common-ion effect (on rates)

A reduction in the rate of certain reactions of a substrate RX in solution [by a path that involves a pre-equilibrium with formation of R⁺ (or R⁻) ions as reaction intermediates] caused by the addition to the reaction mixture of an electrolyte solute containing the 'common ion' X⁻ (or X⁺). For example, the rate of solvolysis of diphenylmethyl chloride in acetone-water is reduced by the addition of salts of the common ion Cl⁻ which causes a decrease in the quasi-equilibrium concentration of the diphenylmethyl cation in the scheme:

\[
\begin{align*}
\text{Ar-CH₂Cl} & \rightleftharpoons 1 \rightleftharpoons \text{Ar}^+ + \text{Cl}^- \\
\text{Ar}^+ + \text{OH}_2 & \rightarrow 2 \rightarrow \text{Ar-CH₂OH} + \text{H}^+ \\
\end{align*}
\]

(free ions, notion pairs)

This phenomenon is a direct consequence of the mass-law effect on ionization equilibria in electrolytic solution. More generally, the common-ion effect is the influence of the 'common ion' on the reactivity due to the shift of the dissociation equilibrium. It may also lead to an enhancement of the rate of reaction.

Source:
PAC, 1994, 66, 1077 (Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994)) on page 1098