



Doctoral Thesis

Sorption-diffusion in porous solids and the dyeing process

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**SORPTION-DIFFUSION IN POROUS SOLIDS
AND THE DYEING PROCESS**

DISSERTATION

submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY
ZURICH

for the degree of Doctor of Technical Sciences

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SUMMARY AND CONCLUSIONS

In Part I, an analysis in terms of classical concepts of diffusion has resulted in a unifying description of sorption/diffusion behavior of heterogeneous solid substrates. As regards the type of interaction between sorbable solutes and the substrates, this treatment encompasses both "solution" and "adsorption" phenomena, and their combined existence, as well as the entire spectrum of interactions characterized by isotherms from the case of weak sorption (Nernst) to the case of irreversible strong sorption (shell-progression), and including what are intermediate cases described by Freundlich and Langmuir isotherms.

In spite of seemingly complex and diverse formal mathematical solutions which normally would apply to the analysis of many specific cases of type of interaction, it was shown by physical reasoning alone how a major modification of the classical Fick relaxation time is universally applicable to sorption/diffusion systems. This modification introduces the experimentally accessible quantity c_f/c_o (the ratio of the total equilibrium quantity of sorbate on the sorbing medium to the sorbate concentration in solution), and geometric correction factors P , the porosity fraction, and b , a tortuosity correction. Rigorous mathematical treatment was used to confirm the analysis and its conclusions.

The analysis has provided a basis for the quantitative interpretation of the course of sorption in terms, for example, of the true classical diffusivities. Furthermore, such interpretation can now be made even in the absence of detailed

knowledge of the isotherm behavior, within a factor of better than 1.6 in diffusivity.

The study has provided a basis with which to examine experimental observations, in order to determine whether there is need and justification for invoking added complicating factors beyond classical diffusion behavior: It is shown that the apparent concentration dependence of diffusivity sometimes observed in sorptive systems can result as a mathematical formality without having any special physico-chemical significance with respect to molecular motion per se. The need for considering additional phenomena, such as physical size hindrance of molecular mobility due to small pore passages, etc., should be recognizable upon comparison of experimental observations with the results of this classically based analysis.

This analysis also made possible a review of the information content of concentration profile studies in the progression of molecules into sorbing solid substrates.

The results and conclusions have applicability to diverse fields of science and technology where sorption processes occur. The process of sorption of dyes on fibers, as encountered in the technology of dyeing is a prominent example to which these considerations are applicable.

In Part II, rigid porous inorganic substrates were used as rigid "model" substrates with definable pore structure and subjected to dyeing with a number of dyes, in non-aqueous and aqueous

dye baths. It was possible to demonstrate differences in apparent diffusivity varying over several orders of magnitude arising for variations in substrate, choice of dye, composition of solvent, etc.; and how in most cases these are resolved to be indirect effects due to changes in the factor c_f/c_o , with the true diffusivity actually varying little or not at all.

It was possible to demonstrate that added phenomena depressing the classical diffusivity can exist in water, and that, however, they are alleviated by raising the temperature. It is suggested that the effect is a result of formation of molecular aggregates as large or larger than pore dimensions, and/or a result of molecular ordering through hydrogen bonding of the water solvent into a partially frozen state of higher viscosity in the neighborhood of solid surfaces. Whichever the mechanism of depressing dyeing rate, the experimental demonstrations suggest that increase of diffusivity with temperatures should not necessarily be interpreted to be due to a mechanism of activated diffusion, but as resulting from the removal of an inhibition phenomenon from the normal classical diffusion mechanism.

In Part III, a cross-section of past studies concerning dyeing rates on organic fibers is re-analyzed in the light of the analysis of Part I and the experimental studies with rigid substrates of Part II. The findings suggest the adequacy of classical diffusive processes for describing the dyeing behavior

in a majority of systems, at temperatures near the boiling point of water, and the existence in a given substrate of an additional physical size impediment for the diffusion of some large dye structures.

The work reported in Parts I, II, and III increases the ability to analyze and interpret many types of experimental observations, and to devise further penetrating studies in connection with various phases of the rate-of-dyeing problem, including the behavior of "composite" systems (e.g. the "Yarn Problem"), competitive dye sorption, the effect of dye bath additives, etc.

Zusammenfassung

Im Teil I wird das Sorptions- und Diffusionsverhalten in heterogenen festen Substraten auf Grund der klassischen Gesetze auf einer einheitlichen Basis interpretiert, die Lösungs- und Adsorptionsmechanismen für schwache Wechselwirkungen (Nernst'sche Verteilungen), Schalenaufbaumechanismen (Shell-progression) wie auch die dazwischen liegenden Fälle von Langmuir- und Freundlich-Sorptionsvorgängen umfasst. Die mathematisch begründete Einführung von Gleichgewichtstermen und von Faktoren, die die Geometrie des heterogenen Substrates berücksichtigen, führt zu den wahren Diffusionskoeffizienten (D), die nicht mehr konzentrationsabhängig sind. Die so erhaltenen numerischen Werte für D lassen sich bezüglich des Diffusionsmechanismus quantitativ interpretieren.

Im Teil II wird in einer Reihe von experimentellen Untersuchungen über die Diffusion von gelösten Farbstoffen in porösen anorganischen Substraten gezeigt, dass die scheinbaren Diffusionskoeffizienten (D_{app}) je nach Bedingungen um mehrere Zehnerpotenzen variieren können, dass die wahren Koeffizienten D gemäss Teil I jedoch gar nicht oder nur sehr wenig von den Reaktionsverhältnissen abhängig sind. Abweichungen lassen sich auf zusätzliche Effekte (Assoziationen etc.) zurückführen.

Im Teil III wird eine grosse Zahl von Literaturdaten über Färbegeschwindigkeiten auf Wolle, Cellulose-, Polyamid-, Polyester- und Celluloseacetat-Fasern auf Grund der Prinzipien von Teil I neu analysiert. Es ergibt sich, dass in allen diesen Fällen die Diffusion in einer wässrigen Phase in der Faser erfolgt. Auf

Zusammenhänge mit technologischen Problemen (Durchfärben von Garn, Wirkung von Egalisier- und andern Zusätzen, gegenseitige Beeinflussung der gleichzeitigen Diffusion von mehreren Farbstoffen etc.) wird hingewiesen.