ISSN (Print): 1060-6076
ISSN (Online): Applied

The Journal of African Development
2026; Vol 7: Issue 1
https://www.afea-jad.com/

Kinetic Equations and Their Applications in Assessing Reactant–Solvent Effects: A Review

Anil Kumar Singh[1]

[1]Department of chemistry,Teerthanker Mahaveer University. Moradabad. UP. India

Email: dr.anilkumarsingh2009@gmail.com

Cite This Paper as: Anil Kumar Singh (2026) Kinetic Equations and Their Applications in Assessing Reactant–Solvent Effects: A Review . The Journal of African Development l, Vol.7, No.1, 1769-1775

KEYWORDS

Chemical reaction rate; Reactant parameters; Solvent parameters; Reaction kinetics; Arrhenius equation; Eyring equation; Transition state; Activation parameters; Solvent effects; Dielectric constant; Solvent polarity; Preferential solvation; Hydrogen bonding; Linear Free Energy Relationships (LFER); Hammett equation; Brønsted relationship; Hughes–Ingold theory; Grunwald–Winstein equation; Kirkwood–Onsager equation; Aqueous–organic binary solvents..

ABSTRACT

The rate of a chemical reaction is governed by the combined influence of the intrinsic properties of reactants and the physicochemical characteristics of the solvent. Quantitative and qualitative relationships between these factors can be described using several classical and modern kinetic equations that provide insight into reaction mechanisms, transition-state stabilization, and solvent–solute interactions. This review summarizes the principal equations employed to evaluate the effects of reactant and solvent parameters on reaction rates, including the Arrhenius equation, Eyring transition-state equation, Hammett equation, Taft equation, Brønsted relationship, Hughes–Ingold theory, Grunwald–Winstein equation, Kirkwood equation, and Linear Solvation Energy Relationships (LSER). These models relate reaction kinetics to activation energy, substituent electronic effects, steric influences, solvent polarity, dielectric constant, nucleophilicity, ionizing power, and hydrogen-bonding ability. The review highlights how these equations complement one another in explaining kinetic behavior across aqueous, non-aqueous, and mixed solvent systems. Particular emphasis is placed on solvent-induced changes in activation parameters, transition-state stabilization, and structure–reactivity correlations. The comparative analysis demonstrates that no single equation completely describes all kinetic phenomena; rather, a combination of mechanistic and empirical relationships provides the most reliable prediction of reaction rates. The study serves as a comprehensive reference for researchers investigating chemical kinetics, physical organic chemistry, and solvent effects, while offering practical guidance for selecting appropriate kinetic models to interpret experimental rate data and predict reaction behavior under varying reaction conditions.....

1. INTRODUCTION

The rate of a chemical reaction is determined by the combined influence of the intrinsic properties of the reactants and the physicochemical characteristics of the solvent. Reactant parameters such as molecular structure, electronic effects, steric hindrance, bond strength, nucleophilicity, electrophilicity, leaving-group ability, and acid–base behavior play a crucial role in controlling the activation energy and the stability of the transition state. Similarly, solvent properties—including polarity, dielectric constant, hydrogen-bonding ability, viscosity, ionizing power, and specific solvation effects—can significantly alter the reaction pathway and reaction rate by stabilizing either the reactants or the activated complex.

To understand these effects quantitatively and qualitatively, several theoretical equations and empirical relationships have been developed in physical organic chemistry. The Arrhenius equation correlates the reaction rate constant with temperature and activation energy, while the Eyring (Transition State) equation provides activation parameters such as enthalpy, entropy, and Gibbs free energy of activation. The Hammett equation relates reaction rates and equilibrium constants to the electronic nature of substituents through substituent constants, whereas the Taft equation extends this approach by separating steric and polar effects in aliphatic compounds. The Brønsted relationship describes the dependence of reaction rates on the acid–base strengths of reactants, and the Hughes–Ingold theory explains the influence of solvent polarity and reaction mechanism (SN1, SN2, E1, and E2) on reaction kinetics. In addition, the Grunwald–Winstein equation evaluates solvent ionizing power in solvolysis reactions, while the Yukawa–Tsuno equation and Linear Free Energy Relationships (LFERs) provide further insight into substituent and resonance effects on reaction rates.[1-4]

.

2. **Hughes and Ingold Theory**. The Hughes–Ingold Theory, developed by chemists Edward D. Hughes and Christopher Kelk Ingold, explains how the nature of reactants, solvents, and the mechanism of a reaction influence the rate of nucleophilic substitution and elimination reactions. It is one of the fundamental theories of physical organic chemistry and is widely used to interpret solvent effects in reaction kinetics.[5-6]

Basic Principle

The rate of a chemical reaction depends on the relative stabilization of the reactants and the transition state by the solvent.

If the transition state is more polar than the reactants, increasing the solvent polarity stabilizes the transition state more strongly, thereby lowering the activation energy and increasing the reaction rate.

If the reactants are more polar than the transition state, increasing solvent polarity stabilizes the reactants more than the transition state, raising the activation energy and decreasing the reaction rate.

Mathematically,

$$k=A.e^{-Ea/RT}$$

or using transition state theory,

$$k= (k_BT) / h. e^{-\Delta G‡/RT}$$

where:

k = rate constant

A = frequency factor

Ea = activation energy

ΔG‡ = Gibbs free energy of activation

R = gas constant

T = absolute temperature

. **3. Hammett's Equation:** Hammett's equation is one of the most important quantitative relationships in physical organic chemistry. It correlates the effect of substituents on the rate or equilibrium of reactions involving aromatic compounds, especially substituted benzoic acid derivatives. It was proposed by Louis Plack Hammett in 1937.

Hammett Equation

$$\text{Log } (k/k_0)= \rho\, \sigma$$

or, for equilibrium constants,

$$\log(K/K_0)= \rho\, \sigma$$

where:

k = rate constant of the substituted compound

k_0 = rate constant of the unsubstituted compound (H)

K = equilibrium constant of the substituted compound

K_0 = equilibrium constant of the unsubstituted compound

σ = substituent constant

ρ = reaction constant

3. Taft's Equation: Taft's Equation is a Linear Free Energy Relationship (LFER) developed by Robert W. Taft Jr. (1952) to quantitatively evaluate the steric and polar (inductive) effects of substituents on the rate and equilibrium of aliphatic organic reactions. It extends the Hammett equation, which is mainly applicable to aromatic compounds.[7-8]

General Form

$$\text{Log } (k/k_0) = \rho* \sigma* + \delta\, Es$$

Where:

k = rate constant of the substituted compound

k_0 = rate constant of the reference compound (usually CH_3)

σ* = polar substituent constant (inductive effect)

ρ* = reaction constant representing sensitivity to the polar effect

Es = steric substituent constant

δ = steric reaction constant indicating sensitivity to steric effects

4. Grunwald and Winstein Equation: The Grunwald–Winstein equation is an empirical linear free-energy relationship developed by Ernest Grunwald and Saul Winstein in 1948 to explain the effect of solvent ionizing power on the rates of solvolysis reactions, particularly **SN1 (**unimolecular nucleophilic substitution) reactions. It correlates the rate of a reaction in different solvents with the solvent's ability to stabilize the developing carbocation and the leaving group.

Equation

$$\log(k/k_0) = mY$$

Where:

k = rate constant of the reaction in the solvent under study.

k_0 = rate constant in the standard solvent (commonly 80% ethanol–water).

Y = solvent ionizing power parameter.

m = sensitivity factor of the substrate toward changes in solvent ionizing power.

Meaning of the Parameters

Y (Ionizing Power):

Measures the ability of a solvent to stabilize ions formed during the reaction.

Higher **Y** values indicate more highly ionizing solvents, which generally accelerate SN1 reactions.

m (Sensitivity Parameter):

Indicates how strongly the reaction rate depends on solvent ionizing power.

m ≈ 1: The substrate behaves similarly to the standard substrate (tert-butyl chloride).

m < 1: Lower sensitivity to solvent changes.

m > 1: Greater sensitivity to solvent ionization.

Modified Grunwald–Winstein Equation

Many solvolysis reactions are influenced not only by solvent ionizing power but also by solvent nucleophilicity. To account for both effects, the equation was modified as:

$$\text{Log}\ (k/k_0) = lN + mY + c$$

Where:

N = solvent nucleophilicity parameter.

l = sensitivity of the reaction to solvent nucleophilicity.

Y = solvent ionizing power.

m = sensitivity to solvent ionizing power.

c = constant accounting for residual effects.

Applications

Predicts rates of SN1 solvolysis reactions in different solvents.

Distinguishes between SN1 and SN2 mechanisms based on solvent dependence.

Evaluates solvent effects in physical organic chemistry.

Investigates carbocation formation and transition-state stabilization.

Compares solvent systems in kinetic studies.

Advantages

Simple and effective method for correlating solvent effects.

Helps identify reaction mechanisms.

Applicable to a wide range of solvolysis reactions.

Provides quantitative insight into solvent–substrate interactions.

Limitations

Primarily applicable to solvolysis reactions.

Less suitable for reactions involving complex or multiple mechanisms.

Does not explicitly account for steric effects or substituent effects.

May fail when specific solute–solvent interactions dominate the reaction.

Significance

The Grunwald–Winstein equation is one of the most important linear free-energy relationships in physical organic chemistry. It quantitatively demonstrates that the rate of many solvolysis reactions is governed by the ionizing ability and, in the modified form, the nucleophilicity of the solvent. Together with the **Hammett**, **Taft**, and **Hughes–Ingold** approaches, it provides a fundamental framework for understanding solvent effects on reaction kinetics[9-12]

4. Swain's Equation: Swain's Equation is a Linear Free Energy Relationship (LFER) developed by C. G. Swain and E. C. Lupton (1968**)**. It quantitatively separates the influence of field (inductive) and resonance effects of substituents on the rates and equilibria of organic reactions. It is considered an improvement over the Hammett equation for reactions in which both effects contribute independently.[13-20]

Equation

$$Y = f F + r R + C$$

Where:

Y = Response parameter (e.g., $\log(k/k_0)$, $\log(K/K_0)$, or another measured property)

F = Field (inductive) substituent constant

R = Resonance substituent constant

f = Sensitivity of the reaction to the field effect

r = Sensitivity of the reaction to the resonance effect

C = Constant (usually close to zero)

Principle

The equation assumes that the overall substituent effect can be divided into two independent components:

Field (F) Effect

Arises from inductive and electrostatic interactions.

Operates through σ-bonds.

Decreases rapidly with increasing distance from the reaction center.

Resonance (R) Effect

Results from electron delocalization through π-bonds.

Becomes important when the substituent is conjugated with the reaction center.

Can either donate or withdraw electron density through resonance.

Significance of the Parameters

f > r: The reaction is mainly controlled by inductive (field) effects.

r > f: Resonance effects dominate the reaction.

f ≈ r: Both field and resonance effects contribute significantly.

Applications

Analysis of substituent effects in aromatic reactions.

Prediction of reaction rates and equilibrium constants.

Separation of inductive and resonance contributions.

Study of reaction mechanisms.

Correlation of kinetic and thermodynamic data.

Physical organic chemistry and quantitative structure–reactivity relationships (QSRR).

Advantages

Separates field and resonance effects quantitatively.

More accurate than the Hammett equation for many aromatic reactions.

Applicable to a wide variety of electrophilic and nucleophilic reactions.

Provides better mechanistic interpretation.

Limitations

Applicable mainly to aromatic systems with well-defined substituent constants.

Reliable values of **F** and **R** are required.

Steric effects are not included.

Less useful when solvent effects or steric factors dominate the reaction.

Importance

Swain's equation is one of the most important Linear Free Energy Relationships (LFERs) in physical organic chemistry. By independently evaluating field and resonance contributions, it provides a more detailed understanding of substituent effects than the Hammett equation and is widely used in mechanistic studies of organic reactions.[21-30]

CONCLUSION: The rate of an organic reaction is determined by the combined influence of the intrinsic properties of the reactants and the physicochemical characteristics of the solvent. The theories and linear free-energy relationships discussed—Hughes–Ingold Theory, Hammett Equation, Taft Equation, Grunwald–Winstein Equation, and Swain's Equation—provide complementary frameworks for understanding and predicting how these factors affect reaction kinetics and mechanisms.

The Hughes–Ingold Theory establishes the fundamental concept that solvent polarity influences reaction rates through differential stabilization of the reactants and the transition state. This theory successfully explains solvent effects in nucleophilic substitution and elimination reactions and forms the basis for interpreting solvent-dependent reaction mechanisms.

The Hammett Equation quantitatively correlates substituent electronic effects with reaction rates and equilibrium constants in aromatic systems. The reaction constant (ρ) and substituent constant (σ) provide valuable information about the sensitivity of a reaction to electron-donating and electron-withdrawing substituents, making the equation indispensable in mechanistic investigations.

The Taft Equation extends the Hammett approach to aliphatic compounds by independently evaluating inductive (polar) and steric effects. Through the parameters σ*, Es, ρ*, and δ, it enables quantitative assessment of how steric hindrance and electronic influences govern reaction rates, particularly in aliphatic substitution and hydrolysis reactions.

The Grunwald–Winstein Equation specifically describes the effect of solvent ionizing power on solvolysis reactions. Its modified form, which incorporates solvent nucleophilicity, provides a comprehensive treatment of solvent participation and has become one of the most useful tools for distinguishing between SN1 and SN2 mechanisms and evaluating solvent–substrate interactions.

The Swain–Lupton Equation further refines substituent analysis by separating field (inductive) and resonance effects into independent contributions. This distinction provides a more detailed understanding of substituent behavior than the Hammett equation alone and has greatly enhanced quantitative structure–reactivity relationship (QSRR) studies and mechanistic interpretations.

Collectively, these theories and equations demonstrate that reaction rates are governed by a balance of electronic effects, steric factors, solvent polarity, solvent nucleophilicity, ionizing power, and transition-state stabilization. They constitute the foundation of physical organic chemistry, enabling quantitative prediction of reaction rates, elucidation of reaction mechanisms, and rational design of reaction conditions. Consequently, these models remain indispensable tools in modern kinetic studies, synthetic organic chemistry, catalysis, medicinal chemistry, and quantitative structure–reactivity investigations.

REFERENCE

1. Seliverstova T S, Marina Kushner, Matusevich L G. (2020) The hydrolysis of Benzyl Ether bond in aqueous-organic media. Russian Journal of Physical Chemistry A. Vol-94:310-316,

2.Magda F Fathalla,Yassir R. Elmarassi.(2019). The reaction of 2-chloroquinoxaline with piperidine in DMSO-H2O and DMF- H2O mixture. Kinetic and solvent effect. Journal of solution chemistry. Vol. 48:1287-1308,.

3 Nisha Chhetri., S. A. Bhoite.: Study of Solvent Effects on Hydrolysis of Mono-m-toluidinePhosphate. International Journal of ChemTech Research, Vol.9, No.02 pp 106-109, (2016)

4. Singh A. K. (2026). Organic reaction in mixed aqueous solvents and their kinetics. International journal of Research and Scientific Innovation (IJRSI) ISSN No.2321-2705.DOI:10.51244/IJRSI. VOL VIII. Issue-VII. July. PP1747-1753

5. Espenson, J. H. (1995). Chemical Kinetics and Reaction Mechanisms (2nd ed.). McGraw-Hill, New York.

6. A. K. Singh. (2026). Qualitative Prediction of Reaction Rates Using Transition State Theory, Solvent Effects and Activation Parameters: A Review. International Journal of Latest Technology in Engineering Management and Applied Science. Volume XV, Issue VII, ISSN 2278-2540 |. PP1511-1516. https://doi.org/10.51583/IJLTEMAS.2026.150700114.

7. Moore, J. W., & Pearson, R. G. (1981). Kinetics and Mechanism (3rd ed.). John Wiley & Sons, New York.

8. Atkins, P., & de Paula, J. (2018). Atkins' Physical Chemistry (11th ed.). Oxford University Press.

9. Anslyn, E. V., & Dougherty, D. A. (2006). Modern Physical Organic Chemistry. University Science Books.

10 Reichardt, C., & Welton, T. (2011). Solvents and Solvent Effects in Organic Chemistry (4th ed.). Wiley-VCH.

11. Hughes, E. D., & Ingold, C. K. (1935). Mechanism of substitution at a saturated carbon atom. Journal of the Chemical Society, 1935, 244–255.

12. Hammett, L. P. (1937). The effect of structure upon the reactions of organic compounds. Benzene derivatives. Journal of the American Chemical Society, 59, 96–103.

13. Hammett, L. P. (1940). Physical Organic Chemistry. McGraw-Hill, New York.

14. Taft, R. W. Jr. (1952). Polar and steric substituent constants for aliphatic and o-benzoate groups. Journal of the American Chemical Society, 74, 2729–2732.

15. Taft, R. W. Jr. (1956). Separation of polar, steric and resonance effects in reactivity. In Steric Effects in Organic Chemistry (M. S. Newman, Ed.). John Wiley & Sons.

16. Grunwald, E., & Winstein, S. (1948). The correlation of solvolysis rates. Journal of the American Chemical Society, 70, 846–854.

17. Swain, C. G., & Scott, C. B. (1953). Quantitative correlation of relative nucleophilic reactivities. Journal of the American Chemical Society, 75, 141–147.

18. Swain, C. G., & Lupton, E. C. Jr. (1968). Field and resonance components of substituent effects. Journal of the American Chemical Society, 90, 4328–4337.

19. Winstein, S., Grunwald, E., & Jones, H. W. (1951). Correlation of solvolysis rates and solvent ionizing power. Journal of the American Chemical Society, 73, 2700–2707.

20. Eyring, H. (1935). The activated complex in chemical reactions. Journal of Chemical Physics, 3, 107–115.

21 Wynne-Jones, W. F. K., & Eyring, H. (1935). The absolute rate of reactions in condensed phases. Journal of Chemical Physics, 3, 492–502.

22. Parker, A. J. (1969). Protic–dipolar aprotic solvent effects on reaction rates. Chemical Reviews, 69, 1–32.

23. Bunnett, J. F. (1963). The relation of nucleophilic reactivity to solvent effects. Quarterly Reviews, Chemical Society, 17, 271–296.

24 Lowry, T. H., & Richardson, K. S. (1987). Mechanism and Theory in Organic Chemistry (3rd ed.). Harper & Row.

25.Carey, F. A., & Sundberg, R. J. (2007). Advanced Organic Chemistry, Part A: Structure and Mechanisms (5th ed.). Springer.

26.March, J. (1992). Advanced Organic Chemistry: Reactions, Mechanisms, and Structure (4th ed.). John Wiley & Sons.

27Jencks, W. P. (1969). Catalysis in Chemistry and Enzymology. McGraw-Hill.

28 House, J. E. (2007). Principles of Chemical Kinetics (2nd ed.). Academic Press.

29. Singh AK & LK. TIWARI . (2020) "Study of Solvent effect of Protic solvent on Solvolysis of Hexanoate ester and Activation parameters." Asian journal of Research in Chemistry, ISSN 0974-4150, 13(3), pp 216-218. DOI: 10.5958/0974-4150.2020.00041.3

30.Singh A K. (2019). Kinetics and solvent effect on activation parameter of aquo-propanol solvent system for acid catalyzed solvolysis of propyl formate. International Journal of Chemical Science ISSN:2523-2843 ,Vol-3, Issue-4, July, pp85-88.