

# A thermodynamic approach to study hydrogen-bonding interactions in solvent/solvent/polymer ternary systems

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## Abstract

A thermodynamic approach based on both the classical Flory–Huggins (FH) formalism and the association equilibria (AE) theory has been developed to study the solubility properties of a system formed by a proton-donor solvent (A), a proton-acceptor solvent (B) and a proton-acceptor polymer (C). The miscibility of this ternary system is attained by competitive specific interactions via hydrogen-bonding established between the hydroxyl and carbonyl interacting groups of either solvent–solvent (AB) or solvent–polymer (AC) system components. The binary AB and AC specific interactions and their dependence with the system composition as well as with the extent of the association equilibrium have been quantified by means of two new parameters,  $\Delta g_{AB}$  and  $\Delta g_{AC}$ . These excess functions have appeared to be equivalent to the combinatorial or entropic term of the Gibbs free energy of the complex formation process, which accounts for the entropy of mixing plus the intermolecular specific interactions. The theoretical predictions have reasonably agreed with experimental data on preferential solvation of two systems taken from literature: methanol(A)/1,4-dioxane(B)/poly(alkyl methacrylate)(C) and *n*-alcohol(A)/heptan-3-one(B)/poly(vinyl pyrrolidone)(C).

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## 1. Introduction

The preferential or selective sorption of a polymer by a solvent is a very common phenomenon in ternary polymeric systems (TPS) formed by a polymer solved in a mixture of two single liquids. A great variety of TPSs have been studied from this

viewpoint, mainly those containing, at least, one polar component such as an alcohol. In some systems, the intermolecular specific interactions established between the polar interacting groups are so important that hydrogen-bonding formation has to be taken into account in order to interpret their thermodynamic properties. Moreover, for TPSs with specific interactions, random mixtures cannot be supposed to occur, and, therefore, the classical thermodynamic theories such as the Flory–Huggins (FH) formalism [1], the FH generalized by Pouchly

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(FHP), the Flory–Prigogine–Patterson (FPP) or equation of state theories [2–7] cannot be appropriate to thermodynamically study the system. For these TPSs, several authors have developed a more adequate theory based on multiple association equilibria [8–15].

For the association equilibria (AE) theory, the existence of association complexes is assumed, and the thermodynamic functions of mixture, such as the Gibbs free energy, are deduced from the association equilibrium constants. This formalism is really useful and appropriate to study the thermodynamic equilibrium reached between complexes formed from single molecules via hydrogen-bonding (or any other strong specific interactions) and the non-associated species [13]. In this sense, Pouchly et al. [8] pioneered the application of the AE theory to the prediction of sorption equilibrium in benzene/methanol/poly(methyl methacrylate) system for which hydrogen bonding interactions between the alcohol and polymer take place. Additional complications arise in other TPS for which, besides solvent–polymer, also solvent–solvent interactions occur, as in the system formed by 1,4-dioxane/methanol/poly(alkyl methacrylate) [9]. For this system, the authors derived a theoretical relationship between the solvation parameter,  $\lambda$ , and the association constants corresponding to all the simultaneous equilibria taking part in the mixing process.

Therefore, up to now, the AE theory has been successfully applied to two main types of TPSs: (i) those in which one of the liquids of the solvent mixture is an active solvent, that is a self-associating specie with proton donor character that also interacts specifically with the polymer (a proton-acceptor) [8]; (ii) a more usual picture consists on one solvent being self-associating and H-donor (as before) but the other liquid and the polymer being both proton-acceptor species [9,13]. Thermodynamically speaking, the specific interactions are of entropic–enthalpic mixed nature and are included in the  $g_{ij}$  functions, derived with the classical FH lattice theory, which refer to all type of interactions, specific and non-specific. In this paper the combination of both the FH and the AE models provides a new parameter named  $\Delta g_{ij} = g_{ij} - g'_{ij}$  that serves to evaluate the contribution of all the possible binary specific interactions established between the three components of the system (being the non-specific interactions represented by the parameter  $g'_{ij}$ ). Specifically, the  $\Delta g_{AB}$  and  $\Delta g_{AC}$  are excess functions that will quantify the AB and AC intermolecular

specific interactions, respectively, and should also be very useful to predict the compatibility or miscibility between the system components as a function of the composition. In this sense, we relate, for the first time, published experimental data on the preferential solvation parameter,  $\lambda$ , [9,13] with calculated  $\Delta g_{ij}$  values for solvent(A)/solvent(B)/polymer(C) systems with specific interactions. Concretely, the proposed approach has been successfully applied to the systems: (i) methanol(A)/1,4-dioxane(B)/poly(alkyl methacrylates)(C) being the alkyl = methyl, ethyl and isobutyl; and (ii) *n*-alcohol(A)/heptan-3-one(B)/poly(vinyl pyrrolidone)(C) where the alcohols are methanol, ethanol and propanol. The reasonable agreement observed between theoretical predictions and experimental data has confirmed the usefulness of the  $\Delta g_{ij}$  magnitude for assessing the selective sorption of a solvent by a polymer. Moreover, a similar approach based on the combination of both FH and AE models has been recently developed for solvent(A)/polymer(B)/polymer(C) systems with H-bonding that pretends to calculate free energy surfaces and, therefore, to predict phase diagrams and to interpret the miscibility or immiscibility regions as a function of the system composition [16,17].

## 2. Theory

### 2.1. Nomenclature

Throughout the text and for the clarity of presentation, we will denote the components of the ternary system as: solvent(A)/solvent(B)/polymer(C). The component A is a self-associating molecule and has proton-donor character whereas components B and C are proton-acceptors, so specific interactions (hydrogen bond) can account between A and B or A and C components. Moreover,  $V_i$ ,  $N_i$ ,  $n_i$ ,  $\phi_i$ ,  $v_i$  and  $r_i$  (with  $i = A, B$  or  $C$ ) will refer to the molar volume, number of molecules, number of moles, volume fraction, nominal concentration of components in moles per mole of lattice sites, and number of segments involved in the complex calculated as the ratio of molar volumes ( $r_i = V_i/V_A$ ), respectively.

### 2.2. Flory–Huggins (FH) lattice theory

For a ternary polymer system, and assuming that 1 molecule of component A (solvent) occupies one site in the lattice, the Gibbs free energy function

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