Determination of Absolute Individual Ion Mobilities with Regard to Electroosmosis

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In the first tests of a device for electromigration measurements in free electrolytes [1], it was observed that the mobilities of $^{99m}TcO_4^-$, $^{18}F^-$, $^{137}Cs^+$ and $^{57}Co^{2+}$ ions in inert aqueous electrolytes at 298K were influenced by the apparition of electroosmosis in the migration tube. Electroosmosis can be explained by the presence of an electric double layer at the charged surface of the glass (ionisation of surface silanol groups). These negative surface charges are neutralised by the cations in the diffuse layer. Under the influence of an electric field, the hydrated cations in the double layer migrate to the cathode moving the bulk solution by viscous drag. As a result of this, the cations migrate faster and the anions slower than expected. The electroosmotic mobility depends on the nature (viscosity, dielectric constant) of the electrolyte and on the potential at the glass/solution interface.

In order to obtain absolute migration data, u_{abs}, the experimental ion mobility, u_{exp}, for a given ionic strength, μ, of the electrolyte was corrected for the electrosomosis as follows:

$$u_{abs} = u_{exp} \pm u^{\infty}_{osm} + \left(1 - \frac{u^{\infty}_{osm}}{u^{\infty}_{exp}}\right) k_{exp} \sqrt{\mu} \qquad (1)$$

(- for cations, + for anions)

where u^{∞}_{exp} and k_{exp} are the experimental value of the ion mobility at infinite dilution of the electrolyte and the slope coefficient obtained from the linear fit $u_{exp} = f(\sqrt{\mu})$ (Tab.1), respectively. $u^{\infty}_{osm} = \left| u^{\infty}_{exp} - u^{\infty}_{Lit} \right|$ represents the electroosmotic mobility at infinite dilution of the electrolyte, u^{∞}_{Lit} being the literature value of the ion mobility in pure water (Tab.1). The third term on the right side of expression (1) is a correction factor which takes into account the change of the mobility function d(ω) [2] caused by the electroosmosis and the variation of the electroosmotic mobility with the ionic strength. The fact that the values of u^{∞}_{osm} agree well with each other within the limit of experimental uncertainties indicates the constancy of the data collected in the migration experiments. Hence the mean value u^{∞}_{osm} = 1.71(6) 10^{-4} $cm^2 s^{-1} V^{-1}$, was used for the correction of the electroosmosis effect. As an example, the variation of u_{exp} and u_{abs} with the square root of the overall ionic strength for $^{18}F^-$ and $^{57}Co^{2+}$ ions is shown in Fig.1. For all the ions studied, the absolute migration data were found to encompass well the values given by the extended limit law [3] which is derived from the Onsager theory [2] and takes into account finite ion-size effects in connection with dielectric saturation and hydration of the ions. The linear extrapolation of the absolute migration data to μ=0 leads to values of the absolute ion mobility at infinite dilution, u^{∞}_{abs}, which agree well with the literature data (Tab.1). From these results eq. (1) can be assumed to give a fairly good correction for electrosmosis, but it may be subject to some criticism because of its semi empirical form. In a future article we show the possibility to suppress the electroosmosis by chemical surface modification of the migration tube with tetramethylchlorosilan in order to directly measure absolute ion mobilities [4]. The migration data obtained in this way were found in reasonable agreement with the values calculated with eq. (1).

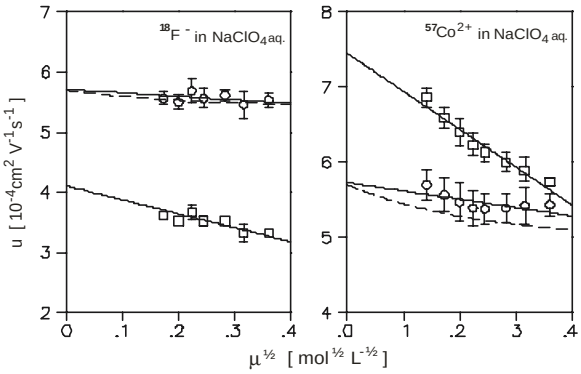

Fig. 1. Ion mobility of $^{18}F^-$ and $^{57}Co^{2+}$ versus $\sqrt{\mu}$ at 298K. Experimental migration data (squares); data corrected for electroosmosis (circles); extended limit law (dashed line).

Table 1. Experimental and literature data used in eq. (1) for the calculation of absolute ion mobilities. u^{∞}_{abs} is the absolute infinite ion mobility obtained after correction for electroosmosis. u_{exp}, u_{osm}, u_{abs} in 10^{-4} $cm^2 s^{-1} V^{-1}$.

Ion	u^{∞}_{exp}	k_{exp}	u^{∞}_{Lit} [ref]	u^{∞}_{osm}	u^{∞}_{abs}
TcO_4^-	3.99(8)	5.20(46)	5.75 [5]	1.76(8)	5.69(8)
F^-	4.11(25)	2.32(57)	5.74 [6]	1.63(15)	5.71(14)
Cs^+	9.71(4)	2.57(20)	8.00 [6]	1.71(4)	8.00(5)
Co^{2+}	7.45(11)	5.05(47)	5.70 [6]	1.75(11)	5.73(11)

References

[1] Mauerhofer E., Kling O., Rösch F., submitted to Radiochim. Acta.
[2] Onsager L., N. Y. Acad. Sci. **46**, 241 (1945).
[3] Stockes R. H., Woolf E. A., Mills R., J. Phys. Chem. **61** 1634 (1957).
[4] Mauerhofer E., Kling O., Rösch F., in preparation.
[5] Schwochau K., Astheimer L., Z. Naturforschg. **17a**, 820 (1962).
[6] Handbook of Chemistry and Physics, 78th Ed., CRC Press LCC, Boca Raton New York, (1997-1998).