

Letters

Historical Scientific Literature and the Spreading of Oil on Water

Marcos Gugliotti, in his recent article (1), discusses Benjamin Franklin's 1774 observations concerning the spreading of oil on the surface of water. One of Gugliotti's main points is that using historical scientific literature in the modern classroom has certain advantages: Students can see how principles now taken for granted were originally established, and they can appreciate the historical continuity of scientific exploration and progress. However, there are drawbacks as well. Older articles sometimes feature prose that is difficult to decipher, terminology that is no longer in use, or figures and data that are presented in ways difficult for modern scientists to follow. Grappling with these issues through the lens that Gugliotti applies to Franklin's 18th century article is an informative exercise and raises two interesting questions: How can a modern reader of historical literature be led astray, and why does certain terminology become obsolete?

In his 1774 article, Franklin observed that "when [a drop of oil] is put on water it spreads instantly...as if mutual repulsion between its particles took place as soon as it touched the water". Gugliotti argues that Franklin, with his "repulsion between particles" explanation, "took the right direction towards another impressive conclusion". Citing Irving Langmuir's famous 1917 *JACS* article (2), Gugliotti writes that "the repulsion between surfactant molecules on the water surface that leads to the spreading of a film is due to the secondary valence of atoms of the polar head group of the molecules....This explains not only why ionic surfactants spread on the water surface (in this case due to primary valence too), but also why nonionic surfactants do it."

I found Gugliotti's explanation confusing in two ways: First, it is unlikely that nonionic surfactant molecules would repel each other and second, the exact meaning of the outdated terms primary versus secondary valence was not clear to me. With the encouragement of Gugliotti, I consulted Langmuir's classic 1917 article¹ (2). Langmuir explains the spreading of oleic acid on water thusly: "[the charged carboxylate head group] portion of the oil² molecule is attracted to the water, while the [non-polar hydrocarbon chain] remainder is more attracted to other oil molecule [chains] than to the water" (2, p 1863). Note that Langmuir does not invoke repulsion among molecules, but attraction, between head groups and water and among hydrocarbon chains. Although to Franklin the oil spreading on water behaved "as if mutual repulsion between its particles took place", Langmuir and others have shown that the spreading is due to the maximization of attractive forces, rather than the minimization of repulsion. Charles Tanford, in his book³ *Ben Franklin Stilled the Waves* (4), devoted a chapter to this problem of repulsion versus attraction. Tanford argued that although 18th century scientists lacked the molecular knowledge necessary to choose between repulsion and attraction, Franklin's invocation of repulsion was "internally inconsistent": His observation of the cohesiveness of a drop of oil on a solid surface shows that oil molecules do not repel, but attract one another. The misuse of repulsion in explanations of hydrophobicity was also recently discussed by Goss and Schwarzenbach in this *Journal* (5).

As for secondary and primary valence, these vague terms

were employed by Langmuir, Werner, and others to describe a wide variety of interactions. Most of these interactions had nothing to do with the primary valence value assigned to an element based on its group in the periodic table. As Smith has argued in this *Journal* (6), this is why these valency terms, "whose definition has been the source of much confusion since they were introduced—were superseded [by terms currently in common usage]....Werner's terminology should by now be regarded as of purely historic interest." For a detailed discussion of the historical complexities of the secondary or auxiliary valence concept, see the monograph by Russell (7). Regarding the spreading of oil on water, Langmuir's use of secondary valence refers to what we would now call the hydrogen bonding that occurs between a surfactant's polar head group and surface water molecules. These interactions, similar to most intermolecular forces, are attractive, not repulsive.

The pedagogical use of historical scientific literature has its advantages and its drawbacks. The advantages include the many tie-ins that Gugliotti was able to make between Franklin's marvelous observations in a 1774 article and the work of scientists who came before and after him, for example, Democritus, Pliny, Newton, Dalton, Avogadro, Rayleigh, and Langmuir. The disadvantages include misreadings (repulsion vs attraction) and obsolete terminology (primary and secondary valence) that appear now and again. Needless to say, teachers must be aware of these potential pitfalls as they plan their classroom discussions.

Acknowledgments

I wish to thank Marcos Gugliotti as well as the other two reviewers of this letter; their suggestions were greatly appreciated and served to improve this piece.

Notes

1. This article was a major part of Langmuir's citation for the 1932 Nobel Prize in Chemistry. Langmuir showed that molecular size and shape could be determined with remarkably simple tools. "To this day, his set of experiments remains one of the simplest and most elegant demonstrations of the reality and properties of molecules" (3).

2. Langmuir's reference to oleic acid as an "oil" differs from modern usage of the term.

3. Gugliotti based a portion of his article (1) on Tanford's book (4), citing it as ref 13.

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Response to Historical Scientific Literature and the Spreading of Oil on Water

While observing the spreading of oil on water, Benjamin Franklin (1) stated: "It seems as if a mutual repulsion between its particles took place as soon as it touched the water." Later, Langmuir (2) concluded that the cause of spreading of oils (fatty acids) is the affinity of the polar head groups (PHGs) of the molecules for water, which "is due to the strong secondary valence" of atoms in the PHGs. In my article (3), I compared Franklin's observations with Langmuir's conclusions and wrote: "According to Langmuir, the repulsion between surfactant molecules...that leads to the spreading of a film is due to the secondary valence". I also stated that secondary valence explains the spreading of nonionic surfactants and that for ionic ones primary valence is important too. In his letter (4), Silverstein finds my statements confusing, probably because of the use of the word "repulsion" in connection to attractive forces such as primary and secondary valences, but I hope the following explanations can avoid any confusion.

Surfactants spread on water as a film because of attraction of their PHGs for water (2). For nonionic surfactants, this attraction is due to secondary (residual) valence, while for ionic surfactants it is due to both primary and secondary valences. The electrostatic repulsion among ionic PHGs also contributes to spreading, whereas a steric repulsion due to hydration of the PHGs can influence both charged and uncharged films (5). Langmuir's theory is based on attraction between PHGs and water molecules and not on repulsion. However, according to Tanford (6, cited in my article as ref 13), Franklin's observation "contains the uncomfortable word repulsion", but "The trouble with this statement, however, is not that it invokes a repulsion force." Thus, Franklin's usage of "repulsion" was not accurate, but his observation was remarkable, and I still think "he took the right direction". Accordingly, my usage of that word may sound as a wrong interpretation of previous articles (1, 2), but it should not be understood this way, for it was used to link Franklin's to Langmuir's explanations, and to me it was not a fatal flaw. Besides, I disagree on many points in Silverstein's letter (4), which are commented below.

In no part of my article (3) did I state that primary or secondary valences are repulsive forces or that nonionic molecules repel each other. To me, Langmuir's usage of the word oil as a reference to fatty acids is acceptable, and his explanations on primary and secondary valences are clear (2), so it is not necessary

to reproduce them here. Langmuir's definitions of such terms were based on Werner's concepts (7), and if this terminology is not clear to Silverstein I encourage him to check other sources. Hydrogen bonding may be one kind of manifestation of secondary valence, but this discussion as well as the possible confusion involving the valence terms are not the subject of my article. The expression "internally inconsistent" used by Tanford in his book (6) was related to the spreading on solids, but I believe Silverstein misread that passage or maybe he is not familiar with surface phenomena, as suggested by a previous letter (8).

Langmuir's article (2) is the basis of the Nobel Prize in Chemistry he received in 1932. To me, Langmuir made proper use of the valence concepts, for he knew them well. In fact, Langmuir defined covalence and electrovalence; he introduced the concept of isosterism and formulated the electroneutrality principle; and he is a co-author of the "octet rule" and coined terms such as covalent bond and polar union, nowadays called ionic bond (9). Unfortunately, the only citation for Langmuir in chemistry textbooks is related to his adsorption isotherm. For these and other reasons, I believe it is useful to discuss historical articles with students and also to cite them, thus giving the pioneers the proper credit.

Finally, I believe Silverstein misinterpreted my explanations and misread or did not correctly check the references cited in my article (3). Some points raised by him are not the subject of my article, and he did not answer the questions that motivated his communication ("How can a modern reader of historical literature be led astray, and why does certain terminology become obsolete?"), but unfortunately the two reviewers he thanks in his letter (4) did not realize that.

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