Advances in Permeation of Solutes into Hair: Influencing Factors and Theoretical Models

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Abstract: The permeation and absorption of solutes into human hair are highly relevant to various applications, including the formulation of hair-care products, the development of water pollution control and remediation, and the risk assessment of environmental exposure. Based on a detailed introduction of the structure and composition of hair, the effects of the properties of hair (structure, composition, and charge properties), the physicochemical properties of solutes (molecular size, shape, and hydrophobicity), and the conditions of the surrounding medium (solvent composition, temperature, and pH) on the permeation and absorption were comprehensively analyzed. Several theoretical models were reviewed, including two-part/two-state, porous media diffusion, homogeneous medium diffusion, heterogeneous medium partition, and diffusion models. Finally, future research directions for the permeation and absorption of solutes in hair were proposed to provide a foundation for the further optimization and application of permeation models.

Keywords: human hair; permeation and absorption; influencing factor; permeation model

1. Introduction

The permeation and absorption of solutes in human hair are closely related to a wide range of applications, including the formulation of hair-care products [1–3], the development of water pollution control and remediation [4], and the risk assessment of environmental exposure [5–7]. According to the latest report released by the U.S. market research firm Transparency Market Research, the market scale of global hair products in 2015 was 81.3 billion USD, and it is expected to reach 105.3 billion USD by 2024. Ingredients in hair products can be adsorbed on the surface of hair or penetrate into hair through permeation and absorption to meet consumers' many daily hair-care needs, such as cleaning, repair, coloring, and styling [8–12]. Studies have shown that hair, as a natural keratin adsorbent, can be used to remove organic pollutants, such as formaldehyde [13–15], phenol [16], and heavy-metal ions [17], from wastewater. The treatment of wastewater with this method has the advantages of low treatment cost, easy design and operation, insensitivity to toxic pollutants, and no secondary pollution [4,13]. In addition, due to the lipophilicity and low biological activity of hair [6,18–20], it can also be used as a bioindicator to evaluate the exogenous exposure of humans to environmental pollutants and to assess exogenous exposure to chemicals in media, such as care agents, pesticides, sewage, and dust [7,21].

The permeation and absorption properties of solutes in the hair are the most important parameters for assessing their absorption amount and speed. Therefore, studying the mechanism of permeation and absorption of solutes in hair and constructing a corresponding permeation mechanism model can provide theoretical guidance for the formula design of hair products and shorten the product development cycle. It can also enrich wastewater treatment and chemical exogenous risk assessment, which have important theoretical and practical significance.

The permeation and absorption properties of solutes, such as surfactants [22–24], phenols [25,26], dyes [27–30], fats [31–33], and metal ions [17,34], have been investigated, and several different permeation mechanism models have been proposed. However, owing to the complex mechanism of solute absorption in hair and the many influencing factors, existing models have certain limitations. In this paper, based on a detailed introduction to the structure and composition of hair, the main factors that influence hair permeation and absorption are summarized, including the physical and chemical properties of hair (structure, composition, and charge characteristics), the physical and chemical properties of solutes (molecular size, shape, and hydrophobicity), and the solvent conditions (composition, temperature, and pH). Several major permeation models of solutes in hair are described in detail, and, based on the current research status, suggestions are made for future research directions to establish a theoretical foundation for further optimization of hair permeation models.

2. Hair Structure and Composition

2.1. Hair Structure

Hair consists of a hair follicle, hair root, and hair shaft. The hair follicle is a cystic tissue surrounding the hair root; the inner layer is an epithelial tissue hair follicle, which is connected with the epidermis; and the outer layer is a connective tissue hair follicle, which is connected with the dermis. The hair roots are hidden in the scalp, and their main function is biosynthesis and directional growth. The hair shaft is the part exposed outside of the skin, and it can be divided into three layers known as the cuticle, the cortex, and the medulla, from outside to inside. The cuticle cells, cortex cells, and the space between them are connected by the cell membrane complex (CMC) (Figure 1) [35,36].
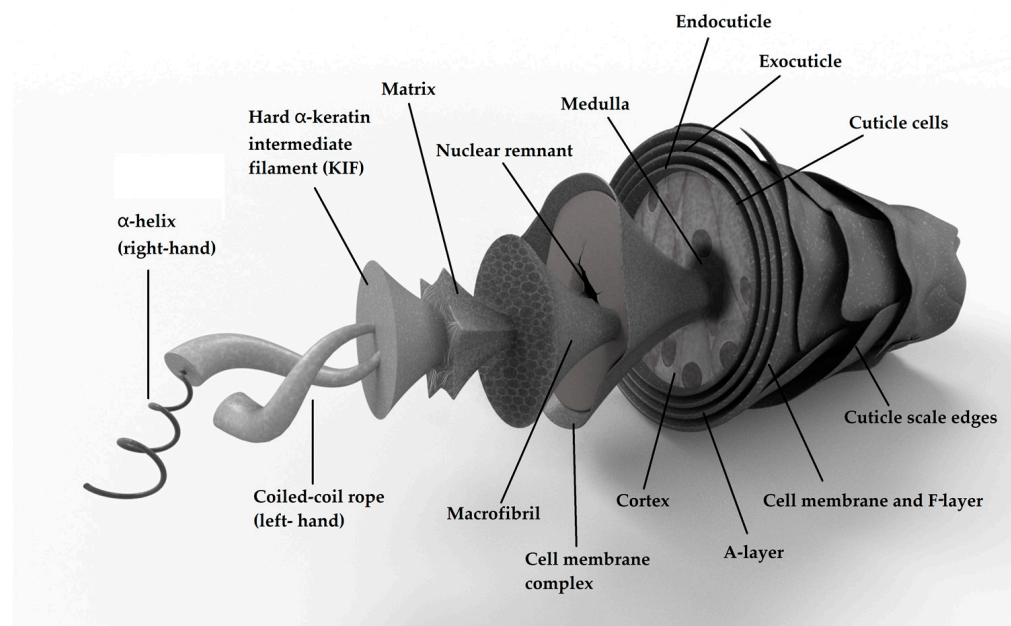

Figure 1. Structure of the human hair shaft.

The cuticle covers the outermost layer of the hair shaft, and it is covered with a stratum corneum layer. It is generally composed of lipid layers and 7 to 10 layers of flat cuticle cells that are staggered and overlapped into fish-scale or tile-like structures. Each cuticle cell has a thickness of 0.5 μm, a length of approximately 5 to 10 μm, and a total thickness of 5 μm in the cuticle layer [37]. The cuticle structure can be divided into 3 parts [11]: the epidermis (cystine content of ~12%), the exocuticle (cystine content of ~15%), and the endo-cuticle (cystine content of ~3%). The epidermis consists of a thin fat layer and a high-sulfur, protein-rich layer (a-layer, cystine content of ~30%) [38]. At the molecular level,

the cuticle is a protein–lipid structure that is severely crosslinked by cystine, and it is not highly organized. This structure provides a barrier to prevent hair damage.

The cortex, which accounts for 70% to 90% of the hair's weight, is the main part of the hair shaft, and it is an important component in determining the physical properties of hair [11]. The cortex cells are spindle-shaped with thicknesses of approximately 1–6 μm and lengths of approximately 50–100 μm [39]. The cells are closely arranged along the direction parallel to the axial direction of the hair, and the edges of the cells are serrated [38]. The cortex cells comprise many macrofibrils, hard α- keratin intermediate filaments, and coiled-coil ropes. They are arranged spirally to each other, embedded in a cell matrix composed of high-sulfur proteins, and form a very tight fiber bundle, giving hair a certain degree of elasticity, strength, and toughness [40].

The medulla is located in the center of the hair shaft. Due to different hair types, the medulla may be continuous, intermittent, or absent [36]. Morphologically, the medulla is a loose structure composed of spongy keratin and amorphous substances, and it is generally considered to have no important physiological function.

The CMC is the only continuous phase in the hair structure [36], and it acts as an adhesive between cuticle cells and cortex cells and has an important influence on the physical and chemical properties of hair. The main components of the CMC are low-sulfur protein and fat, which is the main structural lipid in hair and accounts for 5% to 7% of the hair mass [41]. The CMC lipids are similar to human epidermal keratin lipids, and their main components are ceramide, cholesterol sulfate, cholesterol, fatty alcohols, and free fatty acids [42].

2.2. Chemical Composition of Hair

The main chemical constituents of hair are keratin, fat, water, pigments, and trace elements.

Keratin is the most important component of hair, accounting for more than 90% of dry hair weight [26,43]. Keratin consists of 22 amino acids [11], of which cysteine has the highest content (up to 15.5%). The keratin peptide chain contains many cysteine residues, whose disulfide bonds act as crosslinks, allowing keratin molecules to bind tightly to form a dense structure that can resist the influence of external physical and chemical factors [39]. The mechanism of action of many hair cosmetics and treatment agents is to weaken or break the crosslinking effect of disulfide bonds, thus destroying the stability of the hair fiber structure and changing the curvature of the hair to achieve the effect of hairdressing.

3. Main Factors That Affect the Permeation and Absorption of Solutes in Hair

3.1. Hair

3.1.1. Geometry of Hair

Hair is a biological tissue composed of a variety of biological macromolecules and can be considered to be a heterogeneous porous medium [27]. Some researchers have proposed using porous media theory to describe the permeation properties of solutes in hair [27,28,44]. Chandrashekara et al. [27] studied the diffusion characteristics of solutes in hair using positron annihilation lifetime spectroscopy, and they found that the free-volume channels in hair fibers are the main pathway for solute diffusion. Morel et al. [28] proposed that in the porous structure of hair, the size, shape, and density of the pores all affect the permeation and absorption properties of solutes in hair. Molecules smaller than the pore size are easily transmitted, whereas molecules larger than the pore size are not transmitted. The permeation distance of solutes in damaged hair is generally higher because the pore size of the damaged hair becomes larger, making it easier for solutes to enter the hair.

Solutes penetrate into hair mainly through two channels: transcellular channels and intercellular channels [11,45]. The transcellular channel refers to the permeation of solutes through cuticle cells, which have a dense protein structure and a high degree of crosslinking, thus limiting the permeation of large solutes [1]. The intercellular channel refers to permeation through the glial structures (endocuticle and CMC) between the cuticle cells. As the components of the glial structures are mainly fats and low-sulfur proteins,

which are prone to swelling, they are the preferred channel for lipophilic and non-polar solutes [1,11,38]. Gummer [46] found that hydrophilic substances can enter all of the structures in hair. The CMC can be considered to be a small compartment with the ability to swell and direct the solute from the hair surface to the cortex through capillary forces. It is believed that the outermost part of the cuticle is an open compartment structure, which explains the phenomenon of the rapid loss of dye in the rinsing process after hair dyeing, and it is inferred that the solute enters the cuticle from the external environment through the endocuticle. Kelch et al. [38] also found that the endocuticle and CMC are the main permeation pathways for solutes in hair.

3.1.2. Charge Characteristics of Hair

Keratin is the most important component of hair, and its isoelectric point is approximately 3.67 [11]. When the solvent pH is <3.67, the amino and carboxyl groups in the amino acids that make up keratin are protonated, and the hair appears to be positively charged externally, which increases the absorption of anionic solutes and decreases the absorption of cationic solutes. When the solvent pH = 3.67, the degree of protonation of the free amino groups is equal to the degree of dissociation of the carboxyl groups, the net charge is zero, and the hair is not charged. When the solvent pH is higher than 3.67, the free carboxyl group dissociates, the protonated amino group becomes deprotonated, and the hair appears to be negatively charged externally. Consequently, the absorption of cationic solutes increases while the absorption of anionic solutes decreases [23,26]. Therefore, the charge force can be considered one of the main driving forces for solute permeation and absorption in hair.

3.2. Solutes

3.2.1. Size and Shape of Solute Molecules

The size and shape of solute molecules affect their permeation in hair [28,44,47,48]. Assuming that the shape of the solute molecule is spherical, Holmes [44] determined that the maximum diameter of a molecule that can penetrate into hair is 1.48 nm. Sakai et al. [47] studied the penetrating distance of hair dyes of different sizes. The critical dimension of molecules that can enter hair was calculated to be 1 nm using the longest diagonal of the molecular minimum projected area as a measure of the size and shape of the molecule. However, the study had a single object of interest; the staining time was too long; and the permeation of cationic, anionic, and neutral molecules was not discussed separately. Morel et al. [28] considered the effect of the solute charge characteristics on the permeation and absorption of solutes based on the model of Sakai et al. [47]. They found that the critical sizes for the permeation of anionic, cationic, and neutral solutes into hair are approximately 1.2–1.3, 1.4, and 0.95 nm, respectively.

3.2.2. Solute Hydrophobicity

Some studies have reported that the permeation and absorption characteristics of solutes in biological substrates (e.g., hair, skin, and nails) are mainly related to the hydrophobicity of the solute [26,49–52]. Hydrophobic interaction is an important way that solute molecules and hair interact. Steinhardt et al. [53] found that the adsorption capacity of wool fibers for cationic surfactants increases with increasing hydrophobic structure. Scott et al. [54] determined the absorption characteristics of cetyl trimethyl ammonium bromide (CTAB) and dodecyl trimethyl ammonium bromide (DTAB) in hair. The results showed that CTAB with strong hydrophobicity has greater absorption in hair than DTAB with weak hydrophobicity. Robbins et al. [55] found that when the solvent pH is 3.6 (close to the isoelectric point of hair), the hair fibers are neutral, the absorption of solutes in hair is mainly caused by the hydrophobic effect, and the absorption capacity increases with increasing molecular weight and hydrophobic structure of the solute.

3.3. Solvent

3.3.1. Solvent Composition

Robbins et al. [55] found that increasing the fat content of hair product formulations can increase the adsorbed amount of cationic surfactants. Han et al. [56] found that when water is used as a solvent, the absorption of HC RED3 (a cationic semipermanent dye) in hair is 5–15 times higher than when the water/ethanol volume ratio is 1:1. This is because when water is used as a solvent, the polarity of the solvent is higher than that of a mixed solvent of water/ethanol, and the solubility of HC RED3 in water is lower than that in a mixed solvent of water/ethanol. This increases the amount of HC RED3 absorbed in hair. Therefore, the amount of the solute absorbed by hair can be increased by controlling the formulation of the solvent.

3.3.2. Solvent Temperature

Increasing the temperature decreases the viscosity of the liquid and increases the permeation rate of solutes in hair [44]. Han et al. [56] studied the absorption and diffusion coefficients of HC RED3 in hair at solvent temperatures of 25, 42, and 60 °C. They found that the diffusion coefficient of HC RED3 in hair increases with increasing temperature, and absorption of HC RED3 in hair slightly decreases with increasing temperature. Wortmann et al. [23] studied the permeation and absorption properties of anionic and cationic surfactants in hair at different temperatures. They found that the diffusion coefficients of anionic and cationic surfactants in hair increase with increasing temperature. In addition, the variation in the diffusion coefficient and temperature was in accordance with the Arrhenius equation.

3.3.3. Solvent pH

Changing the pH of the solvent can change the charge characteristics of ionic solutes, and it can also change the type and density of the charges carried by hair, thereby changing the interaction between hair and the solute molecules, which ultimately affects the permeation and absorption properties of the solute in hair. By combining scanning electron microscopy and micro-X-ray fluorescence analysis, Wortmann et al. [23] found that the diffusion coefficients and diffusion activation energies of anionic surfactants in hair decrease with the increasing pH of the solvent, while that of cationic surfactants increase. Furthermore, they found that the diffusion coefficients and diffusion activation energies of cationic and anionic surfactants are approximately the same at pH = 3.5 (close to the isoelectric point of hair). Using solvents with pH of 5.1, 6.0, and 10.4, Han et al. [56] found that the amount of HC RED3 absorbed by hair decreases with increasing pH due to the difference in the degree of ionization of the cationic HC RED3 dye. Morel et al. [28] found that under alkaline conditions, due to the force of the charge, the permeation distances of anionic, cationic, and neutral dyes in hair are different, and cationic dyes have the largest permeation distance and can penetrate the endocuticle and the δ-layer of the CMC to the cortex. Robbins et al. [55] suggested that the permeation and absorption of solutes in hair are driven by both hydrophobic and charge forces. When the solvent pH is close to the isoelectric point of the hair, solute permeation is mainly driven by hydrophobic forces. Conversely, when the pH of the solvent is greater or less than the isoelectric point of the hair, solute permeation is mainly driven by the charge force.

The pH of the solvent can also affect the swellability of hair. Robbins [11] and Valko et al. [57] found that in an alkaline solvent, the degree of swelling of hair significantly increases, which leads to an increase in the pore size of the hair, which favors solute absorption in hair. Otsuka et al. [58] pointed out that hair dyeing is usually performed under alkaline conditions, as the expanded hair fibers facilitate the rapid permeation of dyes.

The wettability of the hair surface can be changed by absorbing solutes under different pH conditions. Vickerstaff [59] and Robbins et al. [55] found that dyes mainly adsorb to the surface of hair fibers through charge or hydrophobic interactions depending on the pH of the solvent, which in turn changes the hydrophilic and hydrophobic properties of the hair

surface. For anionic dyes, when the pH is lower than the isoelectric point, hydrophobic fibers are formed on the hair surface after dye absorption. When the pH is higher than the isoelectric point, hydrophilic fibers are formed on the hair surface after dye absorption, and the reverse is true for cationic dyes.

Faucher et al. [60,61] found that the electrolyte components (e.g., sodium salt, potassium salt, and calcium salt) in the solvent occupy part of the adsorption sites of the cationic polymer on hair, resulting in competitive inhibition, thereby reducing the amount of adsorption under alkaline conditions.

Thus, the solvent pH is a key factor that affects the permeation and absorption of solutes in hair, and changing the solvent pH causes changes in the physicochemical properties of the solute and hair, which in turn affect the permeation and absorption of the solute.

In conclusion, the main factors that affect the permeation and absorption of solutes in hair are summarized in Table 1.

Table 1. Main factors that affect permeation and absorption of solutes in hair.

	Factors	References
Hair	Pore size, shape, and density	[27,28,44]
	Transcellular/intercellular channel	[1,11,38,45,46]
	Charge characteristics	[11,23,26]
	Swellability	[11,57,58]
	Wettability of surface	[55,59]
	Keratin binding	[51]
Solute	Size and shape	[28,44,47,48]
	Charge characteristics	[23,26,28,55]
	Hydrophobicity	[26,49–52]
Solvent conditions	pH	[11,23,28,55–61]
	Temperature	[23,44,56]
	Composition of solvent	[55,56]

4. Permeation Models of Solutes in Hair

The permeation models of solutes in hair include the two-part/two-state model proposed by Nagase et al. [62] and Sakai et al. [47], the porous media diffusion model proposed by Morel et al. [28], the homogenous medium diffusion models proposed by Holmes [44] and Han et al. [56], and the heterogeneous media distribution and diffusion models proposed by Wang et al. [26] and Li et al. [63]. The permeation models of solutes in hair are summarized in Table 2.

Table 2. Main permeation models of solutes in hair.

Permeation Model of Solute in Hair	Factors under Consideration	Factors out of Consideration	References
Two-Part/Two-State Model	Hair structure and composition, hair moisture content, solvent temperature, and pH	Hair cuticle, the physical and chemical properties of solute, hair charge characteristics	[47,62]
Porous Media Diffusion Model	The size, shape, and charge properties of solute	Limited data, hair composition, solute hydrophobicity	[28]
Homogeneous Diffusion Model	Fick diffusion law	Hair microstructure and composition, physicochemical properties of solute, and solvent pH	[44,56]
Heterogeneous Partition and Diffusion Model	Hair microstructure and composition; solute hydrophobicity; solute dissociation constant	Limited data, charge characteristics, and solvent pH	[26]
	Hair composition and charge properties, solute hydrophobicity, dissociation, charge properties, and solvent pH	Hair permeation channel and solvent temperature	[63]

4.1. Two-Part/Two-State Model

Considering the influence of the hair structure and composition on the hair permeation and mechanical properties, Nagase et al. [62] observed the position of absorption of erythrosin B dye in hair and developed a two-part/two-state model based on heat-setting and relaxation experiments and transmission electron microscopy experiments.

Based on the transition temperatures of the hair components, the model [47] divides the hair into two structural parts, which are called the high-temperature parts (high-Tc parts) and low-temperature parts (low-Tc parts). The corresponding transition temperatures of the two parts are 70 and 0 °C. The high-Tc parts are mainly composed of macrofibrils and exo-cuticles consisting of keratinous proteins; the low-Tc parts are mainly composed of inter-macrofibrillar materials, CMC, and endo-cuticles of non-keratinous proteins and lipids. For any part, when the temperature is higher than the transition temperature, the structures become soft and plastic; when the temperature is lower than the transition temperature, the structures are in a hard and elastic solid state. The high- and low-temperature transition temperatures are caused by temperature-induced breakage of S–S bonds, hydrogen bonds, and ionic bonds.

The transition temperature is related to the hair's moisture content and the solvent's pH. The transition temperature is higher for lower hair moisture content and solvent pH. The moisture content of the hair and the pH of the solvent affect the permeation and absorption properties of the solute in the hair by affecting the transition temperature.

To calculate the diffusion coefficient (D) of a solute in hair, the model assumes that the high-Tc parts are discretely distributed in the continuous phase composed of the low-Tc parts without considering the action of the cuticle. The diffusion coefficient of a solute in hair is calculated using the following equation [47]:

$$D = \frac{(X_H D_H + X_L D_L) D_L}{X_H D_L + X_L (X_H D_X + X_L D_L)} \tag{1}$$

where X_H and X_L are the volume fractions of the high-Tc parts and low-Tc parts, respectively, and $X_H + X_L = 1$. D_H and D_L are the diffusion coefficients of the solute in the high-Tc parts and low-Tc parts, respectively:

$$D_H = n_H exp(-\Delta E_H / RT) \tag{2}$$

$$D_L = n_L exp(-\Delta E_L / RT) \tag{3}$$

where ΔE_H and ΔE_L are the activation energies of the high-Tc parts and low-Tc parts, respectively ($\Delta E_H > \Delta E_L$). n_H and n_L are the diffusion constants of the high-Tc parts and low-Tc parts, respectively. In the model, the diffusion coefficient increases with increasing temperature.

Because the high-Tc parts are mainly composed of high-sulfur proteins, the disulfide bonds between the proteins form a net-like structure inside the region, which limits the permeation of macromolecules in the high-Tc parts. The critical size of molecules that can penetrate the network structure of the high-Tc parts is 1 nm. When the size of the solute molecule is less than 1 nm, the molecule can diffuse in both the high- and low-Tc parts. When the molecular size is larger than 1 nm, the low-Tc parts are its only diffusion channel [47].

The two-part/two-state model considers the effects of the hair structure and composition, solvent temperature and pH, and hair moisture content on the hair permeation characteristics based on the phase-transition temperatures of the hair components. However, the physicochemical properties of the solute and the hair charge characteristics are not considered, and the effect of the cuticle layer is ignored when calculating the diffusion coefficient of the solute in hair.

4.2. Porous Media Diffusion Model

Inspired by the catalytic action of enzymes in chemical reactions and the adsorption of zeolites, Morel et al. [28] assumed that the hair is porous and the pores are continuously distributed on the hair surface. In their model, the size and shape of the solute are described by the longest edge of the smallest cross-section that can enclose the parallelepiped of the molecule (L_D), and the effects of the solute charge characteristics on the permeation and absorption characteristics are considered. The permeation distances of anionic, cationic, and neutral dyes in hair are calculated based on L_D using Boltzmann sigmoidal theory, and the critical sizes of anionic, cationic, and neutral dyes entering hair are approximately 1.2–1.3, 1.4, and 0.95 nm, respectively.

The model considers the influence of the size, shape, and charge characteristics of the solute on its penetrating properties in hair, and it calculates the permeation distance of the solute in hair. However, due to the limited experimental data of cationic and neutral dyes, the equations for the permeation distances of the two in hair cannot be determined. In addition, the model does not consider the hair composition, and it also does not simulate the dynamic absorption process of the solute in hair.

4.3. Homogeneous Diffusion Model

The homogeneous diffusion model treats a hair as an infinitely long homogeneous cylinder with a radius R. The permeation process of a solute in hair can be described by Fick's diffusion law [44]:

$$\frac{dC}{dt} = \frac{d}{dr}\left(D\frac{dC}{dr}\right) \tag{4}$$

where C is the concentration of the solute in the hair at time t, r is the distance from the center of the hair, and D is the diffusion coefficient of the solute in the hair.

Generally, the data obtained from the solute permeation experiment of hair can be divided into two categories. The first category is data obtained using the concentration difference method (soak the hair in a solvent containing a certain concentration of a certain solute and calculate the amount of solute absorbed by the hair based on the change in the concentration of the solute in the solvent before and after soaking) or extraction method (the solute extracted from soaked hair) to determine solute absorption in hair with absorption time data. The second category is data obtained using spectral imaging or microscopy techniques to obtain experimental data about the concentration distribution of the solute in hair.

For the two types of data, using Equation (4), two types of solutions can be obtained [56]:

(1) The change in absorption of the solute in hair with time:

$$\frac{M_t}{M_\infty} \approx 4\sqrt{\frac{Dt}{\pi R^2}} \qquad \text{Early solute absorption process} \tag{5}$$

$$\frac{M_t}{M_\infty} \approx 1 - 0.692\exp\left(-5.785\frac{Dt}{R^2}\right) \qquad \frac{M_t}{M_\infty} > 0.31 \tag{6}$$

where M_t is the absorption of the solute by hair at time t, and M_∞ is the maximum absorption of the solute when the absorption equilibrium is reached.

Substituting the experimental data (M_t and t) into Equation (5) or (6), the diffusion coefficient of the solute in hair (D) and the maximum equilibrium absorption (M_∞) can be calculated.

(2) The concentration distribution of the solute in hair:

$$D_{(C=C_1)} = -\frac{1}{2t}\frac{dx}{dC}\int_0^{C_1} x\, dC \tag{7}$$

where $D_{(C=C1)}$ is the diffusion coefficient of the solute in the hair when the concentration of the solute in the hair is C_1, and x is the distance from the inside to the surface of the hair.

Substituting the experimental data (C_1, x, and t) into Equation (7), the diffusion coefficient of the solute in the hair (D) can be calculated.

This model mainly relies on experimental data and fits Equations (5)–(7) to obtain the diffusion coefficient and maximum absorption of the solute in the hair. However, the model does not consider the microstructure and composition of the hair, the physicochemical characteristics of the solute, the pH of the solvent, and other factors.

4.4. Heterogeneous Partition and Diffusion Model

Based on Fick's second law, Wang et al. [26] developed an equation for calculating the maximum equilibrium absorption (M_∞) and effective diffusion coefficient (D_e) of solutes in hair based on full consideration of the composition of hair:

$$\frac{M_t}{M_\infty} \approx 1 - exp\left(-2.405^2 \frac{D_e}{R^2}t\right) \tag{8}$$

where M_t and M_∞ are the absorption of the solute in the hair at time t and the balance of absorption, respectively, and D_e is the effective diffusion coefficient of the solute in the hair. Using this equation to process the experimental data, the partition coefficients and effective diffusion coefficients of five tea polyphenols in hair were calculated.

Since hair mainly comprises keratin, fat, and water, the amount of solute absorbed in hair is the sum of solute absorbed in these three parts. Considering the influences of the oil–water partition coefficient, the dissociation constant of the solute, and the solvent pH on the partition coefficient, a quantitative structure–property relationship (QSPR) model of the solute partition in hair/water was developed according to linear free energy theory [64–67]:

$$PC = \theta_k\left[f_{\text{non}} \times 5.72(K_{\text{ow}})^{0.35} + (1 - f_{\text{non}}) \times 1.17(K_{\text{ow}})^{0.0019}\right] + \theta_l \times f_{\text{non}} \times (K_{\text{ow}})^{0.7} + \theta_w \tag{9}$$

where θ_k, θ_l, and θ_w are the volume fractions of keratin, fat, and water in hair, respectively; f_{non} is the mass fraction of the solute that has not dissociated at a specific pH; and K_{ow} is the oil–water partition coefficient of the solute.

Wang et al. [26] hypothesized that the CMC and aqueous phase in hair are the main permeation channels of solutes in hair, the CMC is the limiting factor for permeation of charged ions in hair, and the effective diffusion coefficient of the solute in hair is not only related to the size of the solute molecules but also to the dissociation constant of the solute and its partition coefficient in hair. Based on comprehensive consideration of the above-mentioned influencing factors, they developed a QSPR model of the effective diffusion coefficient of a solute in hair (D_e):

$$\frac{D_e}{D_w} = exp[0.16 \times (f_{non}K_{ow}) - 10.71] \tag{10}$$

where D_w is the diffusion coefficient of the solute in water.

The QSPR models comprehensively consider the influence of hair microstructure and composition, solute oil–water partition coefficient and dissociation constant, and solvent pH, and it can initially realize rapid prediction of the absorption amount and absorption rate of a solute in hair. However, there are also some limitations of this model:

(1) The QSPR model can only predict the partition coefficient and effective diffusion coefficient of a solute in hair, and it cannot predict other parameters, such as the concentration distribution and cumulative absorption amount in the permeation process.

(2) The dataset of this model only includes five anionic solutes and the applicability of cationic and neutral solutes cannot be determined.

(3) The model fails to consider the effect of the charge interaction on the permeation and absorption properties of a solute in hair.

Based on the study by Wang et al. [26], Li et al. [63] studied the influencing mechanisms of the solvent pH, hair charge characteristics, solute charge characteristics, and hydrophobicity on the partition behaviors of porous hair media through absorption equilibrium experiments. Based on the influencing mechanisms of the electrostatic and hydrophobic effects, a QSPR model of hair partition was constructed according to linear free energy theory:

$$
\begin{aligned}
PC_{\mathrm{hair/w}} = 4.07 K_{\mathrm{ow}}{}^{0.41} \Bigg[&f_{\mathrm{neu}} + f_{\mathrm{cat}} \left(\frac{1.13 - 0.09 \times 10^{3.67 - \mathrm{pH}}}{1 + 10^{3.67 - \mathrm{pH}}} \right) \\
&+ f_{\mathrm{ani}} \left(\frac{0.06 + 1.84 \times 10^{3.67 - \mathrm{pH}}}{1 + 10^{3.67 - \mathrm{pH}}} \right) \Bigg]
\end{aligned}
\tag{11}
$$

where $PC_{hair/w}$ is the hair–water partition coefficient of the solute; K_{ow} is the octanol–water partition coefficient of the solute; and f_{neu}, f_{cat}, and f_{ani} are the mass fractions of neutral, cationic, or anionic species of a chemical at a given pH, respectively.

The model comprehensively considers the influencing mechanisms of the hair characteristics (keratin composition, isoelectric point, and net charge ratio), the solute characteristics (hydrophobicity, dissociation, and positive and negative charge mass fractions), and the solvent pH change on the hair-water partition coefficient. Taking 17 neutral, anionic, and cationic solutes as research objects, a total of 90 data in the range of solvent pH 2–8 were collected as model datasets, and the universality and accuracy of the partition coefficient model significantly improved. However, this model has the limitation of not simultaneously considering the influences of the hair permeation channel and solvent temperature.

5. Conclusions

Due to the importance of the permeation and absorption characteristics of hair in the formulations of hair-care products, prevention of water pollution, and risk assessment of environmental exposure, investigation of the permeation, and absorption characteristics of different types of solutes in hair has received increasing attention. However, because of the complexity of hair microstructure and composition, as well as the diversity of factors affecting solute permeation, there is not a unified view of the mechanism of solute permeation in hair. Although the existing models consider the influence of some factors on the process of solute permeation, they still have some limitations. Given the problems in the current research, it is suggested that future research focuses on the following aspects.

(1) The solvent pH is an important factor that affects the permeation and absorption of solutes in hair. Changing the pH will also cause changes in the solute and hair charge characteristics, resulting in attractive or repulsive forces, thereby significantly affecting the absorption rate and amount of solute in the hair. Therefore, studies should be conducted on the permeation and absorption characteristics of a variety of neutral, cationic, and anionic solutes in hair to expand the existing database of diffusion coefficients, and the mechanism of the effect of the charge on the solute permeation process should be discussed in detail. Based on the influence of the charge, the existing diffusion coefficient model should be optimized.

(2) Keratin is the main component of hair, accounting for more than 90% of the dry weight of hair. The binding of a molecule to keratin slows down steady-state permeation of the solute while maintaining the presence of the solute in hair. Therefore, the binding properties of keratin and solutes should be studied to analyze the permeation and absorption mechanism of solutes from a microscopic point of view.

(3) The development process for formulating new products mainly depends on experimental methods, such as the screening of functional solute species and the selection of appropriate product-use conditions. Therefore, a kinetic mechanism model for the permeation and absorption of solutes in hair should be developed. Simulation of the dynamic change of solute absorption in hair will have great theoretical significance for the development and optimization of hair-care formulations.

(4) Existing research on the permeation and absorption properties of hair is mostly limited to using water as the solvent. However, in practical applications, both the product formulation system and the contaminated water system are compound systems. Therefore,

it is of practical importance to study the effects of other solvents with different polarities and mixed solvents on the permeation and absorption properties of solutes in hair.

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