Zones of Sparingly Soluble Inorganic Salts with Membrane Properties in Gels

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Crystal Growth / Electrochemistry / Membranes / Nucleation / Precipitate

Polyacrylamide gels containing potassium oxalate (sodium oxalate) are brought into contact with aqueous solutions of Pb(NO₃)₂, CaCl₂, SrCl₂ and BaCl₂ respectively. The electrolyte concentrations in the gel phase and in the solutions are varied systematically. There exists a system specific characteristic concentration \tilde{c}_s below which advancing precipitation zones of PbOx, CaOx, SrOx, and BaOx (Ox: oxalate) within the gel are observed. Above \tilde{c}_s the precipitation zones do not grow after advancing for about 2 mm maximally. Such precipitation zones have membrane properties (e.g. impermeability to ions forming the precipitate, osmotic property). \tilde{c}_s corresponds to a supersaturation ratio of the order 10³. The experiments indicate that the precipitation zones with membrane properties are generated by homogeneous nucleation. — The kinetics of formation of oxalate precipitates in cellophane skins is studied by measurements of the membrane potential as function of time. In these systems precipitate is formed by interdiffusion of two solutions containing the appropriate ions. A system specific delay time Δt_{del} is observed after which the precipitation zones acquire membrane properties. It is found that this time is related to the rate of formation of precipitate which is a function of the solubility product and the square of electrolyte concentration. The precipitation zone acquires membrane properties as soon as the local concentration of precipitate has reached a value of the order 10⁻³ mol cm⁻³. The existence of the characteristic concentration \tilde{c}_s and of the delay time Δt_{del} are interpreted in terms of an absorption charge model proposed by Hirsch-Ayalon.

1. Introduction

Anorganic crystalline precipitation zones with membrane properties can be formed by interdiffusion within a porous matrix (e.g. cellophane skin) of two aqueous electrolyte solutions containing ions which can form a sparingly soluble precipitate. The membrane properties manifest themselves in a non-ohmic current/voltage characteristic and characteristic membrane potentials. This has been observed first by Hirsch-Ayalon [1] who has studied extensively the properties of BaSO₄ precipitation zones. BaSO₄, SrSO₄ and PbSO₄ precipitation zones with membrane properties can also be generated in gels using an experimental arrangement similar to that in which periodic precipitation pattern are observed [2].

Further experiments have shown [3] that most precipitation zones formed by 2, -2 valent precipitates in an inert matrix can acquire membrane properties under appropriate conditions. It is the aim of this contribution to study in detail the properties of precipitation zones formed by different sparingly soluble salts of oxalic acid: Calcium, strontium, barium and lead oxalate (abbreviated: Ox) which have quite different solubility products [4] (see Table 3, column 2).

2. Precipitation Zones within Polyacrylamide Gel

Precipitation zones of PbOx, CaOx, SrOx and BaOx in polyacrylamide gels are produced in the following way [2]: Test tubes (length: 10 cm, diameter: 1 cm) completely filled with polyacrylamide (water content: about 90%) containing Na₂Ox (or K₂Ox) of known concentration ($c_s(gel)$) are brought into contact with well stirred aqueous solutions of CaCl₂, SrCl₂, BaCl₂ and Pb(NO₃)₂ of known concentration ($c_s(aq)$) respectively. The temperature of the systems are kept constant (room temperature). The test tubes are positioned vertically with the open end facing up. Three different types of experiments are carried out: $c_s(\text{gel}) = c_s(\text{aq})$; $c_s(\text{gel}) < c_s(\text{aq})$; $c_s(\text{gel}) > c_s(\text{aq})$. At the beginning of an experiment $(c_s(\text{gel}) = c_s(\text{aq}); c_s(\text{gel}) < c_s(\text{aq}))$ precipitation of the sparingly soluble salt sets in at the phase boundary gel/aqueous solution (e.g. Ba(Cl)₂(aq) + Na₂Ox(gel) = BaOx(s,gel) + NaCl(aq,gel)) and slowly extends into the gel phase. The thickness of the precipitation zone (distance between the phase boundary gel/aqueous solution and the front of the advancing precipitation zone within the gel) increases with time. Fig. 1 shows a typical experimental result.



Position ξ of the front of a precipitation zone relative to the phase boundary gel/aqueous solution as a function of the square root of time $t^{1/2}$. $c_s(SrCl_2, aq) = c_s(Na_2Ox, gel) = 0.2 c^+, c^+ = 1 \text{ mol dm}^{-3}$ $(T = 25^{\circ}C)$

There is a linear relation between the thickness ξ of the precipitation zone and the square of the diffusion time $t^{1/2}$. It holds for $\xi/L < 0.3$ (L: length of the gel phase) corre-

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sponding to a duration of the experiment of about 30 d. For larger values of ξ/L (longer diffusion times) the thickness of the precipitation zone begins to grow faster (see below). The straight lines (for $\xi/L < 0.3$) do not pass through the origin. This is due to the uncertainty of the location of the phase boundary gel/aqueous solution.

Periodic precipitation patterns have been observed occasionally, e.g. with the system $c_s(Pb(NO_3)_2, aq) = 0.01 c^+$, $c_s(Na_2Ox, gel) = 0.02 c^+$, $c^+ = 1 \text{ mol dm}^{-3}$.



Concentration profiles of mobile particle species A and B within a polyacrylamide gel for two different diffusion times calculated from $c_A = c_A^0 (1 - \operatorname{erf}(z)/K)$ for $x < \xi$ and $c_B = c_B^0 ((\operatorname{erf}(z) - K))/(1 - K))$ for $x > \xi$ with $z = x/(2(Dt)^{1/2})$ and $K = \operatorname{erf}(\xi/(2(Dt)^{1/2}))$. erf(z): error function; x: space coordinate; D: effective diffusion coefficient, c_A, c_B : molar volume concentration of particle species A and B, respectively; ξ_1, ξ_2 : space coordinate of the front of the precipitation zone relative to the phase boundary gel/aqueous solution at two different diffusion times t_1 and t_2 . $D = 1 \cdot 10^{-5}$ cm² s⁻¹; $c_A^0 = c_B^0 = 0.1 \ c^+$; t_1 : 7.35 $\cdot 10^4$ s; $t_2 = 8.64 \cdot 10^5$ s; $c^+ = 1$ mol dm⁻³

Table 1Effective diffusion coefficients D in polyacrylamide gels obtained from measurements of the thickness of precipitation zones as a function of time (see Fig. 1). The alkali oxalates are contained in the gel phase. For the meaning of f see heading of Table 2

| System | $\frac{c_{\rm s}({\rm aq})}{c^+}$ | $\frac{c_{\rm s}({\rm gel})}{c^+}$ | $\frac{D\cdot 10^6}{\mathrm{cm}^2\mathrm{s}^{-1}}$ | ſ |
|---------------------------------------|-----------------------------------|------------------------------------|--|-----|
| $Pb(NO_3)_2/K_2Ox$ | 0.05 | 0.05 | 6.96 ± 0.12 | 0 |
| $Pb(NO_3)_2/K_2Ox$ | 0.1 | 0.1 | 6.63 ± 0.17 | 0 |
| CaCl ₂ /Na ₂ Ox | 0.1 | 0.1 | 5.90 ± 0.10 | 0 |
| CaCl ₂ /Na ₂ Ox | 0.2 | 0.2 | 6.69 <u>+</u> 0.11 | 0 |
| CaCl ₂ /K ₂ Ox | 0.3 | 0.3 | (3.10 ± 0.14) | 1 |
| CaCl ₂ /K ₂ Ox | 0.4 | 0.4 | (2.63 ± 0.11) | 1 |
| SrCl ₂ /Na ₂ Ox | 0.1 | 0.1 | 5.80 ± 0.2 | 0 |
| SrCl ₂ /Na ₂ Ox | 0.2 | 0.2 | 6.11 ± 0.15 | 0 |
| BaCl ₂ /K ₂ Ox | 0.2 | 0.2 | 4.84 ± 0.13 | 0 |
| BaCl ₂ /K ₂ Ox | 0.3 | 0.3 | 5.70 ± 0.10 | 0.1 |

Assuming that (a) the formation of the precipitation can be represented by the scheme A(aq) + B(gel) = AB(s); (b) that the influence of osmotic volume flow on the formation of precipitate can be neglected, (c) the species A and B have the same diffusion coefficient and (d) the formed precipitate AB does not impede the diffusion process the concentration profile of A and B respectively with the gel can be calculated [2, 5, 6]. Fig. 2 shows a graphical representation of the results of such a calculation assuming that the concentration of B (gel) far from the front of the advancing precipitation zone still has the original value $c_{\rm B}^0$ (gel phase of infinite length). In this model precipitation occurs only at the point at which $c_A(gel) = c_B(gel) = 0$ (neglecting the finite solubility of the precipitate). Eq. (1) describes the position of the front of the precipitation zone within the gel as function of time.

$$c_{\rm A}^0/(c_{\rm A}^0 + c_{\rm B}^0) = \operatorname{erf}(\xi/2(Dt)^{1/2})) \tag{1}$$

D: effective diffusion coefficient; erf(x): error function; t: time.

Eq. (1) together with known values of c_A^0 , c_B^0 and the slope $m (= \xi/t^{1/2})$ of the experimental versus $t^{1/2}$ curve is used to calculate the value of the effective diffusion coefficient *D*. Typical results of such a data analysis are compiled in Table 1.

The observation that the slope of the versus $t^{1/2}$ curve increases for $\xi/L > 0.3$ is interpreted as the influence of the finite length of the gel phase. For $\xi/L > 0.3$ the decrease of $c_B^0(Ox^{--})$ becomes noticable (see Fig. 2): The ratio $c_A^0/(c_A^0 + c_B^0)$ increases as well as the ratio $\xi/t^{1/2}$ for a constant value of the effective diffusion coefficient D (see Eq. (1)).

3. Precipitation Membranes in Polyacrylamide Gels

If experiments are carried out with equal concentrated electrolyte solutions in the gel phase and in the aqueous bulk phase as function of concentration $(c_s(gel) = c_s(aq) = c_s)$ it is observed that within a narrow concentration range around a characteristic concentration \tilde{c}_s the growth of the precipitation zone stops after it has reached a thickness of maximal 2 mm. In some cases the precipitation zone is very thin, only visible as a sleightly opaque layer at the phase boundary gel phase/aqueous bulk phase. The experiments are carried out with groups of ten test tubes filled with polyacrylamide gel under identical conditions. The fraction of the number of the test tubes in which the precipitation zone does not grow after the test tubes have been brought into

Table 2

Fraction f of the number of test tubes in which the precipitation zone as stopped to grow as a function of concentration $c_s(aq) = c_s(gel) = c_s$. The test tubes are filled with polyacrylamide gels containing K₂Ox (or Na₂Ox, indicated by #) of known concentration and brought into contact with aqueous solutions of Pb(NO₃)₂, CaCl₂, SrCl₂ and BaCl₂ respectively

| | f | | | | | | | |
|--|------|------|------|------|------------------|------|------|------|
| | 0.02 | 0.05 | 0.10 | 0.15 | 0.20 | 0.25 | 0.30 | 0.40 |
| Pb(NO ₃) ₂ (aq) | 0 | 0 | 0 | 0.1 | 0.2 [*] | 1* | 1* | 1* |
| CaCl ₂ (aq) | _ | _ | 0.1 | _ | 0.5 | 1* | - | - |
| SrCl ₂ (aq) | - | _ | 0 | _ | 0* | 0.2* | 0.4* | 1* |
| BaCl ₂ (aq) | _ | | 0 | | - | 0.1* | 0.1* | 1* |

contact with the aqueous bulk phase is compiled in Table 2. It has never been observed that a precipitation zone which has stopped to grow started to grow again ("all nor nothing" process). The observation that the thickness of precipitation membranes does not grow with time (to a first approximation) is evidence for its impermeability for the ions forming the precipitate.

Visual observation of the size of the crystalline conglomerates forming the precipitation zones indicate that their dimensions decrease with increasing values of c_s . The precipitation zones which have stopped to grow are formed by densely packed crystallites. It is noteworthy that the concentration range of c_s is fairly narrow in which a transition from growing precipitation zones to precipitation zones which do not grow takes place. The observation is interpreted by assuming that precipitation zones which are not able to grow are formed by small tightly packed crystallites generated by homogeneous nucleation. This tight packing of crystallites is one of the necessary conditions for the precipitation zone to acquire membrane properties (see below). Indeed, the supersaturation ratio \tilde{S} (=($\tilde{c}_s/c_s(sat), c_s(sat)$): saturation concentration of the precipitate) which must be reached to produce precipitation zones which do not grow has a value of the order of $\tilde{S} \sim 10^3$ (see Table 3, column 5). Closer inspection of the data shows that \tilde{S} increases with decreasing values of K_s (i.e. \tilde{S} is smaller for the precipitate with the larger solubility.

The existence of a characteristic concentration \tilde{c}_s is not caused by an impedement of the diffusional processes by the mass of precipitate with increasing values of c_s . The effective diffusion coefficient D at concentrations c_s in the vicinity of \tilde{c}_s where some of the precipitation zone in an ensemble of gels still grow but others have stopped to grow ($c_s = \tilde{c}_s - \delta c_s$) has the same value within the accuracy of the measurement as that found in growing precipitation zones at concentrations $c_s \ll \tilde{c}_s$.

Precipitation zones which have stopped to grow exhibit osmotic properties. If the osmotic value Π of the electrolyte



Isoosmotic concentrations of the systems $Pb(NO_3)_2/Na_2Ox$ (curve 1), $CaCl_2/Na_2Ox$ (curve 2), $SrCl_2/Na_2Ox$ (curve 3); $BaCl_2/Na_2Ox$ (curve 4) obtained from osmotic vapour pressure measurements at room temperature. Calibration with $CaCl_2$ solutions. $c^+ = 1 \mod dm^{-3}$

solution in the aqueous bulk phase ($\Pi(aq) = RT\Phi(aq)$) $\Sigma c_i(aq), \Phi$: osmotic coefficient) is higher than that in the gel phase (Π (gel) = $RT\Phi$ (gel) Σc_i (gel), i.e. $\Delta \Pi = \Pi$ (aq) - $\Pi(\text{gel}) > 0$) the volume of the gel which is free of precipitate shrinks (decrease of the volume of the gel as function of time). The data in Fig. 3 show the conncentration dependence of isoosmotic concentrations of the electrolytes used in this study. They were determined by vapour pressure osmometry. The osmotic difference $\Delta \Pi$ is the driving force of an osmotic volume flow J_{v} directed from the gels phase into to the aqueous bulk phase. The shrinking of the gel causes the electrolyte solution of the aqueous bulk phase to surround the shrunken gel thereby generating a layer of precipitate around the outer surface of the shrinking gel plug. An increase of the thickness of this layer of precipitate with time can not be observed visually. That newly formed precipitation membrane has also osmotic properties. The rate at which the volume of the gel free of precipitate shrinks is accelerated.

For the system CaCl₂(aq)/K₂Ox(gel) ($c_s = 0.3 c^+$, $c_s = 0.4 c^+$) the coefficient *D* given in Table 1 is not a diffusion coefficient. (It is given in brackets.) At the stated concentrations the precipitation zones of these systems have membrane properties (osmotic properties). The "diffusion coefficient" characterizes the growth of the area of the precipitation membrane at the cylindrical surface of the shrinking gel plug.

The direction of the osmotic volume flow J_{y} can be reversed by reversing the sign of the osmotic difference $\Delta \Pi$ (= Π (aq) - Π (gel)). If $\Delta \Pi < 0$ the volume flow is directed into the gel phase. The hydrostatic pressure within the gel increases. Finally, the thin, osmotically active precipitation zone cannot withstand the hydrostatic pressure difference and cracks. A volume flow formed mainly by the electrolyt solution contained within the gel phase reaches the aqueous bulk phase. This triggers a precipitation of the sparingly soluble salt at the phase boundary gel/bulk phase. This precipitate has different appearences in the different systems studied. The precipitate of PbOx has a cauliflower like appearence covering the entire area at the opening of the test tube. The new precipitate of CaOx forms thin hollow hairs (outer diameter: about 1 mm; length several centimeter). They grow at certain areas of the interphase and extend into the aqueous bulk phase.

With the system NaOx(aq)/Pb(NO₃)₂(gel) several experiments have been carried out under the condition $c_s(aq) \neq c_s(gel)$. The results are shown in Fig. 4. It turns out that for $c_s(gel)/c_s(aq) > 3$ but $c_s(gel)$, $c_s(aq) < \tilde{c}_s$ precipitate (PbOx) is only formed at the phase boundary gel/bulk phase and no advancing precipitation zones are observed. The amount of precipitate at the phase boundary increases with time. The question whether this layer of precipitate finally acquires membrane properties cannot be answered definitely. The observation of hollow hairs of CaOx in the system CaCl₂(gel)/Na₂Ox(aq) ($c_s(Na_2Ox)(aq) = 0.05 c^+ c_s(CaCl_2)(gel) = 0.15 c^+$ suggest that thick precipitation layers could have osmotic properties.

Is the characteristic concentration \tilde{c}_s related to the extent of supersaturation necessary to produce homogeneous nucleation in free solution? To answer this question the fol-



Study of precipitation zones in the system Na₂Ox(gel)/Pb(NO₃) with $c_s(gel) \neq c_s((aq))$. $\blacktriangle: f = 0; \blacksquare: 0 < f < 0.4; \boxdot: f = 1. f:$ fraction of the number of tests tubes in which precipitation zones do not advance into the gel phase. The experiments are carried out with groups of 10 test tubes; $c^+ = 1 \mod dm^{-3}$



Fig. 5

Electric current *I*/voltage $\Delta \varphi (= \varphi' - \varphi'')$ characteristic of a CaOx precipitation membrane generated by interdiffusion of equal concentrated CaCl₂ and K₂Ox solutions ($c_s = 0.1 c^+$) in a polyacrylamide gel plug (diameter: 7 mm, thickness 5 mm. $\Delta \varphi_0$: membrane potential at I = 0

lowing experiments are carried out: Equal volumes of equal concentrated aqueous solutions of Pb(NO₃)₂, CaCl₂, SrCl₂ and BaCl₂ (concentration c_s) are rapidly mixed in a spectral photometric cell (optical path length: 1 cm), and placed into a spectral photometer at room temperature (mixing time: 0.8 s). The extinction of the solution is measured as a function of time. The time (delay time τ) at which the extinctions starts to increase due to scattering of the primary light intensity at the growing crystallites is determined. The experiments are carried out as a function of concentration. For each experiment a new cell is used to avoid contamination with crystal seeds. The concentration c_s at which the delay time for the formation of precipitate approaches 1 s is taken arbitrarily as the concentration c_s (hom.nucl.) of homogeneous nucleation. The results of the experiments are shown in Fig. 5 and Table 3 (column 6). From these findings the following conclusions are drawn:

- a) The supersaturation ratio \tilde{S} necessary to produce a precipitation zone with membrane properties (e.g. osmotic properties, impermeability to ionic species forming the precipitate) is higher by a factor of about 10 than the supersaturation $S (= c_s (homog. nucl)/c_s (sat))$ necessary to trigger homogeneous nucleation (see Table 3, compare column 4 and 6). This finding reflects the fact that the gel phase contains about 10% of solid material (water content about 90%) at which heterogeneous nucleation can occur. Therefore, a higher supersaturation is necessary to trigger homogeneous nucleation within the gel.
- b) The values of \vec{S} as well as of S (see Table 3) increase with decreasing values of the solubility product of the precipitate.
- c) System specific properties are also observed: The value of \tilde{c}_s for SrOx and BaOx is about the same. The same is approximately true for \tilde{S} and S. Going from BaOx and SrOx to CaOx the value of c_s decreases by about a factor of 2. \tilde{S} and S increase also by a factor of about 2. On the basis of this finding it is expected that the value of \tilde{c}_s of the system PbOx should be smaller by a factor of 5 $(S(PbOx)/S(CaOx) \sim 5)$. But this is not observed experimentally.

The membrane properties of the precipitation zones which do not grow show up clearly in measurements of their electrochemical properties: A glas tube (length: 10 mm, both

Table 3 Compilation of experimental data.

 \tilde{S} : Supersaturation ratio in polyacrylamide gels with precipitation zones which have stopped to grow. ($\tilde{S} = \tilde{c}_s/c_s(sat)$; c_s : concentration at which f = 1; For the meaning of f see heading of Table 2. $c_s(sat)$: saturation concentration of the precipitate in water; $c_s(sat) = K_2^{1/\nu}/v_{\pm})c^+$; $\nu = \nu_{\pm} + \nu_{-}$; $\nu_{\pm} = \nu_{\pm}^{\nu_{\pm}} + \nu_{\pm}^{\nu_{-}}$; ν_{\pm}, ν_{\pm} : number of cations and anions respectively from which a molecule of the precipitate is formed; K_s : solubility product; c_s (homog. nucl.): concentration at which homogeneous nucleation is observed in free solution (for details see text); S: supersaturation ratio for homogeneous nucleation; ($S = c_s(homog. nucl)/c_s(sat)$); c_s^* : concentration at which the delay time Δt_{del} diverges in measurements of membrane potential as function of time (see Fig. 6)

| 1 | $\frac{2}{\frac{K_{\rm s}}{(c^{*})^2}}$ | $\frac{3}{\frac{c_{s}(sat)}{c^{+}}}$ | $\frac{4}{\frac{\tilde{c}_{s}}{c^{+}}}$ | $\tilde{S} = \frac{\tilde{c}_{s}}{c_{s}(\text{sat})}$ | $\frac{c_{\rm s}(\rm hom.nucl)}{c^+}$ | $S = \frac{c_{\rm s}(\rm hom.nucl)}{c_{\rm s}(\rm sat)}$ | $\frac{c_s^*}{c^+}$ |
|------------------------------|---|--|---|---|--|---|---|
| PbOx CaOx SrOx BaOx | $2.74 \cdot 10^{-11} (18^{\circ}\text{C}) 2.57 \cdot 10^{-9} (25^{\circ}\text{C}) 5.61 \cdot 10^{-8} (18^{\circ}\text{C}) 1.2 \cdot 10^{-7} (18^{\circ}\text{C})$ | $5.2 \cdot 10^{-6} 5.1 \cdot 10^{-5} 2.4 \cdot 10^{-4} 3.5 \cdot 10^{-4}$ | 0.25 0.25 0.4 0.4 | $\begin{array}{c} 4.8 \cdot 10^4 \\ 4.9 \cdot 10^3 \\ 1.7 \cdot 10^3 \\ 1.2 \cdot 10^3 \end{array}$ | $3.4 \cdot 10^{-3} 6.3 \cdot 10^{-3} 1.5 \cdot 10^{-2} 2.5 \cdot 10^{-2}$ | $\begin{array}{c} 6.5 \cdot 10^2 \\ 1.3 \cdot 10^2 \\ 0.6 \cdot 10^2 \\ 0.7 \cdot 10^2 \end{array}$ | $4 \cdot 10^{-3} \\ 1.5 \cdot 10^{-2} \\ 2.5 \cdot 10^{-2} \\ 2.5 \cdot 10^{-2} \\ 2.5 \cdot 10^{-2} \\ 10^{-2$ |

ends open) filled with a polyacrylamide gel (free of electrolyte) is brought into contact with two equal concentrated aqueous solutions of CaCl₂ (left bulk phase, index (')) and K₂Ox (right bulk phase, index (")); $c'_s = c''_s$). The gel plug has a length of about 5 mm. The membran potential $\Delta \varphi (= \varphi' - \varphi'')$ between the bulk phases is measured with two identical calomel electrodes. At the beginning of the experiment a potential difference of a few millivolts is observed typically for diffusion potentials. After about 2.5 h the potential difference begins to rise and reaches a time independent value of about $\Delta \varphi = 110$ mV after about ~8 h. At that time a narrow band of precipitate has been formed



Fig. 6 Concentration dependence of delay time Δt_{del} as a function of logarithm of concentration c_s . Left bulk phase: ('), Pb(NO₃)₂, CaCl₂, SrCl₂, BaCl₂, right bulk phase ("), K₂Ox; $c'_s = c''_s$





Double logarithmic plot of delay time τ of onset of turbidity after rapid mixing (mixing time about 0.8 s) of equal concentrated aqueous solutions of K₂Ox and Pb(NO₃)₂, CaCl₂, SrCl₂ and BaCl₂ respectively as function of concentration

at about the middle of the plug. Its thickness (visual observation) does not increase with time. After $\Delta \varphi$ has reached a time independent value the stationary electric current/ voltage characteristic is measured under galvanostatic conditions. The curve shown in Fig. 6 demonstrates that the current/voltage characteristic is non-ohmic. This is typical for precipitation membranes generated within cellophane skins by interdiffusion of two aqueous electrolyte solutions containing ions which can form a sparingly soluble 2, -2 valent precipitate [7]. Hirsch-Ayalon has proposed a bipolar adsorption charge model which explaines this behaviour [1b]. The model has been described in detail repeatedly in the literature (e.g. [1c, 3]). The available experimental data which are mainly obtained with BaSO₄ precipitation membranes give support to this model [8].

4. Generation of Precipitation Membranes in Cellophane Skins

The kinetics of formation of oxalate precipitation membranes in cellophane skins is studied by measuring the electrical potential difference $\Delta \varphi (= \varphi' - \varphi'')$ between the bulk phases of a cellophane skin (Kalle, cellulose hydrate foil, 350 **P** 16, thickness in equilibrium with water: 50 μ m; thickness in the dried state: 22 μ m; water content: 61%) as a function of time after the skin has been brought into contact with aqueous solution containing Pb++, Ca++, Sr++ and Ba++ ions respectively (left bulk phase: (')) and Ox^{--} ions (left bulk phase: (")). It is found that there exists a characteristic time interval Δt_{del} (delay time) between the start of an experiment and the onset of build-up of a membrane potential, leading finally to a time independent value of the order of $\Delta \phi \sim 100 \text{ mV}$ [9]. Fig. 7 shows the concentration dependence of the delay time Δt_{del} for the systems studied in this investigation. For each concentration c_s ($c'_i = c''_{Ox}$, i = Pb, Ca, Sr, Ba) a new cellophane skin is used. The delay time is larger by a factor of about 10 than the characteristic time of diffusion to obtain stationary concentration profiles within the cellophane skin) $t = \delta^2/D$, δ : thickness of the swollen cellophane skin ($\delta = 50 \ \mu m$; D: effective diffusions coefficient, $D \simeq 5 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). Therefore, it is concluded that the delay time is related to the kinetics of the precipitation process taking place within the cellophane skin. The delay time diverges at a certain system specific concentration $c_{\rm s}$. The values of the characteristic concentrations $c_{\rm s}^*$ (referring to $\Delta t_{del} = 20$ min) are compiled in Table 3 (column 8).

What is the cause of the existence of the characteristic concentration c_s^* ? To answer this question the maximal production rate of precipitate AB (solubility product K_s) in a convection free layer (gel plug) separating two bulk phases with fixed concentration c_A and c_B of uncharged species A and B is calculated. The calculation is based on a simple model proposed by Helfferich and Katchalsky (Ref. [10], Eq. (13)) which neglects the influence of supersaturation. For the calculation it is assumed that the diffusion coefficient of species A and B within the gel plug have the same value $(D_A = D_B = D = 5 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1})$ and that the concentrations of the species A and B in the bulk phases have the same values ($c_A = c_B = c_s$). Under these conditions the maximal production rate of precipitate j_{max} is located in the middle of the gel plug and is given by Eq. (2) [10]. j_{max} depends on the square of electrolyte concentration.

$$j_{\rm max} = (Dc_{\rm s}^2)/(K_{\rm s}^{1/2}\delta^2)$$
(2)

 j_{max} : maximal production rate of precipitate at $\delta/2$; δ : thickness of convection free layer; D: effective diffusion coefficient; K_s : solubility product.

Calculations of the maximal production rate density j_{max} of precipitate within the cellophane skin at the system dependent concentration c_s^* (with $D = 5 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$; $\delta =$ 50 μ m) shows that for all systems j_{max} has similar values: $j_{\text{max}}(\text{Pb}(\text{NO}_3)_2)/j^+ = 6.1 \cdot 10^{-7}; j_{\text{max}}(\text{CaOx})/j^+ = 8.8 \cdot 10^{-7};$ $j_{\max}(\text{SrOx}) = 5.3 \cdot 10^{-7}; j_{\max}(\text{BaOx}) = 3.6 \cdot 10^{-7} (j^+ = 1 \text{ mol})$ $cm^{-3} s^{-1}$). c_s^* is the electrolyte concentration (see Table 3, column 8) at which Δt_{del} diverges. With $\Delta t_{del} = 20$ min (see Fig. 6) this corresponds to a local concentration of precipitate of the order of 10^{-3} mol cm⁻³. This finding is interpreted by assuming that at that concentration the counter ion clouds of the adsorption charges on the crystallites forming the precipitation zone overlap effectively (adsorption charge model, see e.g. Ref. [8]) and the precipitation zone acquires membrane properties. Indeed, it can be estimated that in a precipitation zone with membrane properties a local concentration of precipitate of the order of 10^{-3} cm⁻³ does exist: Scanning electron microscop pictures show [3] that the thickness of a precipitation membrane is about 10 μ m. It containes an amount of substance of about 10⁻³ mol cm^{-2} (determination of the mass of precipitate per unit area of cellophane skin after removing the organic material of the cellophane matrix by combustion).

Our study of precipitation membranes was started after Dr. P. Hirsch-Ayalon drew our attention to these systems. We thank him for his continued interests in our work. Beate Schaaf determined the delay times from measurements of membrane potentials and the isoosmotic concentrations. R. D. Reinhardt measured the electrical current/voltage characteristic. We thank them for their help.

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(Eingegangen am 5. Juli 1988)

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Water Desorption Kinetics from Alumina Supported Copper Studied by FTIR Spectroscopy

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Adsorption / Catalysis / Chemical Kinetics / Desorption / Spectroscopy, Infrared / Surfaces

The desorption of water from an alumina-supported copper catalyst has been followed by FTIR spectroscopy. On the catalyst, an exponential decrease of the 2400 cm⁻¹ (O-D stretching) absorption is observed subsequent to loading of the sample with a D_2O pulse. The rates and activation energies of desorption are found to be different in N_2 and H_2 carrier gases. On the pure alumina support the desorption is non-exponential, and is well described by a Temkin-type desorption kinetics: A distribution of sites, which are characterized by different desorption enthalpies, are contributing to the broad O-D stretching band. This is evidenced by different desorption rates for various parts of the band.

Introduction

One important advantage of multichannel detection techniques, in which the entire spectral range of interest is being recorded simultaneously, is the possibility to study timedependent systems. Together with the inherently high sensitivity, this advantage contributes to the increasing importance of Fourier Transform Infrared (FTIR) spectroscopy in catalytic research [1,2]. In this note we would like to emphasize the possibility that desorption kinetics from individual sites can be studied by FTIR even if the desorbing product is the same, provided the sites are distinguished by different IR absorption frequencies. If there is a distribution of sites which gives rise to an inhomogeneously broadened line, different parts of the absorption band will decrease due to desorption at different rates. In this case the overall absorption intensity exhibits a non-exponential time dependence, as described e.g. by a Temkin isotherm.

The paper is organized as follows. First, the desorption of water from an alumina-supported copper catalyst is discussed where simple exponential desorption, with a remark-

Ber. Bunsenges. Phys. Chem. 92, 1553-1557 (1988) - © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1988. 0005-9021/88/1212-1553 \$ 02.50/0