

Aspen Technology Inc.

Benefits of the new Electrolyte Models in *Aspen Plus*[®] V7.2

Best in Class Electrolyte Thermodynamics

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Aspen Plus(R)V7.2 includes significant improvements in electrolyte thermodynamics enabling greater accuracy for a wider range of electrolyte solutions, including mixed-solvent solutions.

Synopsis

AspenTech rose to prominence in the chemical simulation market because our products are able to solve our customer's most challenging problems. AspenTech has always been a leader in physical properties, especially in the area of electrolyte thermodynamics.

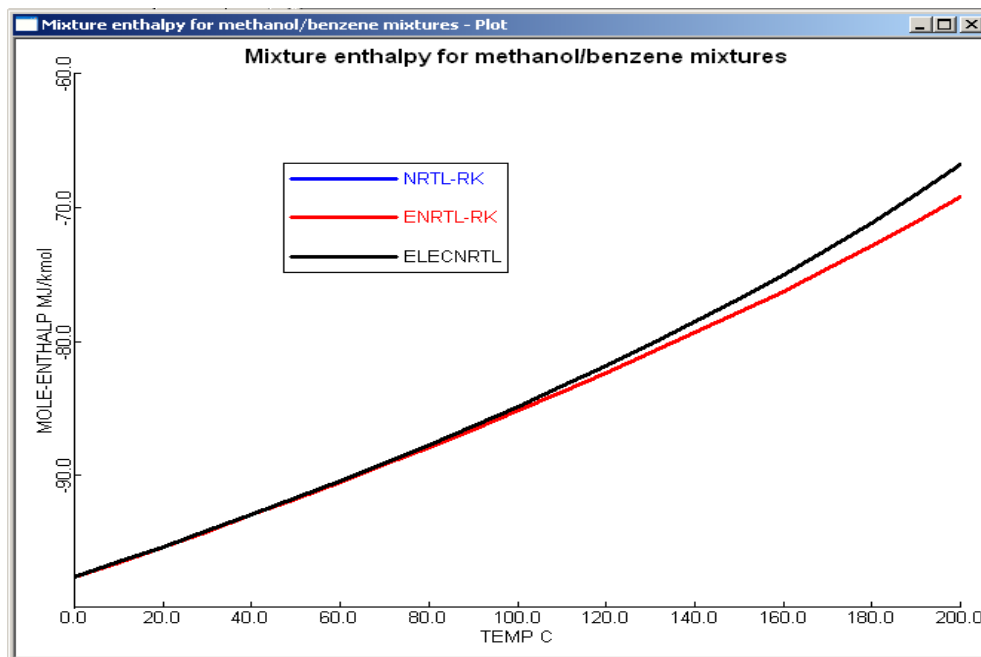
The electrolyte NRTL model, also known as the Chen electrolyte model, was originally formulated with unsymmetric reference state, i.e., aqueous phase infinite dilution, for modeling aqueous electrolytes. Using the same unsymmetric reference state, the model was later extended for modeling mixed solvent electrolytes. Although the electrolyte NRTL model has served well for over twenty years, the unsymmetric model formulation has caused difficulties in modeling liquid-liquid equilibrium of mixed solvent electrolytes and phase behavior of non-aqueous electrolytes. In addition, there are a number of shortcomings in the implementation of the electrolyte NRTL model as ELECNRTL option. We have been able to overcome these shortcomings with the new electrolyte NRTL model and associated options available in V7.2.

The new electrolyte NRTL model provides a comprehensive electrolyte thermodynamic framework to model thermophysical properties of all kinds of electrolyte systems. Retaining the key concepts of the original electrolyte NRTL model, the new model is a reformulation of the electrolyte NRTL model with a different mixing rule for multiple electrolytes. The reference state for ionic species can be either unsymmetric, i.e., aqueous phase infinite dilution or symmetric, i.e., pure fused salt state. The reformulation makes the model much more robust and convenient to use in modeling liquid-liquid equilibrium of mixed solvent electrolyte systems and phase behavior of non-aqueous electrolytes.^[1]

Two option sets are available in V7.2 with the new electrolyte NRTL model: ENRTL-RK and ENRTL-SR. ENRTL-RK is developed based on the new electrolyte NRTL model with the unsymmetric reference state while ENRTL-SR is developed based on the new electrolyte NRTL model with the symmetric reference state.

Shortcomings of the original electrolyte NRTL model implementation

The original electrolyte NRTL model has been available in Aspen Plus as the ELECNRTL option. Implemented as a special option for aqueous electrolytes, ELECNRTL is not fully consistent with the standard NRTL option for non-electrolytes. For example, the predicted enthalpies of mixtures of organic solvents are different between ELECNRTL and NRTL options. The same issues exist for the entropy and Gibbs free energy calculations. This in turn leads to slight differences in phase equilibrium calculations with Gibbs flash or non-TP flash.



The liquid phase enthalpies predicted with ELECNRTL are slightly different from the enthalpies predicted with NRTL-RK. The new electrolyte ENRTL-RK option is fully consistent with the NRTL-RK option for non-electrolyte systems and they yield the same results with non-electrolyte systems.

Aspen Plus® V7.2 includes an improved option for aqueous electrolytes

Incorporating the new electrolyte NRTL model, the new ENRTL-RK option provides an improved implementation for aqueous electrolytes. Unlike the older ELECNRTL option, the new ENRTL-RK option collapses to NRTL-RK when the fluid becomes free of ionic species.

The ENRTL-RK option is based on the traditional unsymmetric reference state, e.g., aqueous phase infinite dilution. This model should only be used to simulate aqueous electrolyte systems and mixed solvent electrolyte systems with the presence of water.

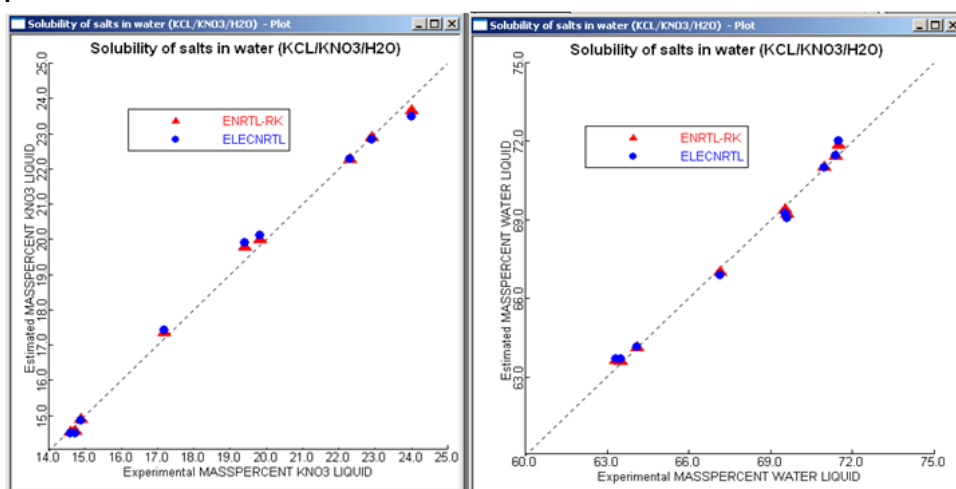
The original ELECNRTL property method is retained for upward compatibility purposes.

The binary molecule-molecule parameters and the pair molecule-electrolyte parameters previously used with the ELECNRTL option can be re-used with the new ENRTL-RK option. The pair electrolyte-electrolyte parameters may be different between ENRTL-RK option and ELECNRTL option because they use slightly different mixing rules for multiple electrolytes. Note that, usually, the electrolyte-electrolyte pair parameters are set to zero for both options.

ENRTL-RK is an improvement over the original ELECNRTL option.

ENRTL-RK is consistent with NRTL-RK for non-electrolyte systems.

ELECNRTL is retained for upward compatibility.



Both *ELECNRTL* and the new *ENRTL-RK* options can accurately predict salt solubility in aqueous solution; the *ENRTL-RK* option does a slightly better job for the cases shown and has the additional advantage of being consistent with the *NRTL-RK* option for non-electrolyte systems.

The new *ENRTL-SR* option offers major new capabilities

A significant improvement in V7.2 is the introduction of a new electrolyte option, *ENRTL-SR*, based on the symmetric reference state (pure liquids and pure fused salts) and the new electrolyte *NRTL* model. As such, the option is applicable to all types of electrolyte solutions including aqueous electrolytes, non-aqueous electrolytes, and mixed-solvent electrolytes.

The symmetric reference state option *ENRTL-SR* uses the same binary molecule-molecule parameters and pair molecule-electrolyte parameters as the *ENRTL-RK* option. However, Chemistry reaction parameters, on the other hand, depend on the reference state. Chemistry parameters fit using the *ELECNRTL* option or the *ENRTL-RK* option should not be re-used with the *ENRTL-SR* option.

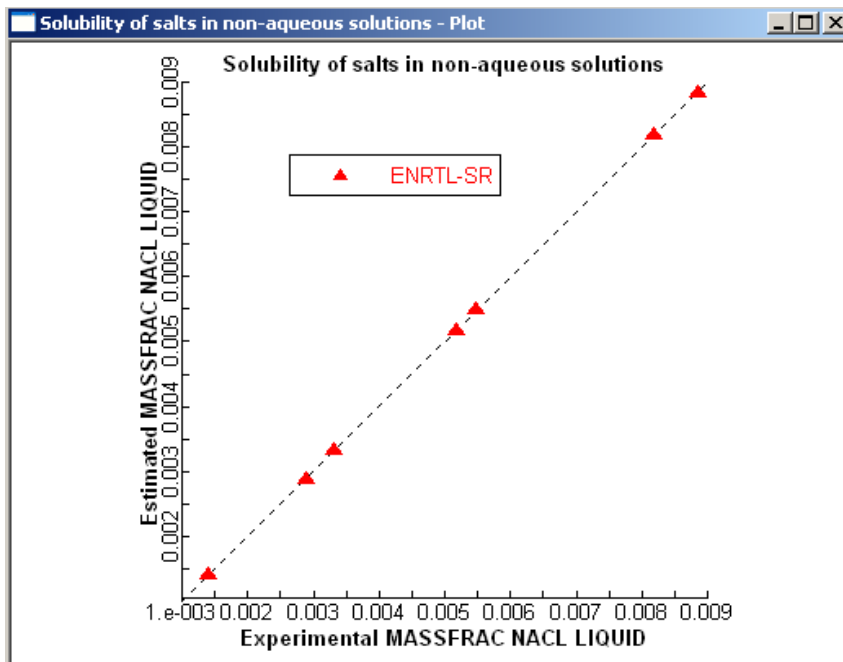
In the V7.2 implementation, the reference state must be declared globally for the simulation as a whole to ensure a single, consistent thermodynamic framework is used within the simulation flowsheet¹. In other words, the *ENRTL-RK* option and the *ENRTL-SR* option cannot both be used within the same process flowsheet model.

Aspen Plus[®] V7.2 includes a full set of chemistry parameters for both reference states. The chemistry wizard will select the

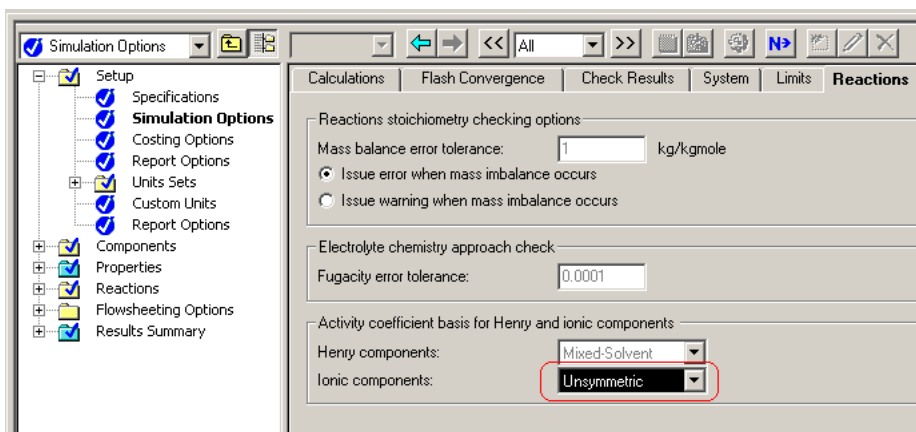
ENRTL-SR applies to *all types of electrolyte solutions*, including non-aqueous electrolyte solutions.

¹ The reference state is related to entropy and Gibbs energy and related variables such as excess properties and activity coefficients – this should not be confused with the enthalpy reference state.

appropriate set of parameters depending on the reference state declared on the simulation options form.



The symmetric reference state ENRTL-SR option can accurately characterize the solubility of salts in non-aqueous electrolytes. Based on aqueous phase infinite dilution reference state, ELECNRTL and ENRTL-RK options cannot be used to characterize this system, the data cannot be fit and the data regression process will fail.



The activity coefficient reference state declared on the Simulation Options | Reactions tab sheet must be consistent with the selected activity coefficient model. Aspen Plus® will report errors if you try to use an activity coefficient model that is inconsistent with the declared basis.

The NRTL-SAC model has been extended to electrolytes

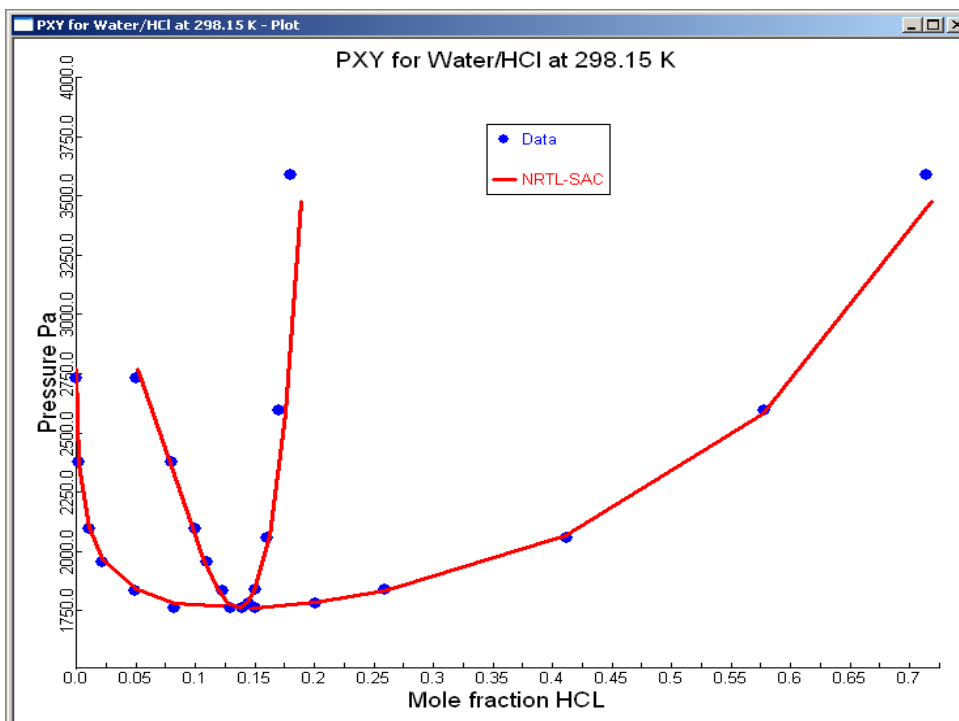
AspenTech's NRTL-SAC method is based on a semi-predictive activity coefficient model that characterizes the properties of molecules in terms of a small number of representative 'segments'. The segments represent hydrophilicity, solvation strength, polarity, and hydrophobicity of the target molecules. The segment parameters are determined by fitting the solubility of the target compound against a handful of well-characterized reference solvents.

In V7.2, the NRTL-SAC model has been extended to include anionic and cationic segments. This extends the range of applicability of the NRTL-SAC model to electrolytic systems including salts in aqueous and non-aqueous solutions.

The new NRTL-SAC model can be used with either the symmetric or the traditional aqueous phase infinite dilution reference states (the reference state is set using an option code in the model; the aqueous phase infinite dilution reference state is used by default).

NRTL-SAC is a semi-predictive model used for solvent screening applications.

V7.2 extends this model to electrolytic solutes.



The semi-predictive NRTL-SAC model has been extended for electrolytes; the new model can be used to predict the solubility of organic and inorganic salts in aqueous, non-aqueous, or mixed solvents.

Summary

Aspen Plus[®] V7.2 includes two new electrolyte options which provide significant upgrades over the ELECNRTL option. These two new options are implementations of the new symmetric electrolyte NRTL model^[1]. The ENRTL-RK option is consistent with the NRTL-RK option for non electrolytes. It is based on the aqueous phase infinite dilution reference state and is applicable to aqueous electrolytes and mixed-solvent electrolytes with the presence of water. The new *ENRTL-SR* option is based on the symmetric reference state (pure fused salts and pure liquids). It is applicable to all kinds of electrolyte systems including aqueous electrolytes, mixed-solvent electrolytes and non-aqueous electrolytes.

The semi-predictive *NRTL-SAC* model has been extended to cover electrolytic solutes and solutions. The new version of the NRTL-SAC model defaults to the aqueous phase infinite dilution reference state, but may be optionally set to the symmetric reference state.

Taken together, these three electrolyte options represent a significant advance in Aspen's capability to model electrolyte solutions. No other commercial simulation tool can address as wide a range of electrolyte problems as Aspen Plus.

Like our competitor's simulators, including UNISIM and PRO/II, Aspen Plus includes optional links to the aqueous and mixed-solvent electrolyte (MSE) models sold by OLI Systems Inc. We believe our new electrolyte NRTL model provides a fundamentally simpler, better and more rigorous thermodynamic framework than the MSE model. However, we concede that OLI may have more sets of fitted interaction parameters in their database.

We believe the new electrolyte NRTL model holds great promise for the future. We have already made significant progress using this new model, including the new scaling models delivered with *Aspen Plus*[®] V7.2.

[1] Song, Y., Chen, C.-C., "Symmetric Electrolyte Nonrandom Two-Liquid Activity Coefficient Model," *Ind. Eng. Chem. Res.*, **2009**, 48, 7788-7797.