

**ACES: CALCULATION OF ACTIVITY COEFFICIENTS
IN MULTICOMPONENT ELECTROLYTE SOLUTIONS
USING THE ZDANOVSKII METHOD**

Slavinskiy K.A., Stepanov S.I.

D.I. Mendeleev University of Chemical Technology of Russia
125047, Moscow, Miusskaya sq., 9

Thermodynamic modeling of liquid–liquid extraction equilibria for lanthanide separation requires activity coefficients and water activity for the aqueous phase, which typically contains several electrolytes (lanthanide nitrates, mineral acids) at once. The Zdanovskii–Stokes–Robinson (ZSR) isopiestic mixing rule [1, 2] provides a way to calculate these quantities from published data on constituent binary solutions; however, no freely available calculator with a database of lanthanide electrolyte parameters has been reported so far.

We present ACES (Activity Calculation for Electrolyte Solutions), an open-access web calculator implementing the complete ZSR calculation scheme for electrolyte mixtures at 25 °C. When molar concentrations are supplied, the algorithm first determines the mixture density via the Zdanovskii criterion and converts to molalities. Water activity a_w is found iteratively from $\Sigma(m_i/m_i^*) = 1$, where m_i^* is the isopiestic molality of the i -th binary solution at the same a_w . Each isopiestic molality is obtained by inverting the relation between water activity and osmotic coefficient, the latter expressed as a four-term polynomial in molality with the third approximation of the Debye–Hückel equation. Binary activity coefficients γ_i^* are calculated from analogous polynomials and converted to mixture values via ZSR proportionality; mean ionic activities are then obtained accounting for the common-ion composition.

The database currently covers 33 electrolytes including the full lanthanide nitrate series from $\text{La}(\text{NO}_3)_3$ to $\text{Lu}(\text{NO}_3)_3$, HNO_3 , H_2SO_4 , NaOH , NaCl , NH_4NO_3 , and others relevant to hydrometallurgical practice. Polynomial coefficients for the osmotic coefficient, activity coefficient, and density were fitted to published isopiestic data [3, 4]. The database can be extended: a built-in fitting module accepts experimental data for new binary systems.

Verification against the original VBA implementation (Mendeleev University, 1997) for the system $\text{Tb}(\text{NO}_3)_3\text{--HNO}_3\text{--NH}_4\text{NO}_3$ showed agreement within 0.015% across 23 compositions; for binary lanthanide nitrate solutions, calculated activity coefficients reproduced the experimental values from [3] within 1–2%. ACES supports manual input and batch calculation via Excel upload/download. The calculator is available at <http://aces-thermo.duckdns.org>

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3. Rard J.A., Shiers L.E., Heiser D.J., Spedding F.H. // J. Chem. Eng. Data. 1977. Vol. 22. P. 337–347.
4. Mikulin G.I. Physical Chemistry of Electrolyte Solutions. Leningrad, Khimiya, 1968 (in Russian).