

Electronic Supplementary Information, Part B, to:

ACTIVITY COEFFICIENTS IN MIXED ELECTROLYTE SOLUTIONS

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The IPBE algorithm – How to use the enclosed computation program.

The original program was written in FORTRAN IV ca. 20 years ago, thus it is quite rigid and not friendly. However, it works reasonably well, and despite the intrinsic limits of the model and statistical treatment that it is based on, it is still one of the most effective treatments capable of predicting the thermodynamic behavior of the different kinds of electrolytes (including high-charge electrolytes and some kinds of mixtures of electrolytes, see later) using –as its only parameter– the average distance of closest approach (a) of the ions to one another. Results for 2:2, as well as for 2:3, 3:2 and 3:3 salts since also the latter have finally become available, proved to be surprisingly faithful.^{Sb1, Sb2, Sb3} A previous version of the algorithm was used to study the kinetic salt effect in the reactions of ions of even sign,^{Sb4} and demonstrated once and for all the electrostatic nature of the Olson-Simonson salt effects. The relevant algorithm has always been made freely available to users on request. It is now provided once and for all as a part of the present supplementary information. We provide here some general remarks and the instructions for use. More details can be found in the original paper that described the algorithm.^{Sb5}

IPBE develops the same physical model as the Debye-Hückel theory (restricted primitive model),^{Sb6} following the same imperfect (and not completely consistent) thermodynamic approach known as the Poisson-Boltzmann equation (PBE). However, while the Debye-Hückel theory finds the solution of the approximate form of PBE which only retains the linear term of the series expansion of the Boltzmann exponential term, IPBE solves the complete equation by numerical methods (a mathematically improved version of Guggenheim's approach to numerical integration of PBE).^{Sb7} The differences between the Debye-Hückel theory and IPBE become very evident when dealing with high charge system (with which the linear approximation no longer holds and can even fail to predict the correct sign of the second derivative of $\ln \gamma_{\pm}$ at the limit of infinite dilution).

The input of data occurs via the keyboard in the form of a dialogue with a self-explaining menu selection. The possible options are: (1) theoretical activity coefficients for single ions and the corresponding mean activity coefficient (as natural logarithms); (2) osmotic coefficients ϕ (as $1 - \phi$); (3) partial and apparent molar volume (for the part that exceeds the infinite dilution limiting value) in $\text{cm}^3 \text{mol}^{-1}$; (4) partial and apparent relative molar enthalpies (kJ mol^{-1}). Depending on the selected option, the program asks for:

- (i) the dielectric constant of the solvent, D (plus the derivative $D^{-1}\partial D/\partial p$ and the compressibility coefficient of the solvent $-V^{-1}\partial V/\partial p$, in bar^{-1} units, or $D^{-1}\partial D/\partial T$ and the thermal expansion coefficient of the solvent $-V^{-1}\partial V/\partial T$, in K^{-1} units, if the volume or enthalpy options are selected). The values that the program suggests for water at $T = 298.15 \text{ K}$ are from B. B. Owen, R. C. Miller, C. E. Milner, H. L. Cogan, *J. Phys. Chem.*, 1961, **65**, 2065 (D , $D^{-1}\partial D/\partial p$, $D^{-1}\partial D/\partial T$); G. S. Kell, E. Whalley, *Phil. Trans. A*, 1956, **258**, 565 ($-V^{-1}\partial V/\partial p$); F. T. Gucker, *J. Amer. Chem. Soc.*, 1934, **56**, 1017 ($-V^{-1}\partial V/\partial T$).
- (ii) the distance of closest approach selected, a (in ångström units)
- (iii) the type of solute, i.e., the number of kinds of distinguishable cations and of anions (in two different steps, separated by more detailed questions concerning the multiplicity and charge of the ions, see item iv). In the hypothetical case of an electrolyte $\text{Na}_2\text{KLaCa}_0[\text{Co}(\text{CN})_6]_2(\text{SO}_4)_0$, the numbers to be answered are 3 for the cations and 2 for the anions, since the electrolyte contains three distinguishable kinds of cations ($\text{M}^+ = \text{Na}^+$ and K^+ together, undistinguishable;^{Sb8} Ca^{2+} , a fictitious component whose concentration has been set at zero; and La^{3+}) and two distinguishable anions, SO_4^{2-} (a fictitious component set at null concentration), and $[\text{Co}(\text{CN})_6]^{3-}$. Null species introduced in the formula of the electrolyte, like fictitious Ca_0 and $(\text{SO}_4)_0$ in the example, are a trick that forces the program to extend the calculation to the corresponding ions too, although the corresponding concentrations have been set at zero. (The situation recalls a trace ion in a supporting electrolyte.)

^{Sb1} F. Malatesta, S. Trombella, A. Giacomelli, M. Onor, *Polyhedron*, 2000, **19**, 2493.

^{Sb2} F. Malatesta, F. Bruni and N. Fanelli, *Phys. Chem. Chem. Phys.*, 2002, **4**, 121

^{Sb3} F. Malatesta and R. Zamboni, *J. Solution Chem.*, 1997, **26**, 791; F. Malatesta, L. Carbonaro, N. Fanelli, S. Ferrini, A. Giacomelli, *J. Solution Chem.*, 1999, **28**, 593.

^{Sb4} R. Zamboni, A. Giacomelli, F. Malatesta, A. Indelli, *J. Phys. Chem.*, 1976, **80**, 1418.

^{Sb5} F. Malatesta, T. Rotunno, *Gazz. Chim. Ital.*, 1983, **113**, 783.

^{Sb6} The ion-ion interactions – which are controlled by the ion-ion distances – make the natural variable of IPBE (like DHT and other ion interaction theories) the molar and not molal concentration. Substitution of molal concentrations for molar concentrations results in slight differences in the results, which, however, are nullified by the presence of the empiric parameter a . The same applies to the kind of activity coefficient that IPBE calculates, a rational scale (rather than molal scale) activity coefficient and – to all appearances – referring to MacMillan-Mayer's, rather than Gibbs' reference system; the empiric parameter, and model roughness, make such distinctions unimportant.

^{Sb7} E. A. Guggenheim, *Trans. Faraday Soc.*, 1960, **56**, 1152; *ibid.*, 1962, **58**, 86.

^{Sb8} As IPBE (like DHT) does not consistently admit different values of a for the different ions of a solution, all ions having the same charge are automatically treated as indistinguishable.

- (iv) For as many kinds of ions as declared in the previous step, the program asks for the stoichiometric coefficient (i.e., how many ions of that kind have to appear in the real or fictitious formula of the electrolyte), and the charge. In the example of $\text{Na}_2\text{KLaCa}_0[\text{Co}(\text{CN})_6]_2(\text{SO}_4)_0$, the answers are, for the first cation (Na^+ and K^+ together): 3, 1 ; second cation (La^{3+}): 1, 3; third cation (Ca^{2+}): 0, 2. The same questions, when asked for anions, are to be answered: 2, -3 (or 2, 3) for $[\text{Co}(\text{CN})_6]^{3-}$; 0, -2 (or 0, 2) for SO_4^{2-} . As a matter of fact, the program is capable of recognizing indistinguishable ions that have wrongly been declared as distinguishable, and automatically makes corrections. The formulae that do not correspond to electrically neutral systems are rejected, and requested again. Provided the electrical neutrality be preserved, the formulae that contain non integer instead of integer numbers of ions $n_1, n_2 \dots, n_i \dots$ are freely allowed, and can be used to simulate a mixture of different ionic species, whose different n_i are proportional to the respective ionic fractions $x_i = n_i / \sum_j n_j$. E.g., a mixed solution of 0.1 m Na_2SO_4 and 0.001 m $\text{La}_2(\text{SO}_4)_3$ can be treated as a 0.1 m solution of the fictitious salt $\text{Na}_{2.00}\text{La}_{0.02}(\text{SO}_4)_{1.03}$. When starting calculations, the program keeps the different n_i constant and varies the overall concentration, as if a mixture with a corresponding ionic composition were progressively diluted by adding a solvent. In such a case, the mean activity coefficients that the program still calculates lack significance, and the mean activity coefficients of the component electrolytes – Na_2SO_4 and $\text{La}_2(\text{SO}_4)_3$ in the example – are to be obtained by combining by hand the output values listed for single ions.
- (v) A selection is possible among a series of possible options of input units – molar concentrations or ionic strength or the corresponding square roots. (A further selection, not necessarily the same, is subsequently requested, between items vi and vii, for the output units.) Further, the program asks for the highest concentration (or ionic strength, square root of concentration..., as appropriate) at which calculations are to be performed (for activity coefficients, the program also asks for the lowest concentration limit; by entering the digit 0 one selects the default option).
- (vi) The computation chain automatically creates a natural set of concentrations to be treated. However, the user is allowed to introduce additional concentrations at which he wishes the calculations to be performed. The program asks for the number of these additional, user-defined concentrations, and their values, if any (enter the digit 0 for none; otherwise, enter the relevant number and their values, in decreasing order).
- (vii) The program then starts calculating, and results are written into a file (ipbout) which can be opened using e.g. Microsoft Word or any other file editors.