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Separations with Protein Liquid Crystals

A lyotropic protein liquid crystal was studied experimentally to evaluate its potential as a selective liquid membrane. Concentrated solutions of fibrinogen had nematic like properties under shear and exhibited graded selectivities toward solutes of widely differing sizes when subjected to a two-dimensional velocity field. The magnitude of the selectivity differences was found to depend on the shear orientated direction of the liquid crystal layer. The selectivity seems to be both a solubility phenomena and a relative diffusion phenomena. These anisotropic layers may have potential as controlled variable selectivity membranes.

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SCOPE

Many biological materials, particularly enzymes, cannot be purified by conventional methods which employ large gradients of temperature, pressure, *p*H, or shear. Such harsh treatments can cause protein denaturation and the consequent loss of biological activity. Therefore, milder means of purification are needed. The development of artificial membranes was hoped to provide a new selective separation technique for liquid solutions. However, in practice the thin synthetic membrane has become most useful as a concentrating tool—separating solutes from solvent. The fixed and rather wide selectivity cutoff has made it ineffective for many solute-solute separations.

Developments with liquid membranes have shown more selective solute-solute separations, although not in commercially useful systems. For example, Bangham (1967) has shown selective separation of K^+ and Na^+ with phospholipid vesicles. Bangham's work was part of a recent large effort to duplicate with phospholipid bilayers the highly selective separations performed by natural membranes. Green (1970), however, has pointed out that these highly charged bilayers do not have sufficient diversity of characteristics to be wholly satisfactory models for natural membranes. More specifically, the selectivity of these phospholipid bilayers does not respond in a controlled manner to changes in environment.

These phospholipids, however, are members of a larger class of materials called *liquid crystals*, some members of which potentially have the properties necessary to overcome the limitations of fixed membranes and phospholipid bilayers. The liquid crystal is a phase of matter which exhibits the long-range order of a solid, but has the response of a fluid to shear. For many liquid crystals, whether charged or uncharged, the structure is very sensitive to perturbations in the environment, particularly force fields. The long-range structure of a liquid crystal results in physical properties which are directionally dependent. The orientation of phase structure and, thus, the properties of the phase can be changed relative to a fixed reference by applying force fields on the phase.

This study used the liquid crystal formed from concentrated solutions of the protein fibrinogen to determine the potential of protein liquid crystals for selective solute-solute separations and to determine if control of this selectivity could be exercised by manipulating the orientation of the phase. The study also provides new information on the role of structure in protein liquid crystals for use in developing better natural membrane models.

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CONCLUSIONS AND SIGNIFICANCE

Concentrated solutions of the protein fibrinogen exhibited liquid crystal properties. The solubility of a small solute in the liquid crystal fibrinogen phase was significantly different from that in an isotropic fibrinogen solution. Thin layers of fibrinogen liquid crystals were used in a flowing system as a selective liquid membrane for two different solutes, tyrosine and lysozyme. A two-dimensional flow field provided sufficient shear force to control the orientation of the liquid crystal layer relative to the direction of mass transfer. No effect of orientation was found on the transfer of the small symmetric solute tyrosine or on the transfer of water. However, transfer of lysozyme, a larger less symmetric protein, was significantly affected by the orientation of the liquid crystal layer. When the long axis of the fibrinogen liquid crystal was parallel to the direction of transfer, the rejection of lysozyme was half the rejection observed when the axis of the fibrinogen liquid crystal was perpendicular to the direction of mass transfer. Thus, the selectivity of the fibrinogen liquid crystal was demonstrated to be variable in a controlled manner for a selected solute.

This initial work suggests the possibility that liquid crystal membranes could be used as controlled molecular gates to separate mixtures of similar solutes which are difficult to separate by other methods. Other force fields such as electric or magnetic instead of shear fields may provide the precise control necessary to separate solutes of nearly identical properties such as optical isomers.

In addition, these results indicate that a new interpretation could be given to natural membrane structures. The function of proteins present in all cellular membranes can be expanded beyond just a structural role to include transport control. The permeation and selectivity character of proteins in membranes when in a liquid crystal state would be highly environment dependent and, for example, would cause one to predict a drop in permeability of blood cells in high shear fields.

Of the two large classifications of liquid crystals, the lyotropic are of major interest for effecting separations of mixed solutes because these liquid crystals exist as multicomponent solutions. The other classification, thermotropic, exists only as single component phases. Lyotropic systems are typically two component systems in which mesophase forms as the result of increasing solvation of a solid composed of asymmetric molecules. Flory (1956) has shown that this results in parallel orientation being a minimum free energy state beyond a critical concentration of the asymmetric solute.

The ordering of molecules in the liquid crystal state leads to directionally dependent physical properties. Optically, liquid crystals are highly birefringent, a property which is often used to characterize liquid crystals. The transport properties are also anisotropic. This results in the effective viscosity coefficient typically exhibiting a maximum at the transition from isotropic to meso phase (Hermans, 1962). This property is also often used to detect a liquid crystal state. The diffusion coefficients for the transport of a small solute have also been found to be directionally dependent (Yun and Fredrickson, 1970). In the flux equation,

$$J_m = -\underline{\underline{D}}\nabla c \qquad (1)$$

the transport coefficient is a tensor with the three diagonal elements being the directional diffusion coefficients for the coordinate space. This neglects such coupling fluxes such as thermal diffusion and momentum diffusion.

Liquid crystals, as separate phases, have exhibited highly selective thermodynamic potentials for various solutes. Bangham (1967) found that phospholipid vesicles displayed graded permeabilities to a number of ionic solutes. Meta and para disubstituted benzene derivatives were separated by chromatography using a liquid crystal support (Dewar and Schroeder, 1964). These effects are a result of structure and should be independent of orientation.

In the following discussions, experimental studies which attempted to use the unique properties of liquid crystals to effect controlled separations of mixed solutes are described. The experimental studies first determined and verified the conditions under which a specific liquid crystal mesophase may be formed and the conditions necessary for the control of the orientation. These results were then used to investigate the use of the formed mesophases for controlled transport of specific biological species.

LIQUID CRYSTAL SYSTEM AND PROPERTIES

The liquid crystal system we wanted for mass transfer studies had to be compatible with biological materials. This eliminated most known liquid crystal systems. As shown by Flory's (1956) work, any sufficiently asymmetric solute in solution should form a liquid crystal phase at high solute concentrations. Large known globular proteins look particularly attractive because of their well defined spheroidal shape, their single unique molecular weight for each unique protein, and their nonamphiphilic conformation. The protein, fibrinogen, was used in this study. Some of its properties are shown in Table 1.

Flory's model, Equation (2),

$$\Psi = (8/x)(1 - 2/x) \qquad (2)$$

predicts that fibrinogen should form a liquid crystal phase at aqueous concentrations of 25 wt. % fibrinogen. Solutions of fibrinogen bracketing this critical concentration point were prepared in 0.03 M arsenate buffer, $pH = 6.1$.

Standard optical birefringence tests were made on samples of these solutions. The samples were placed between microscopic slides and tested with crossed polarizers and a Gilford Spectrophotometer. Long-range structure was detected in solutions containing at least 22 wt% fibrinogen. The birefringence measurements for a 25 wt% solution shown in Figure 1 suggest an optical axis which is orientated at about 10° to the polarizer axes. This can be either of two possible orientations. The absolute orientation can-

Table 1. Molecular Species

Molecule	Type	Mol. wt.	Isoelect.	Asym.
Fibrinogen	Protein	339,700	5.5	31.0
Lysozyme	Enzyme	17,000	11.0	4.3
Tyrosine	Amino acid	181	5.6	1.0

not be determined from this experiment alone. However, the important result is that structural order exists in concentrated solutions of fibrinogen. In addition, no rotary optical activity was detected for these samples.

The existence of the liquid crystal was confirmed by viscosity measurements. These measurements also indicated the conditions needed for control of the liquid crystal layer during the mass transfer measurements. Capillary viscometers in a range of sizes were used with a pressure driving force to measure the viscosity of these solutions. The true rates of shear were calculated using the Rabinowitsch correction (Van Wazer, 1963). Shown in Figure 2 is the viscosity coefficient as a function of fibrinogen concentration. The discontinuty on the viscosity occurs at about 21 wt% fibrinogen. Solutions at concentrations above this discontinuity concentration exhibited optical birefringence while those below it did not. The discontinuity is usually interpreted as being due to the extremely high levels of dissipation encountered in a concentrated isotropic solution

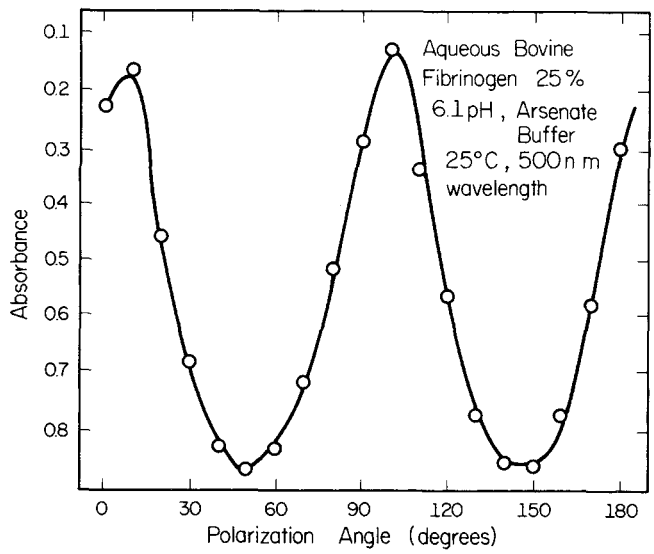

Fig. 1. Birefringence of aqueous fibrinogen solution.

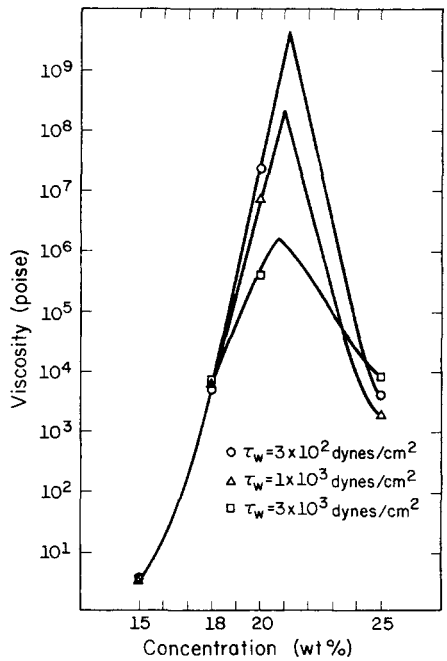

Fig. 2. Viscosity of fibrinogen.

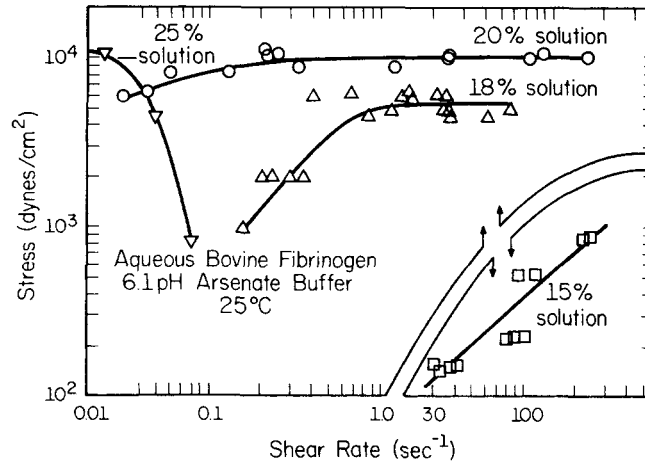

Fig. 3. Rheology of fibrinogen.

of large asymmetric particles (Hermans, 1962). Once the liquid crystal transition occurs, the regular order of the solutes results in significantly lower levels of dissipation. High shear rates can also induce order in the concentrated isotropic solutions, commonly called *flow birefringence*, and reduce the discontinuity at the liquid crystal transition. This is shown in Figure 2 for the fibrinogen solutions.

As noted earlier, the liquid crystal has directionally dependent transport coefficients. For momentum transport in a fluid with symmetries consistent with a nematic liquid crystal, there are six coefficients which have dimensions of a viscosity (Aslaksen, 1971). These can be combined into three effective viscosities η_1 experienced when the molecules slide past each other in their long direction η_2 experienced when they slide past side to side and η_3 the effective viscosity when they slide past each other side against side. The viscosity coefficient values reported here for the orientated solutions are essentially the effective coefficients for movement in the direction of flow with the long axis of the molecules orientated parallel to the flow. Close to the mesophase transition point shear rates of less than 10^{-4} s^{-1} were sufficient to orient the solutions in the direction of flow. This is shown in the stress-strain data of Figure 3. No birefringence was observed for the isotropic solutions. These data agree with literature values for dilute isotropic solutions which show that flow birefringence is observed only at shear rates greater than 10^4 s^{-1} (Tanford, 1961). However, as the concentration of fibrinogen approaches the transition point, induced order is observed at progressively lower shear rates. After the liquid crystal transition, induced order in the direction of flow was observed for shear rates of less than 10^{-4} s^{-1}. This agrees with other published results (Peters, 1955) which show that only infinitely small shear rates are required to orient a liquid crystal. A more detailed discussion of the viscosity data for fibrinogen and other liquid crystals will be published in the future.

EXPERIMENTAL TRANSFER MEASUREMENTS

Selectivity Studies

The thermodynamic selectivities of these fibrinogen solutions were determined for two solutes. A summary of the pertinent properties of the selected solutes are tabulated in Table 1. The tyrosine represents a small symmetric solute while the lysozyme is a larger asymmetric solute. A special cell was constructed as shown in Figure 4. A sample of fibrinogen solution, 1.5 mm thick, was trapped between two PSED membranes (Millipore tradename) and their supports. An aqueous solution of the test solute was then placed, under controlled pressure, in contact with one side of the sandwich. The membrane was impermeable to the fibrinogen but essentially completely permeable to water,

lysozyme, and tryosine. This isolated the fibrinogen solutions as test phases in a one-dimensional flow field with well-defined boundaries. The pressure on the system was held constant at 50 lb./sq.in.abs. ± 0.2 lb./sq.in.abs. for the duration of a test. Water permeation rates were measured with a calibrated capillary tube while the concentrations of lysozyme or tyrosine were measured with a Gilford UV-Vis spectrophotometer. In addition, after the run the fibrinogen solutions were removed from the cell and analyzed for concentrations of fibrinogen and test solute by measuring the absorbance at two wavelengths and assuming additivity of the individual absorbances. The technique was checked by separating one sample by gel chromatography techniques.

The slow approach to equilibrium normally associated with liquid crystals was circumvented by using the forced convection cell. Admittedly, the solutes are at true equilibrium only at the phase interfaces since a gradient of solute concentration will exist across the liquid crystal layer. However, this is a small error compared to the relative magnitudes of the observed solubilities.

Selectivity Control Studies

Selectivties for tyrosine and lysozyme were also determined for the fibrinogen liquid crystal as a function of phase orientation. The orientation of the major axis of the fibrinogen phase was controlled relative to a contacting isotropic phase by imposing a two-dimensional flow field on the phase. This was accomplished by using a continuous flow ultrafiltration cell. The device designed for this study was a stagnation flow ultrafiltration cell which is shown in Figure 5. A porous ultrafiltration membrane which rejects fibrinogen while passing water and other solutes was used in the cell to create a highly concentrated layer of fibrinogen at the membrane surface. By adjusting conditions, the surface concentration exceeded that necessary

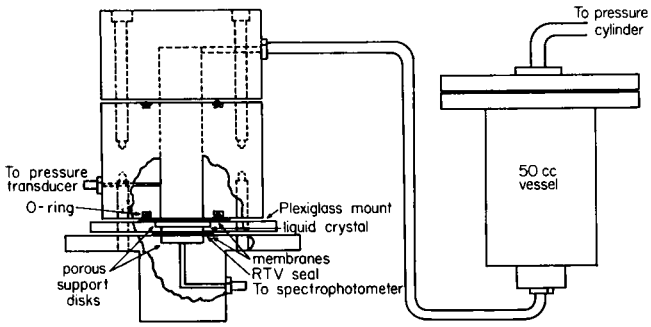

Fig. 4. Filtration cell detail.

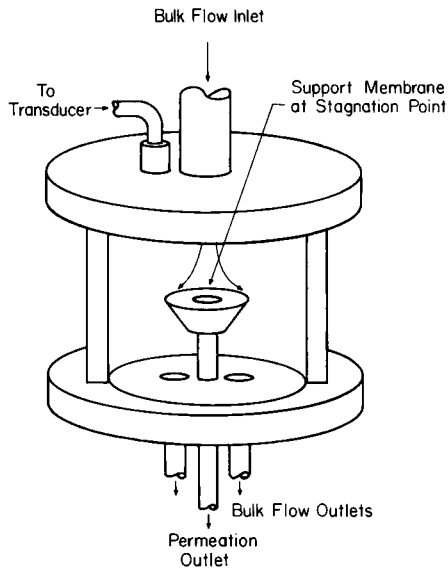

Fig. 5. Stagnation flow filtration cell.

to form a liquid crystal phase. The phase thus formed at the membrane surface will be in a two-dimensional velocity field composed of the permeation velocity through the membrane and the cross velocity across the membrane.

The stagnation flow geometry has the property that for a Newtonian fluid the permeation velocity, concentration, and shear are independent of radial position. Thus macroscopic measurements can be described by a microscopic analysis. A boundary layer analysis for this system was developed by Kozinski and Lightfoot (1973) and is summarized in the following equation:

$$V_w \cong (Re)^{1/2}\, Sc^{-2/3} \left(\frac{c_w}{c_\infty} \right)^{1/3} \qquad (3)$$

The equation relates permeation velocity, cross velocity, and surface concentration for a totally rejected solute. Optical dye studies and standard benzoic acid mass transfer measurements, Kozinski and Lightfoot (1973), for our cell agreed within adequate accuracy with this analysis of stagnation flow. While the liquid crystal is obviously non-Newtonian, the isotropic solution above the liquid crystal layer is Newtonian. Thus this Newtonian boundary layer analysis is useful for determinng concentration variations at the liquid crystal phase—isotropic phase interface.

The selectivity tests were conducted using the same solutes as in the previous tests, namely tyrosine and lysozyme. A solution containing 0.5 g of fibrinogen/100 cc of solution at a *p*H of 7 and in a 0.5M phosphate buffer was mixed with each of the test solutes. The support membrane on the stagnation surface was an Amicon XM-50 which passed 100% of the tyrosine and about 90% of the lysozyme but none of the fibrinogen. The outlet concentrations of the solutes in the permeate streams were monitored continuously using the Gilford UV-Vis spectrophotometer.

The cell was run at constant pressure with the ratio of cross velocity to permeation velocity varied by controlling the outlet resistance on the cross-flow stream with a microvalve. For the flow conditions and pressure used in this study, the shear rate $\partial v_r/\partial z$ parallel to the porous surface varied from 10^{-5} to 10^{-1} s^{-1}. The previously discussed birefringent and viscosity studies suggest that the fibrinogen liquid crystal when subjected to a shear rate greater than about $10^{-4}s^{-1}$ should be oriented at an angle of about 10° from the flow vector. Thus, in this system when the cross flow is at a very low value corresponding to a shear rate $< 10^{-5}s^{-1}$, the fibrinogen should be oriented at a small angle to the permeation flow vector or approximately perpendicular to the membrane surface. At high cross-flow rates the shear rate is about $10^{-1}s^{-1}$ and the fibrinogen liquid crystal should be oriented at a small angle to the cross velocity or approximately parallel to the membrane surface. Hence, by changing the ratio of the cross flow to permeation flow we should be able to change the orientation of the primary axis of the fibrinogen liquid crystal layer relative to the surface. About 30 min. were allowed between changes to ensure that steady state operations had been achieved. As in the other cell, permeation velocities were measured with a calibrated capillary tube. The cross velocities were determined by measuring the total flow into the cell and then calculating the boundary layer velocity from the analytical model.

DISCUSSION OF RESULTS

The one-dimensional flow cell studies allowed us to determine the basic transfer differences between the isotropic and structured fibrinogen solutions. For these tests, the orientation of the liquid crystal layer was always assumed to be perpendicular to the support membrane.

Permeation rates of pure water essentially did not differ between the concentrated isotropic (18 wt%) fibrinogen solution and the liquid crystal (25 wt%) fibrinogen solutions as shown in Figure 6. This indicated that the hydraulic permeation was not affected by the type of solute present. Structure did affect the permeation rate slightly.

The tests with lysozyme indicated that neither the isotropic or liquid crystal layers were permeable to any detectable levels of this protein. Subsequent studies in our

two-dimensional flow system indicated that the layer in this test was too thick for the period of observation.

The tyrosine was not rejected by either of the concentrated layers. However, the rate of passage of tyrosine was about 1.5 times as rapid through the liquid crystal layer as through the isotropic layer. This enhanced transport, as measured by the time required to reach a steady state outlet concentration, is shown in Figure 7. This could be the result of reduced resistance of the structured phase to transport of tyrosine.

The results of measuring the concentrations of fibrinogen and solute in the layer after the run are shown in Table 2. These solubility results were subsequently confirmed by equilibrium measurements over a period of weeks in a non-flow cell. For the small symmetric solute, tyrosine, there was no difference between the isotropic and liquid crystal phase solubilities. However, the concentration in both phases was about 100 times greater than the aqueous tyrosine solution used in the tests. This is undoubtedly just a manifestation of the well-known fact that large macromolecules have a high equilibrium capacity for small ions.

The tests with lysozyme, a larger asymmetric solute, showed no small ion effect as the concentration of lysozyme in buffer and isotropic fibrinogen solution were nearly the same. However, the solubility increased by a factor of 15 for the liquid crystal phase. This can be interpreted in terms of a steric effect as follows: For concentrated solutions of large asymmetric solutes, more particles can fit into a structured media than an unstructured media. This is a simplified interpretation of Flory's Lattice Model, in which the free energy will be lower for a structured phase than an unstructured phase. The results indicate that compared to a similar isotropic phase, a structured phase shows a significantly higher affinity for an asymmetric solute.

The above tests, with regard to mass transfer, were conducted under unsteady state conditions which make them

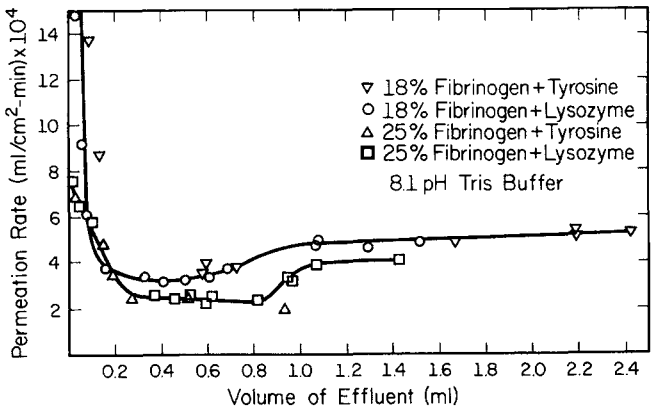

Fig. 6. Water permeation of aqueous bovine fibrinogen.

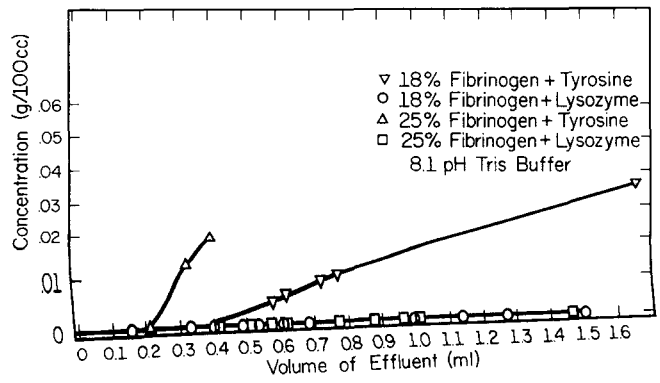

Fig. 7. Solute permeation of aqueous bovine fibrinogen.

TABLE 2. SOLUBILITY IN FIBRINOGEN LAYERS

	Feed	Fibrinogen layers Isotropic 18, wt %	Liquid crystal 25, wt %
Tyrosine conc., C_T (g/100 cc)	0.0200	2.96	9.12
Lysozyme conc., C_L (g/100 cc)	0.0672	0.064	0.963
Fibrinogen conc., C_F (g/100 cc)	0	11.17	22.26

TABLE 3. SOLUTE REJECTION IN PRESENCE OF CONCENTRATED FIBRINOGEN LAYERS

Solute	Perm. flow,* cm/min.	Cross flow Perm. flow	Rej.
Lysozyme	0.009	0.8	0.11
	0.009	15.0	0.18
Tyrosine	0.009	0.2	0.11
	0.012	14.0	0.11

unreliable for predicting any rate determined selectivity. The tests with the two-dimensional flow cell, in addition to orientation effects, would reveal any selectivity whether due to relative transfer rates or the affinity of the layer. The results shown in Table 3 are a summary of these tests.

The data in Table 3 show that the permeation velocity did not change as the cross velocity was changed. This allows one to state that the observed rejection effects are not due to the well-known boundary layer effects commonly observed during ultrafiltration. If a boundary layer of rejected small solute were present, the analysis of Kozinski and Lightfoot (1973) summarized here as Equation (3), would indicate that the permeation velocity should vary as the cross velocity to the ½ power. For the cross-velocity changes in this study, the permeation velocities should have changed minimally by a factor of 3 with the surface concentration of rejected small solute consequently also reduced. Then, the change in surface concentration would change the potential for mass transfer across the membrane which would appear as a change in rejection. This would be the well-known observation in ultrafiltration that at high Reynolds numbers rejection of a solute appears to be better. The permeation velocities in our tests did not vary and, thus, these boundary layer effects were not significant. In our system, the surface concentration of fibrinogen exceeded that necessary to form the liquid crystal at all test conditions. The observed effects may then be attributed to the presence of the liquid crystal fibrinogen layer. Later studies have confirmed in situ, the existence of a structured layer on the surface.

The data for tyrosine indicated that about 10% of the tyrosine is rejected by the liquid crystal layer at both the high and low cross-velocity conditions. This result indicates that the diffusion of tyrosine through this phase is reduced relative to water. The observed rejection is the result of a relative diffusion difference since the solubility measurements indicated no rejection should have occurred. The orientation of the liqud crystal layer did not affect the rejection of this symmetric solute. The data also confirm the lack of a significant boundary layer resistance since the change in cross velocity did not change the rejection of tyrosine.

For the lysozyme, the test data indicated a change by a factor of 2 as a result of a change in orientation of the layer. Under the conditions of our tests, a solute the size

of lysozyme will be randomly orientated in the bulk solution and will thus not confound the orientation effects we attributed to the fibrinogen liquid crystal layer. When the orientation of the fibrinogen solution was approximately perpendicular to the bulk solution, the rejection of lysozyme was about 10%, which indicates that the lysozyme mass transfer resistance of the liquid crystal layer in this orientation is not significantly different from that of the supporting membrane. Remember that the solubility of the lysozyme in the liquid crystal layer is about 15 times the bulk concentration and, thus, only an order of magnitude reduction in diffusion rate would significantly alter the observed rejection.

When the orientation of the fibrinogen solution was changed to approximately parallel to the bulk solution, the rejection rose to about 20%, or double the previous value. While a change in the solubility of the lysozyme in this changed orientation cannot be eliminated based on our data, it is inconceivable that the equilibrium chemical potential of a solute will be dependent on the orientation of a phase relative to an external reference. Thus, one concludes that the increased rejection is due to increased resistance to transfer when the solute must move in a direction perpendicular to the axis of the liquid crystal. This is represented schematically in Figure 8. The effect should be continuously variable although this was not demonstrated in this study. Also, the larger the solute the greater should be the change in rejection. Qualitative tests with an unidentified lipid solute of about 80,000 Mwt indicated a larger effect of orientation.

These results can be expressed in terms of the transfer resistance of the two regions.

$$\frac{1}{K_i} = \frac{1}{k_{BL}} + \frac{\delta}{D_i S}$$

k_{BL} is negligible

Then the ratio of transfer rates for the two directions can be expressed as follows:

$$\frac{K_{\underline{1}}}{K_{11}} = \frac{D_{\underline{1}}\,\delta_{11}}{D_{11}\,\delta_{\underline{1}}}$$

The liquid crystal layer thickness is determined by the dynamics of the layer and currently cannot be expressed in terms of more fundamental quantities such as viscosity. Thus the observed change in transfer rates can not be attributed solely to the anisotropic diffusivity.

In conclusion, then, a solution of large asymmetric proteins was observed to form a structured, so-called *liquid crystal* phase. The properties of the structural phase were quite distinct from those of the isotropic phase. The transport properties were directionally dependent, particularly the diffusion rates of small solutes. In a typical ultrafiltration system, a liquid crystal phase was formed such that the orientation of the structure relative to a fixed reference was controlled. The relative rate of transfer of a solute was found to be a function of the liquid crystal phase orientation as well as the solute type. This work is being pursued to determine if the continuously controllable selectivity of a liquid crystal layer, as indicated by our data, can be exploited for practical separations.

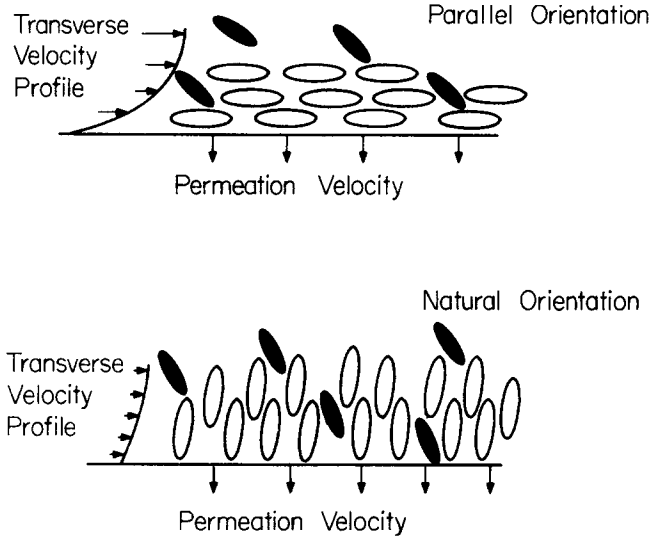

Fig. 8. Schematic of liquid crystal membrane.

NOTATION

C = mass concentrations, g/cc
D_i = diffusion coefficient, cm²/s
J_m = mass flux, g/cm²s
K_i = overall mass transfer coefficient, cm/s
Re = Reynolds number
S = solute solubility in liquid crystal layer, $\frac{\text{g/cc LC.}}{\text{g/cc isot.}}$
Sc = Schmidt number
V = fluid velocity through membrane, cm/s
X = ratio of major to minor axis of a solute
∇ = gradient operator
δ = thickness of liquid crystal layer, cm
η_i = component viscosity, g cm/s
Ψ = critical volume fraction for phase formation

Subscripts

BL = bulk phase boundary layer resistance
W = evaluated at phase boundary
∞ = bulk value
$\underline{1}$ = evaluated in direction perpendicular to main axis of liquid crystal
11 = evaluated in direction parallel to main axis of liquid crystal

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