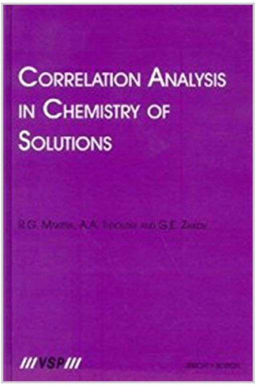

Correlation Analysis in Chemistry of Solutions

By Roman Makitra, Anatolij Turovsky, Gennady Zaikov

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The behavior of substances in solutions may not be adequately characterized by the effect of any single physicochemical parameter of solvents, nor are numerous semi-empirical scales of the solvent effect (their â€˜polarityâ€™) suitable for their limited selections only. In recent decades, it has been found that the variation of reaction rate constants in solutions or that spectral parameters of dissolved substances are determined by the total effect of different solvation processes. This monograph presents numerous examples of such an approach and characterizes various empirical and semi-empirical scales of solvent properties. It is shown that additional consideration of some structural parameters of solvents, namely, their cohesive energy and the molar volume, may provide for spreading this approach on homolytical and catalytic reaction.
It is also shown that for the solvolysis reaction, one of the excessive reagents may represent either a reagent or a solvent, which requires additional consideration of its structural characteristics in the Hammeth equation.
The application of the principle of free energy linearity also allowed adequate generalization of data on the effect of solvents on different physicochemical processes, such as dissolution of gases and solids in various solvents, swelling of polymers and solid fossil fuels, coal extraction, adsorption, absorption, diffusion, and chromatography. Special attention is paid to substance distribution between two immiscible phases. Properties of both an extractive phase and an active extractant dissolved in inert diluter are taken into account. The majority of these processes indicate the efficiency of solvent self-association factor that defines the energy consumption for formation of a void for an alien molecule injection.

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- Published on: 2004-07-01
- Released on: 2004-07-01
- Format: Kindle eBook

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