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Letter to the Editor

Isotachophoresis of metal-neutral ligand complexes

II. Corrected R and K values for 18-crown-6

Sir,

Two errors appear in my paper on the theory and application of 18-crown-6 electrolytes for the isotachophoretic separation of alkali metals¹. In the Onsager equation for single ion conductances (eqn. 6), the correct value for the coefficient of the electrophoretic term, B , is $30.32 \text{ S cm}^2/\text{equiv. (l/mole)}^{1/2}$. Also, the correct value for the single ion conductance of the reference ion, tetramethylammonium (TMA), is $45.0 \text{ S cm}^2/\text{equiv.}^2$. Revised calculations for the theoretical relative step heights of the $\text{K}^+/\text{18-crown-6}$ system give slightly higher conductances in the leader and sample zone resulting in somewhat lower R values. Using the proper R_s value for TMA, 8.01, also lowers the experimental R values. The corrected results are given in Table I.

TABLE I (corrected)

CALCULATED AND OBSERVED RELATIVE STEP HEIGHTS AND CALCULATED CONCENTRATIONS AND CONDUCTANCES FOR $\text{K}^+/\text{18-CROWN-6}$ COMPLEX

Leading electrolyte = HCl ; $c_L = 10 \text{ mM}$; $K = 107 \text{ l/mole}$; $\lambda_L^\circ = 349.8$, $\lambda_y^\circ = 76.35$, $\lambda_M^\circ = 73.5$, $\lambda_{\text{MC}}^\circ = 25.3 \text{ S cm}^2/\text{equiv.}$ $\lambda_L = 338.7$; $\lambda_y^L = 71.6$; $k_L = 4103 \text{ } \mu\text{S/cm}$.

$\bar{c}_C \text{ (mM)}$	$\bar{c}_M \text{ (mM)}$	$\bar{\lambda}_M \text{ (S cm}^2/\text{equiv.)}$	$k_M \text{ (}\mu\text{S/cm)}$	R	
				Calc.	Obs.
0	5.94	69.9	846	4.85	4.66
1	5.80	66.9	810	5.06	5.01
3	5.55	61.6	746	5.50	5.45
10	4.84	48.6	589	6.96	7.08
30	3.93	35.2	427	9.61	9.76
100	3.29	27.4	332	12.4	> 12.5

The average relative difference between observed and calculated step heights is 1.3%, and this accuracy remains sufficient for the prediction of neutral ligand effects on isotachophoresis separations.

Calculations using the correct R_s and B values have been performed to obtain formation constants, K , giving the best fit to the experimental R values for K^+ , NH_4^+ and Na^+ . Corrected K values are 114 ± 9 for K^+ , 11.4 ± 0.2 for NH_4^+ and

3.6 ± 0.3 for Na^+ . Only small increases in K values are seen and they remain in agreement with literature constants.

Finally, an apology is extended to M. Tazaki, M. Takagi and K. Ueno who first presented isotachophoretic separations of alkali metals using 18-crown-6 electrolytes³. Reference to their work was omitted in the original paper.

*Corporate Research Laboratories,
Monsanto Company,
800 N. Lindbergh Blvd.,
St. Louis, MO 63167 (U.S.A.)*

FREDERICK S. STOVER

1 F. S. Stover, *J. Chromatogr.*, 298 (1984) 203.

2 H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolyte Solutions*, Reinhold, New York, 3rd ed., 1976, p. 231.

3 M. Tazaki, M. Takagi and K. Ueno, *Chem. Lett.*, (1982) 639.

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