

EXTERNAL CONVECTIVE MASS TRANSFER IN NON-NEWTONIAN FLUID

PART I

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Аннотация—Сообщаются результаты аналитического и экспериментального исследования массопереноса в пограничном слое эластовязкой неньютоновской жидкости.

В первой части приводятся результаты аналитического исследования массопереноса продольно-обтекаемой пластины, описывается также методика экспериментального исследования. Излагаются результаты исследования диффузии, оптических и реологических свойств электрохемиллюминесцирующего раствора (ЭХЛ) с добавками НКМЦ.

NOMENCLATURE

$x, y, z,$	rectangular co-ordinates of a boundary layer;	$\Delta V,$	voltage difference between anode and solution;
$n, k,$	rheological parameters of a constitutive formula;	$T,$	light transmission coefficient;
$\tau,$	shear stress;	$L_i^{(r)}; L_{ik},$	phenomenological transfer coefficients;
$P_{ik}, \dot{\epsilon}_{ik}$	deviators of tensors stress and deformation rates;	$C_0,$	active agent bulk concentration (H_2O_2) in electrolyte;
$\mu,$	shear viscosity of steady-state flow;	$d,$	cylinder diameter;
$\eta,$	similarity variable;	Nu_{mx}	$= \frac{jx}{DC_0}$, local Nusselt number (mass transfer);
$\psi,$	stream function;	Pe_{mx}	$= \frac{U_\infty x}{D}$, local Péclet number (mass transfer);
$\lambda_r,$	delay period;	$Re,$	$= \frac{U_\infty^2 - n_x^n}{k/\rho}$, generalized Reynolds number.
$\tau_r,$	relaxation period;		
$G,$	shear modulus;		
V and $P,$	consistent rheological variables;		
$\rho,$	density;		
u and $v,$	velocity vector components along co-ordinate axes x and y , respectively;		
$h_0,$	length of passive section;	Subscripts	
$U_\infty,$	velocity of incoming flow;	$m,$	referred to mass transfer;
$j,$	local value of a diffusion flux at electrode surface;	lim,	limiting value;
$\beta_1,$	formparameter of the dynamic boundary layer;	0,	referred to bulk phase outside a boundary layer;
		$w,$	referred to wall;

x, dimension, according to which a number is composed.

DURING the last years the interest in the problems of convective transfer in non-Newtonian fluids has grown considerably. The interest in the transfer processes in moving non-linear viscous and elastic fluids is caused by the fact that such complex systems with more general laws of physical and mechanical behaviour may display many new phenomena. These may be not only purely mechanical (Weissenberg, Key, Merryngton's effects) but also physical, due, for example, to turbulent substance transfer. Many new and sometimes unexpected properties of such systems (e.g. melts, concentrated polymer solutions) are conditioned by comparatively great time intervals of the order of seconds and more of the relaxation of the stress-deformation state and by memory effects. Thus, strictly speaking, hydrodynamics of the modern high altitude, high-speed vehicles should be based on the rheological concepts since atmospheric air at altitudes above 9 km has distinct viscoelastic properties [1]. Against the background of numerous publications on rheodynamics and heat transfer in general liquid systems, the absence of theoretical and experimental works on mass transfer is specially noticeable. At the same time such problems are important not only in their practical but also in their theoretical applications, since diffusion in non-Newtonian disperse systems and polymer solutions has its specific features, which make it different from heat conduction. In particular, the diffusion coefficient of a polymer admixture in a low molecular medium is not only by some orders smaller than the thermal diffusivity of the same solution but also displays an extremely strong and non-linear dependence upon concentration while the thermal diffusivity varies very weakly and linearly. Up to now the influence of rheological characteristics of shear flow upon admixture convection in the external and internal problem is not sufficiently studied.

The so-called power law for describing inter-

nal friction is used in the majority of works on pure viscous non-Newtonian fluids. Consequently, such systems are based on the law of the Newtonian internal friction with some correction in the form of the empirical exponent n in the formula (modified Newton's law)

$$P_{ik} = k \left| \frac{1}{2} \dot{\epsilon}_{mr} \dot{\epsilon}_{rm} \right|^{\frac{n-1}{2}} \dot{\epsilon}_{ik} \quad (1)$$

From the thermodynamics of irreversible processes it is known that the law of viscous Newton flow corresponds to the validity of the linear phenomenological Onsager laws. Work [2] presents the generalized relation between fluxes J_i and thermodynamic forces X_k , which is valid for current systems with different rheological models

$$J_i = L_i^{(r)} J_i + \Sigma (L_{ik} X_k + L_{ik}^{(r)} X_k) \quad (2)$$

Hence, for example, we have the well-known Oldroyd formula [3] which was proposed for describing visco-elastic fluid with zero yield stress ($L_i^{(r)} = -\tau_r$; $L_{ik}^{(r)} = \lambda_r$; $L_i = \mu$)

$$P_{ik} = \mu \dot{\epsilon}_{ik} + \lambda_r \left(\frac{d\dot{\epsilon}}{dt} \right)_{ik} - \tau_r \left(\frac{dP}{dt} \right)_{ik} \quad (3)$$

Here P_{ik} and $\dot{\epsilon}_{ik}$ are the deviators of the tensor stresses and the deformation rates, μ , λ_r , τ_r are the material constants, η is the shear viscosity of the steady-state flow, λ_r is the delay period characterizing the rate of exponential decrease in shear velocity when shear stresses are taken off, τ_r is the stress relaxation period when shear flow is stopped instantaneously. These constants are determined by the viscosity of a continuous phase, bulk concentration and elasticity modulus of a disperse phase. The rheological law (3) has a physical meaning only when it satisfies the inequality $\tau_r > \lambda_r \geq 0$ and includes the classical model of a visco-elastic Maxwell fluid ($\lambda_r = 0$) as a particular case.

The principal difference between laws (1) and (3) is that if in the first case the rheological system under the action of shear displays one

fundamental property, i.e. it approximates a pure viscous fluid obeying the modified Newtonian law, then in the second case the model is given properties of a Newtonian fluid and also of a non-ideal elastic solid (second and third terms in the right-hand side of formula (3) characterize the instantaneous and the delayed τ , elasticity†).

From the rheological point of view there is no principal difference between an elastic solid and fluid, the difference is only in the magnitudes of periods of stress relaxation and elastic recoil. In the first case the relaxation period of the shear stresses τ , is large and in the second case is negligibly small in the usual time scale.

The constitutive equation (3) is well confirmed by experimental data on the flow of structured systems, emulsion type, high-polymer solutions and elastic particle suspensions. Elastic elements (drops, flexible macromolecules, etc) suspended in such a system are deformed under the action of shear stresses and accumulate energy of elastic deformations. According to [3] in fluid (3) in steady shear flow normal stresses must appear not equal one to the other. Non-zero differences of normal stresses along and across the stream lines lead to the Weissenberg effect [4].

Thus, the Oldroyd law makes it possible to explain, although to a first approximation, new physical and mechanical effects which may be predicted on the basis of the classical Newtonian viscosity concept. Rheological systems of type (3) are not difficult to obtain by introducing polymer additives into a Newtonian fluid. In particular, we have used a fluid which is a solution of sodium-carboxy-methylcellulose in water (Na-CMC). Elastic elements are formed in water by polymer macromolecules with additional immobilization of the solution by "solvent" cells. Deformation of such an element

under the influence of a velocity gradient is not instantaneous due to resistibility of a macromolecule to a change in its shape. The time, during which a change occurs in the macromolecule configuration is determined by the relaxation period and depends upon the sizes, shape and flexibility of the chain. The mechanical behaviour of such a solution should, in principle, be described by relations (2) and (3).

Kotaka *et al.* [5] have studied viscoelasticity of Na-CMC solutions by means of the rotational instrument "paralleldisks" ("plate-plate"). Even for comparatively small shear rates of the order of 10 sec^{-1} , viscoelastic properties appear very effective. For shear velocities of the order of 10^3 sec^{-1} the viscoelastic stresses P_b become greater than the shear ones P_c . The commensurability of the quantities P_b and P_c is achieved more rapidly at small Na-CMC concentrations.

In Ernst's recent experiments [6] it has been found that in turbulent flow of Na-CMC aqueous solutions in circular tubes at $\dot{\epsilon} = (0.5 + 3.5) 10^3 \text{ sec}^{-1}$ the viscoelastic properties are strongly displayed at 0.1 per cent concentrations.

For steady laminar shear flows where the longitudinal pressure gradients $\partial P/\partial x$ are small (plate in flat-parallel flow, translational motion in long constant cross-section channel), as it is known [7, 8], the velocity field and friction resistance are independent of viscoelastic properties and may be calculated on the basis of the so-called flow curve, in particular, by using equation (1). Where the values of $\partial P/\partial x$ change sharply along the flow surface (nozzles, diffusers, inlet sections of rectangular tubes and channels, flow past blunt bodies, etc.) one should expect an increasing role of the viscoelastic properties of a flowing medium in the general dynamic and energy flow balance.

The present paper deals with the results of an analytical and experimental study of mass transfer in a boundary layer along a plate in longitudinal flow (Part I) and with the experimental investigation of mass transfer from a circular cylinder (Part II) to an elastoviscous non-Newtonian fluid.

† If the viscosity coefficient is large ($\mu \rightarrow \infty$), we obtain the formula of Hooke's law in shear $P_{ik} = G(e_{ik})$, i.e. $\tau = \mu/G$ where G is the shear modulus (see [2]).

**ANALYTICAL STUDY—FLAT PLATE
IN LONGITUDINAL FLOW**

The initial system is formulated as follows:

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = kn \left| \frac{\partial u}{\partial y} \right|^{n-1} \frac{\partial^2 u}{\partial y^2} \quad (4)$$

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \quad (5)$$

$$\tau = k \left| \frac{\partial u}{\partial y} \right|^{n-1} \frac{\partial u}{\partial y} \quad (6)$$

$$u \frac{\partial C}{\partial x} + v \frac{\partial C}{\partial y} = \frac{\partial}{\partial y} \left[D \frac{\partial C}{\partial y} \right] \quad (7)$$

The velocity distribution defined by equations (4)–(6) is considered to be known. Work [9] contains it in the form of tables and charts. Equation (7) will be solved assuming that the diffusion kinetics process occurs in a region, i.e. under the boundary conditions of a limiting diffusion flux. Assume also that diffusion occurs not at the whole wetted surface but starts at some distance h_0 calculated from the leading edge of a plate. Consequently, the section of a plate $0 \leq x \leq h_0$ is characterized by the equality $j_w = 0$ (passive section of a plate). For all $x > h_0$ (active section) the condition $C = 0$ is valid. From physical considerations it is clear that the regime of the limiting flux at this section is established not immediately behind the passive section. At some portion of the active surface there will occur transition to the limiting flux values and here diffusion mass transfer will be higher than the appropriate limiting one achieved at $x \gg h_0$. This region will be called the stabilization region where tangential mass transfer makes a greater contribution to the full diffusion flux than to the region of the steady limiting regime. After changing from the physical co-ordinates x and y to the variables x and ψ , equation (7) can be re-written as:

$$\left(\frac{\partial C}{\partial x} \right)_\psi = \frac{\partial}{\partial \psi} \left[Du \frac{\partial C}{\partial \psi} \right] \quad (8)$$

The new abscissa x is now read along the stream line $\psi = \text{const.}$ (from now on the subscript ψ will be omitted). The variable ψ is above the wall ($\psi = 0$). Equation (8) should be solved for the following boundary conditions

$$\frac{\partial C}{\partial \psi} = 0 \quad \text{at } \psi = 0 \quad (x < h_0) \quad (9a)$$

$$C = 0 \quad \text{at } \psi = 0 \quad (x > h_0) \quad (9b)$$

$$C = C_0 \quad \text{at } \psi = 0 \quad (x = 0) \quad (9c)$$

$$C = C_0 \quad \text{at } \psi \rightarrow \infty. \quad (9d)$$

To combine the quantities u, x, ψ we shall use the well known similar solutions of the dynamic problem for a plate [9]

$$\eta = yx^{-\frac{1}{1+n}} \left[\frac{U_\infty^{2-n} \rho}{n(n+1)k} \right]^{\frac{1}{1+n}} = yx^{-\frac{1}{1+n}} M^{\frac{1}{1+n}} \quad (10)$$

$$\left. \begin{aligned} u &= U_\infty \frac{\partial F(\eta)}{\partial \eta}; \\ \psi &= x^{\frac{1}{1+n}} U_\infty M^{-\frac{1}{1+n}} F(\eta); \\ M &= \left[\frac{U_\infty^{2-n} \rho}{n(n+1)k} \right] \end{aligned} \right\} \quad (10a)$$

$$(F'')^{n-1} F''' + FF'' = 0 \quad (11)$$

$$F(0) = F'(0) = 0 \quad \lim_{\eta \rightarrow \infty} F'(\eta) = 1. \quad (11a)$$

The unknown relation $\eta(\psi)$ is found from the equalities

$$u = \frac{\partial \psi}{\partial y} \quad \text{and} \quad v = -\frac{\partial \psi}{\partial x} \quad (12)$$

which satisfy the continuity equation (5).

As it is known, all liquids (especially high-viscous) are characterized by the condition $Pr_m \gg 1$. The the diffusion boundary layer appears to be much thinner than the dynamic

one and occupies a narrow near-wall region. While finding the concentration field by equation (8), not the whole velocity profile should be taken into account but only that part of it which is "submerged" in the diffusion boundary layer. For this purpose, the one-parameter linear velocity family is normally used

$$\left. \begin{aligned} \frac{u}{U_\infty} = \beta_1(x, n) y = \left[\frac{\partial(u/U_\infty)}{\partial \eta} \right]_{\eta=0} \eta, \\ \text{where} \\ \beta_1 = a = \left(\frac{\partial u}{\partial \eta} \right)_{\eta=0} x^{-\frac{1}{1+n}} M^{\frac{1}{1+n}} \end{aligned} \right\} \quad (13)$$

combining equations (10)–(13) we have the relation

$$\eta = 2^{\frac{1}{2}} x^{-\frac{1}{2(n+1)}} a^{-\frac{1}{2}} M^{\frac{1}{2(1+n)}} U_\infty^{-\frac{1}{2}} \psi^{\frac{1}{2}}. \quad (14)$$

Equation (8) is now simplified

$$x^{\frac{1}{2(n+1)}} \frac{\partial C}{\partial x} = B \frac{\partial}{\partial \psi} \left[(\sqrt{\psi}) \frac{\partial C}{\partial \psi} \right]. \quad (15)$$

Here

$$B = 2^{\frac{1}{2}} D a^{\frac{1}{2}} U_\infty^{\frac{1}{2}} M^{\frac{1}{2(n+1)}} \quad (16)$$

Introduce new variables

$$\xi = \frac{n+1}{2(2n+1)} B x^{\frac{2n+1}{2(n+1)}}; \quad \varphi = \sqrt{\psi} \quad (17)$$

As a result we come to a new notation

$$\frac{\partial C}{\partial \xi} = \frac{1}{\varphi} \frac{\partial^2 C}{\partial \varphi^2} \quad (18)$$

$$C \rightarrow C_0 \quad \text{at} \quad \varphi \rightarrow \infty \quad (19)$$

$$\left. \begin{aligned} \frac{\partial C}{\partial \varphi} = 0 \quad \text{at} \quad \xi < \frac{n+1}{2(2n+1)} B h_0^{\frac{2n+1}{2(n+1)}} \\ \text{and} \quad \varphi = 0 \end{aligned} \right\} \quad (20)$$

$$\left. \begin{aligned} C = 0 \quad \text{at} \quad \xi > \frac{1}{2} \cdot \frac{n+1}{2n+1} B h_0^{\frac{2n+1}{2(n+1)}} \\ \text{and} \quad \varphi = 0. \end{aligned} \right\} \quad (21)$$

Following Meuman [10], the solution of the limiting boundary-value problem is sought in terms of the variables ξ and φ for a semi-infinite plate without a passive section ($h_0 = 0$). Then, the boundary conditions are simplified as:

$$C \rightarrow C_0 \quad \text{at} \quad \varphi \rightarrow \infty \quad (22)$$

$$C = 0 \quad \text{at} \quad \varphi = 0 \quad (23)$$

$$C = 0 \quad \text{at} \quad \xi = 0; \quad \varphi = 0. \quad (24)$$

The replacement of the variables

$$\omega = \varphi(9\xi)^{-\frac{1}{3}} \quad (25)$$

leads to the equation

$$\frac{\partial^2 C}{\partial \omega^2} + 3\omega^2 \frac{\partial C}{\partial \omega} = 0. \quad (26)$$

The solution of equation (26) is

$$\left. \begin{aligned} C_{\text{lim}} = \frac{C_0 \int_0^\omega e^{-\lambda^3} d\lambda}{\int_0^\omega e^{-\lambda^3} d\lambda} \\ = C_0 \left[\frac{1}{3} \Gamma\left(\frac{1}{3}\right) \right]^{-1} \int_0^\omega e^{-\lambda^3} d\lambda. \end{aligned} \right\} \quad (27)$$

The initial system is obviously invariant with respect to the group of transformations $\xi + \xi_0$ ($\xi_0 = \text{const}$). Choose

$$\xi_0 = \frac{B}{2} \frac{n+1}{2n+1} h_0^{\frac{2n+1}{2(n+1)}}$$

The function

$$\left. \begin{aligned} C = C_0 \left[\frac{1}{3} \Gamma\left(\frac{1}{3}\right) \right]^{-1} \int_0^\omega \exp(-\lambda^3) d\lambda; \\ \omega = \frac{\varphi}{\sqrt[3]{9 \left(\xi - \frac{B}{2} \frac{n+1}{2n+1} h_0^{\frac{2n+1}{2(n+1)}} \right)^{\frac{1}{3}}}} \end{aligned} \right\} \quad (28)$$

satisfies equation (18) and the conditions (19)–(21). In terms of the physical variables the solution has the form:

Here it is interesting to dwell upon two important consequences of the solution obtained. Firstly, the influence of the passive section is

$$C(x, y) = \begin{cases} C_0 & \text{at } x < h_0 \\ C_0 \left[\frac{1}{3} \Gamma\left(\frac{1}{3}\right) \right]^{-1} \int_0^p \exp(-\lambda^3) d\lambda & \text{at } x > h_0 \end{cases}$$

$$P = \frac{1}{\sqrt{2}} \left[\frac{2n+1}{9(n+1)} \right]^{\frac{1}{3}} D^{-\frac{1}{3}} a^{\frac{1}{3}} U_{\infty}^{\frac{1}{3}} M^{\frac{1}{3(n+1)}} y x^{-\frac{n+2}{3(n+1)}} \left[1 - \left(\frac{h_0}{x} \right)^{\frac{2n+1}{2(n+1)}} \right]^{-\frac{1}{3}} \quad (29)$$

The value of the diffusion flux density at the active section is determined by the relation

$$j = D \left(\frac{\partial C}{\partial y} \right)_{y=0} = C_0 \left[\frac{1}{3} \Gamma\left(\frac{1}{3}\right) \right]^{-1} \left[\frac{2n+1}{36(n+1)} \right]^{\frac{1}{3}} B^{\frac{1}{3}} x^{-\frac{n+2}{3(n+1)}} \left[1 - \left(\frac{h_0}{x} \right)^{\frac{2n+1}{2(n+1)}} \right]^{-\frac{1}{3}} \quad (30)$$

For $n = 1$ (Newtonian fluid) relations (29) and (30) automatically convert into Meuman's solution [10].

The relation of real and limiting ($h_0 = 0$) diffusion fluxes is expressed by a simple formula:

$$\frac{j}{j_{\text{lim}}} = \left[1 - \left(\frac{h_0}{x} \right)^{\frac{2n+1}{2(n+1)}} \right]^{-\frac{1}{3}} \quad (31)$$

Thus, the excess of the real flux j over j_{lim} and the length of the stabilization region depend not only on the relation h_0/x but also on the non-Newtonian behaviour index n .

As compared with Newtonian fluids, the pseudoplastic ones ($n < 1$) require a larger length x to achieve j_{lim} . The dilatant system ($n > 1$) exhibits a reverse tendency. The exponent of the relation h_0/x varies from $\frac{1}{2}$ (limiting pseudoplasticity $n = 0$) to 1 (extreme dilatancy $n \rightarrow \infty$). For a fixed value of h_0 , on the abscissa where j and j_{lim} differ between themselves by 5 per cent for limiting pseudoplastic fluid $x_{5\%} \cong 10 h_0$, for Newtonian fluid $x_{5\%} \cong 5 h_0$ and for limiting dilatant system $x_{5\%} \cong 3 h_0$.

the greater, the lower is the value of the non-Newtonian behaviour index n . This is caused by the higher contribution of the tangential j -component to the cross mass flux. For great h_0/L the cross-mass flux transferred over the whole active portion of a plate will differ considerably from j_{lim} despite the fact that the process still proceeds in a diffusion region and the condition $C|_{y=0} = 0$ is fulfilled.

Secondly, the presence of a passive section may serve as a means for exerting deliberately influence upon convective mass transfer in a non-Newtonian fluid. New possibilities are created for optimal control of technological mass-transfer processes in the production and processing of polymers and plastics in a liquid state.

The solution obtained is transformed into a dimensionless form

$$Nu_{mx} = \frac{a}{0.89^3 \cdot 18} \frac{2n+1}{1+n} [n(n+1)]^{\frac{1}{3}} \left[1 - \left(\frac{h_0}{x} \right)^{\frac{2n+1}{2(n+1)}} \right]^{-\frac{1}{3}} \times Re_x^{\frac{1}{1+n}} Pr_{mx}^{\frac{1}{3}} \quad (32)$$

Let us determine the average values of j -fluxes on the portion $x - h_0$

$$\bar{j}_x = \frac{1}{x - h_0} \int_{h_0}^x j \, dx = \frac{3(n + 1)}{2n + 1} A h_0^{-\frac{n+2}{3(n+1)}} \times \frac{\left[\left(\frac{x}{h_0} \right)^{\frac{2n+1}{2(n+1)}} - 1 \right]^{\frac{1}{3}}}{\frac{x}{h_0} - 1} \quad (33)$$

Here

$$A = C_0 \sqrt[3]{ \left\{ \frac{a_1 D^2 U_{\infty}^{\frac{3}{n+1}} (2n + 1)}{0.89^3 \cdot 18 \cdot (n + 1) \left[\frac{nk}{\rho} (n + 1) \right]^{1/1+n}} \right\} } \quad (34)$$

The formulae obtained contain the velocity field formparameter β_1 being the only characteristic unamenable to direct measurement.

The quantity

$$\beta_1(x, n) = \left| \frac{\partial u/U_{\infty}}{\partial y} \right|_{y=0} = a \cdot \eta/y$$

is the dynamic formparameter dependent on the longitudinal co-ordinate of the layer, the velocity distribution in the external potential flow and the rheological properties of the medium.

In general, the quantities a should be determined from the solution of a non-linear system of the equations for a boundary layer in case of the arbitrary law of a change in external potential flow $U(x)$ and of the prescribed equation of a rheological state. It is still very difficult to obtain a strict solution of this problem owing to great mathematical difficulties. Let us briefly describe a new method for calculating β_1 similar to the Meksyn method [19].

Solutions (11)-(12) will be sought in the form of the McLoren expansion with increasing powers i.e.

$$F = \sum_{\alpha=0}^{\infty} \frac{a_{\alpha}}{\alpha!} \eta^{\alpha} \quad (35)$$

Owing to the first two conditions (12)

$$a_0 = a_1 = 0. \quad (36)$$

Moreover, by means of the consecutive differentiation (11) we obtain additional conditions

$$F^{III}(0) = F^{IV}(0) = 0. \quad (37)$$

Consequently,

$$a_3 = a_4 = 0. \quad (38)$$

Substitution of series (35) into equation (11) allows all the coefficients a_{α} to be expressed in terms of $a_2 = a$.

From (36) and (38)

$$F(\eta) = \sum_{i=0}^{\infty} \frac{a_{3i+2}}{(3i + 2)!} \eta^{3i+2}. \quad (39)$$

Present (11) as

$$F''' + (F'')^{1-n} FF'' = 0. \quad (40)$$

Substitution of series (39) into (40) and equating the coefficients of the same powers η give

$$\left. \begin{aligned} a_5 &= -a^{3-n} \\ a_8 &= (21 - 10n)a^{5-2n} \end{aligned} \right\} \quad (41)$$

Consequently,

$$F = \frac{a}{2!} \eta^2 - \frac{a^{3-n}}{5!} \eta^5 + \frac{(21 - 10n)a^{5-2n}}{8!} \eta^8 + \dots \quad (42)$$

We shall consider the quasi-linear equation (40) as a differential equation in terms of the

derivative F'' which quickly decreases across the layer. The product

$$(F'')^{1-n} F = \varphi(\eta) \tag{43}$$

is formally interpreted as some variable coefficient, i.e.

$$(F'')' + \varphi(\eta) F'' = 0. \tag{44}$$

Then

$$F'' = A_1 e^{-\phi} \tag{45}$$

$$F' = A_1 \int_0^\eta e^{-\phi} d\eta. \tag{46}$$

Here A is the integration constant and

$$\phi = \int_0^\eta (F'')^{1-n} f d\eta. \tag{47}$$

The quantity A_1 is found from the wall condition

$$A_1 = F''(0) = a.$$

To calculate $\phi(\eta)$, transform the integrand

$$(F'')^{1-n} = \left[a - \frac{a^{3-n}}{3!} \eta^3 + \frac{10(2-n)+1}{6!} \times a^{5-2n} \eta^6 + \dots \right]^{1-n} = \sum_{k=0}^\infty C_k \eta^k \tag{48}$$

$$\left. \begin{aligned} C_0 &= a^{1-n} \\ C_1 &= 0 \\ C_2 &= 0 \\ C_3 &= -\frac{1-n}{3!} a^{3-2n} \\ C_4 &= 0 \\ C_5 &= 0 \\ C_6 &= \frac{(1-n)[20(1-n)+1]}{6!} a^{5-3n} \end{aligned} \right\} \tag{49}$$

Multiplication of equation (34) by (47) gives

$$\begin{aligned} \varphi &= \frac{a^{2-n}}{2!} \eta^2 - \frac{10(1-n)+1}{5!} a^{4-2n} \eta^5 \\ &+ \frac{[11+(1-n)(654-560n)]}{8!} a^{6-3n} \eta^8 \\ &+ \dots \end{aligned} \tag{50}$$

Upon integration

$$\begin{aligned} \phi(\eta) &= \frac{a^{2-n}}{3!} \eta^3 - \frac{10(1-n)+1}{6!} a^{4-2n} \eta^6 \\ &+ \frac{[11+(1-n)(654-560n)]}{9!} a^{6-3n} \eta^9 \\ &+ \dots \end{aligned} \tag{51}$$

Thus, to calculate $F''(0, n) = a(n)$ the asymptotic condition at the upper boundary of the layer should be satisfied in equation (46)

$$F' = a \int_0^\infty e^{-\phi} d\eta = 1. \tag{52}$$

Generally speaking, the power series (42) and (51) have a limited interval of convergence and therefore the upper limit in (52) should also be finite. However, in this case the calculation of the quadratures (45) and (52) is considerably simplified by the fact that the integrand has a stationary (saddle) point ($\eta = 0$) and quickly decreases away from it along the positive direction η (direction of steepest descent). Due to monotony and positivity of $\phi(\eta)$ the main contribution of the value of the integral (52) is formed in the vicinity of a stationary point by some first terms of the series $\phi(\eta)$. This very circumstance justifies the use of an infinite upper limit. In a general case of a non-similar boundary layer with a longitudinal pressure gradient, in Meksyn's method Euler's transformation is used which increases the series convergence interval (42) and (51) together with the method of steepest descent.

Let us make the inversion of series (51) by means of the formula

$$\eta = \sum_{m=0}^{\infty} \frac{Am}{m+1} \Phi^{\frac{1}{3}(m+1)} \tag{53}$$

In such a case

$$\left. \begin{aligned} A_0 &= \left(\frac{a^{2-n}}{6}\right)^{-\frac{1}{3}} \\ A_1 &= A_2 = 0 \\ A_3 &= \frac{10(1-n)+1}{15} \left(\frac{a^{2-n}}{6}\right)^{-\frac{1}{3}} \\ A_4 &= A_5 = 0 \\ A_6 &= \frac{-4+(1-n)(186-140n)}{720} \left(\frac{a^{2-n}}{6}\right)^{-\frac{1}{3}} \end{aligned} \right\} \tag{54}$$

From equalities (52)–(54) we obtain

$$1 = \frac{1}{3}(6a^{1+n})^{\frac{1}{3}} \left[\Gamma\left(\frac{1}{3}\right) + \frac{10(1-n)+1}{15} \Gamma\left(\frac{4}{3}\right) + \frac{-4+(1-n)(186-140n)}{720} \Gamma\left(\frac{7}{3}\right) + \dots \right] \tag{55}$$

Hence

$$a(n) = \left\{ 6^{\frac{1}{3}} \frac{1}{3} \Gamma\left(\frac{1}{3}\right) \left[1 + \frac{10(1-n)+1}{45} + \frac{-4+(1-n)(186-140n)}{1620} + \dots \right] \right\}^{-\frac{3}{1+n}} \tag{56}$$

Figure 6 shows a comparison of the approximate values of $a(n)$ with their exact ones taken from [2]. The first approximation, based on the presence of only the first term in series (42) has an error of +2 per cent near $n = 1$, achieving almost 100 per cent at $0 \leq n \leq 2$. The second approximation gives an accuracy (<10 per cent) for all the values of the flow index n . The three-term series (42) ensures accuracy, on the average, of order of 1 per cent over the whole theoretically possible range of the parameter n . In the most important range $0.5 \leq n \leq 1.5$ the deviation from the exact values of “ a ” does not exceed 0.2 per cent.

EXPERIMENTAL STUDY—DESCRIPTION OF A LIQUID SYSTEM

The present method for studying convective mass transfer also allows observation of the flow past solid surfaces without introducing any disturbances into it. This method is based on electrochemiluminescence.

If voltage is supplied to two electrodes submerged into electrochemiluminiscent solution, then there appears blue glow on the anode usually shaped as an investigated body.

In [11] it is shown that in laminar flow of electrochemiluminiscent solution at a fixed voltage between the electrodes the brightness of the glow of different portions of the anode surface is directly proportional to the local intensity of mass transfer j/x of the active

electrolyte (H_2O_2) to a wetted anode surface. ECL-glow is excited in the region some light wavelengths in width which is adjacent to the anode surface, i.e. at a distance much smaller than the boundary layer thickness [12]. Thus, the ECL-methods are especially useful to study wall phenomena (solid and liquid interface, films, etc.). In definite ECL-regimes glow is observed in a moving medium, and the flow pattern is distinctly visualized at a distance from the wall in bulk (downstream region, traces, cavities, jets, eddy formation, etc.).

The addition of a high-polymer into the

Newtonian ECL-system noticeably influences all the electrolyte properties (physical, mechanical and electrochemical). Even a small amount of macromolecules in solution changes its internal friction and diffusion sharply and non-linearly. At the same time the conditions of ion transport through such anomalously viscous solution vary and the ECL-reaction takes place. We shall discuss this problem in more detail:

(a) *Voltage-current characteristic*

The curve in Fig. 1 shows the relationship of the current in external circuit to the applied

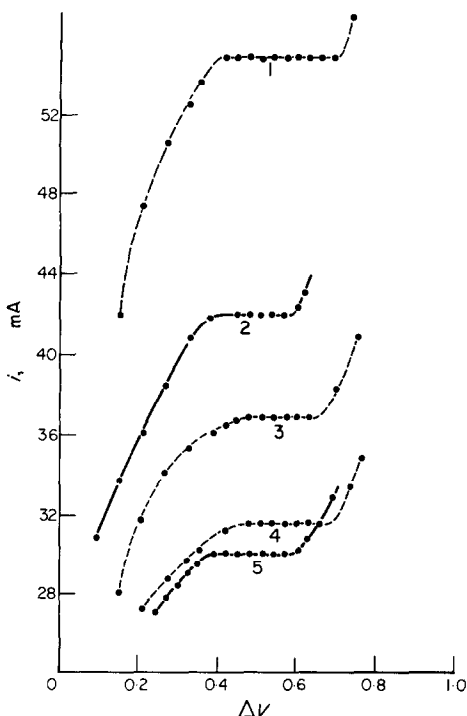


FIG. 1. Current in the external circuit v. potential difference between anode and solution

- 1— $C_{CMC} = 0.5\%$; $h_0 = 2.3$ cm; $U_\infty = 0.5$ m/sec; $C_{H_2O_2} = 0.9$ ml/lit
- 2— $C_{CMC} = 0\%$; $h_0 = 0.7$ cm; $U_\infty = 0.5$ m/sec; $C_{H_2O_2} = 0.6$ ml/lit
- 3— $C_{CMC} = 0.25\%$; $h_0 = 2.3$ cm; $U_\infty = 0.17$ m/sec; $C_{H_2O_2} = 0.9$ ml/lit
- 4— $C_{CMC} = 1\%$; $h_0 = 2.3$ cm; $U_\infty = 0.17$ m/sec; $C_{H_2O_2} = 0.9$ ml/lit
- 5— $C_{CMC} = 0\%$; $h_0 = 0$; $U_\infty = 0.17$ m/sec; $C_{H_2O_2} = 0.6$ ml/lit.

voltage difference. The almost linear dependence of both quantities upon each other is valid for small potential differences ΔV . At large ΔV the current achieves some limiting values (the plateau in chart in Fig. 1) and does not depend upon the applied potential difference. Zero concentration of ions discharging near the anode surface corresponds to the regime of the so-called limiting flux, i.e. the condition $C_w \approx 0$ is fulfilled. The ECL-solution composition and designation of each chemical are given in Table 1.

In all our experiments, the limiting current and at the same time maximum glow intensity are achieved when the potential difference between anode and non-Newtonian ECL-solution is approximately 0.63 V (Figs. 1 and 2).

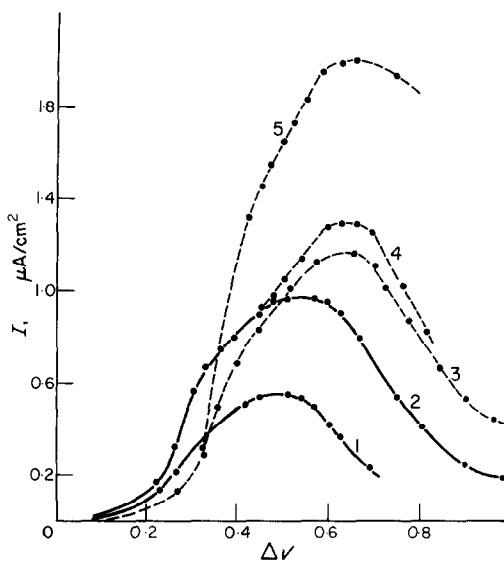


FIG. 2. Glow intensity as function of the potential difference between anode and solution

- 1— $C_{CMC} = 0\%$; $h_0 = 0$; $U_\infty = 0.17$ m/sec; $x = 2.2$ cm; $C_{H_2O_2} = 0.6$ ml/lit
- 2— $C_{CMC} = 0\%$; $h_0 = 0.7$ cm; $U_\infty = 0.17$ m/sec; $x = 1.4$ cm; $C_{H_2O_2} = 0.6$ ml/lit
- 3— $C_{CMC} = 1\%$; $h_0 = 2.3$ cm; $U_\infty = 0.17$ m/sec; $x = 3$ cm; $C_{H_2O_2} = 0.9$ ml/lit
- 4— $C_{CMC} = 0.25\%$; $h_0 = 2.3$ cm; $U_\infty = 0.17$ m/sec; $x = 5$ cm; $C_{H_2O_2} = 0.9$ ml/lit
- 5— $C_{CMC} = 0.5\%$; $h_0 = 2.3$ cm; $U_\infty = 0.5$ m/sec; $x = 3$ cm; $C_{H_2O_2} = 0.9$ ml/lit.

(b) Optical properties

ECL-solution turbidity and its refraction increase with concentration of thickening non-Newtonian additive. Consequently, the fraction of light absorption in the total light flux received by a photodevice (photomultiplier, photoelement, etc.) does not remain constant and varies together with the polymer content from one experiment to another. In order that the influence of the variable refraction and light absorption upon "useful" photocurrent be eliminated, we have found in separate experiments the concentration dependence of the refraction factor and relative attenuation of the light beam passing through the Newtonian ECL-solution and through the same solution with a high-molecular additive.

The data of the measurement of the transmission coefficient are presented in Fig. 3 and are approximated by the equation

$$T_i^{-1} = 1 + 24 C \quad (57)$$

where C is measured in g/cm^3 .

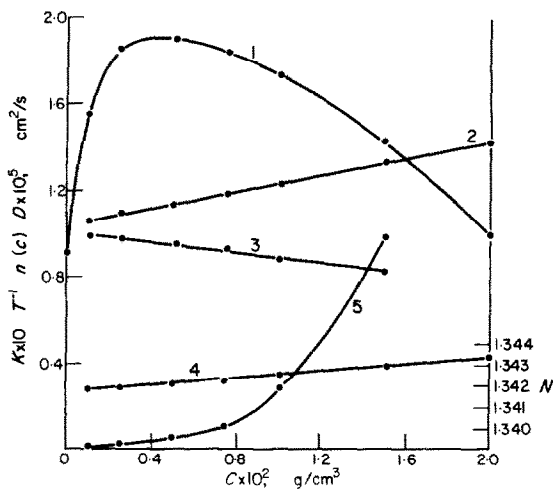


FIG. 3. ECL-solution properties versus polymer additive concentration

1—change in diffusion coefficient; 2—change in "flow index"; 3—change in transmission coefficient; 4—change in refraction coefficient; 5—change in index of liquid consistency.

Thus, up to the quantities $C = 2\%$ the absorption of the passing light is directly proportional to the Na-CMC concentration.

The refraction coefficient linearly depends upon Na-CMC concentration in the solution

$$N = 1.3413 + 0.124 C \quad (58)$$

(c) Diffusion

The majority of the modern experimental methods for determining the diffusion coefficient D is based on measuring the concentration gradient of the solution under consideration with the help of optical methods. In particular, we use the dependence of the refraction index N of the solution upon the concentration C of a diffusing substance

$$\frac{\partial N}{\partial C} = v_1 \quad (59)$$

where v_1 is the increment of refraction index.

In a case of one-dimensional unsteady diffusion the concentration field at the time moment t is characterized by a distribution

$$C = C_1 + \frac{\Delta C}{2} \left(1 + \frac{2}{\sqrt{\pi}} \int_0^y e^{-y^2} dy \right) \quad (60)$$

where

$$y = \frac{x}{2\sqrt{Dt}} \quad \text{and} \quad \Delta C = C_2 - C_1.$$

From equality (60) the value of D is simply determined by the experimental curve $c(x)$. However, for this purpose it is more convenient to use not the concentration itself but its gradient dC/dx (Boltzmann's method). The calculation is made by the formula

$$\frac{dC}{dx} = \frac{\Delta C}{\sqrt{(2\pi\sigma)}} e^{-x^2/2\sigma^2} \quad (61)$$

where $\sigma^2 = 2Dt$.

In the refractometric method the gradient of the refraction index dN/dx is measured, and with the help of it (since $dN/dx = v_1(dC/dx)$) the value of D is calculated from relation (62) [13]

$$\frac{dN}{dx} = \frac{N - N_0}{2\sqrt{(\pi Dt)}} e^{-x^2/4Dt}. \quad (62)$$

In refractational diffusometers the initial clear interface of liquids being in contact is established by means of depositing the lighter liquid (solution-solvent) on the more heavy one or vice versa. The light beam passing through a medium with a non-zero gradient of the refraction index deflects to the side of an increase in the refraction index and follows the curve, whose radius of curvature R is inversely proportional to the concentration gradient dC/dx at this point [14]. Consequently, the cuvette, along which there exists a change in the medium refraction index N determined by equation (60) (C is proportional to N) is in its optical properties similar to a non-uniform material prism having a refraction angle different from the points on the x -axis and proportional to the gradient dN/dx determined by equation (62). The small angle of the beam deviation in the cuvette is equal to $\delta dN/dx$ where δ is the cuvette size with respect to the direction of the incident light beam. Substituting the value of equation (62) for dN/dx , we have the relation

$$\alpha = \delta \frac{N - N_0}{2\sqrt{(\pi Dt)}} e^{-x^2/4Dt}. \quad (63)$$

The maximum beam deviation takes place at $x = 0$, i.e.

$$\alpha_{\max} = \delta \frac{N - N_0}{2\sqrt{(\pi Dt)}}. \quad (64)$$

Thus, the value of the diffusion coefficient determined for two different time moments is equal to

$$D = \frac{\delta^2(N - N_0)^2}{4\pi(t_2 - t_1)} \left(\frac{1}{\alpha_2^2} - \frac{1}{\alpha_1^2} \right). \quad (65)$$

To find the value of D by formula (65), it is sufficient to have two pairs of values t_1, α_1 and t_2, α_2 . However, to achieve greater accuracy, it is necessary to make more measurements. When

calculating D , to avoid a systematic error, different α_1 and α_2 (but not the relations of different α_2 to one and the same α_1) are combined. To decrease the relative error in the calculations, values of α_1 not very close to each other are used.

The results obtained by formula (65) are given in Fig. 3. The diffusion coefficient of ions of the active electrolyte (H_2O_2) for the ECL-system under consideration increases with the polymer concentration up to $C_{Na-CMC} = 0.5$ per cent where a maximum is achieved. With a further increase in the polymer concentration, a monotonous decrease in D is observed.

It is interesting to compare our data with the results calculated by the method of the polarization interferometer of two solutions being in contact. The experiments based on this method [15] reveal sharp changes in the diffusion coefficient of chain macromolecules in a non-ideal solvent with an increase in the solution concentration. Bisschops' experiments [16] with a polyacrylonitrile-dimethylformamide system have revealed also a non-monotonous change of the diffusion coefficient with an increase in the polymer concentration. The same effect is also observed in other polymer-solvent systems.

(d) Rheological systems

The real liquids with a non-linear curve of shear flow, for which the shear velocity at each point is uniquely related to tangential shear stress at the same point, may be described by the rheological constitutive equation (one-dimensional conditions)

$$\dot{\gamma} = f(\tau). \quad (66)$$

We have determined rheological characteristics of non-Newtonian ECL-solution in a capillary constant-pressure viscometer by simultaneous measurement of the volume velocity Q in tube cross-sections and of the corresponding longitudinal pressure drop ΔP at a prescribed length.

At present, when treating data of capillary

viscosimetry the consistent rheological variables are widely used

$$V = \frac{4Q}{\pi R^3} = \frac{32Q}{\pi d^3}; \quad P = \frac{R \cdot \Delta P}{2L} = \frac{d\Delta P}{4L} \quad (67)$$

Here Q is the volume rate through a tube per second; ΔP is the pressure drop of stabilized flow over the tube length L .

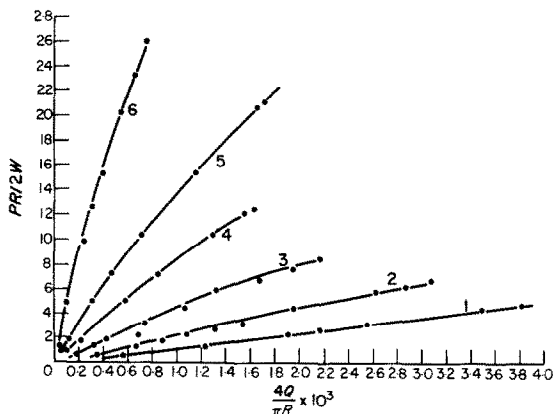


FIG. 4. Consistent curves of Na-CMC solution flows

- 1— $C_{CMC} = 0.1\%$;
- 2— $C_{CMC} = 0.25\%$;
- 3— $C_{CMC} = 0.5\%$;
- 4— $C_{CMC} = 0.75\%$;
- 5— $C_{CMC} = 1\%$;
- 6— $C_{CMC} = 1.5\%$.

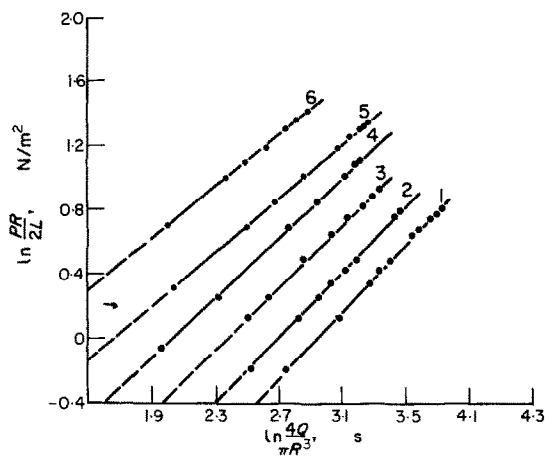


FIG. 5. Curves of Na-CMC solution flows

- 1— $C_{CMC} = 0.1\%$;
- 2— $C_{CMC} = 0.25\%$;
- 3— $C_{CMC} = 0.5\%$;
- 4— $C_{CMC} = 0.75\%$;
- 5— $C_{CMC} = 1\%$;
- 6— $C_{CMC} = 1.5\%$.

Table 1

Substance	Concentration	Notes
1	2	3
H ₂ O	—	Solvent
KCl	74.56 g/lit	Main electrolyte (phone)
NaOH	0.87 g/lit	Regulator pH (luminol dissolves and luminiscences only in alkali solution at pH > 8.5)
H ₂ O ₂	0.6 ml/lit (30% solution)	Oxidiser (active electrolyte), its concentration greatly influences the flow intensity
	0.9 ml/lit (30% solution)	For non-Newtonian solutions
Luminol	0.15 g/lit	Chemiluminescent substance
Na-CMC	(0.1-2)%	Pseudoplastic and viscoelastic non-Newtonian thickening additive

Table 2

Nos.	C (g/cm ³)	n	K · 10 ³ (n · sec ⁿ /m ²)	K · ρ ⁻¹ · 10 ⁶ (m ² /sec ²⁻ⁿ)
(1)	0	1	0.93	0.92
(2)	0.001	0.99	1.172	1.12
(3)	0.0025	0.98	2.384	2.28
(4)	0.005	0.96	5.355	5.124
(5)	0.0075	0.94	12.13	11.61
(6)	0.01	0.88	29.32	28.057
(7)	0.015	0.83	99.3	95.04

Consistent values of the mean gradient of the shear velocity V and the tangential shear stress P were calculated on the basis of the measurements of Q and ΔP by formula (67). In Figs. 4 and 5 are presented the consistent curves of flow of aqueous Na-CMC solutions with ECL-additives in ordinary and logarithmic co-ordinates. As it is seen from the plot in double logarithmic co-ordinates within more than one decimal order ($10^2 \div 5 \cdot 10^3$) sec⁻¹ the relation $P(V)$ appears to be linear with the tangent of the angle of inclination between zero and unity.

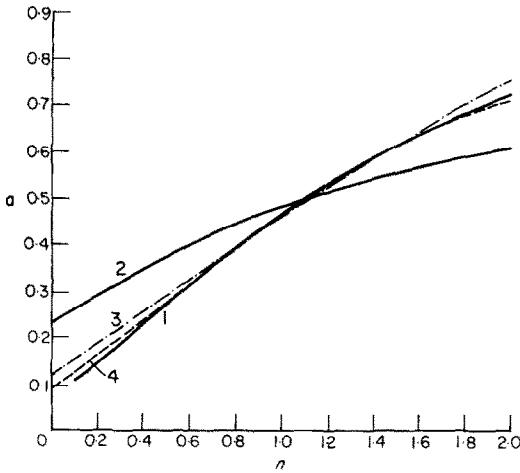


FIG. 6. Comparison of the approximate and exact values of

the form parameter $a = \left(\frac{\partial^2 f}{\partial \eta^2}\right)_{\eta=0}$

- 1—exact solution of similar problem
- 2—first approximation

$$a^{(1)} = \left(\frac{1}{6^{\frac{1}{3}}\Gamma(\frac{4}{3})}\right)^{3/1+n}$$

- 3—second approximation

$$a^{(2)} = \left\{ \frac{1}{\Gamma(\frac{4}{3}) 6^{\frac{1}{3}} \left[1 + \frac{10(1-n)+1}{45} \right]} \right\}^{3/1+n}$$

- 4—third approximation

$$a^{(3)} = \left\{ \frac{1}{6^{\frac{1}{3}}\Gamma(\frac{4}{3}) \left[1 + \frac{10(1-n)+1}{45} + \frac{-4+(1-n)(186-140n)}{1620} \right]} \right\}^{3/1+n}$$

Thus, the rheological behaviour of the ECL-solution with polymer additives has distinct pseudoplastic character and is well described by the law (I). Table 2 comprises values of the rheological parameters n and K .

The relation between the index of liquid consistency and Na-CMC concentration is

$$k = e^{315.65C - 6.86} \tag{68}$$

The dependence of consistency K upon CMC-polymer concentration appears to be linear

(Fig. 3) and is approximated by the equation

$$n = 1 - 12C. \tag{69}$$

In equations (68) and (69) C is measured in g/cm^3 .

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Abstract—The results of the analytical and experimental study of mass transfer in a boundary layer of an elastic-viscous non-Newtonian fluid are reported.

Part I includes the results of the analytical study of mass transfer in longitudinal flow along a plate. The methods of the experimental study are also described. Also presented are results on diffusion, optical and rheological properties of an electrochemiluminescence solution (ECL) with Na-CMC additives.

Résumé—Les résultats de l'étude théorique et expérimentale du transport de masse sont donnés pour une couche limite d'un fluide non-newtonien elastico-visqueux.

La première partie comprend les résultats de l'étude théorique du transport de masse dans l'écoulement longitudinal le long d'une plaque. Les méthodes de l'étude expérimentale sont également décrites. On présente aussi les résultats des propriétés de diffusion, optiques et rhéologiques d'une solution électrochimiluminescente (ECL) avec des additifs de Na-CMC.

Zusammenfassung—Es wird über eine analytische und experimentelle Untersuchung des Stoffübergangs in der Grenzschicht einer elastisch-zähen Nicht-Newtonschen Flüssigkeit berichtet.

Der Teil I behandelt die Ergebnisse der analytischen Untersuchung des Stofftransports in der Strömung längs einer Platte. Die Versuchsmethoden werden ebenfalls beschrieben. Weiterhin werden Ergebnisse geliefert für die Diffusion und optische und rheologische Eigenschaften einer elektrochemischen Lumineszenzlösung (ECL) mit Na-CMC-Zusätzen.