A Kinetic Study of the Formation of Trilaurylamine Hydrochloride at the Decanol–Water Interface

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A kinetic study of the formation of trilaurylamine hydrochloride at the n-decanol–water interface was carried out using a rotating diffusion cell technique. The reaction between hydrogen chloride and the amine appears to be fast and of zeroth order with respect to hydrogen ion. The slow step is either the binding of chloride ion to the initially formed protonated amine or the desorption of ion-paired trilaurylamine hydrochloride into the decanol phase. At a pH lower than 3.6 the rate-determining step is the diffusion of trilaurylamine in the decanol phase. To maintain a stable and reproducible interfacial region an excess of sodium chloride (>0.01 M) was needed. This finding suggests that chloride ions are adsorbed at the interface.

In a previous paper[1] we studied the extraction and fractionation of a polydisperse polyelectrolyte, lignosulfonate, using a supported liquid membrane. A separate study[2] was done to find out the suitable solvent and carrier for this purpose. These studies showed that decanol as a solvent and trilaurylamine as a carrier are a proper combination for the extraction and fractionation of lignosulfonate from aqueous media. Even though decanol has been used previously in supported liquid membrane (SLM) studies,[3] it presents some special features compared to the solvents usually used, viz. its relative permittivity is comparatively high ($\varepsilon_r = 8.1$) and its interfacial tension is low. Also, decanol dissolves water (1.5 mol per dm³ of decanol), although much less than, for example, octanol and pentanol.

The overall reaction of the formation of trilaurylamine hydrochloride at the interface is shown in reaction (1),

$$HCl(aq) + TLA(o) \rightleftarrows TLAHCl(o) \qquad (1)$$

where aq denotes the aqueous phase and o decanol. When developing the model for the extraction process in Ref. 1 it was assumed without direct evidence that this interfacial reaction is fast in comparison with diffusion processes. The validity of this assumption needs to be reconsidered in order gradually to improve the model; therefore it was decided to study reaction (1) separately without lignosulfonate.

TLA is a common extractant in liquid–liquid extraction. Some kinetic studies of the interfacial reaction (1) have been presented, e.g. Refs. 4 and 5. These studies have concerned non-polar solvents such as toluene ($\varepsilon_r = 2.4$),

and there is reason to suspect that the reaction mechanism may be different when decanol is used as a solvent instead of these more non-polar solvents. Firstly, aggregation of amine hydrochlorides is not so obvious in decanol as in, for example, alkanes.[6] Secondly, the structure of the decanol–water interface is probably organized, owing to the presence of a hydroxyl group in decanol that is at least partly oriented towards the water phase. This is reflected in the low interfacial tension between decanol and water; according to our measurements the value is 8.2 mN m^{-1} at 21°C. Thirdly, decanol may form a compound together with TLA and HCl. Muhammed[7] has observed that octanol forms a mixed compound with TLA and HCl when octanol is added to benzene. In addition, decanol dissolves large quantities of water[3] and may give rise to micellar structures.

Albery et al.[8] have introduced a method which is especially suitable for studying the kinetics of reactions at the interfaces of a supported liquid membrane. This method allows the study of the system under the same type of steady-state conditions which occur in a supported liquid membrane during extraction. The liquid membrane is placed in a diffusion cell which can be rotated at a controlled rate. The well known Levich equation[9] can then be used to calculate the thicknesses of the diffusion layers and the rate of mass transport. The kinetic contribution can be extrapolated from the data of experiments in which the rotation rate is varied while other conditions are maintained.

Transport in the aqueous phases must be considered in all experiments that use supported liquid membranes. The most common way to treat the problem has been to increase the stirring in the aqueous phases until a limiting flux is observed.[10–13]

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Experimental

Apparatus. The rotating diffusion cell apparatus is manufactured by Oxford Electrodes (Fig. 1). When the cylinder is rotated, a convective flow is directed towards the membrane from both sides, so that the Levich equation can be applied to the two diffusion layers thus formed.[14] A membrane is placed at the bottom of a perspex cylinder. Millipore GS filters (pore size 0.22 μm, porosity 80%, thickness 150 μm) made of mixed esters of cellulose were used as membranes. During the preparation of the membranes the procedures developed by Albery *et al.*[15] were used. The membrane was glued to the cylinder with Acrifix 106 (Röhm), so that the shiny side of the membrane was directed towards the aqueous phase. Part of the membrane was destroyed by an organic solution (33% n-hexane, 33% 1,4-dioxane, 33% 1,2-dichloroethane, 1% water) leaving an active porous area in the center with a radius of ca. 1.5 cm. The membrane was thoroughly washed with Milli-Q water (Waters) and left to soak for at least 2 h. The membrane was then dried in a vacuum desiccator.

Measurements. The aqueous phase (250 ml) containing 10^{-4} M HCl and in most cases sodium chloride (Merck, p.a.) was pre-equilibrated at 25°C with the organic phase (50 ml) consisting of trilaurylamine (Tokyo Kasei, 95%) dissolved in decanol (Sigma, 98%). The membrane was wetted with a few drops of the organic solution and levelled into position. Both phases were then added simultaneously, so that the levels of the liquids were the same at all times. This ensured a small hydrostatic overpressure on the aqueous side, which was found necessary to keep the interface stable during rotation. The pH electrode and the titration tube were positioned and the rotation rate was set to 1.8 Hz (rotations per second) for 1 h in order to ensure a constant temperature (25°C) in the cell.

The pH (at this point above 5.5) was then adjusted near the set point by pipetting an appropriate amount of 1 M HCl into the aqueous phase. Fine adjustment of the pH
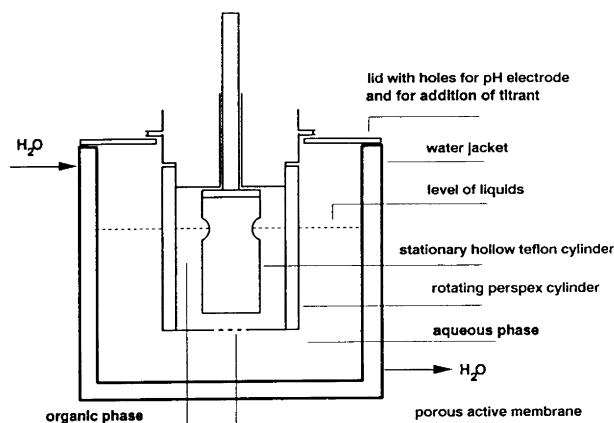
was made by titration, after which the experiment was started. The reaction was followed for 2 h. During that time six rotation rates were selected at random between 1.8 and 6.5 Hz. The rate of the reaction was followed by a pH-stat apparatus (Radiometer VIT90 titrator and ABU91 autoburette). A Radiometer GK2401 C combined electrode was used to monitor the pH. The rate of reaction (1) was calculated from the rate of addition of the titrant to the aqueous phase.

The effects of the concentrations of HCl, NaCl and TLA on the flux were determined under conditions close to those used earlier in the liquid membrane experiments.[1] For each system at least two consecutive experiments were done. Fresh solutions and membranes were used for each set of two experiments. Measurements at pH > 4 were repeated under nitrogen to make sure that carbon dioxide did not interfere with the results. The effective thickness of the membrane was determined by measuring the tracer diffusion of H^+ in 1 M KCl.

Results and discussion

The steady-state transport has been analyzed using linear concentration gradients as presented in Fig. 2.

Use of the Levich equation requires that the hydrodynamic flows to the surfaces of the porous membrane must be laminar and uniform over the whole surface, which means that they should be independent of the radius of the porous membrane. The fulfillment of the latter condition was checked by performing the following experiment. The rate of consumption of HCl was measured for three different areas of the interface, keeping all other parameters constant. The result shown in Fig. 3 indicates that this rate is indeed directly proportional to the membrane area.

Next, the influence of the kinetics of reaction (1) was studied. The effect of chloride ion was investigated by varying the amount of NaCl in the aqueous phase while the pH was held at 3.50 and the concentration of TLA was 0.1 M. When extraction with a supported liquid membrane is considered, the most interesting condition for reaction (1) is the absence of NaCl, because Cl^- is a competing ion for lignosulfonate.[1] The transport of H^+ is
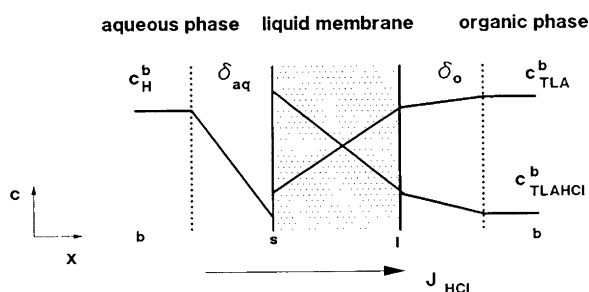

Fig. 1. The rotating diffusion cell.

Fig. 2. The steady-state transport in the rotating diffusion cell. $c_H{}^b$, $c_T{}^b$ and $c_{TH}{}^b$ are the concentrations of HCl, TLA and TLAHCl in the bulk, respectively. The concentration gradients are indicated in the figure. δ_{aq} and δ_o are the thickness of the aqueous and organic diffusion layers, respectively.
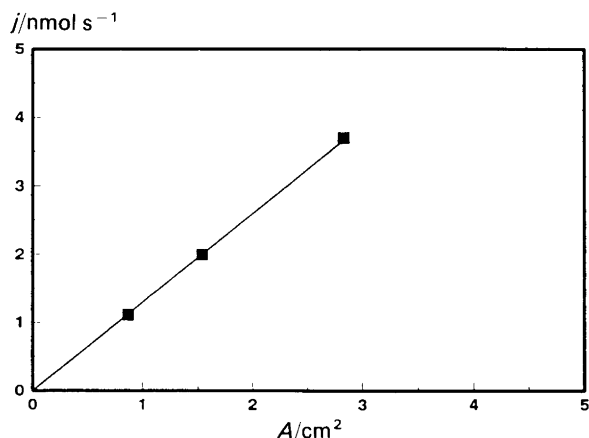
Fig. 3. The rate of the consumption of hydrogen chloride as a function of the membrane area at pH 3.500. $c_{NaCl}{}^{b} = 0.1$ M, $c_T{}^{b} = 0.1$ M and $\omega = 4.7$ Hz.

reduced because the diffusion of HCl is much slower than the tracer diffusion of H⁺. To determine the order of reaction with respect to Cl⁻, measurements using low concentrations of NaCl were carried out. However, when the concentration of NaCl was lower than 0.01 M the system was unstable during measurement: the flux of HCl corresponding to a specific rotation rate rose constantly in consecutive measurements, in which the same membrane and solutions were used, for as long as three days before a steady value was reached. The difference between the flux values was usually about 20% in two consecutive measurements. Several attempts were made to overcome this instability by varying the pH, the concentration of TLA, the method of equilibration, the hydrophobicity and material of the membrane and the levels of the phases in the cell. A stable system was finally achieved by keeping the Cl⁻ concentration at a minimum value of 0.01 M in the aqueous phase with NaCl. The chloride ions evidently stabilize the system, possibly by forming an adsorbed layer at the interface. From the results presented in Fig. 4
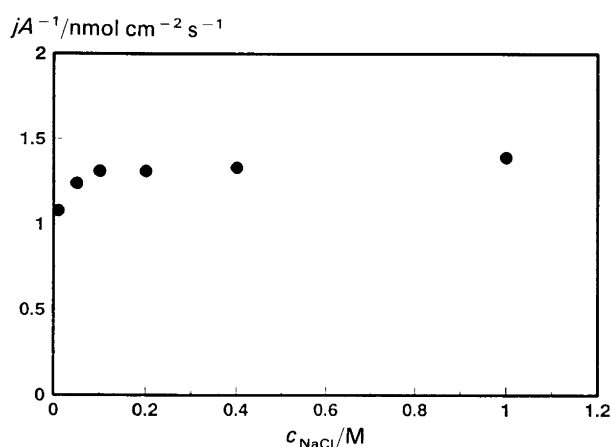
it can be seen that at values between 0.01 and 0.1 M the concentration of NaCl clearly has an effect on the flux of HCl. This indicates that the reaction is not of zeroth order with respect to Cl⁻. It can be concluded from the response of the flux of HCl to the rotation rate that the diffusion of NaCl does not affect the flux.

Next, the effect of hydrogen ion on the flux of HCl was studied by varying the concentration of HCl and using constant concentrations of 0.1 M NaCl in the aqueous phase and 0.1 M TLA in decanol. The results at a low concentration of HCl (pH ⩾ 4) are presented in Fig. 5, which shows the inverse of flux of HCl as a function of the inverse of the square root of the rotation rate.

The plots at pH > 4.135 have a common intercept. The fact that this intercept, which corresponds to the hypothetical condition of infinite rotation rate, is not zero indicates that the kinetics of reaction (1) is involved. The values of the intercepts in Fig. 5 obtained by linear regression vary between 0.35 and 0.41 cm² s nmol⁻¹. The variation in the values is most probably due to the uncertainty in the measurement of the area of the porous membrane. The value of the intercept corresponding to pH 5.00 is 0.6 cm² s nmol⁻¹, but in this case the standard error of the value is an order of magnitude larger (0.2 cm² s nmol⁻¹) than in the other cases.

The common intercept indicates that reaction (1) is of zeroth order with respect to H⁺. The maximum flux set by the kinetics is about 2.3 nmol cm⁻² s⁻¹ (from Fig. 5). It can be seen from Fig. 6, which shows the flux of HCl as a function of HCl concentration, that other rate-limiting steps reduce the flux before this limit is reached. It must be pointed out that Danesi *et al.*[4] have studied this reaction at the toluene–water interface and found that the reaction of H⁺ with TLA is a slow step and that the order with respect to chloride is zero.

The results in Fig. 5 can be explained by taking into account the diffusion of H⁺ in the aqueous diffusion layer and the kinetics of the interfacial reaction (1), which is of

Fig. 4. The effect of concentration of NaCl on the flux of HCl at pH 3.500. $c_{TLA}{}^{b} = 0.1$ M and $\omega = 3.5$ Hz.
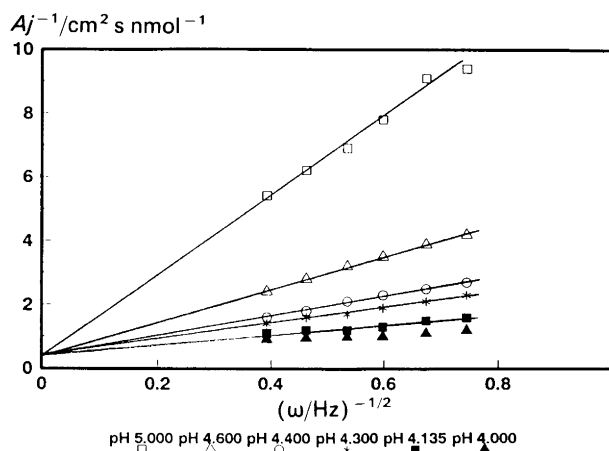

pH 5.000 pH 4.600 pH 4.400 pH 4.300 pH 4.135 pH 4.000

Fig. 5. The inverse of the flux of HCl as a function of the inverse of the square root of the rotation rate at various pH values. $c_{NaCl}{}^{b} = 0.1$ M, $c_{TLA}{}^{b} = 0.1$ M.

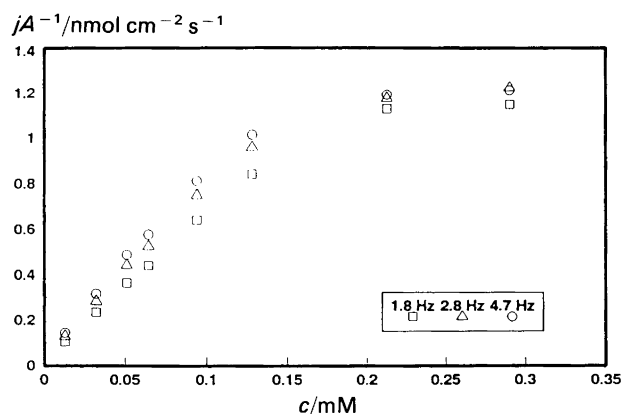$jA^{-1}/\text{nmol cm}^{-2}\,\text{s}^{-1}$

Fig. 6. The flux of HCl as a function of the bulk HCl concentration.

zeroth order with respect to H^+. Assuming that these processes control the overall transport of HCl under the above experimental conditions, a plot of the results of Fig. 5 as $c_H{}^b Aj^{-1}$ vs. $\omega^{-1/2}$ should yield straight lines with equal slopes. This is confirmed in Fig. 7, where the line passing through the origin has been calculated using the Levich equation (pure mass transport control), eqn. (2),

$$\left(\frac{c_H{}^b A}{j}\right) = 0.643 D_H{}^{-2/3} v^{1/6} \omega^{-1/2} \tag{2}$$

where c_H (mol cm^{-3}) is the concentration of HCl equal to that of H^+, D_H (cm^2 s^{-1}) is the tracer diffusion coefficient of H^+,[16] and v (cm^2 s^{-1}) is the kinematic viscosity of the aqueous solution. ω is the rotation rate (Hz) and j/A (mol cm^{-2} s^{-1}) is the flux of HCl. $c_H{}^b$ was determined from the measured pH using the Debye–Hückel theory. The mean slope of the five experimental lines (Fig. 7) is 157 cm Hz$^{1/2}$ s^{-1}, and the theoretical slope according to eqn. (2) is 155 cm Hz$^{1/2}$ s^{-1}.

Furthermore, simple calculations show that the surface concentration of TLA does not affect on the rate of the interfacial reaction at high pH, because the surface
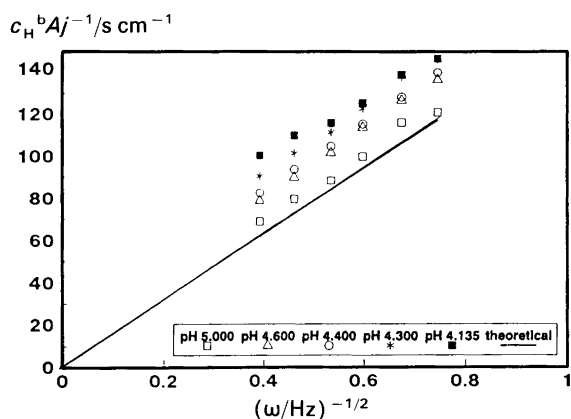
concentration of TLA at pH 5 is about two times higher than the concentration at pH 4.3, and yet the kinetic term remains constant. The rate-determining step in the reaction is therefore most likely the binding of chloride ion to TLAH$^+$ at the interface.

The results in Figs. 5 and 7 indicating limiting values for the flux of HCl are evidently due to the fact that the concentration of TLA drops to zero at the interface. This was checked by studying the influence of the concentration of TLA in the organic phase on reaction (1) at a fixed pH 3.50 and using a constant concentration of 0.1 M NaCl in the aqueous phase. The effect of the amine concentration is seen in Fig. 8, where the inverse flux of HCl is presented as a function of the inverse of the square root of the rotation rate. The results clearly show that the limiting flux, which is insensitive to changes in the concentrations at the aqueous side, can be increased by the addition of TLA to the organic phase (Fig. 8), indicating the domain of the transport of TLA in the decanol phase. Furthermore, measurements of interfacial tension in the presence of TLA were carried out to identify the possible adsorption of TLA on the interface. These measurements gave no evidence of surface adsorption of TLA, but the interfacial tension remains constant in spite of the addition of TLA into the oil phase. Thus it is obvious that the conclusion presented above is correct.

The zero surface concentration of amine corresponds to the overall flux [eqn. (3)]. In order to calculate the

$$\frac{j}{A} = \frac{D_T}{(\delta_o + l)} c_T{}^b \tag{3}$$

theoretical flux of TLA in the organic phase the diffusion coefficient of TLA (D_T) has to be estimated. Kontturi *et al.* have measured the diffusion coefficient of TLAHCl in dichloroethane.[17] Applying Walden's rule and assuming that the diffusion coefficients of TLA and TLAHCl are the same, the value of D_T was estimated to be 4×10^{-7} cm^2 s^{-1} in decanol. The effective thickness, l, of the porous membrane determined from measurements of
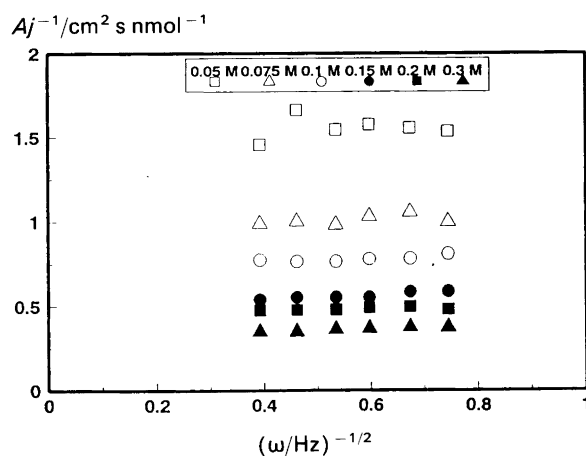
$c_H{}^b Aj^{-1}/\text{s cm}^{-1}$

Fig. 7. $c_H{}^b Aj^{-1}$ as a function of the inverse of the square root of the rotation rate. Full line calculated according to eqn. (2).

$Aj^{-1}/\text{cm}^2\,\text{s nmol}^{-1}$

Fig. 8. The effect of amine concentration on the inverse of the flux of HCl at pH 3.500. $c_{NaCl}{}^b = 0.1$ M.
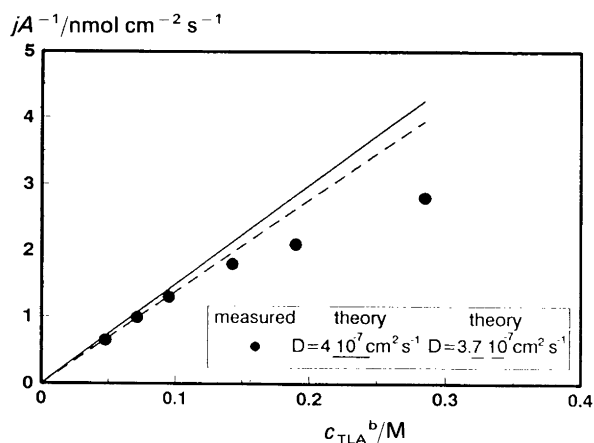
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$jA^{-1}/\text{nmol cm}^{-2}\,\text{s}^{-1}$

Fig. 9. The flux of HCl as a function of concentration of TLA. The straight lines are calculated using eqn. (3). pH 3.500. $c_{\text{NaCl}}{}^{b} = 0.1$ M, $\omega = 3.5$ Hz.

the tracer diffusion of H^+ in 1 M KCl was found to be 250 μm. The value for the tracer diffusion coefficient of H^+ was taken from Ref. 16.

When the concentration of TLA is 0.1 M this limiting flux has the value 1.4 nmol cm^{-2} s^{-1}, which is very close to the limiting fluxes observed in Figs. 4 and 6. The average value for the increase in the flux obtained by changing the rotation rate from 1.8 to 6.5 Hz is 3.7 % from the measurements in Fig. 8. A theoretical value of 4 % is obtained by using eqn. (3). When the value of j/A calculated from eqn. (3) is compared with the measured fluxes as a function of concentration of TLA (Fig. 9) only a small deviation is observed, which may be due to the uncertainty in the value of the diffusion coefficient of TLA. The deviation increases at concentrations above 0.1 M, which may be due to the aggregation of amine hydrochloride or a change in the viscosity of the organic phase.

The addition of an equivalent concentration of the reaction product (TLAHCl) to the organic phase when the concentration of TLA was 0.05 M lowered the flux by only 9 %. This means that the diffusion of TLAHCl from the interface can be neglected and that the rate-determining diffusion process is the diffusion of TLA to the interface.

Finally, the possibility of the transport of HCl into decanol owing to micelle formation was ruled out by making three sets of experiments in which three different kinds of aqueous phases were equilibrated with a 0.1 M solution of TLA in decanol. The three aqueous phases were 0.01 M HCl, 0.001 M HCl and 0.001 M HCl + 0.1 M NaCl. Equilibration studies with different volume ratios of aqueous and organic phases showed no evidence of micelle formation.
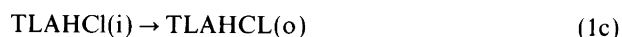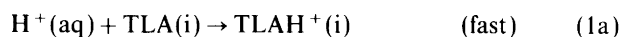
Conclusions

The rotating diffusion cell method works well; almost identical results are obtained in consecutive measure-

ments in cases where the transport in the aqueous phase determines the flux, while a much poorer reproducibility is observed in the measurements of diffusion in the oil phase. For example, extrapolation to infinite rotation rate is not physically meaningful in this case (cf. Fig. 8).

Referring to earlier work,[1] the assumption that reaction (1) is fast compared to the diffusion processes involved is correct at the conditions of the liquid membrane extraction of lignosulfonate. Also, the assumption that the diffusion of lignosulfonate–TLA complex in the liquid membrane is rate-determining seems reasonable in the light of the behaviour of TLA in the decanol phase, because the diffusion coefficient of this complex is bound to be smaller than that of TLA.

According to the measurements presented the mechanism of reaction (1) consists of a fast step in which H^+ reacts to form TLAH$^+$ at the interface (1a). This step is followed by the binding of the adsorbed Cl$^-$ (1b), after which the desorption of TLAHCl takes place (1c).

$$H^+(aq) + TLA(i) \rightarrow TLAH^+(i) \qquad \text{(fast)} \qquad \text{(1a)}$$

$$Cl^-(ads) + TLAH^+(i) \rightarrow TLAHCl(i) \qquad \text{(slow)} \qquad \text{(1b)}$$

$$TLAHCl(i) \rightarrow TLAHCL(o) \qquad \text{(1c)}$$

TLAH$^+$ cannot diffuse into decanol until its charge is suppressed by ion-pairing to Cl$^-$ because of the low relative permittivity of the decanol phase. The slow reaction of Cl$^-$ is in accordance with our assumption concerning the stripping reaction in the extraction of lignosulfonate in the counter-transport mode, where the chloride ion acts as a stripping agent (Ref. 1). However, the facts that TLAHCl has some effect on the flux and that the system is unstable at low concentrations of Cl$^-$ indicate that the detailed reaction mechanism may be complicated. A fast reaction step involving H^+ inevitably produces a charged interface, and the local potential of this interface has to be taken into consideration.

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