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Wetting Anomalies on Kaolin Particles Highlighting Limits of the Thin-Layer Washburn Technique

Abstract:

The determination of surface free energy and wetting characteristics of powdered minerals remains a methodological challenge due to the inability to apply conventional contact-angle techniques to porous and highly absorbent materials. Kaolin is widely used as a model aluminosilicate system, yet its complex surface chemistry raises questions concerning the applicability of classical approaches such as the Washburn equation. The present study investigates the wetting behaviour of thin kaolin layers using water and cyclohexane, with the aim of evaluating deviations from Washburn-type capillary rise dynamics. A thin-layer wicking method was employed, combining controlled sample preparation, high-resolution video tracking, and statistical analysis of capillary kinetics. The work builds on established research by Chibowski, Newby, Danchenko, Rybka and others, who have highlighted both the utility and the limitations of the Washburn method for powders. The results show that the initial wetting front is strongly non-uniform and influenced by adsorption-driven and inertial effects, while subsequent stages reflect a transition to capillary-controlled motion accompanied by the formation of a diffuse partially saturated region. Despite this heterogeneity, repeated measurements demonstrated high reproducibility, yielding a consistent average capillary rise rate of approximately 4460 $\mu m^2/s$ for water. However, a pronounced divergence from theoretical predictions was observed: cyclohexane permeated the kaolin layer significantly faster than water, contradicting Washburn-based expectations derived from assumed contact angles. These findings indicate that the classical Washburn model does not adequately describe wetting in kaolin layers and suggest that additional factors — such as ionic interactions, partial pore saturation, or dissolved-gas effects — may govern the observed anomalies. The study thus defines clear limitations of the thin-layer Washburn technique and outlines directions for refining wetting analysis in complex mineral powders.

Keywords: kaolin, wetting, contact angle, hydrophilic, Washburn equation.

Introduction

It is well established that surface free energy represents the effective potential governing how dispersed solids interact with liquids, gases, or foreign bodies, serving as a quantitative measure of interfacial reactivity (*Danchenko et al., 2018*). Although numerous techniques for flat surfaces—such as the sessile drop, Wilhelmy plate, or du Noüy ring methods—are based on contact angle measurements (*Kwak et al., 2018*; *De Farias et al., 2025*), they cannot be applied to powders (*Alghunaim et al., 2015*). Thus, reliable determination of surface free energy for particulate materials remains a significant challenge (*Kirdponpattara et al., 2013*).

For powders undergoing mechanical treatment, surface reactions, oxidation, or hydrophobization, such measurements become particularly important. However, adapting flat-surface methods—e.g., sessile-drop analysis on compressed powder beds—is usually infeasible, as droplets are immediately absorbed by the porous structure, preventing equilibrium contact angle formation.

Since the 1950s, the Washburn method has been widely used to address this issue. A porous body formed from powder—either on a thin plate or within a narrow capillary—is successively wetted with a nonpolar liquid such as diiodomethane or hexane and with water (*Chibowski & Holysz, 1992*). The Washburn equation relates the squared penetration height to time, allowing estimation of contact angles when corrected for liquid viscosity and surface tension (*Myronyuk et al., 2020*).

For materials such as quartz or silica, contact angles obtained by the Washburn technique match those measured on equivalent flat surfaces, supporting its validity for simple systems. However, other studies show deviations for silicate-based materials, indicating that the method does not universally apply to more complex chemistries or morphologies.

In particular, preliminary results by the authors revealed similar limitations for dispersed kaolin. The present work was therefore designed to demonstrate systematic deviations from the classical Washburn prediction when kaolin is wetted by the commonly used probe liquids, water and cyclohexane.

The present investigation focuses on the wetting behaviour of kaolin in a thin-layer configuration using water and cyclohexane.

The object of study is the wetting behaviour of kaolin powder layers—specifically, how liquids penetrate and interact with kaolin surfaces under capillary conditions modelled by the Washburn equation.

The principal subject of analysis is the deviation of the experimentally observed wetting dynamics from those predicted by the Washburn equation.

The study aims to critically evaluate the applicability and limitations of the classical Washburn equation for describing capillary rise and wetting kinetics in kaolin-based systems. The study seeks to identify and explain the observed deviations between theoretical predictions and experimental measurements obtained via thin-layer wicking experiments.

According to the purpose, following tasks are set:

- fabricate and characterise thin kaolin layers suitable for reproducible wicking experiments with both polar (water) and non-polar (cyclohexane) liquids.
- measure and statistically analyse capillary rise kinetics using a calibrated video-based system to ensure methodological precision;

- compare experimentally determined wetting rates with those predicted by the classical Washburn model;
- identify potential physicochemical factors (ionic interactions, partial pore saturation, evaporation effects, gas retention) that may cause observed deviations;
- determine the methodological boundaries of the Washburn approach when applied to complex aluminosilicate materials such as kaolin.

To this end, thin-layer kaolin plates were fabricated to enable repeated measurements in different media. A calibrated video-based procedure was developed to track capillary infiltration, and statistical datasets were obtained for water and hexane.

The results consistently show departures from Washburn behavior, confirming that the method is significantly limited for this aluminosilicate powder.

Materials and Methods

In the study to create the thin layer of powders the approach was used. The kaolin powder was obtained from a local supplier (KC-1 of Ukraine kaolin company), dried in oven for 5 h at 105°C and cooled. The slurry for coating was formed by taking 5 g of dry kaoline and 95 g of water, mixing powder with water with slow speed stirrer, disparaged with laboratory high-speed blender for 3 min and poured into the microscopic laboratory glasses. The poured slurry was left to dry overnight and the obtained uniform layer was additionally dried for 6 h at 105°C, then the layer was vertically segmented to obtain straight lines from the kaoline powder on the glass by remove of the layers' fraction with blade. The setup of wetting speed measurement includes the microscope UCMOS 1300 digital camera, optical tube and the probe liquid inside the transparent cuvette. Depending on the measurement either water of the cyclohexane was used. At the start of measurement, the microscopic glass mounted in the holder was immersed into the liquid. The wicking layer started to move upwards and from this moment the recording was started and kept at 20 fps rate for 20 sec for each sample. The video files then were analysed with Toup View software, that was calibrated to identify precisely an object scale and the frame duration. The measurement was kept from the line of wetting to the highest point of the wetting front in several points of the sample. The real ratio of h^2/m was calculated basing on the average of 4–6 experimental results using the ANOVA analysis tool built in Origin software.

Literature Review

The determination of surface free energy and wettability parameters for powdered materials remains a significant methodological challenge in surface science. Traditional contact-angle measurement techniques, such as the sessile drop, Wilhelmy plate, or du Noüy ring methods, are applicable to smooth, impermeable surfaces but cannot be reliably used for porous or particulate media, where immediate absorption prevents equilibrium contact formation (*Kwak et al., 2018*; *De Farias et al., 2025*). Consequently, researchers have developed alternative approaches capable of describing the interaction between liquids and heterogeneous solids, among which the Washburn capillary rise method has gained particular prominence. By relating the square of penetration height to time under controlled conditions, this technique offers an indirect yet practical way to estimate surface free energy and contact angles in powders (*Alghunaim et al., 2015*).

The Washburn equation assumes uniform cylindrical capillaries, constant fluid properties, and ideal wetting behaviour governed solely by capillary forces. Early studies demonstrated its validity for homogeneous materials such as quartz and silica, where the experimentally obtained contact angles closely matched theoretical predictions (*Chibowski & Holysz, 1992*). However, later investigations revealed that deviations from the ideal model become significant for systems with irregular pore structures, mixed wettability, or complex surface chemistries. In such cases, the linear relation between squared penetration height and time begins to fail, indicating that other processes—adsorption, partial saturation, or evaporation—affect the infiltration dynamics.

A growing body of work has therefore focused on quantifying and interpreting these discrepancies. Kirdponpattara, Phisalaphong, and Newby (*2013*) demonstrated that the Washburn method systematically overestimates contact angles for fibrous and granular materials due to dynamic effects at the wetting front. Similarly, Danchenko et al. (*2018*) designed an automated system for measuring surface energy in epoxy composites and reported that results obtained through classical Washburn analysis must be corrected for material-specific characteristics. Myronyuk, Baklan, and Nudchenko (*2020*) further showed that the Owens–Wendt theory, when combined with experimental data, allows a more accurate evaluation of surface energy for dispersed aluminium oxide, illustrating the need for hybrid models that bridge theoretical and empirical approaches.

Experimental observations of capillary rise often reveal phenomena that contradict the assumptions underlying the Washburn model. Tullis and Wright (*2007*) observed three-dimensional instabilities in wetting fronts propagating through granular media, while Benner and Petsev (*2017*) demonstrated that evaporation can create diffuse, partially saturated regions that alter the apparent rise rate. Mampallil et al. (*2018*) described how inertial effects, adsorption, and surface heterogeneity contribute to transient deviations from classical capillary behaviour, producing complex patterns of liquid advance similar to those detected in kaolin layers. These studies collectively suggest that the dynamics of wetting are governed not only by capillary pressure and viscosity but also by physicochemical factors intrinsic to the solid matrix.

Kaolin serves as a particularly illustrative model for studying such effects. As a layered aluminosilicate mineral, it exhibits high surface heterogeneity, hydrophilicity, and pronounced ionic activity. The surface hydroxyl groups of kaolin participate in hydrogen bonding and electrostatic interactions with both polar and non-polar liquids, significantly affecting interfacial energy and adsorption capacity. Kwaśniewska et al. (*2020*) demonstrated that kaolin additives can substantially modify the mechanical and structural properties of polymer matrices, underscoring its strong interfacial reactivity. When subjected to capillary infiltration, these same properties yield complex wetting patterns that diverge from classical Washburn predictions.

The literature therefore converges on a consistent conclusion: while the Washburn equation remains an essential analytical tool, its straightforward application to complex mineral powders such as kaolin is limited. The assumptions of uniform capillary geometry and constant contact angle do not adequately represent systems with variable pore sizes, surface heterogeneity, or competing adsorption phenomena. The discrepancies reported in recent studies cannot be dismissed as experimental artefacts; rather, they point to fundamental physicochemical processes—ionic interactions, gas retention, partial pore saturation, and surface restructuring—that must be incorporated into revised models. Accordingly, the refinement of the Washburn approach through integrated experimental and theoretical methods represents a promising direction for advancing the characterisation of wetting and surface energy in heterogeneous mineral systems.

Results

At the onset of wetting of a kaolin particle layer, the infiltrating liquid fills the interparticle pores, leading to a change in the optical transparency of the layer. This transparency variation enables visual tracking of the height to which the wetting front rises and the rate at which it propagates.

In Figure 1 (*Appendix*), it can be observed that the wetting front begins to advance from the top downward. This motion is distinctly non-uniform, as it was previously pointed out in the work of B.P. Tullis and S.J. Wright (*2007*). Along the entire length of the wetting front shown in Figure 1a, two pronounced protrusions appear on the left and right sides, whereas the central region forms a depression. This pattern corresponds to the initial stage of wetting, during which the process is governed primarily by adsorption phenomena. The front is inertial, as its shape is also influenced by the velocity at which the substrate enters the wetting liquid. As a result, the non-uniformity of the wetting front is highly evident at this stage and cannot be compensated rapidly.

However, after a certain period of time, the wetting rate begins to decrease. This slowdown is partly attributable to gravitational forces and partly to the progressive homogenisation of the wetting process (*Mampallil et al., 2018*). At this stage, inertial effects no longer dominate; instead, capillary forces govern the motion of the liquid front. As illustrated in Figure 1D, the wetting front becomes more uniform over time. Additionally, the boundary of this front becomes increasingly diffuse.

This diffuse boundary is a noteworthy phenomenon. It arises because liquid evaporation occurs directly from the advancing front. As a result, there exists a transitional region in which the pores are not fully saturated with liquid, yet they contain a measurable amount of adsorbed moisture deposited during evaporation (*Benner et al., 2017*). This effect is more distinctly visible in Figure 1C.

Figure 1 clearly demonstrates that the wetting rate varies considerably across different regions of the sample. Therefore, when comparing the wetting kinetics of different liquids, it is reasonable to measure the rise velocity at a single, well-defined point on the specimen. This observation also raises questions regarding the overall reproducibility of such measurements.

To evaluate and illustrate this reproducibility, we performed nine independent measurements of the capillary rise kinetics of water in different locations of the same kaolin layer. The resulting kinetic curves are presented in Figure 2 (*Appendix*).

The results presented in Figure 2 are rather unexpected. They show that the slope of the main kinetic dependence—not at the initial moment of wetting, but within the interval from approximately 5 to 20 seconds, and in some cases even longer—remains effectively constant. This behaviour is particularly evident when the data are plotted in the coordinates $h^2 = f(t)$. Under these conditions, the capillary rise of water proceeds at a constant rate.

From these measurements, an average capillary rise velocity of approximately 4460 μm²/s can be derived for water. This value is consistently reproduced across a broad range of measurement points within the same sample.

Thus, the method demonstrates sufficiently high reproducibility, provided that an appropriate level of statistical processing is applied and an adequate number of repeated measurements are performed. We then proceed to examine whether the experimentally obtained average imbibition rates for the polar liquid (water) and the nonpolar liquid (hexane) correspond to the values predicted by the Washburn equation.

To estimate the expected velocities using the Washburn model, we assumed a water–kaolin contact angle of approximately 45°C (*Kwaśniewska et al., 2020*). Based on this assumption, the theoretical wetting curves were calculated, and these predicted dependencies are presented in Figure 3a.

In Figure 3a (*Appendix*), it is clearly seen that the predicted wetting rate of kaolin by water should exceed that of cyclohexane. This expectation is reasonable, given that a polar solid is anticipated to exhibit stronger affinity toward a polar liquid. However, the experimental results shown in Figure 3b (*Appendix*) reveal the opposite trend: cyclohexane wets the kaolin layer considerably faster than water.

One could suggest that the discrepancy arises from the initial assumptions—namely, that the kaolin–water contact angle is approximately 45°C, whereas the hypothetical contact angle for hexane might be as low as ~3° or even less. It is also possible that kaolin is more hydrophilic than assumed, which would shift the expected water curve upward. Yet, the more hydrophilic the kaolin surface is, the higher the predicted water wetting curve should lie. Consequently, even for a strongly hydrophilic kaolin surface, the trend observed experimentally in Figure 3b cannot be reconciled with the prediction of the Washburn equation.

Discussion

The experimental results obtained in this study deviate markedly from the behavior predicted by the Washburn equation. Moreover, the measurements were performed with sufficient statistical rigor, including a substantial number of repetitions, to ensure the reliability of the observed trends. Consequently, the discrepancy between the experimentally measured values and those forecasted by the Washburn model cannot be attributed to statistical uncertainty, as it lies well beyond the limits of experimental error.

The results of this study leave unresolved the question of whether the Washburn equation can be reliably applied to predict the wetting behavior of materials with complex surface architectures, such as kaolin, including the estimation of their specific surface energy and contact angle. Additionally, the underlying origin of the pronounced discrepancy between the theoretical predictions and the experimental observations remains unclear and warrants further investigation.

Only by addressing these two key questions can the actual limits of applicability of the Washburn equation to different mineral systems be determined. At the same time, the very factors responsible for the deviation from the theoretical model represent a valuable subject of study in their own right. These deviations provide important insights into the physicochemical nature of such materials when examined through the Washburn method and the technique of thin-layer capillary rise.

For example, if the source of such deviations is the ionic character of the material—i.e., its ability to retain water through specific association mechanisms—then this very property could be probed and quantified using the thin-layer capillary rise method.

Conclusion

The present study systematically investigated the wetting behaviour of thin kaolin layers using water and cyclohexane as probe liquids, with particular attention to the applicability and limitations of the classical Washburn equation for such mineral systems. The experimental analysis demonstrated that the initial stage of wetting is strongly non-uniform and dominated by adsorption and inertial effects, as manifested by irregular propagation of the wetting front. As the process progresses, capillary forces become the prevailing driving mechanism, resulting in gradual homogenization of the wetting profile and the appearance of a diffuse transition zone attributed to liquid evaporation and partial pore saturation.

Repeated measurements of the capillary rise kinetics revealed that, despite the local non-uniformities of the wetting front, the method exhibits high reproducibility when adequate statistical treatment is applied. The experimentally observed linearity of the $h^2 = f(t)$ dependence within defined time intervals enabled estimation of an average capillary rise velocity of approximately 4460 $\mu m^2/s$ for water. This value was consistently reproduced across multiple locations on the same kaolin layer, confirming that the thin-layer method can reliably provide kinetic parameters.

However, a major outcome of this work is the discovery of a pronounced discrepancy between the experimentally determined wetting rates and those predicted by the Washburn equation. According to the theoretical model, water—due to higher polarity and expected stronger affinity to kaolin—should exhibit faster infiltration than cyclohexane. In contrast, the experiments revealed the opposite behavior: cyclohexane permeated the kaolin layer significantly more rapidly. Attempts to reconcile this discrepancy through variations in assumed contact angles or increased kaolin hydrophilicity remained insufficient, demonstrating that the classical Washburn framework does not capture the actual dynamics for this material.

These findings raise two fundamental issues: (1) whether the Washburn equation is appropriate for estimating surface energy and contact angles of minerals with complex physicochemical characteristics such as epokaolin, and (2) what specific material properties or interfacial phenomena give rise to the observed deviations. Potential contributing factors include ionic interactions, water retention via specific adsorption, pore blocking by dissolved gases, or changes in surface hydrophobicity following exposure to organic liquids. Each of these mechanisms represents a promising direction for further research and may itself be quantifiable through refined thin-layer capillary rise measurements.

Overall, the study highlights that while thin-layer wicking experiments offer high reproducibility and valuable kinetic insights, the Washburn equation should be applied to kaolin and similar minerals with considerable caution. The deviations observed are not random artifacts but systematic effects intrinsic to the material's interfacial behavior. Understanding these deviations provides a pathway to expanding the method's diagnostic capabilities and refining theoretical models for predicting wetting in complex porous mineral systems.

References:

Alghunaim, A., Kirdponpattara, S., & Newby, B. Z. (2015). Techniques for determining contact angle and wettability of powders. *Powder Technology*, *287*, 201–215. https://doi.org/10.1016/j.powtec.2015.10.002

Benner, E. M., & Petsev, D. N. (2017). Evaporation effect on two-dimensional wicking in porous media. *Journal of Colloid and Interface Science*, *514*, 21–29. https://doi.org/10.1016/j.jcis.2017.12.004

Chibowski, E., & Holysz, L. (1992). Use of the Washburn equation for surface free energy determination. *Langmuir*, *8*(2), 710–716. https://doi.org/10.1021/la00038a066

Danchenko, Y., Andronov, V., Teslenko, M., Permiakov, V., Rybka, E., Meleshchenko, R., & Kosse, A. (2018). Study of the free surface energy of epoxy composites using an automated measurement system. *Eastern-European Journal of Enterprise Technologies*, *1*(12(91)), 9–17. https://doi.org/10.15587/1729-4061.2018.120998

De Farias, E. C. C., Fermam, R. K. S., & De J Souza Marques De Mendonça, A. (2025). Comparison between the Wilhelmy surface tension measurement method and the pendant drop shape analysis method. *Acta Polytechnica*, *65*(3), 276–281. https://doi.org/10.14311/ap.2025.65.0276

Kirdponpattara, S., Phisalaphong, M., & Newby, B. Z. (2013). Applicability of Washburn capillary rise for determining contact angles of powders/porous materials. *Journal of Colloid and Interface Science*, *397*, 169–176. https://doi.org/10.1016/j.jcis.2013.01.033

Kwak, W., Park, J. K., Yoon, J., Lee, S., & Hwang, W. (2018). Measurement of surface tension by sessile drop tensiometer with superoleophobic surface. *Applied Physics Letters*, *112*(12). https://doi.org/10.1063/1.5011439

Kwaśniewska, A., Chocyk, D., Gładyszewski, G., Borc, J., Świetlicki, M., & Gładyszewska, B. (2020). The influence of kaolin clay on the mechanical properties and structure of thermoplastic starch films. *Polymers*, *12*(1), 73. https://doi.org/10.3390/polym12010073

Mampallil, D., Sharma, M., Sen, A., & Sinha, S. (2018). Beyond the coffee-ring effect: Pattern formation by wetting and spreading of drops. *Physical Review. E*, *98*(4). https://doi.org/10.1103/physreve.98.043107

Myronyuk, O., Baklan, D., & Nudchenko, L. (2020). Evaluation of the surface energy of dispersed aluminium oxide using owens-wendt theory. *Technology Audit and Production Reserves*, *2*(1(52)), 25–27. https://doi.org/10.15587/2312-8372.2020.200756

Tullis, B. P., & Wright, S. J. (2007). Wetting front instabilities: a three-dimensional experimental investigation. *Transport in Porous Media*, *70*(3), 335–353. https://doi.org/10.1007/s11242-007-9103-x

Appendix

a b c

Figure 1. Tracking images of kaolin layer wetting with cyclohexane: (a) initial stage, (b) slow down to uniform speed; (c) diffuse wetting

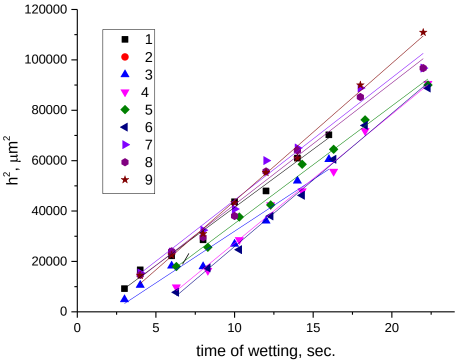
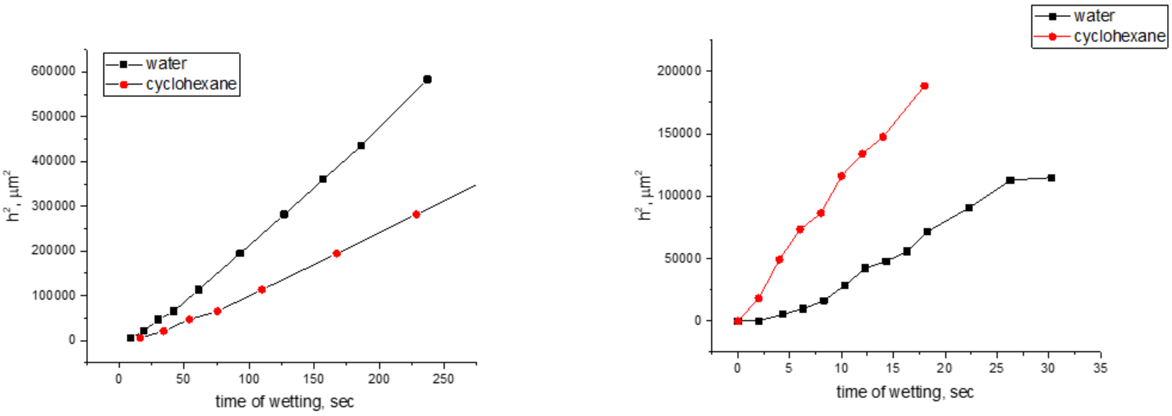


Figure 2. Wetting kinetics of kaolin layer (water as a probe liquid)



a b

Figure 3. Wetting kinetics of water/hexane: (a) predicted with Washburn equation for kaolin surface, (b) obtained experimentally