

kinetic electrolyte effect (kinetic ionic-strength effect)

Also contains definitions of: primary kinetic electrolyte effect, secondary kinetic electrolyte effect

The general effect of an added electrolyte (i.e. an effect other than, or in addition to, that due to its possible involvement as a reactant or catalyst) on the observed rate constant of a reaction in solution. At low concentrations (when only long-range coulombic forces need to be considered) the effect on a given reaction is determined only by the ionic strength of the solution and not by the chemical identity of the ions. For practical purposes, this concentration range is roughly the same as the region of validity of the Debye–Hückel limiting law for activity coefficients. At higher concentrations, the effect of an added electrolyte depends also on the chemical identity of the ions. Such specific action can usually be interpreted as the incursion of a reaction path involving an ion of the electrolyte as reactant or catalyst, in which case the action is not properly to be regarded just as a kinetic electrolyte effect. Kinetic electrolyte effects are usually (too restrictively and therefore incorrectly) referred to as 'kinetic salt effects'. A kinetic electrolyte effect ascribable solely to the influence of the ionic strength on activity coefficients of ionic reactants and transition states is called a 'primary kinetic electrolyte effect'. A kinetic electrolyte effect arising from the influence of the ionic strength of the solution upon the pre-equilibrium concentration of an ionic species that is involved in a subsequent rate-limiting step of a reaction is called a 'secondary kinetic electrolyte effect'. A common case encountered in practice is the effect on the concentration of hydrogen ion (acting as catalyst) produced from the ionization of a weak acid in a buffer solution. Synonymous with kinetic equivalence.

See also: common-ion effect, order of reaction, kinetic ambiguity

Source:

PAC, 1994, 66, 1077 (*Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994)*) on page 1133