World Academy of Science, Engineering and Technology
International Journal of Mathematical and Computational Sciences
Vol:14, No:12, 2020

# Thermodynamics of Aqueous Solutions of Organic Molecule and Electrolyte: Use Cloud Point to Obtain Better Estimates of Thermodynamic Parameters

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**Abstract :** Electrolytes are often used to bring about salting-in and salting-out of organic molecules and polymers (e.g. polyethylene glycols/proteins) from the aqueous solutions. For quantification of these phenomena, a thermodynamic model which can accurately predict activity coefficient of electrolyte as a function of temperature is needed. The thermodynamics models available in the literature contain a large number of empirical parameters. These parameters are estimated using lower/upper critical solution temperature of the solution in the electrolyte/organic molecule at different temperatures. Since the number of parameters is large, inaccuracy can bethe creep in during their estimation, which can affect the reliability of prediction beyond the range in which these parameters are estimated. Cloud point of solution is related to its free energy through temperature and composition derivative. Hence, the Cloud point measurement can be used for accurate estimation of the temperature and composition dependence of parameters in the model for free energy. Hence, if we use a two pronged procedure in which we first use cloud point of solution to estimate some of the parameters of the thermodynamic model and determine the rest using osmotic coefficient data, we gain on two counts. First, since the parameters, estimated in each of the two steps, are fewer, we achieve higher accuracy of estimation. The second and more important gain is that the resulting model parameters are more sensitive to temperature. This is crucial when we wish to use the model outside temperatures window within which the parameter estimation is sought. The focus of the present work is to prove this proposition. We have used electrolyte (NaCl/Na2CO3)-water-organic molecule (Iso-propanol/ethanol) as the model system. The model of Robinson-Stokes-Glukauf is modified by incorporating the temperature dependent Flory-Huggins interaction parameters. The Helmholtz free energy expression contains, in addition to electrostatic and translational entropic contributions, three Flory-Huggins pairwise interaction contributions viz., and (w-water, p-polymer, s-salt). These parameters depend both on temperature and concentrations. The concentration dependence is expressed in the form of a quadratic expression involving the volume fractions of the interacting species. The temperature dependence is expressed in the form .To obtain the temperature-dependent interaction parameters for organic molecule-water and electrolyte-water systems, Critical solution temperature of electrolyte -water-organic molecules is measured using cloud point measuring apparatus The temperature and composition dependent interaction parameters for electrolyte-water-organic molecule are estimated through measurement of cloud point of solution. The model is used to estimate critical solution temperature (CST) of electrolyte water-organic molecules solution. We have experimentally determined the critical solution temperature of different compositions of electrolyte-water-organic molecule solution and compared the results with the estimates based on our model. The two sets of values show good agreement. On the other hand when only osmotic coefficients are used for estimation of the free energy model, CST predicted using the resulting model show poor agreement with the experiments. Thus, the importance of the CST data in the estimation of parameters of the thermodynamic model is confirmed through this work.

**Keywords :** concentrated electrolytes, Debye-Hückel theory, interaction parameters, Robinson-Stokes-Glueckauf model, Flory-Huggins model, critical solution temperature
**Conference Title :** ICSRD 2020 : International Conference on Scientific Research and Development
**Conference Location :** Chicago, United States
**Conference Dates :** December 12-13, 2020