MATHEMATICS/CHEMISTRY

ELECTROKINETIC EFFECTS IN A NETWORK OF CAPILLARIES II

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Theorem 3. $\Delta^1\Omega = 0$ for arbitrary ΔF_{ij}, ΔL_{ij}.

$\Delta^2\Omega \gtreqless 0$ if ΔF_{ij} and ΔL_{ij} are subject to a relation (34) with a $\chi \lessgtr 0$.

Proof: First we remark that on account of the symmetry of L^{-1} and D we may write

$$\Omega_2 = (H^{-1}i, i)\,(H^{-1}(DL^{-1}i), (DL^{-1}i)) - (H^{-1}i, (DL^{-1}i))^2.$$

Since H^{-1} is n.d. we find as a consequence of the fundamental inequality for n.d. operators (cf. 1.) that $\Omega_2 \geqslant 0$. Hence $\Omega_2(L^0, F^0, D) = 0$ is a minimal value for Ω_2, and therefore $\Delta^1\Omega_2 = 0$. Hence we have only to prove that $\Delta^1\Omega_1 = 0$.

For that purpose we expand L^{-1}, H^{-1} as follows

$$(35)\qquad \begin{cases} L^{-1} = (L^0 + \Delta L)^{-1} = L^{0-1} + \Delta(L^{-1}) + \Delta^2(L^{-1}) + \dots \\ H^{-1} = (H^0 + \Delta H)^{-1} = H^{0-1} + \Delta(H^{-1}) + \Delta^2(H^{-1}) + \dots \end{cases}$$

Here $\Delta^k(\dots)$ denotes the aggregate of terms of order k in ΔL_{ij}, ΔF_{ij}; to be more precise $\Delta^k(\dots)$ is a homogeneous polynomial of degree k in ΔF_{ij}, ΔL_{ij}, with operators as coefficients. By (35) we find

$$\Delta^1\Omega_1 = (\Delta(H^{-1})i, i)\,(L^{0-1}i, i) - (L^{0-1}D\Delta(H^{-1})i, i)\,(D^{-1}i, i) + (H^{0-1}i, i)\,(\Delta(L^{-1})i, i) - (\Delta(L^{-1})DH^{0-1}i, i)\,(D^{-1}i, i).$$

Since both L^0, F^0 are multiples of D, H^0 is also a multiple of D (cf. (31)), and thus it will be seen that $\Delta^1\Omega_1 = 0$. So we have proved that $\Delta^1\Omega = 0$ for arbitrary ΔF_{ij}, ΔL_{ij}.

In order to calculate $\Delta^2\Omega_i$ we must insert again (35) into the expression for Ω_i (cf. (31)) and collect the second order terms in ΔF_{ij}, ΔL_{ij}. Doing thus it may be seen, that $\Delta^2\Omega_i$ may be decomposed into a sum Σ_{i1} which contains the terms with $\Delta(L^{-1})$ and $\Delta(H^{-1})$ and a sum Σ_{i2} which contains the terms with $\Delta^2(L^{-1})$, $\Delta^2(H^{-1})$. Σ_{i2} can be obtained from $\Delta^1\Omega_i$ by replacing in the latter expression $\Delta(L^{-1})$ and $\Delta(H^{-1})$ by $\Delta^2(L^{-1})$ and $\Delta^2(H^{-1})$ respectively. Since $\Delta^1\Omega_i = 0$ for arbitrary $\Delta(L^{-1})$ and $\Delta(H^{-1})$ Σ_{i2} is also $= 0$. Hence we have only to calculate Σ_{i1}. Taking into account that L^0, F^0, H^0 are multiples of D, say a ϱ-, a σ- and a τ-tuple respectively, we find after a somewhat lengthy but elementary calculation,

$$(36)\quad \begin{cases} \Delta^2\Omega_1 = (\Delta(H^{-1})i, i)\,(\Delta(L^{-1})i, i) - (\Delta(L^{-1})D\Delta(H^{-1})i, i)\cdot(D^{-1}i, i) \\ \Delta^2\Omega_2 = \tau^{-2}[(D^{-1}i, i)\,(\Delta(L^{-1})D\Delta(L^{-1})i, i) - (\Delta(L^{-1})i, i)^2]. \end{cases}$$

Since $\Omega_2 \geqslant 0$, $\Omega_2(L^0, F^0, D) = 0$, $\Delta^1\Omega_2(L^0, F^0, D) = 0$, we find that necessarily $\Delta^2\Omega_2 \geqslant 0$. This result can also be derived from (36) by means of the Cauchy–Schwarz inequality for definite operators. Futhermore it appears from (36), that in order to compute $\Delta^2\Omega$ we need only calculate $\Delta(H^{-1})$ and $\Delta(L^{-1})$.

From

$$(L^0 + \Delta L)^{-1} = (L^0(1 + L^{0-1}\Delta L))^{-1} = (1 + L^{0-1}\Delta L)^{-1}L_0^{-1},$$

and the expansion

$$(I + A)^{-1} = I + \sum_{i=1}^{\infty} (-1)^i A^i$$

which is valid for small operators A, we find

$$(L^0 + \Delta L)^{-1} = L^{0-1} - L^{0-1}\Delta L L^{0-1} + \text{terms of higher order.}$$

And since $L^0 = \varrho D$, this shows that

$$(37)\qquad \Delta(L^{-1}) = -\varrho^{-2}D^{-1}(\Delta L)D^{-1}.$$

In the same way we find

$$(38)\qquad \Delta(H^{-1}) = -\tau^{-2}D^{-1}(\Delta H)D^{-1}\ (H = \tau D!).$$

Furthermore $H = F - DL^{-1}D$, hence

$$(39)\qquad \Delta H = \Delta F - D\Delta(L^{-1})D \overset{(37)}{=} \Delta F + \varrho^{-2}\Delta L \overset{(34)}{=} (\chi + \varrho^{-2})\Delta L.$$

(39), (38) and (37) yield

$$(40)\qquad \Delta(H^{-1}) = (\tau^{-2} + \chi\varrho^2\tau^{-2})\Delta(L^{-1}).$$

Inserting (40) into the expression for $\Delta^2\Omega_1$ we find that

$$\Delta^2\Omega_1 = -(1 + \chi\varrho^2)\Delta^2\Omega_2,$$

and hence

$$\Delta^2\Omega = \Delta^2\Omega_1 + \Delta^2\Omega_2 = -\varrho^2\chi\Delta^2\Omega_2.$$

According to the aforesaid $\Delta^2\Omega_2 \geqslant 0$, and so it appears that $\Delta^2\Omega \geqslant 0$ if $\chi < 0$, and $\leqslant 0$ if $\chi > 0$. This completes the proof of our theorem.

Remark. In the above proof D is kept fixed. If D was also allowed to vary slightly the final result would have remained the same. This may be shown as follows: A variation

$$L^0 \to L_1 = L^0 + \Delta L,$$
$$F^0 \to F_1 = F^0 + \Delta F,$$
$$D^0 \to D_1 = D^0 + \Delta D,$$

may be performed in two separate steps

$$L^0 \to L_2 = \varrho D_1 = L^0 + \varrho \Delta D,$$
$$F^0 \to F_2 = \sigma D_1 = F^0 + \sigma \Delta D,$$
$$D^0 \to D_1 = D^0 + \Delta D$$

and

$$L_2 \to L_1 = L_2 + \Delta_2 L, \text{ with } \Delta_2 L = \Delta L - \varrho \Delta D,$$
$$F_2 \to F_1 = F_2 + \Delta_2 F, \text{ with } \Delta_2 F = \Delta F - \sigma \Delta D,$$
$$D_1 \to D_1.$$

The first step does not change Ω. The second step is precisely a variation such as is studied above.

In 4. 1. it will be shown that for a cylindrical capillary under the condition $D =$ constant, L and F vary in opposite senses. Hence in (34) ΔL_{ij} and ΔF_{ij} have opposite sign, and consequently $\chi < 0$. This leads to

Theorem 4. Given a network with cylindrical capillaries of equal diameters. Then if the diameters and lengths of the capillaries are slightly changed the resulting network will display at most an apparent ζ-depression but not an apparent rise of ζ apart from third order terms in the deviations.

3. 2. In this section we shall calculate the capacity of conductance of a network $\mathfrak{N}$. In practice this quantity is determined by measuring the conductivity of $\mathfrak{N}$ if $\mathfrak{N}$ is immersed in a concentrated solution of an electrolyte. In that case surface conductance may be neglected and $L_{ij} = \varkappa C_{ij}$, $\varkappa$ being the specific conductivity of the liquid, and hence $\alpha L = D$ with $\alpha = \varkappa^{-1} Z$. The formulae (22) yield

$$(41) \qquad \begin{cases} K_{12} = -\alpha K_{22}, \ (K_{12} i, i) = (K_{21} i, i) = -\alpha (K_{22} i, i) \\ K_{11} = L^{-1} + \alpha^2 K_{22}. \end{cases}$$

Now we may determine by means of (26) the electric current through $\mathfrak{N}$, and using (41) we find

$$\lambda \alpha \left[- \frac{((L^{-1} i, i) + \alpha^2 (K_{22} i, i))(K_{22} i, i)}{\alpha (K_{22} i, i)} + \alpha (K_{22} i, i) \right] = E,$$

so

$$-\lambda (L^{-1} i, i) = E.$$

Since $L = \varkappa C$, the conductivity of $\mathfrak{N}$ turns out to be $-\varkappa (C^{-1} i, i)^{-1}$ and hence the capacity of conductance is $-(C^{-1} i, i)^{-1}$.

4. 1. In this section we shall examine more closely the quantities L_{12}, F_{12}, D_{12} for a network with two nodes, i.e. for a single capillary. Therefore we shall omit subscripts.

Putting $p_1 - p_2 = p$, $e_1 - e_2 = e$, $I =$ electric current in the direction

$1 \to 2$, V = flow of liquid in the direction $1 \to 2$, the equations of steady state for an electrokinetic process may be written as

$$\left\{\begin{aligned} Le + Dp &= I \\ De + Fp &= V. \end{aligned}\right. \tag{42}$$

From these equations it appears that

$$L = \left(\frac{I}{e}\right)_{p=0}, \quad D = \left(\frac{V}{e}\right)_{p=0}.$$

F is the hydrodynamic conductivity and may be taken as $\pi R^4/8\eta l$, where R = radius of the capillary, η = viscosity of the liquid, l = lenght of $(1, 2)$.

Before deriving more explicit formulas for L and D we remark that I consists of a transport of electricity by conduction and a transport of the electric double-layer-charge in the boundary layers by the streaming liquid.

Now introducing cylindrical coordinates in the obvious way we find

$$\left\{\begin{aligned} I &= \pi\varkappa\, E R^2 + \int_0^R 2\pi\, r\, \varrho v\, dr \quad ^{1)} \\ V &= \int_0^R 2\pi\, r\, v\, dr \end{aligned}\right. \tag{43}$$

where

$\varrho(r)$ = double-layer-charge density } at distance r from the axis
$v(r)$ = velocity of the liquid }
$\varkappa$ = specific conductivity of the liquid
$E = \dfrac{e}{l}$
l = length of capillary.

v and ϱ satisfy the following differential equation and boundary conditions

$$\left\{\begin{aligned} &\frac{1}{r}\frac{d}{dr}\left(r\,\frac{dv}{dr}\right) + \frac{E\varrho}{\eta} = 0 \\ &\left(\frac{dv}{dr}\right)_{r=0} = 0\,, \quad v(R) = 0. \end{aligned}\right. \tag{44}$$

So we find

$$\left\{\begin{aligned} L &= l^{-1}\cdot\left(\pi\varkappa R^2 + \int_0^R 2\pi\, r\varrho\,\frac{v}{E}\,dr\right) \\ D &= l^{-1}\cdot\int_0^R 2\pi r\,\frac{v}{E}\,dr. \end{aligned}\right. \tag{45}$$

Supposing that $\varrho \neq 0$ only in the boundary layers it is easily seen that L and D may be approximated by the following formulae (cf. [1])

$$\left\{\begin{aligned} L &= l^{-1}\cdot\pi\, R^2\left(\varkappa + \frac{2\lambda}{R}\right) \\ D &= l^{-1}\cdot a\pi\, R^2, \end{aligned}\right. \tag{46}$$

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1) An additional surface conductance of the form $2\pi\sigma ER$ would only make the following proofs (conclusions) more stringent.

where λ may be interpreted as a surface conductance and α equals the constant Z (cf. 3. 1). In this case it is easily seen that L/D and F/D vary in opposite senses, a result which we needed for theorem 4.

4. 2. Our object in this section is to show that the energy dissipation of an electrokinetic process calculated with L and D according to (45) is positive. This shows that these quantities such as they are given by (45) are compatible with the requirements of thermodynamics.

The energy dissipation in an electrokinetic process is obviously

$$Ie + Vp = Le^2 + 2Dep + Fp^2.$$

The requirement that this should always be positive unless $e = p = 0$ is equivalent to

$$LF > D^2. \tag{47}$$

Taking $l = 1$ for simplicity we have

$$LF > \frac{\pi R^4}{8\eta} \int_0^R 2\pi r\, \varrho \frac{v}{E}\, dr.$$

Hence it is sufficient to show that

$$\frac{\pi R^4}{8\eta} \int_0^R 2\pi\, r\varrho \frac{v}{E}\, dr \geqslant \left(\int_0^R 2\pi r \frac{v}{E}\, dr\right)^2. \tag{48}$$

Integrating by parts and using $v(R) = 0$ we find

$$\int_0^R 2r\, v\, dr = -\int_0^R r^2 \frac{dv}{dr}\, dr. \tag{49}$$

Using (44) and integrating by parts we find

$$\int_0^R r\varrho v\, dr = -\frac{\eta}{E}\int_0^R v \frac{d}{dr}\left(r\frac{dv}{dr}\right) dr = \frac{\eta}{E}\int_0^R r\left(\frac{dv}{dr}\right)^2 dr. \tag{50}$$

By (49) and (50), (48) becomes

$$\frac{\pi^2 R^4}{4E^2}\int_0^R r\left(\frac{dv}{dr}\right)^2 dr \geqslant \frac{\pi^2}{E^2}\left(\int_0^R r^2\left(\frac{dv}{dr}\right) dr\right)^2. \tag{51}$$

Put $r = R\sqrt{t}$ then (51) becomes

$$\tfrac{1}{2}\int_0^1 t\left(\frac{dv}{dt}\right)^2 dt \geqslant \left(\int_0^1 t\left(\frac{dv}{dt}\right) dt\right)^2. \tag{52}$$

Putting $t^{\frac{1}{2}}\left(\frac{dv}{dt}\right) = f(t)$ this inequality may be rewritten as

$$\int_0^1 (t^{\frac{1}{2}})^2\, dt \int_0^1 f(t)^2\, dt \geqslant \left(\int_0^1 t^{\frac{1}{2}} f(t)\, dt\right)^2 \tag{53}$$

which is a special case of the Schwarz-inequality.

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