An Electrochemical Study of Long-Chain Aliphatic Amines

A. K. Kontturi,[a] K. Kontturi,[*,a] L. Murtomäki[a] and D. J. Schiffrin[b]

[a] Laboratory of Physical Chemistry and Electrochemistry, Helsinki University of Technology, Kemistintie 1 A, SF-02150 Espoo, Finland and [b] Chemistry Department, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, UK

Kontturi, A. K., Kontturi, K., Murtomäki, L. and Schiffrin, D. J., 1992. An Electrochemical Study of Long-Chain Aliphatic Amines. – Acta Chem. Scand. 46: 47–53.

Cyclic voltammetry has been applied in the study of the behaviour of long-chain aliphatic amines at the interface between two immiscible electrolyte solutions. The organic phase was 1,2-dichloroethane, which has a relatively low relative permittivity resembling those of solvents used in extraction processes. For the oil-soluble amine hydrochlorides the stability constants were evaluated after the estimation of the standard Gibbs energy of transfer of the hydrogen ion. Assisted ion transfer explained the behaviour of the oil-soluble amines at high pH values, but at low values results gave evidence for Cl^- ion transfer across the interface. For the water-soluble amine hydrochloride the results were in reasonable accordance with earlier observations.
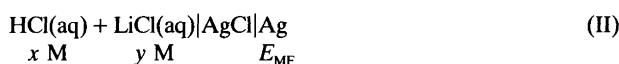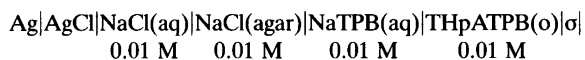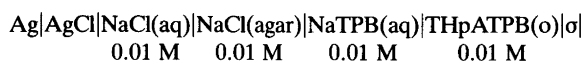
The behaviour of amines at liquid–liquid interfaces is of importance because of their many practical applications, for instance in industrial extractions processes[1] and in the pharmacological characterization (partition between water and 1-octanol) of amines as drugs.[2]

Electrochemistry at the interface between two immiscible electrolyte solutions (ITIES) provides a versatile way to study the interfacial behaviour of charged species.[3] In the case of amines, several studies have been carried out when the organic phase is nitrobenzene.[4-7] However, when considering extraction processes, nitrobenzene is not an interesting solvent because its relative permittivity is high compared with usual extraction solvents, and many important properties, such as ion pairing, acid–base equilibria etc. are different in nitrobenzene from solvents having low relative permittivity.

Electrochemistry at ITIES can be used to investigate interfacial transport mechanisms, to determine the stability constant of the amine and to calculate the partition coefficient after determination of the Gibbs energy of transfer for the amine.[8-10]

Experimental

The four-electrode potentiostat, signal generator and cell employed in the measurements have been described elsewhere.[11] The potentials refer to cells (I) and (II). Electric

Ag|AgCl|NaCl(aq)|NaCl(agar)|NaTPB(aq)|THpATPB(o)|σ|
　　　　 0.01 M 　 0.01 M 　　 0.01 M 　　 0.01 M

$$LiCl(aq) + buffer|AgCl|Ag \qquad (I)$$
0.01 M 　　　　　　 E_{MF}

---

* To whom correspondence should be addressed.

Ag|AgCl|NaCl(aq)|NaCl(agar)|NaTPB(aq)|THpATPB(o)|σ|
　　　　 0.01 M 　 0.01 M 　　 0.01 M 　　 0.01 M

$$HCl(aq) + LiCl(aq)|AgCl|Ag \qquad (II)$$
x M 　　 y M 　　 E_{MF}

current is defined to be positive when flowing from the aqueous to the organic phase. The Galvani potential differences $\Delta_o^w\varphi = \varphi(w) - \varphi(o)$ were calculated from the measured potentials as described before.[12]

THpA and TPB are tetraheptylammonium and tetraphenylborate, respectively, and σ refers to the interfacial region. Trilaurylamine hydrochloride (TLAHCl) and dilaurylamine hydrochloride (DLAHCl) where added to the organic phase in concentrations of 0.1 or 0.2 mM; owing to its very low solubility in 1,2-dichloroethane, laurylamine hydrochloride (LAHCl) was added to the aqueous phase. Since the adsorption of LAH^+ at the interface distorted voltammograms, this compound was used in a concentration of only 0.1 mM.

Cell (I) was used in the pH range 5–7 and cell (II) in the more acidic solutions. The buffer was a solution of $NaHPO_4$ and KH_2PO_4, and the total concentration of the salts was chosen to be 0.01 M, since there was no need for a greater buffer capacity and in order to avoid salting-out effects.[13] In cell (II) HCl was used to adjust the pH of the solution, and LiCl to adjust the total chloride concentration. When measuring the effect of pH, $x + y$ was 0.01 M, and when measuring the effect of the chloride concentration, x was kept constant.

NaCl, LiCl, Na_2HPO_4 and KH_2PO_4 (Merck p.a. grade) were used without further purification, and HCl was diluted from a Merck Titrisol solution; NaTPB (Aldrich Gold Label) was recrystallized according to Ref. 14. THpATPB was precipitated from aqueous solutions of THpABr (Fluka A.G. purum) and NaTPB and recrystallized from
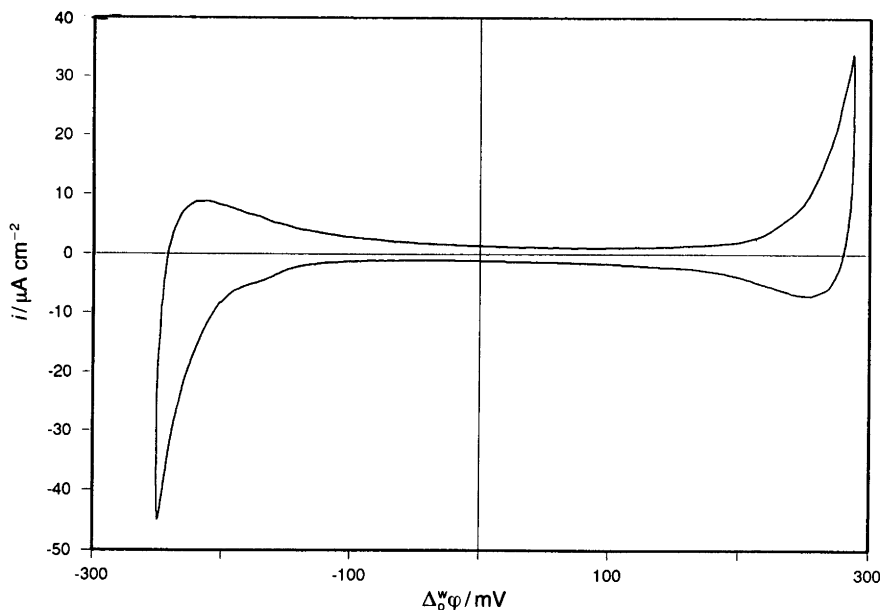
Fig. 1. A cyclic voltammogramm corresponding to cell (II) when $x = 0$ and $y = 0.01$ M (see text). The scan rate is 25 mV s^{-1}.

acetone (M & B *p.a.*). 1,2-Dichloroethane (DCE, Rathburn HPLC grade) was used as received, and water was distilled and ion-exchanged (Millipore milli-Q system).

TLAHCl and DLAHCl were prepared by dissolving TLA (Aldrich tech. grade) and DLA (K & K, 80%) in absolute ethanol, adding a concentrated aqueous HCl solution in excess, recrystallizing the filtered precipitates from acetone and drying them in a vacuum because of their thermal lability. LAHCl was prepicitated in an analogous manner (K & K, 80%) from aqueous solutions.

Results

Fig. 1 shows a voltammogram corresponding to cell (II) with $x = 0$ and $y = 0.01$: at the negative polarisation limit Cl$^-$ is transferred reversibly from the aqueous to the organic phase ($\Delta_o^w \varphi^\circ_{Cl^-} = -481$ mV,[9,15] while $\Delta_o^w \varphi^\circ_{THpA^+} = -604$ mV[16]). At the positive limit, the current is due to TPB$^-$ transfer from DCE to water ($\Delta_o^w \varphi^\circ_{TPB^-} = 364$ mV,[17] $\Delta_o^w \varphi^\circ_{Li^+} = 398$ mV[15] from water to nitrobenzene).

The width of the polarisation window determines the range of stability constant values K_s that can be studied, because a change of 1 pK_s unit results in a ca. 60 mV/n shift in the half-wave potential of the electrochemical process involved[3] (where n is the number of charges transferred). The use of THpATPB as a base electrolyte instead of the more widely used TBATPB (TBA = tetrabutylammonium) expands the potential window at the negative limit by ca. 200 mV.

In Fig. 2 a typical voltammogram of a system containing TLAHCl is presented. When the water phase is made more positive, a positive current flows, showing that in the absence of redox reactions either a cation is transferred from water to DCE or an anion is transferred in the opposite direction; the peak separation is ca. 60 mV, showing that the process is reversible and that $n = 1$. The peak current is

proportional to the square root of the scan rate, implying diffusion control; separate measurements also showed that the current is proportional to the amine concentration. From these observations it can be concluded that the process is controlled by the diffusion of the amine in the organic phase.

Because the facilitated transfer of protons by amines has been reported in the literature,[4,5] the pH dependence of the half-peak potential, $\Delta_o^w \varphi_{p/2}$, was measured. The results for
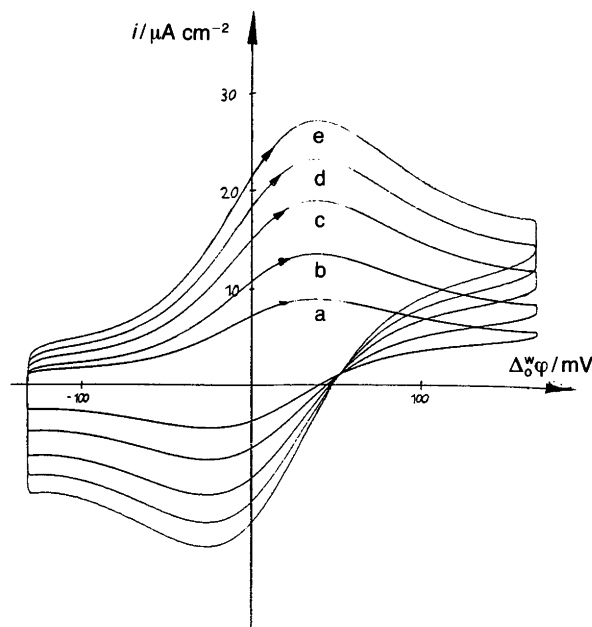

Fig. 2. Cyclic voltammetry showing reversible ion transfer across the DCE/water interface in the presence of TLAHCl. $C_{TLAHCl}(0) = 0.1$ mM. Potentials and conditions refer to cell (I). The pH is 6.77 and the scan rates are (a) 10, (b) 25, (c) 50, (d) 75 and (e) 100 mV s^{-1}.
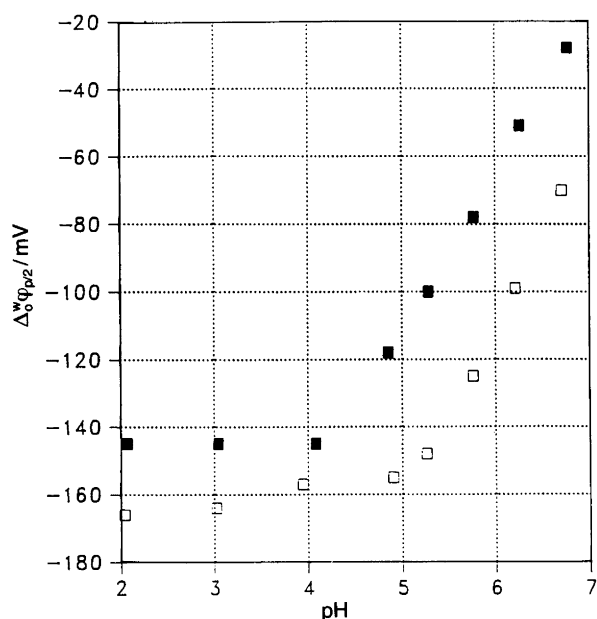
Fig. 3. Half-peak potentials due to ion transfer for TLA (■) and DLA (□) as a function of pH. $\Delta_0^w\varphi_{1/2} = \Delta_0^w\varphi_{p/2} + 28$ mV.
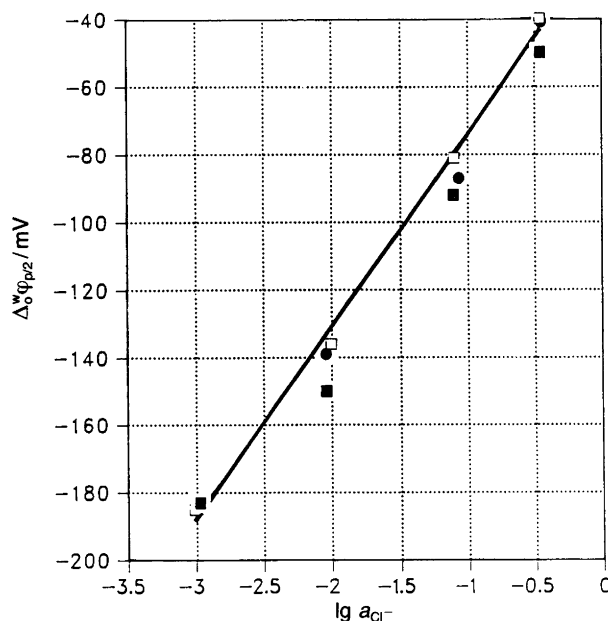

Fig. 4. Dependence of the half-peak potential on chloride activity for TLA: ●, pH 2; □, pH 3; ■, pH 4. The line is drawn for pH 3.

TLA and DLA are presented in Fig. 3. The half-wave potential for a reversible process can be calculated from[18] eqn. (1). It can be seen that for neutral and slightly acidic

$$\Delta_0^w\varphi_{1/2} = \Delta_0^w\varphi_{p/2} + 28 \text{ mV}/n \tag{1}$$

solutions the dependence is about 60 mV/pH unit, while in the pH range 2–4, the half-peak potentials remain constant. Peak currents remain constant in the whole pH range studied. An interesting result is that the transfer potentials for DLA are more negative than for TLA. If the currents were due to amine transfer, the opposite effect should be observed; TLA is a tertiary amine and its standard transfer potential should be more negative than that of DLA. The results imply facilitated proton transfer taking place above pH 5.

In order to evaluate the transfer mechanism in the acidic region, the effect of the aqueous chloride concentration on the half-peak potentials was studied for TLA: on the basis of the direction of the current, chloride transfer from DCE to water could be another possibility. The results for three different pH values are shown in Fig. 4, and a shift of 58 mV/lg a_{Cl^-} in half-peak potentials is observed between pH 2 and 4. Peak currents were independent of chloride concentration. These results indicate that a chloride transfer process that could not be observed in the absence of amine is taking place (see Discussion below).

The organic base electrolyte THpATPB is partially ion-paired with an association constant of approximately 1000.[16] The effect of THpATPB concentration on half-peak potentials was also measured for TLA. A shift of ca. 30 mV/lg $a_{THpATPB}$ was observed, corresponding to the formation of an ion pair TLAH⁺TPB⁻.[3] Since the concentra-

tion of the amine is nearly two orders of magnitude smaller than that of the base electrolyte, it is completely ion-paired and does not have any effect on the degree of THpA⁺TPB⁻ ion-pairing.

As mentioned above, LAHCl is sparingly soluble in the oil phase, and its partition equilibrium is in the aqueous phase; therefore it was added to the aqueous phase. Because of the surface-active nature of LAHCl, the organic phase was equilibrated with an aqueous LAHCl solution. Even so, adsorption phenomena slightly distorted the
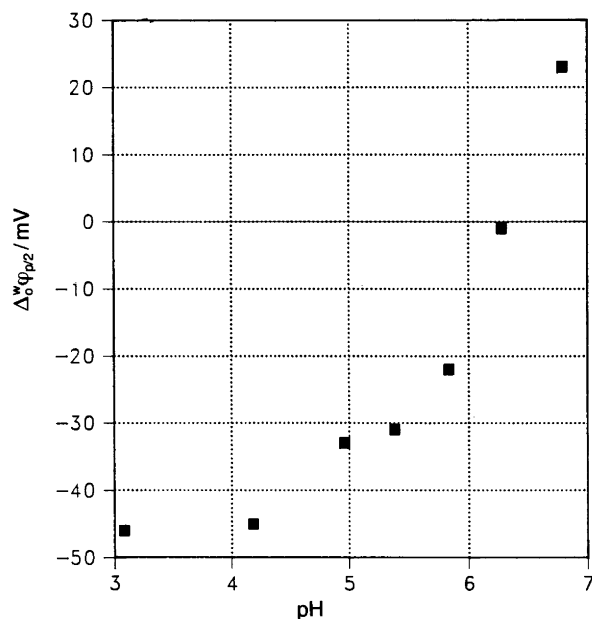

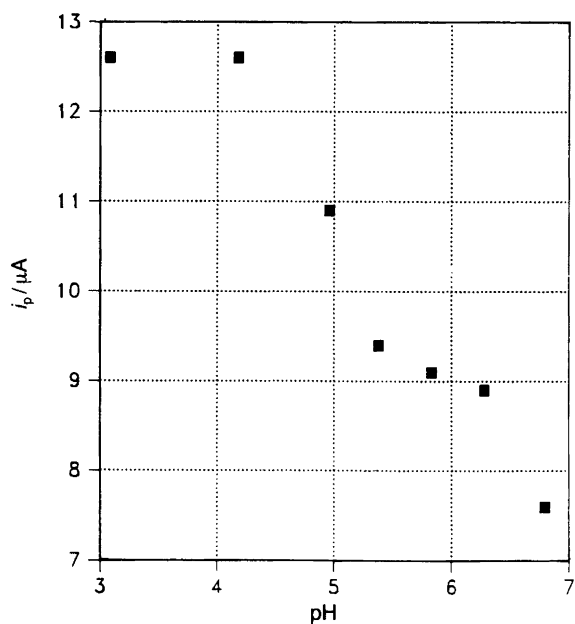Fig. 5. pH dependence of the half-peak potential for LA.

Fig. 6. Dependence of the peak currents due to LAH⁺ transfer on pH. The interfacial area was 0.14 cm² and the sweep rate was 100 mV s⁻¹.

Fig. 8. Dependence of the half-wave potential on base electrolyte concentration for LA.

voltammograms. The pH dependence of the half-peak potential is presented in Fig. 5, where a region of ca. 60 mV/pH unit dependence between pH 7 and 4.5 and a constant-value region at lower pH values can be seen, similar to the results for TLA and DLA.

The relatively low absolute values of the half-peak potentials indicate that the current is due to amine transfer and the pH dependence can be explained in terms of the dissociation equilibrium of LAH⁺ as discussed below. A
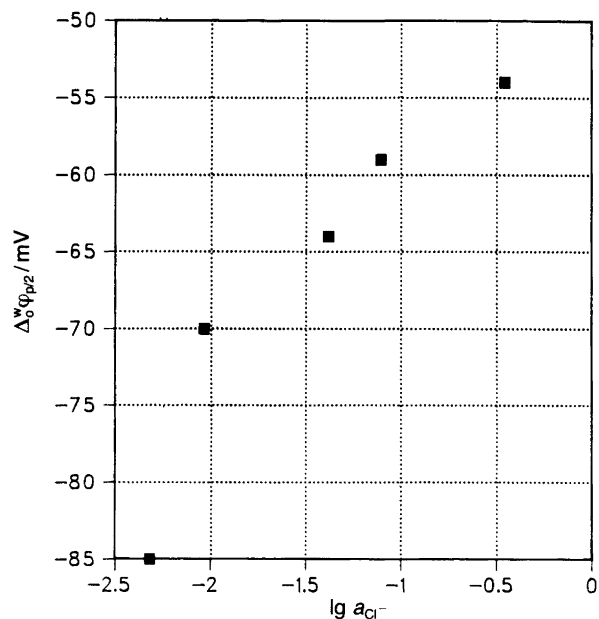

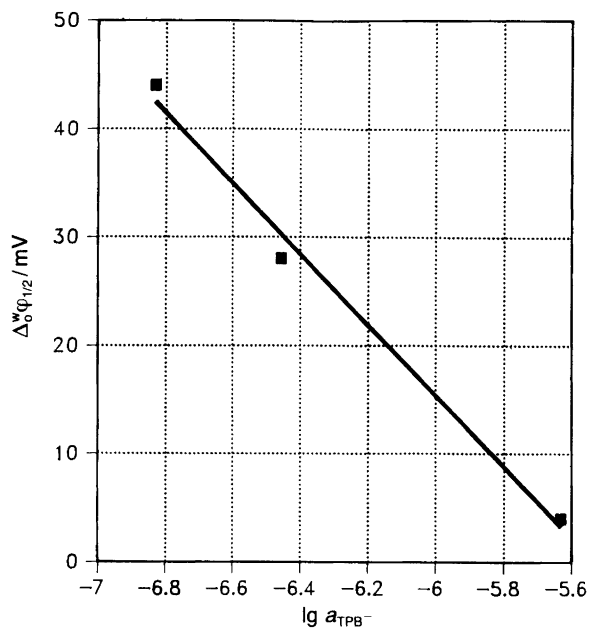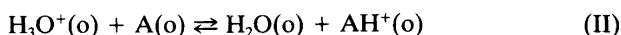*Fig. 7.* Dependence of the half-peak potential on chloride activity for LA.

confirmation of this scheme can be found in Fig. 6, where the peak currents increase in a same way as the half-peak potentials.
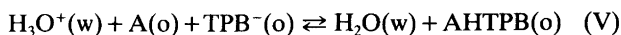
The dependence of the half-peak potential on chloride concentration was also measured, and the results are given in Fig. 7. No mechanistic explanation can be given for the dependence, but the slightly small shift in the potential can be understood by salting-out. Furthermore, the dependence of the half-peak potential on the base electrolyte concentration is shown in Fig. 8, and a slope of ca. -30 mV/lg a_{TPB^-} is obtained, indicating that ion pairing also has to be taken into account for LA.

Discussion

Trilaurylamine and dilaurylamine undergo assisted ion transfer according to[3] reactions (I)–(IV).

$$H_3O^+(w) \rightleftarrows H_3O^+(o) \tag{I}$$

$$H_3O^+(o) + A(o) \rightleftarrows H_2O(o) + AH^+(o) \tag{II}$$

$$AH^+(o) + TPB^-(o) \rightleftarrows AHTPB(o) \tag{III}$$

$$H_2O(o) \rightleftarrows H_2O(w) \tag{IV}$$

The total transfer reaction is given by reaction (V),

$$H_3O^+(w) + A(o) + TPB^-(o) \rightleftarrows H_2O(w) + AHTPB(o) \tag{V}$$

where A denotes the amine and w and o refer to the

aqueous and organic phases, respectively. For reaction (V) the half-wave potential $(\Delta_o^w \varphi_{1/2})$ is given by[3] eqn. (2),

$$\Delta_w^o \varphi_{1/2} = \Delta_w^o \varphi_{H^+}^o - \frac{RT}{2F} \ln \frac{D_{AHTPB}^{(o)}}{D_A^{(o)}} - \frac{2.303RT}{F} \lg K_s'$$

$$+ \frac{2.303RT}{F} pH - \frac{RT}{F} \ln a_{TPB^-}^{(o)} \qquad (2)$$

where $\Delta_o^w \varphi_{H^+}^o$ is the standard Galvani potential difference for the hydrogen ion, $D_A^{(o)}$ and $D_{AHTPB}^{(o)}$ are the diffusion coefficients of the amine and the ion-paired form of the protonated amine, $a_{TPB^-}^{(o)}$ is the activity of TPB^- in the organic phase and the equilibrium constant K_s' is defined by eqn. (3). K_s' is a product of the stability constant of the

$$K_s' = \frac{a_{AHTPB}^{(o)}}{a_A^{(o)} a_{H^+}^{(o)} a_{TPB^-}^{(o)}} \qquad (3)$$

amine, K_s, and the ion pairing constant, K_a, that can be written as eqns. (4) and (5), respectively.

$$K_s = \frac{a_{AH^+}^{(o)}}{a_A^{(o)} a_{H^+}^{(o)}} \qquad (4)$$

$$K_a = \frac{a_{AHTPB}^{(o)}}{a_{AH^+}^{(o)} a_{TPB^-}^{(o)}} \qquad (5)$$

Before K_s' can be evaluated $\Delta_o^w \varphi_{H^+}^o$ must be known. No data for this quantity in 1,2-dichloroethane are available. This value has been assumed to be the same as for Na^+,[19] but this seems very doubtful. Therefore it was estimated as follows.

The standard transfer potential is defined by eqn. (6),

$$\Delta_o^w \varphi_i^o = - \frac{\Delta_o^w G_i^o}{z_i F} \qquad (6)$$

where $\Delta_o^w G_i^o$ is the difference between the ionic Gibbs free energies of solvation from vacuum for water (i.e. hydration) and for DCE, respectively,[15] and is given by eqn. (7).

$$\Delta_o^w G_i^o = \Delta G_{hydr,i}^o - \Delta G_{solv,i}^o \qquad (7)$$

The standard Gibbs energy of hydration for H^+ is -1056 kJ mol^{-1}.[20] The solvation energy in 1,2-dichloroethane was estimated by considering the two different contributions to the solvation energy: a non-electrostatic and an electrostatic part. The scaled particle theory[21] has been sucessfully used in estimating the former, and the Beveridge–Schnuelle theory[22] the latter. The scaled particle theory includes the energies of forming a cavity into a solvent and the interaction of the solute with the solvent resulting from introducing the solute into the cavity. The Beveridge–Schnuelle theory utilizes a one-layer model where the first solvent layer is localized in the immediate vicinity of an ion

and has a relative permittivity value of 2 owing to dielectric saturation. Outside this layer, the bulk solvent relative permittivity is considered; the relative permittivity of the ion is 1 because no electric field can penetrate it.

In its most general form, the theory takes into account the dipole, quadrupole etc. interactions as well, but for an ion without a dipole moment, such as a hydrogen ion, we have eqn. (8), where a and b are the ion and

$$\Delta G_e^o = \frac{1}{2} \left[\left(\frac{1 - \varepsilon_a}{\varepsilon_a} \right) \frac{Z^2}{a} + \left(\frac{1 - \varepsilon_b}{\varepsilon_b} \right) \frac{Z^2}{b} \right] \qquad (8)$$

solvent radii, respectively, and Z is the charge of the ion. Furthermore ε_a', ε_a and ε_b are given by eqns. (9)–(11),

$$\varepsilon_a' = \varepsilon_a \left[1 + \frac{(1 - \varepsilon_a)(1 - \varepsilon_b)}{\varepsilon_b} \frac{a}{b} \right]^{-1} \qquad (9)$$

$$\varepsilon_a = \varepsilon_1 / \varepsilon_i \qquad (10)$$

$$\varepsilon_b = \varepsilon_0 / \varepsilon_1 \qquad (11)$$

where ε_i, ε_1 and ε_0 are the relative permittivities of the ion, the first solvent layer and the bulk solvent, respectively. Because of the way in which eqn. (8) is expressed, all the parameters must be given in c.g.s. units, in order to have the proper dimensions.

Both theories need the value of the naked ion radius and are extremely sensitive to it. The Gibbs energy of transfer of H^+ from water to nitrobenzene is known from partition data to be 32.5 kJ mol^{-1},[15] and therefore the thermochemical radius of H^+ can be estimated. This procedure gives a value of 0.383 Å, which in turn leads to a standard Gibbs energy of transfer from water to 1,2-dichloroethane of 41.8 kJ mol^{-1} corresponding to a standard transfer potential of $\Delta_o^w \varphi_{H^+}^o$ of 433 mV. This value can be considered as a reasonable estimate when comparing the standard transfer potentials of cations between nitrobenzene and 1,2-dichloroethane. In the scaled-particle theory, the only contribution to be considered is the energy of cavity formation, because the polarisability and dipole moment have zero values for a proton. All the other values needed in the calculations were taken from Ref. 22.

With these data it is possible to evaluate K_s' for a given pH, and $a_{TPB^-}^{(o)}$ is estimated as presented earlier.[12] The term containing the ratio of the diffusion coefficients is so small that it has been neglected in the calculations.

The measured equilibrium constants for trilaurylamine and dilaurylamine [eqn. (3)] were $\lg K_s'(TLA) = 16.8$ and $\lg K_s'(DLA) = 17.5$. The Gibbs energy for reaction (V) is given by eqn. (12), where the subscripts of refer to the

$$\Delta G_V = \Delta G_I + \Delta G_{II} + \Delta G_{III} + \Delta G_{IV} \qquad (12)$$
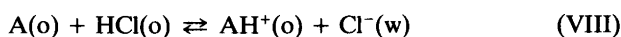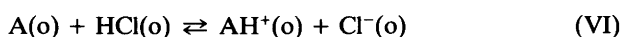
corresponding reactions. This relationship can be used to estimate ΔG_V, since ΔG_I is known from the calculated value of $\Delta_o^w \varphi_{H^+}^o$, $\Delta G_{II} + \Delta G_{III}$ is directly related to K_s', and

ΔG_{IV} can be calculated from the solubility of water in the organic solvent. This procedure gives very negative Gibbs energies ΔG_V for both amines, indicating the known fact that these are excellent acid extractants: $\Delta G_V(\text{TLA})$ = -54.0 kJ mol^{-1} and $\Delta G_V(\text{DLA})$ = -58.0 kJ mol^{-1}.

In order to evaluate the stability constants of the amines, the ion-pairing constants K_a have to be estimated. This can be done using Bjerrum's theory.[23] From the measured diffusion coefficients, using Stokes' law, the radii of the amines can be calculated, and their values are r_{TLA} = 5.6 Å and r_{DLA} = 4.7 Å. In previous work[13] a value of 4.9 Å for r_{TPB^-} was found. Taking the sum of the ionic radii as the parameter of closest approach, the theory gives the association constants lg $K_a(\text{TLAHTPB})$ = 3.01 and lg $K_a(\text{DLAHTPB})$ = 3.07. These seem to be reasonable when compared with the known values of several other electrolytes having TPB$^-$ as the anion.[24] Also, as expected, little difference between K_a for TLA and DLA is observed. The stability constants of the amines can now be calculated as lg $K_s(\text{TLA})$ = 13.8 and lg $K_s(\text{DLA})$ = 14.4. These results clearly show that both amines are very strong bases in DCE.

From the above derivation of the assisted (or facilitated) ion transfer, it is predicted that the pH dependence of the half-wave potential is linear over the whole pH range. As can be seen from Fig. 3, this is only the case above pH 5, while below pH 4, the half-wave potential is independent of pH. This behaviour is considered to be due to the fact that the acid (HCl) is significantly soluble in DCE. This solubility was also verified experimentally by equilibrating DCE with an aqueous acid solution and back-extracting acid from DCE to water.

In this pH range the mechanism proposed is given by reactions (VI) and (VII), resulting in the total reaction (VIII), i.e. Cl$^-$ transfer occurs. For reaction (VIII) the half-wave potential can be derived in the form of eqn. (13).

$$A(o) + HCl(o) \rightleftarrows AH^+(o) + Cl^-(o) \qquad \text{(VI)}$$

$$Cl^-(o) \rightleftarrows Cl^-(w) \qquad \text{(VII)}$$

$$A(o) + HCl(o) \rightleftarrows AH^+(o) + Cl^-(w) \qquad \text{(VIII)}$$

$$\Delta_o^w\varphi_{1/2} = \Delta_o^w\varphi_{H^+}^\circ - \frac{RT}{2F}\ln\frac{D_{AH^+}^{(o)}}{D_A^{(o)}} + \frac{RT}{F}\ln a_{HCl}^{(o)} + \frac{RT}{F}\ln a_{Cl^-}^{(w)} \qquad (13)$$

Eqn. (13) does not take into account ion pairing, the contribution of which must be included for quantitative analysis. However, eqn. (11) shows that the change in the activity of Cl$^-$(w) at constant pH should result in a change of the half-wave potential of ca. 60 mV/decade, which explains the results shown in Fig. 4. Furthermore, measurements without amine did not produce this behaviour, and therefore the results give strong evidence for the above mechanism. It is interesting to point out that the above discussion can serve as the basis of a new type of Cl$^-$ electrode.

Laurylamine hydrochloride is very soluble in water, and therefore its transfer mechanism at the ITIES can be described as a single ion transfer, with ion pairing in the organic phase. When pH > lg K_s, where K_s has been defined by eqn. (14), the half-wave potential can be written in the form of eqn. (15), where $\Delta_o^w\varphi_{AH^+}^\circ$ is the standard

$$K_s = \frac{a_{AH^+}^{(o)}}{a_A^{(o)}\,a_{H^+}^{(o)}} \qquad (14)$$

$$\Delta_w^o\varphi_{1/2} = \Delta_w^o\varphi_{AH^+}^\circ - \frac{RT}{2F}\ln\frac{D_{AHTPB}^{(o)}}{D_A^{(o)}} + \frac{2.303RT}{F}\text{pH}$$

$$- \frac{2.303RT}{F}(\lg K_s + \lg K_a) - \frac{RT}{F}\ln a_{TPB^-}^{(o)} \qquad (15)$$

transfer potential of the protonated amine and K_a is defined by eqn. (3). Eqn. (15) predicts that the slope for the linear relationship between $\Delta_o^w\varphi_{1/2}$ and pH is ca. 60 mV/decade. As can be seen from Fig. 5, this is the case for pH values above 5.5. However, when the pH is low, this linear relationship fails. This is due to the fact that at pH values below lg K_s, the concentration of the protonated amine remains constant, giving simply eqn. (16) for the

$$\Delta_o^w\varphi_{1/2} \approx \Delta_o^w\varphi_{AH^+}^\circ - \frac{2.303RT}{F}\lg K_a - \frac{RT}{F}\ln a_{TPB^-}^{(o)} \qquad (16)$$

half-wave potential, where the correction for the diffusion coefficients has been assumed to be negligible.

From eqns. (15) and (16) a value of lg K_s = 4.10 was found. This K_s value is the inverse of the base constant K_b for laurylamine. pK_b values 3.37 have been measured by potentiometric titration and conductivity in water–ethanol mixtures using extrapolation techniques to obtain the value in water.[25,26] The extrapolation with respect to the relative permittivity is not straightforward and may explain the deviations between these results and those predicted here.

As calculated above, there is only a small difference between the lg K_a values of TLA and DLA. Therefore, we can assume that the corresponding value for LA is probably of the same magnitude, ca. 3.2. $\Delta_o^w\varphi_{LAH^+}^\circ$ can be estimated using this value in eqn. (14). This approach gives $\Delta_o^w\varphi_{LAH^+}^\circ$ of 10 mV, corresponding to a standard Gibbs energy of transfer of ca. -1 kJ mol^{-1}. This very low negative value, combined with the known value for Cl$^-$ (46.4 kJ mol^{-1}) yields a partition coefficient between water and DCE of lg $P(\text{LAHCl,w/DCE})$ = 4.0. In our experience, the solubility of LAHCl in DCE is less than 0.1 mM and in water more than 0.1 M. However, because of its rather complicated phase equilibria in water[27] and its tendency towards micelle formation,[28] it is hard to determine accurately its solubility in water. It is considered that the partition coefficient calculated above can be accepted.

Cyclic voltammetry is a good method to measure diffu-

sion coefficients. As discussed elsewhere,[4,5] the diffusion coefficients for oil-soluble amines (TLA and DLA) can be obtained from the voltammograms, and the results are $D_{TLA}^{(o)} = 5 \times 10^{-6}$ cm^2 s^{-1} and $D_{DLA}^{(o)} = 6 \times 10^{-6}$ cm^2 s^{-1}. For the water-soluble amine (LA), the diffusion coefficient obtained is $D_{LA}^{(w)} = 2.6 \times 10^{-5}$ cm^2 s^{-1}.

It can be concluded that the extraction properties of amines are strongly pH-dependent. For HCl solutions, at pH < 4, Cl$^-$ transfer is observed, whereas for more alkaline solutions, proton transfer is observed.

References

1. Marcus, Y. and Kertes, A. S. *Ion Exchange and Solvent Extraction of Metal Complexes*, Wiley-Interscience, Bristol 1969.
2. Hansch, C. and Drayton, C. J. *Comprehensive Medicinal Chemistry*, Pergamon Press, Oxford 1990, Vol. 6.
3. Schiffrin, D. J. and Girault, H. H. J. In: Bard, A. J., Ed., *Electroanalytical Chemistry*, Marcel Dekker, New York 1989, Vol. 15, Chap. 1.
4. Makrlík, E., Ruth, W. and Vanýsek, P. *Electrochim. Acta 28* (1983) 575.
5. Makrlík, E., Ruth, W. and Vanýsek, P. *J. Colloid Interface Sci. 96* (1983) 548.
6. Homolka, D., Le Quoc Hung, Hofmanová, A., Khalil, M. W., Koryta, J., Mareček, V., Samec, Z., Sen, S. K., Vanýsek, P., Weber, J. and Březina, M. *Anal. Chem. 52* (1980) 1606.
7. Homolka, D., Mareček, V., Samec, Z., Baše, K. and Wendt, H. *J. Electroanal. Chem. 163* (1984) 159.
8. Koryta, J. *Electrochim. Acta 24* (1979) 293.
9. Koryta, J. *Electrochim. Acta 29* (1984) 445.
10. Koryta, J. *Electrochim. Acta 33* (1988) 189.
11. Geblewicz, G., Kontturi, A. K., Kontturi, K. and Schiffrin, D. J. *J. Electroanal. Chem. 217* (1987) 261.
12. Kontturi, A. K., Kontturi, K., Murtomäki, L. and Schiffrin, D. J. *J. Chem. Soc., Faraday Trans. 86* (1990) 819.
13. Kontturi, A. K., Kontturi, K., Murtomäki, L. and Schiffrin, D. J. *J. Chem. Soc., Faraday Trans. 86* (1990) 931.
14. Perrin, D. P., Armarego, W. L. F. and Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed., Pergamon Press, Oxford 1980.
15. Markin, V. S. and Volkov, A. G. *Electrochim. Acta 34* (1989) 93.
16. Kontturi, K. and Murtomäki, L. Unpublished results.
17. Czapkiewicz, J. and Czapkiewicz-Tutaj, B. *J. Electroanal. Chem. 83* (1977) 225.
18. Bard, A. J. and Faulkner, L. R. *Electrochemical Methods*, John Wiley, New York 1980.
19. Yoshida, Z. and Freiser, H. *J. Electroanal. Chem. 162* (1984) 307.
20. Marcus, Y. *Ion Solvation*, Wiley-Interscience, Chichester 1985.
21. Pierrotti, R. A. *Chem. Rev. 76* (1976) 717.
22. Abraham, M. H. and Liszi, J. *J. Chem. Soc., Faraday Trans. 1, 74* (1978) 1604.
23. Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, 2nd ed., Butterworths, London 1959.
24. Abraham, M. H. and Danil de Namor, A. F. *J. Chem. Soc., Faraday Trans. 1, 72* (1976) 955.
25. Hoerr, C. W., McCorkle, M. R. and Ralston, A. W. *J. Am. Chem. Soc. 65* (1943) 328.
26. Slabaugh, W. H. and Cates, V. E. *Anal. Chem. 27* (1955) 151.
27. Broome, F. K., Hoerr, C. W. and Harwood, H. J. *J. Am. Chem. Soc. 73* (1951) 3350.
28. Klevens, H. B. *J. Am. Oil Chem. Soc. 30* (1953) 74.