Transport properties and their coupling with ion aggregate formation

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Abstract – A theoretical approach is presented and applied to transport properties of electrolyte solutions undergoing chemical reactions such as ion-pair formation, micelle destruction and recombination, and ligand exchange reactions. The observable transport coefficients differ from those of chemically inert systems and exhibit kinetic patterns depending on the relative time scales of the superimposed effects. The quantitative description of the phenomena requires to take into account the rates of chemical reactions in the solutions and the deviations from ideality occuring on the same level of approximation.

INTRODUCTION

The common point of view in chemical kinetics is to consider the limitation of rate processes by the transport of either reactants to or products from the zone where the reaction takes place. The reaction step generally is considered to be the non-trivial part of the process, the transport of species is considered inasmuch as it yields conditions for an upper limit of the rate processes (cf. ref. 1).

In the present work, the transport coefficients are considered as the observable quantities, and the problem is studied how they are modified by chemical reactions of the moving particles. This point of view is a novel aspect of transport theory, never adopted before in a systematic way. The transport properties studied in the present contribution are the ion mobilities and the diffusion coefficients of the particles involved in the chemical reactions yielding the equilibria of electrolyte and polyelectrolyte solutions. Examples of application will be the diffusional transport in electrolyte solutions of associated electrolytes, electrophoresis experiments coupled with metal ion-ligand exchange reactions, and diffusion of micelles observed by dynamic light scattering. The process of micelle formation from the separated ions is a fast reaction with respect to the considered transport process.

The crucial point in the study of coupled transport processes and chemical reactions is the consideration of the ratio of characteristic times related to these phenomena.

If the characteristic time of the chemical reaction is shorter than that of the transport process, the transport coefficient depends only on relative rate constants. However this dependence cannot be simply analyzed in terms of mass action law. Diffusional transport under fast exchange conditions is an example of this class of coupled phenomena (ref. 2).

In contrast, if the rate process takes place at a velocity comparable to that of the transport phenomenon, the absolute value of the rate constants can be deduced by deconvolution of the concentration profiles of the moving particles, involving both the propagation of the particles and the sources of particles due to chemical reaction. This situation (slow exchange) can be encountered in electrophoretic migration.

THEORY

Transport phenomena in electrolyte solutions are presented in terms of phenomenological Onsager coefficients, especially in electrolyte mixtures. However the occurence of chemical reactions complicates the analysis of the phenomena in a way that Onsager coefficients hardly can be used to describe the peculiar features of such systems (ref. 3).

We have developed a method, related to that used in the interpretation of dynamic light scattering experiments (ref. 4), apt to give a description of simultaneous transport processes and chemical reactions.

The basic equation of this method is the hydrodynamic continuity equation

$$\frac{\partial c_i}{\partial t} + \vec{\nabla} . \vec{J}_i = \sigma_i \qquad i = 1, 2, \dots k \qquad (1)$$

showing for each particle i the "source" term σ_i due to chemical reactions producing or consuming particles i, and the "flow" term $\vec{\nabla} . \vec{J}_i$ caused by inhomogeneities of concentration, temperature etc., producing transport in the solution. In Eq. (1) c_i is the concentration of particle i ; the source term σ_i is the algebraic sum of the rates of chemical reactions in which the particle i is involved, $\sigma_i = (dc_i/dt)_{chem.react.}$; the flow $\vec{J}_i$ contains the contributions from both transport processes (diffusion, migration) and excess thermodynamic forces (gradients of activity coefficients) as well as hydrodynamic interactions.

Summing up the continuity equations for all particles ($i = 1, 2, \dots$) yields a set of partial derivative equations which generally are non-linear equations and then can only be solved by numerical methods (finite differences) for arbitrary values of the concentration gradients.

Small fluctuations or concentration inhomogeneities permit the linearization of concentrations, flows, and sources in states near to steady and equilibrium states

$$c_i = c_i^o + \delta c_i \quad ; \quad \vec{J}_i = \vec{J}_i^o + \delta \vec{J}_i \quad ; \quad \sigma_i = \sigma_i^o + \delta \sigma_i \qquad (2 \text{ a,b,c})$$

An electric field $\vec{E}$ contributing to $\vec{J}_i$ via the electric force $\vec{F}_i$, $\vec{F}_i = ez_i \vec{E}$, is splited in two parts

$$\vec{E} = \vec{E}^o + \delta \vec{E} \qquad (2d)$$

where $\vec{E}^o$ corresponds to the applied external field and $\delta \vec{E}$ is the fluctuating part producing the macroscopic electroneutrality of the solution.

Keeping only the first order terms in the heterogeneities and fluctuations yields a set of linear partial derivative equations.

This system can be transformed to an eigen-value problem with the help of integral transformations. A convenient way is to use Fourier transformation for the space and Laplace transformation for the time variables:

$$\tilde{c}_i(q) = \int dr\, e^{iqr}\, c_i(r) \qquad \text{Fourier transform} \qquad (3)$$

$$\tilde{c}_i(q,s) = \int_0^\infty dt\, e^{-st}\, \tilde{c}_i(q,t) \qquad \text{Laplace transform} \qquad (4)$$

The system of hydrodynamic equations is then reduced to a system of linear equations and can be written in the matrix form:

$$\mathbf{M}\,\tilde{\mathbf{C}}(q,s) = \tilde{\mathbf{C}}(q,t=0) \qquad (5)$$

The normal modes (relaxation frequencies) of the system are given by the n roots in s of the secular equation:

$$\det(\mathbf{M}) = 0$$

They can be developed according to their dependence in the reciprocal space variable $(-iq)$ to yield relations:

$$s_i(q) = s_i^0 + (-iq)\, s_i^1 + (-iq)^2\, s_i^2 \qquad (6)$$

and may be classified according to the first non zero terms in these developments.

The first non-zero term in Eq. (6) characterizes the nature of the corresponding mode:

- $s_i^0 \neq 0$, characterizes a relaxation mode (either chemical or electrical).
- $s_i^1 \neq 0$ and $s_i^0 = 0$, characterizes a migration mode.
- $s_i^2 \neq 0$ and $s_i^0 = 0$ and $s_i^1 = 0$, characterizes a diffusion mode.

The last two cases characterize propagative modes which can be affected by the chemical reactions.

ION PAIR FORMATION AND DIFFUSION

We consider the superposition of diffusion and an association kinetic process according to the following reaction

$$Y_1^- + Y_2^+ \underset{k_3}{\overset{k_{12}}{\rightleftharpoons}} Y_3 \qquad ; \qquad Y_3 = [Y_1^-\, Y_2^+]^0 \qquad (7\ a,b)$$
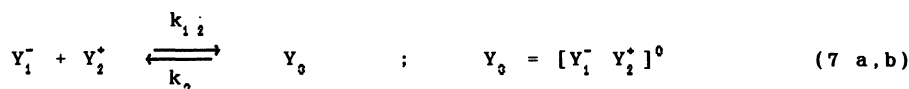
For such a system, the set of continuity equations is given by the relations

$$\frac{\partial c_1}{\partial t} + \vec{\nabla}.\vec{J}_1 = -k_{12}\, c_1\, c_2 + k_3\, c_3 \qquad (8a)$$

$$\frac{\partial c_2}{\partial t} + \vec{\nabla}.\vec{J}_2 = -k_{12}\, c_1\, c_2 + k_3\, c_3 \qquad (8b)$$

$$\frac{\partial c_3}{\partial t} + \vec{\nabla}.\vec{J}_3 = -k_3\, c_3 + k_{12}\, c_1\, c_2 \qquad (8c)$$

The flows involve diffusional and migrational parts

$$\vec{J}_1 = -D_1\, \vec{\nabla} c_1 + c_1\, z_1\, e\, \frac{D_1}{kT}\, \vec{E} \qquad (9a)$$

$$\vec{J}_2 = - D_2 \vec{\nabla} c_2 + c_2 z_2 e \frac{D_2}{kT} \vec{E} \qquad (9b)$$

$$\vec{J}_3 = - D_3 \vec{\nabla} c_3 \qquad \text{(uncharged species)} \qquad (9c)$$

In these equations, e is the charge of the proton, k the Boltzmann constant and D_i are the diffusion coefficients. Ionic mobilities are expressed in terms of diffusion coefficients, with the help of the Einstein relation, $D_i = \omega_i k T$.

To evaluate the electrical field $\vec{E}$ in Eqs. (9), we remember that in microscopic and macroscopic pure diffusion processes without external driving force the electric field originates only from charge inhomogeneities. Taking into account electroneutrality at equilibrium, the diffusion potential is given by the Poisson equation:

$$\vec{\nabla} . \vec{E} = \frac{\mathcal{N}_A e}{\varepsilon_0 \varepsilon} \sum_{i=1,2} c_i z_i = \frac{\mathcal{N}_A e}{\varepsilon_0 \varepsilon} \sum_{i=1,2} z_i \delta c_i \qquad (10)$$

Only the first order terms in the perturbations δc_i are retained and the electroneutrality condition

$$\sum_{i=1,2} c_i^0 z_i = 0 \qquad (11)$$

is used, where c_i^0 is the equilibrium concentration of species i. The linearized hydrodynamic transport equations show three eigen modes:

two relaxation modes
$$s_1 = - (q_1^2 D_1 + q_2^2 D_2) \qquad \text{Debye relaxation} \qquad (12a)$$

$$s_2 = -(k_{12} c_1^0 + k_{12} c_2^0 + k_3) \qquad \text{chemical relaxation} \qquad (12b)$$

one diffusional mode
$$s_3 = - q^2 \mathcal{D} \qquad \qquad (12c)$$

where q is the reciprocal space variable and $\mathcal{D}$ the diffusion coefficient:

$$\mathcal{D} = \frac{D_{NH}}{1 + 2\mathcal{K}_p c_f} + \frac{D_3}{1 + \dfrac{1}{2\mathcal{K}_p c_f}} \qquad (13)$$

In Eq. (13), D_{NH} is the chemical diffusion coefficient of the dissociated part of the electrolyte and D_3 is the diffusion coefficient of the ion pair. D_{NH} is related to the individual ion diffusion coefficients by the Nernst-Hartley equation

$$D_{NH} = \frac{D_1 D_2 (q_1^2 + q_2^2)}{q_1^2 D_1 + q_2^2 D_2} \qquad (14a)$$

where

$$q_i^2 = e^2 z_i^2 \mathcal{N}_A c_i^0 / (\varepsilon_0 \varepsilon kT) \qquad (i=1,2) \qquad (14b)$$

$\mathcal{K}_p$ is the equilibrium constant of ion-pair formation, $\mathcal{K}_p = k_{12}/k_3$, and c_f is the average concentration of the free ions, $c_f = c_1^0 = c_2^0$. This result (ref. 5) is different from that obtained in self-diffusion processes involving the simultaneous diffusion of

free and paired ions and yielding the relationship:

$$\mathfrak{D} = D_{NE}(1 - \beta) + \beta D_{\mathfrak{Z}} \qquad (15)$$

where $\beta = c_{\mathfrak{Z}}^{0} / (c_{\mathfrak{f}} + c_{\mathfrak{Z}}^{0})$ is the degree of association to ion pairs.

In contrast, the asymptotic behaviour of $\mathfrak{D}$, according to Eq. (13), at low pair concentration is given by the relation

$$\mathfrak{D} = D_{NE}(1 - 2\beta) + 2\beta D_{\mathfrak{Z}} \qquad (16)$$

which is smaller than the diffusion coefficient given by Eq.(16) if $D_{\mathfrak{Z}} < D_{NE}$

Figure 1 illustrates results for $D_{\mathfrak{Z}} = D_{NE}/2$ as a function of Log ($X_{p} c_{\mathfrak{f}}$) . The upper curve corresponds to Eq. (15) and the lower curve to Eqs.(16) and (13).
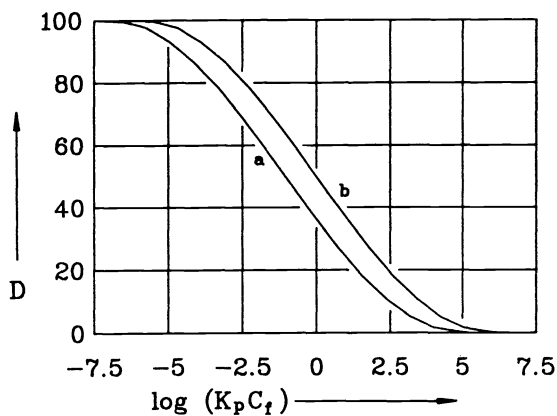

Fig. 1 : Diffusion coefficients according to Eq. (15) and Eqs. (13) and (16) as a function of Log($X_{p} c_{\mathfrak{f}}$) .

Both curves were calculated setting $D_{\mathfrak{Z}} = 0.5 D_{NE}$

INFLUENCE OF MONOMER–MICELLE EXCHANGE ON MICELLE DIFFUSION

The formation-dissolution process for micelles can be written as follows

$$N \, m \quad \underset{k_{m}}{\overset{k_{M}}{\rightleftarrows}} \quad M \qquad (17)$$

if m is the monomer and M the micelle.
For micelles with a large c.m.c. (critical micellar concentration) like sodium hexyl sulfate or sodium octanoate the reactions are very fast. In dynamic light scattering one observes (ref. 6) micellar diffusion over distances comparable to the wavelength of light, during a time $\tau_{D} = (2Dq^{2})^{-1}$ where D is the diffusion coefficient of the micelle . For the two systems investigated τ_{D} is of about 5 µs, the residence time, τ_{E}, of a monomer in the micelle being about 20 ns. The c.m.c. is high (about 0.5 M), and for concentrations just above the c.m.c. (c-c.m.c. $\simeq$ 0.05M) there are 200 times more monomers than micelles. The brownian motion measured by light scattering may be modified by monomer-micelle exchange reactions.
The presence of an excess of uncondensed monomers and counterions ensures a large ionic strength which is able to screen out the coulomb forces and the system can therefore be described by diffusion-reaction equations for uncharged systems. However, the system is far from ideality, owing to the large size of the micellar objects, whose excluded volume corresponds to a volume

fraction ϕ reaching usually a value of about 0.5. At such volume fractions, one has to take into account both thermodynamic excess properties and hydrodynamic interactions. That can be done by considering that the micellar diffusion coefficient should be multiplied by a factor (ref. 4)

$$1 + K \phi \qquad (18)$$

in the expression for the apparent diffusion coefficient as measured by dynamic light scattering. K is a constant very close to 2, and ϕ is the volume fraction of the micellar object.
The diffusion-reaction equations then are written

$$\frac{\partial c_1}{\partial t} + \vec{\nabla}.\vec{J_1} = k_M c_2^{\nu} - k_m c_1 \quad \text{for the micelle} \qquad (19a)$$

$$\frac{\partial c_2}{\partial t} + \vec{\nabla}.\vec{J_2} = N (-k_M c_2^{\nu} + k_m c_1) \quad \text{for the monomer} \qquad (19b)$$

N is the number of monomers in each micelle and ν is the partial order for the formation of the micelle from the monomers.
The equilibrium condition is given by the relation

$$k_M c_2^{0 \nu} - k_m c_1^{0} = 0 \qquad (20)$$

Linearization of the concentrations near equilibrium yields the system of equations for the fluctuating concentrations in the Fourier-Laplace space:

$$(s+q^2 D_1 +k_m) \, \delta\tilde{c}_1 (q,s) - k_m \nu \, \frac{c_1^0}{c_2^0} \, \delta\tilde{c}_2 (q,s) = \delta\tilde{c}_1 (q,t=0) \qquad (21a)$$

$$- k_m N \, \delta\tilde{c}_1 (q,s) + (s+q^2 D_2 +Nk_m \nu \, \frac{c_1^0}{c_2^0}) \, \delta\tilde{c}_2 (q,s) = \delta\tilde{c}_2 (q,t=0) \qquad (21b)$$

which has the diffusive mode

$$\mathcal{D} = \frac{D_1 N \nu \, \frac{c_1^0}{c_2^0} + D_2}{1 + N \nu \, \frac{c_1^0}{c_2^0}} \qquad (22)$$

Taking into account the effect of departure from ideality introduces the factor $D_1^0 (1+K\phi)$ in place of D_1. Moreover, we can take, as a first approximation, c_2^0 equal to the c.m.c. of the system . In the lack of other information we set ν equal to N. We notice that $c_1^0 = \phi / v_1$ where v_1 is the volume of the micelle which can be estimated from its hydrodynamic radius via Stokes formula or any other model yielding the size of the micellar object.
The apparent diffusion coefficient then is given by the relation

$$\mathcal{D} = [D_1^0 N^2 \phi \, (1 + K\phi)/(v_1 c.m.c.) + D_2^0]/[1 + N^2 \phi /(v_1 c.m.c.)] \qquad (23)$$

Eq. (23) is in good agreement with the experimental values of the diffusion coefficients of sodium octanoate and sodium hexyl sulfate, determined by dynamic light scattering (ref. 6).
     A graphical presentation of the corresponding results is given in figures 2 and 3.
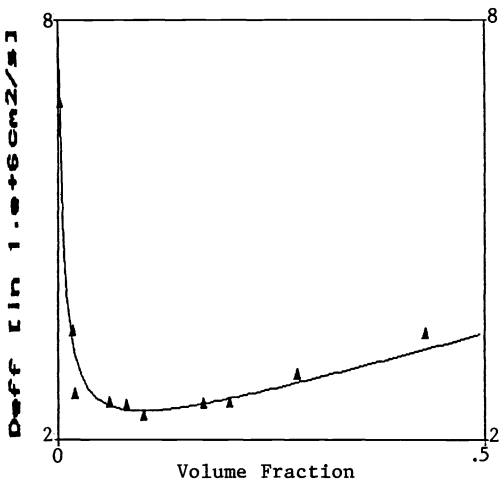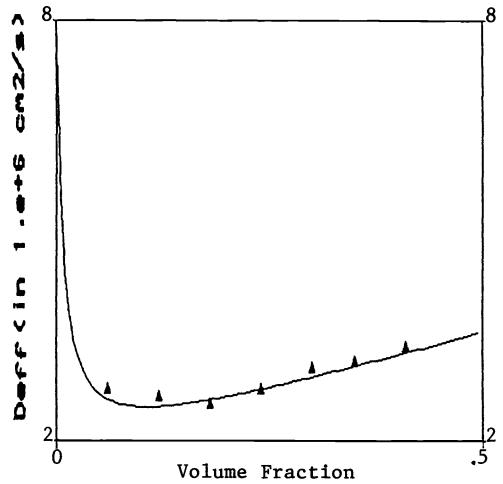
Fig 2

Fig. 3

Fig 2 Diffusion coefficient of sodium hexylsulfate as a function of the volume fraction ϕ. Triangles: experimental values, continuous line calculated by Eq. 23.

Fig. 3 Diffusion coefficient of sodium octanoate as a function of the volume fraction ϕ. Triangles: experimental values, continuous line calculated by Eq. (23).

ELECTROPHORETIC TRANSPORT AND ION AGGREGATION

Exchange reaction of the type:

$$Y_1^{z_1} + L^{z_\ell} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} Y_2^{z_1 + z_\ell} \qquad (24)$$
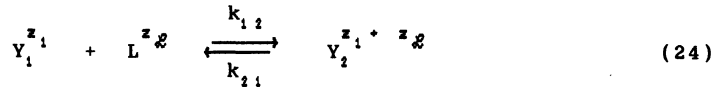
taking place between the complexes Y_1 of charge ez_1 and Y_2 of charge $e \, z_2 = e \, (z_1 + z_\ell)$ in a solution containing an excess of the ligand L^{z_ℓ} are independent of the metal concentration. This simple kinetic situation, exemplified by the reaction

$$RuNO(NO_3^-)^{2+} + NO_3^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} RuNO(NO_3^-)_2^+ \qquad (25)$$
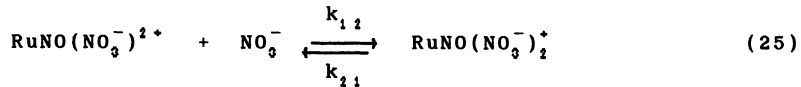
in aqueous solution of HNO_3, is chosen for applying our theory to electrophoresis.

The sources and flows for the electrophoretic transport in an external electrical field which is accompanied by the chemical reaction, are given by the expressions:

$$\sigma_1 = -k_{12} c_1 + k_{21} c_2 \qquad (26a)$$

$$\sigma_2 = k_{12} c_1 - k_{21} c_2 \qquad (26b)$$

$$\vec{J}_1 = D_1 \left[-\vec{\nabla} c_1 + \frac{c_1 z_1 e}{KT} \vec{E} \right] + c_1 \Delta \vec{v}_1 \qquad (27a)$$

$$\vec{J}_2 = D_2 \left[-\vec{\nabla} c_2 + \frac{c_2 z_2 e}{kT} \vec{E} \right] + c_2 \Delta \vec{v}_2 \qquad (27b)$$

At the level of the approximations in this paper $\Delta \vec{v}_i$ contributes only to ionic migration (peak position). This effect can be represented as an increment in the mobility of ions and

does not change the structure of the equations. The effect of $c_i \Delta \vec{v}_i$ will be taken into account afterwards by an appropriate correction. The excess of the supporting electrolyte, HNO_3, permits to neglect the fluctuations of the electrical field, *i.e.* $\vec{E} = \vec{E}^o$ in Eq. (2b). The system of equations (5), for the two migrating compounds involved in the chemical reaction is given under this presupposition by the relationship

$$\begin{Vmatrix} s+\lambda_1 , & -k_{21} \\ -k_{12} , & s+\lambda_2 \end{Vmatrix} \begin{Vmatrix} \tilde{c}_1(q,s) \\ \tilde{c}_2(q,s) \end{Vmatrix} = \begin{Vmatrix} \tilde{c}_1(q,t=0) \\ \tilde{c}_2(q,t=0) \end{Vmatrix} \qquad (28a)$$

where :
$$\lambda_1 = q^2 D_1 - i z_1 \omega_1 e E^o q + k_{12} \qquad (28b)$$
$$\lambda_2 = q^2 D_2 - i z_2 \omega_2 e E^o q + k_{21} \qquad (28c)$$

The two eigenvalues, s_1 and s_2 , of the matrix are given by the relationships:

$$s_1 = \frac{1}{2} [-(\lambda_1 + \lambda_2) + \{(\lambda_1 - \lambda_2)^2 + 4k_{12} k_{21}\}^{1/2}] \qquad (29a)$$
$$s_2 = \frac{1}{2} [-(\lambda_1 + \lambda_2) - \{(\lambda_1 - \lambda_2)^2 + 4k_{12} k_{21}\}^{1/2}] \qquad (29b)$$

determining the observable quantity of this experiment which is the sum of the two time and space depending concentrations c_1 and c_2 :

$$\tilde{c}(q,s) = \tilde{c}_1 + \tilde{c}_2 = \frac{1}{s_1 - s_2} [\tilde{c}(q,t=0) \{s_2 e^{s_2 t} - s_1 e^{s_1 t}\}$$

$$+ \{(\lambda_1 + k_{21})\tilde{c}_2(q,t=0) + (\lambda_2 + k_{12})\tilde{c}_1(q,t=0)\} \{e^{s_2 t} - e^{s_1 t}\}] \qquad (30)$$

The pattern of the observable quantity is obtained by inverse Fourier transform or by Fourier series expansion, the initial pattern is given by the functions at t = 0.
The effect of $\Delta \vec{v}_i$ on ionic velocity $\vec{v}_i$, is taken into account by a correction of ionic mobility u_i ,

$$\vec{v}_i = u_i \vec{E} + <\Delta \vec{v}_i> = u_i^{eff} \vec{E} \qquad (31)$$

where

$$<\Delta \vec{v}_i> = \sum_j c_j \int_0^\infty (g_{ij} - 1) \overset{\leftrightarrow}{T} \vec{F}_j 4\pi r^2 dr \qquad (32)$$

$\overset{\leftrightarrow}{T}$ is the Oseen tensor and g_{ij} is the radial two particles distribution function.
The velocity of particle i is the result of two effects:
- on the one hand the response $\omega_i \vec{F}_i$, to the applied force $\vec{F}_i$.
- on the other hand the dragging of particle i by the local drift at the location of i .

The Oseen tensor relates $\Delta \vec{v}_i$ to the velocity, $\vec{v}_j$, of the particle j at distance $\vec{r}_{ij}$:

$$\Delta \vec{v}_i = \overset{\leftrightarrow}{T} \vec{v}_j \frac{1}{\omega_i} \qquad (33)$$

Using he Oseen expression (ref. 7) for $\overset{\leftrightarrow}{T}$ and the expression of the chemical model (ref. 8) for $g_{ij}(r)$ at low concentrations

yields the relationship:

$$\vec{v}_i = e \; z_i \; \left[\frac{D_i}{k \; T} - \frac{\exp \; (\; -\varkappa \; R \;)}{6 \; \pi \; \eta \; \varkappa^{-1}} \; \right] \vec{E} \qquad (34)$$

R is the center-to-center distance of the Ruthenium ion and the counterion NO_3^- , including the dimension of the ligand shell, $\varkappa^{-1}$ is the Debye length.

From Eq.(34) follows

$$u_i^{eff} = e \; z_i \; \left[\frac{D_i}{k \; T} - \frac{\exp \; (\; -\varkappa \; R \;)}{6 \; \pi \; \eta \; \varkappa^{-1}} \right] \qquad (35)$$

The effect of Δv_i can be formally interpreted either as a change of the diffusion coefficient or of the charge ez_i . We choose the latter possibility by writing:

$$z_i^{eff} = z_i \; \left[1 - \frac{k \; T}{D_i} \; \frac{\exp \; (\; -\varkappa \; R \;)}{6 \; \pi \; \eta \; \varkappa^{-1}} \; \right] \qquad (36)$$

Figs.4 a,b,c show the patterns at various temperatures for the paper electrophoresis of a mixture of $RuNO(NO_3^-)^{2+}$ and $RuNO(NO_3^-)_2^+$ after migration under the experimental conditions of refs. 9 and 10 initial concentration of NO_3^- in the supporting electrolyte (aqueous solution of HNO_3) about 2 mol dm^{-3}, ruthenium as a tracer.

Both ruthenium complexes have the same diffusion coefficient D.
The separation in two peaks, Fig. 4a (T=267K) occurs only for slow exchange reactions, i.e. at low temperatures. Fast exchange reactions do not permit the separation, except at much higher electrical fields which, however, cannot be applied to the highly conducting solutions used in this experiment. The separation of peaks occurs either at high fields or at low temperatures. At higher temperatures we observe one peak more or less broadened (Fig. 4b (T=279K) and 4c.(T=285K)). Under this condition the roots are

$$s_1 = - \; q^2 \; D \; + \; i \; \omega \; e \; E^0 q \; z_2 - k_{2 1} \qquad (37a)$$

$$s_2 = - \; q^2 \; D \; + \; i \; \omega \; e \; E^0 q \; z_1 - k_{1 2} \qquad (37b)$$

they indicate the diminution of the peaks by the relaxation
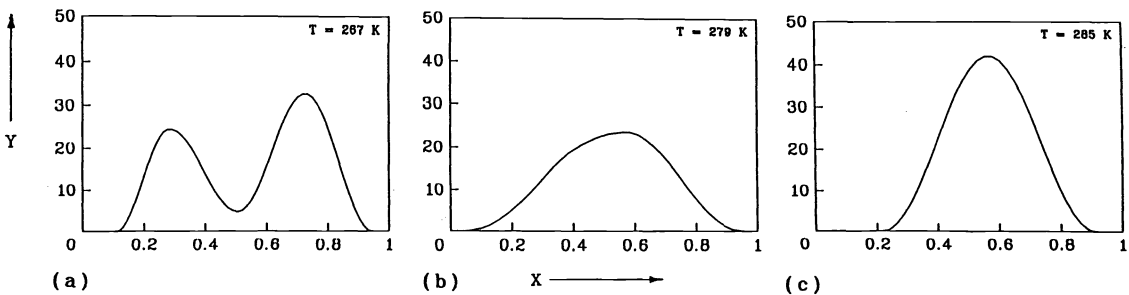

(a)   (b)   X ⟶   (c)

Fig.4 Influence of temperature on the electrophoretic patterns of ruthenium nitrate in HNO_3 (2 mol.dm^{-3}): (a) low temperature (267K), two peaks, separation of the two complexes; (b) & (c) high temperatures (b:279K, c:285K), one peak, no separation. X axis: broadness of the ruthenium zone after migration (relative time scale); Y axis: ruthenium distribution after migration (relative concentration scale).

factors $e^{-k_{12}t}$ and $e^{-k_{21}t}$, respectively, t being the migration time. The term $-q^2 D$ shows the diffusion broading of the peaks, the term $i\omega$ e $E^o q z_i$ characterizes the migrational separation of the two peaks according to the relative values of z_1 and z_2. The high field approximation doesn't exhibit the contribution due to the production of compounds by the exchange reaction to the electrophoretic pattern. This effect can be illustrated by the fast exchange approximation which yields the roots

$$s_1 = -q^2 D + i\omega \ e \ E^o q \ \frac{z_2 k_{12} + z_1 k_{21}}{k_{12} + k_{21}} \tag{38a}$$

$$s_2 = -q^2 D + i\omega \ e \ E^o q \ \frac{z_1 k_{12} + z_2 k_{21}}{k_{12} + k_{21}} - (k_{12} + k_{21}) \tag{38b}$$

Data analysis requires the use of z_i^{eff}, for the correct reproduction of the peak positions, cf. ref. 9.

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