliable results. The large scatter in the drift mobility values, as encountered in literature, is either due to the properties of the materials used, or to the improper application of the methods.

3. THE COMPARISON OF THE MOBILITY AND VISCOSITY TENSOR COMPONENTS FOR 5CB. THE WALDEN'S RULE

The viscosity tensor components have been determined for 5CB either by means of retangular capillary[10,11] or by means of the attenuation of ultrasound waves.[12] The measurements involving rectangular capillary have been made on the same material as used for the drift mobility determination. So, there should not be any speculations about the different purity of the material.

Evidently, when the hydrodynamic friction is dominating, μ and η components should be mutually related by the radius of solvation r_s, eq.:

$$(\mu_i \eta_i)^{-1} \approx const.\ r_{si}$$

where i indicates the parallel or perpendicular orientation.

The dependences of $\mu_{\parallel}\,\eta_{\parallel}$ and $\mu_{\perp}\,\eta_{\perp}$ for 5CB are shown in Figure 3. As one can see for parallel orientation the product $\mu_{\parallel}\,\eta_{\parallel}$ is in the limits of experimental errors temperature independent, meaning that $r_{s\parallel}$ is constant in nematic range—see Figure 4. In contrary, for the product $\mu_{\perp}\,\eta_{\perp}$ significant temperature dependence is observed; the value $\eta_{\perp}$ has been extracted from experimental data by the procedure described in Appendix 2. However, if ultrasound data of viscosity are explored the product of $\mu_{\perp}\,\eta_{\perp}$ is constant, consistently, as in the paper of Herino.[13] Let us look for the reasons of these discrepancies.

If the difference of the temperature dependence of the product $\mu_{\parallel}\,\eta_{\parallel}$ and $\mu_{\perp}\,\eta_{\perp}$ was due to the mechanism of the movement of the ions, this should have an impact in the activation energy. The thermal activation energy values for mobilities and viscosities are shown in Table 1. From Table 1 we can see that the observed effect is due to viscosities. However, two different sets of viscosity data do exist, and one should notice that the conditions of the experiments are different.

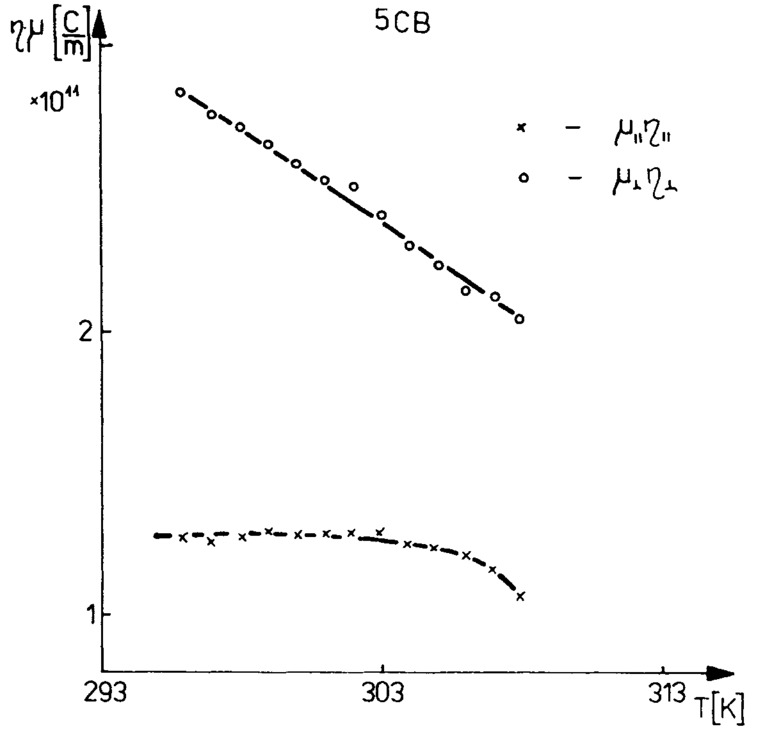

FIGURE 3. The product of $\mu\eta$ in oriented PCB, parallel and perpendicular to the applied electric field.

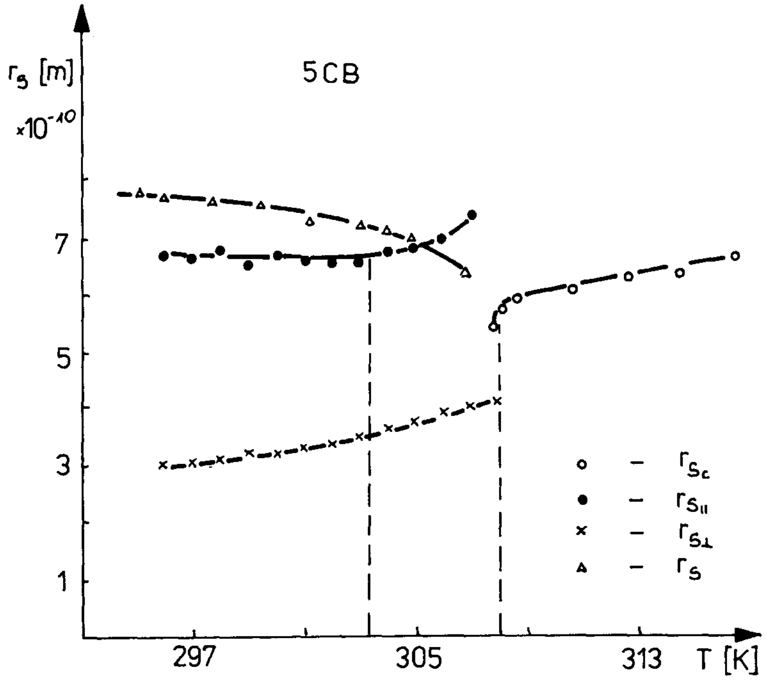

FIGURE 4. Temperature dependence of radii of solvation in 5CB. r_{sc}— in isotropic liquid, $r_{s\parallel}$ and $r_{s\perp}$ for parallel and perpendicular orientation to electric field, r_s— in non-oriented material.

In the rectangular capillary method one can observe macroscopic flow; that is not the case of the method exploring ultrasounds. If one can assume that both of these results are correct, we should consider the existence of macroscopical η_i and microscopical η_{mi} viscosities. In such a case the Walden's rule should be related to microscopical viscosities:

$$\mu_i \, \eta_{mi} = const.$$

TABLE 1

Thermal activation energies of drift mobilities and capillary viscosities

Material	Thermal activation energy		Phase	Orientation
	E_μ [eV]	E_η [eV]		
5CB	0.31 ± 0.07	0.21 ± 0.04	nematic	—
	0.32 ± 0.06	0.27 ± 0.04	nematic	∥
	0.33 ± 0.06	0.49 ± 0.06	nematic	⊥
80CB	0.83 ± 0.16	0.83 ± 0.11	smectic A	—
	0.71 ± 0.08	0.64 ± 0.08	nematic	—

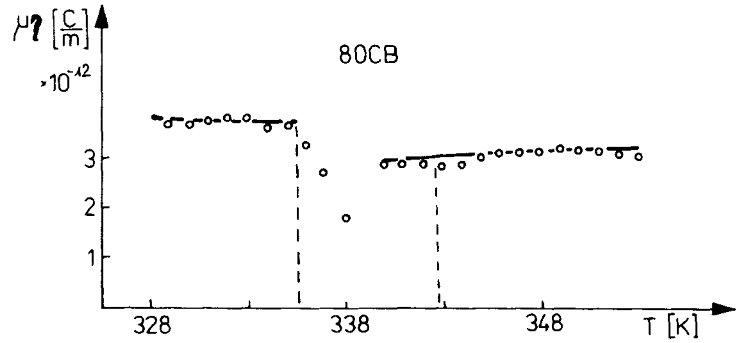

FIGURE 5. The product of $\mu\ \eta$ in non-oriented 8OCB.

It is interesting to mention that for non-oriented liquid crystalline material the Walden's rule is roughly fulfilled as shown in Figure 5 and Appendix 3.

4. FINAL REMARKS

In one assumes the concept of microscopic viscosity and the application of the Walden's rule in the form:

$$\mu\ \eta = const.$$

one can electrically probe the viscosity of liquid crystalline structures where the application of the conventional methods is impossible because of non-Newtonian hydrodynamics. For such a purpose the time of flight method based on ionic injection seems to be very promising. The method has been used by Sazin and Szuwajew[14] for investigating thin polymer films. The investigation of the drift mobility in nematic, cholesteric and smectic A structures[3] has been carried out in our laboratory. We hope it can be applied to any LC structure.

Appendix 1

Due to weak electrolyte theory, the time dependence of the current is as follows[7]:

$$\frac{dj(t)}{dt} = \frac{2j_s}{\tau_T} - \frac{\tau_T j^2(t)}{(2\tau_R)^2\, 2j_s} - \frac{2j(t)}{\tau_T} \tag{1}$$

where

$$\tau_T = \frac{2d}{E(\mu_+ + \mu_-)} \text{ – average time of flight of the ions}$$

$$\tau_R = \frac{1}{2\sqrt{\nu k_D k_R}} \text{ – chemical relaxation time}$$

$j_s = \nu\, k_D\, q\, d$ – the density of saturation current

ν – the density of dissociable particles

k_D – dissociation rate

k_R – recombination rate

q – the charge of an ion

d – thickness of the layer.

Solving of eq. (1) for $j(t)$ (in assumption of $\tau_R >> \tau_T$ too) one obtains:

$$\frac{\tau_T}{2} = -\frac{j(t) - j_s}{\frac{dj(t)}{dt}} \qquad (2)$$

Having in mind that for $dj(t)/dt = 0$, $j_s \cong j_\infty$, one can rewrite eq. 2:

$$\tau_T = -2\frac{j(t) - j_\infty}{\frac{dj}{dt}} \qquad (3)$$

instead of

$$\tau_T = -2\frac{j(t)}{\frac{dj}{dt}}$$ as appeared in.[6]

Appendix 2

For the laminar flow of nematic liquid crystals the effective viscosity is the combination of coefficients: η_1, η_2, η_3 and η_{12} as follows[10]:

$$\eta(\theta, \varphi) = \eta_1 \sin^2\theta \cos^2\varphi + \eta_2 \cos^2\theta + \eta_3 \sin^2\theta \sin^2\varphi + \eta_{12} \cos^4\theta \sin^2\theta$$

where θ is the angle between director and velocity vector, φ—the angle between the velocity gradient and the projection of the director on the plane perpendicular to the flow velocity. Therefore:

$$\eta_\perp\left(\theta = \frac{\pi}{2}, \varphi\right) = \frac{\int_0^{\pi/2} \eta\left(\theta = \frac{\pi}{2}, \varphi\right) d\varphi}{\frac{\pi}{2}} = \frac{\eta_1 + \eta_3}{2}$$

Appendix 3

The Walden's rule is often presented as follows[15]:

$$\mu\, \eta^H = const.$$

where $H = E_\mu / E_\eta$, E_μ and $E\eta$—the thermal activation energy of mobility and viscosity, respectively. The H values obtained in LC are shown in Table 2.

TABLE 2

The values of H for liquid crystals

Material	Phase		Bibliography
	nematic	cholesteric	
PAA	4.0		16
PAA	1.0-1.5		17
MERCK 7a	1.0-1.5		18
MERCK 5	1.0-1.3		18
MBBA	1.0*		19
MBBA	0.4-1.5		20
ch. propionate		1.0*	21
ch. pelargonate		1.0*	21
ch. palmitate		1.0*	21

*—the Walden's rule is fulfilled

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