

LEVENBERG-MARQUARDT METHOD APPLIED TO THE DETERMINATION OF VAPOR-LIQUID EQUILIBRIUM MODEL PARAMETERS

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Abstract— In order to correlate and optimize experimental data either from the laboratory or industry, one needs a robust method of data regression. Among the non-linear parameter estimation methods it may be pointed out of Levenberg, which applies the conversion of an arbitrary matrix into a positive definite one. Later, Marquardt applied the same procedure, calculating λ parameter in an iterative form. The Levenberg-Marquardt algorithm is described and two routine for correlating vapor-liquid equilibrium data for pure component and mixtures, based on this efficient method, have been applied. The routines have been written with an interface very accessible for both users and programmers, using Python language. The flexibility of the developed programs for introducing the desired details is quite interesting for both process simulators and modeling properties. Furthermore, for mixtures with electrolytes, it was obtained a coherent and compatible relation for the structural parameters of the salt species, with the aid of the method and the graphical interface designed.

Keywords— Nonlinear Regression, Levenberg-Marquardt Method, Vapor-Liquid Equilibria, Mixed Solvents Electrolyte Systems.

I. INTRODUCTION

The phenomena and properties involved in the chemical processes present, usually, non-linear behavior. Therefore, it is needed a robust method of non-linear regression for providing the required correlation of the experimental data collected, either from the laboratory or from the industry.

Bard (1974) pointed out three methods of parameter estimation, i.e., least squares, maximum likelihood and Bayesian. The method of least squares is the oldest and most widely used estimation procedure. It can be applied directly to a deterministic model, without any knowledge being taken of the probability distribution of the observations. This feature satisfies quite well the propose of correlating most of the desired thermodynamic properties and process variables.

For solving these unconstrained problems, the Levenberg-Marquardt method has proven very reliable results. In this work the Levenberg-Marquardt algorithm is described in a simple form.

This parameter estimation method has been reproduced and applied for the correlation of vapor-liquid equilibrium (VLE) data using activity coefficient and equation of state approaches (Lazzús, 2010; Camacho-

Camacho *et al.*, 2007). For the first case, an evaluation of the thermodynamic consistency of the data can be provided, since activity coefficient models fulfill the exact definition of partial molar excess Gibbs energy.

Systematic evaluation of thermodynamic properties of solutions of sodium chloride (NaCl) in water, e.g., boiling point and osmotic coefficient, with an extensive experimental database, was provided by Clarke and Glew (1985). VLE calculation for mixed solvents electrolyte systems have been applied using functional group activity coefficient model, i.e., UNIFAC (Kikic *et al.*, 1991). It was taken into account the electrostatic term with Debye-Huckel term, normalized according to the theory of Mc-Millan-Mayer. However, the estimated parameters present scattering and large order of magnitude. Loehe and Donohue (1997) described a survey of the literature models to determine thermodynamic properties of aqueous systems with strong electrolytes. Thomsen *et al.* (2004) have presented a systematic modeling work with mixed electrolytes and mixed solvents systems for solid-liquid-vapor equilibrium data, using UNIQUAC also. Haghtalab and Peyvandi (2009) have proposed a new version of UNIQUAC model for electrolyte solutions that requires just two fitted interaction parameters per binary aqueous system. The structural parameters of the ionic species were evaluated considering solvation for the determination of the radii.

This study aimed to describe the Levenberg-Marquardt computational procedure for estimation of vapor-liquid equilibrium model parameters. Validations of the method are present for pure component vapor pressure and binary VLE data. Application to strong electrolytes in mixed solvents systems has also been performed, using UNIQUAC model. It is proposed a new form to determine structural UNIQUAC parameters of the ions that is compatible with the solvent species parameters.

II. METHODS

A. Levenberg-Marquardt Method

The method presented by Levenberg (1944) utilizes a conversion of an arbitrary matrix into a positive definite one. This method rests on the observation that if \underline{P} is any positive definite matrix, then $\underline{A}_i + \lambda \underline{P}$ is positive definite for λ sufficiently large, no matter what \underline{A}_i . Marquardt (1963) suggested an iterative algorithm for the selection of λ .

The importance of working with a definite positive matrix is to satisfy the necessary and sufficient conditions of minimization in the data regression, where the least square of the residuals (e_i) is to be found.