The Hofmeister order and the concept of bias in anion separations

Bruce A. Moyer,1 Peter V. Bonnesen,1 Jeffrey C. Bryan,1 Tamara J. Haverlock,1 Konstantinos Kavallieratos,2 Tatiana G. Levitskaia,1 Richard A. Sachleben,1 and Thomas Vercouter1

1Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37830-6119
2Dept. of Chemistry, Florida International University, University Park Campus CP 304, 11200 Southwest 8th St., Miami, FL 33199-0001


The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. DE-AC05-00OR22725. Accordingly, the U.S. Government retains a non-exclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for the U.S. Government purposes.

This research was sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract number DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.
The Hofmeister order and the concept of bias in anion separations

Bruce A. Moyer,¹ Peter V. Bonnesen,¹ Jeffrey C. Bryan,¹ Tamara J. Haverlock,¹ Konstantinos Kavallieratos,² Tatiana G. Levitskaia,¹ Richard A. Sachleben,¹ and Thomas Vercouter¹

¹Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37830-6119
²Dept. of Chemistry, Florida International University, University Park Campus CP 304, 11200 Southwest 8th St., Miami, FL 33199-0001

Why do so many anion separation systems follow the Hofmeister order? In considering this question, we have introduced the concept of bias, referring to selectivity behavior that exhibits a monotonic trend vs. recognition. For anions, the term bias characterizes the typically observed monotonic increase in extractability with decreasing ionic charge density. Electrostatic principles predict and experiments confirm that such a relationship can be steep and strongly influenced by ion-pairing and specific interactions via hydrogen bonding. However, such effects rarely override the dominant solvation-based ion-partitioning Gibbs energy term, and the Hofmeister ordering thus persists in many types of separations, including anion exchange, ion-pair extraction, and membrane systems. Bias thus represents either a powerful tool by itself or the background against which specific receptors for anion recognition must operate. Several examples will be discussed from the authors’ research on crown ethers and calix-crowns for ion-pair extraction. In this connection, it is widely understood that non-ionizable cation hosts such as crown ethers extract alkali metal salts most efficiently when the co-extracted anion is large and hydrophobic. It would be useful if this restriction could be lifted so as to permit efficient separations from common acid or salt matrices.

This research was sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract number DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.