The Real Reason Why Oil and Water Don’t Mix

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Background

Most introductory chemistry textbooks include in their discussion of solubility and miscibility the famous rule of thumb, “like dissolves like”. The converse of this rule, that nonpolar solutes are insoluble in polar solvents, is often referred to as the hydrophobic effect. This effect forms the basis for many important chemical phenomena: the cleaning action of soaps and detergents, the influence of surfactants on surface tension, the formation of biological membranes, and the stabilization of protein structure are all based in large part on the hydrophobicity of nonpolar groups. In their explanation of the hydrophobic effect, introductory chemistry textbooks often rely primarily on the concepts of enthalpy and intermolecular forces. Because the solution process is generally discussed after enthalpy, but before entropy or free energy, authors are left with little choice but to emphasize enthalpy over entropy when explaining the thermodynamic basis of “like dissolves like” and the hydrophobic effect.

For example, one text states that octane and carbon tetrachloride are miscible because the nonpolar molecules are both “held together in the liquid phase by weak dispersion forces” and thus “are attracted to one another”. However, for the very reason that both molecules experience similar intermolecular forces, ΔH of mixing should be close to zero. These molecules are thus not “attracted” to one another in the normal enthalpic sense of the word, but rather in an entropic sense. Spontaneous mixing of the two phases is driven *not* by enthalpy, but by entropy.

Regarding the immiscibility of octane and water, another text states that “the value of the overall enthalpy change, $\Delta H_{\text{solution}}$, is likely to be positive, reflecting an endothermic process. In large part, it is for this reason that polar and nonpolar liquids do not mix well.” In the legend of an accompanying figure, this text offers the most common (incorrect) explanation as to why oil and water don’t mix: “The weak intermolecular interactions between the nonpolar molecules and water cannot overcome the very strong forces between water molecules and allow them to be miscible with water.” Another version of this explanation appeared in a recent overhead projector demonstration in this *Journal*, entitled “Why Don’t Water and Oil Mix?” The authors stated the argument this way: “The water molecules are attracted to each other through hydrogen bonding…resulting in the expulsion of the nonpolar oil molecules into a separate layer”. They go on to describe an overhead projector demonstration using magnetic stir bars to simulate the water–water attraction and marbles to simulate nonpolar solutes. Once again, the problem here is the stress these authors place on enthalpy and hydrogen bonding, while omitting any reference to the importance of entropic effects.

This issue has in fact surfaced in the pages of this *Journal* in the past. In a brief note published in 1994, Alger (*2*) pointed out that many organic chemistry textbooks offer the same incorrect explanation for the immiscibility of water and organic liquids. Huque (*3*), writing in this *Journal* in 1989, provided a detailed thermodynamic, statistical-mechanical analysis of the hydrophobic effect. Somehow the ideas stressed in these papers and many others have been largely overlooked in introductory and organic chemistry textbooks.[1] In this paper I will describe the scope of the problem, present thermodynamic data along with a generally accepted model that explains the hydrophobic effect, and recommend how textbook authors should approach the problem.

Discussion

First consider the discussion of the immiscibility of octane and water quoted above. The choice of octane as solute is fortuitous because dissolving octane in water is, as these authors propose, slightly endothermic. However, this is not the main reason why octane does not spontaneously dissolve in water. In fact, dissolving smaller hydrocarbons such as ethane, propane, butane, and pentane in water is actually an *exothermic* process (see Table 1). Even for hexane, benzene, toluene, and xylene, $\Delta H_{\text{solution}}$ is close to zero.

What then is the *correct* explanation for the hydrophobic effect? Consider hexane and water: they are immiscible, yet $\Delta H_{\text{solution}}$ is about zero (see Table 1). The reason for the immiscibility must therefore be entropic and not enthalpic. Seidell’s thermodynamic data (*4*) showing the enthalpy of solution for most organic liquids in water to be negative[2] were already available in 1941. In the 1940s, Butler (*5*) and Frank and Evans (*6*) were the first to point out the importance of increased order in the aqueous phase in explaining the hydrophobic effect. Later, Klotz (*7*), Kauzmann (*8*), Nemethy and Scheraga (*9*), and Tanford (*10*) developed further Frank and Evans’s entropic model. Tanford in particular performed a series of experiments in which he measured changes in enthalpy, entropy, and free energy upon transferring nonpolar solutes from organic to aqueous solvent phases. The data collected in Table 1 clearly show that the thermodynamic barrier to the solution process is entropic rather than enthalpic.

How can we explain this? How is it that $\Delta H_{\text{solution}}$ is zero for dissolving hexane in water (Table 1)? Is it not true that in order to introduce a hexane molecule into bulk solvent, water–water hydrogen bonds must first be broken to create a cavity (*11*), after which the solute molecule may be inserted and allowed to interact with surrounding solvent? For this simple series of steps the entropy should be positive (due to phase mixing) and the enthalpy should also be positive (because the broken hydrogen bonds are much stronger than the newly formed dipole-induced dipole interactions). However, the process does not stop there.

What happens after the nonpolar solute is placed in the aqueous solvent cavity is clearly explained in most modern biochemistry textbooks, especially those devoted to biological membranes (*12–18*). If ΔH is zero for dissolving hexane in water, then after the solvent cavity forms, strong attractive interactions must be created to counterbalance the positive enthalpy of water–water hydrogen bond breaking. Furthermore, if the process is endergonic and ΔH is zero, then ΔS must be negative. Both of these facts may be explained if one considers the change in structure that takes place in the water “cage” surrounding the solute molecule. Water

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Table 1. Thermodynamic Functions for Transferring Nonpolar Solutes at 25 °C from Organic Solvent to Water

Solute	Solvent	ΔH	$-T\Delta S$	ΔG^a	ΔG^b	ref
CH_4	CCl_4	−10.5	+22.6	+12.1		*28*
CH_4	C_6H_6	−11.7	+22.6	+10.9		*28*
CH_4	ether	−10.0	+23.7	+13.8		*3*
CH_4	cyclohexane	−10.0	+17.6	+7.6		*3*
CH_4	1,4-dioxane	−11.9	+17.9	+6.0		*3*
CH_4	CH_3OH	−8.0	+14.7	+6.7		*3*
CH_4	C_2H_5OH	−8.2	+14.9	+6.7		*3*
C_2H_6	CCl_4	−7.5	+23.7	+16.2	+15.9	*16*
C_2H_6	CCl_4	−7.1	+22.4	+15.3	+15.5	*3*
C_2H_6	C_6H_6	−9.2	+24.9	+15.7	+15.1	*16*
C_2H_6	C_2H_6	−10.5	+26.2	+15.7	+16.3	*16*
C_2H_4	C_6H_6	−6.7	+18.8	+12.1		*28*
C_2H_2	C_6H_6	−0.8	+8.8	+8.0		*28*
C_3H_8	C_3H_8	−7.1	+27.4	+20.3	+20.5	*16*
C_3H_8	C_3H_8	−7.5	+28.7	+21.2		*3*
C_4H_{10}	C_4H_{10}	−3.3	+28.7	+25.3	+24.7	*16*
C_4H_{10}	C_4H_{10}	−4.2	+28.7	+24.5		*3*
C_5H_{12}	C_5H_{12}	−2.1	+31.2	+29.1	+28.7	*16*
C_6H_{14}	C_6H_{14}	0.0	+28.4	+28.4	+28.4	*16*
C_6H_6	C_6H_6	+2.1	+17.5	+19.6	+19.3	*16*
C_6H_6	C_6H_6	0.0	+17.2	+17.2		*28*
C_6H_6	C_6H_6	0.0	+17.0	+17.0		*3*
$C_6H_5CH_3$	$C_6H_5CH_3$	+1.7	+21.2	+22.9	+22.6	*16*
$C_6H_5CH_3$	$C_6H_5CH_3$	0.0	+20.0	+20.0		*28*
$C_6H_5CH_3$	$C_6H_5CH_3$	0.0	+19.5	+19.5		*3*
$C_6H_5C_2H_5$	$C_6H_5C_2H_5$	+2.0	+23.7	+25.7	+25.9	*16*
$C_6H_5C_2H_5$	$C_6H_5C_2H_5$	0.0	+23.1	+23.1		*3*
$C_6H_5C_3H_7$	$C_6H_5C_3H_7$	+2.3	+26.2	+28.5	+28.9	*16*
m- or *p*-xylene	xylene	0.0	+24.3	+24.3		*3*

Note: All thermodynamic data are in units of kJ/mol.

[a] Calculated from experimental values of ΔH and ΔS.

[b] Measured experimentally.

molecules at the surface of the aqueous cavity may compensate for their broken hydrogen bonds by making extra hydrogen bonds with nearest neighbors. The resulting structure is often visualized as an icelike clathrate hydrate "in which water provides a hydrogen-bonded framework that contains holes…occupied by solute molecules. The framework resembles ice in the sense that every water molecule is hydrogen-bonded to four other water molecules, but the…geometry of ice is somewhat distorted…[which] gives rise to the types of cavity structures" (*3*, but see discussion below for alternative model).

From this description it is easy to see that the newly made hydrogen bonds in the icelike clathrate structure compensate for the H-bonds that were broken initially to make the cavity; hence ΔH could be zero or even negative. Furthermore, because of the increase in order and rigidity upon formation of the icelike clathrate hydrate, ΔS for the process could easily be negative. Hildebrand (*19*) has provided data that have been used to support this model, showing that at 25 °C, methane's diffusion coefficient in water is 40% less than it is in carbon tetrachloride ($D_{H_2O} = 1.72 \times 10^{-5}$ cm^2/s vs. $D_{CCl_4} = 2.89 \times 10^{-5}$ cm^2/s). Presumably the loose clathrate water "cages" serve to inhibit free diffusion of the nonpolar solute. From these data it seems that both the nonpolar solute (in this case, methane) *and* the aqueous solvent experience a decrease in entropy upon dissolving in water.

Hildebrand's data have been interpreted as supporting the clathrate cage model, but he himself did not accept this model as a logical explanation for the hydrophobic effect. He stressed that if clathrate cages as such really existed, then methane's diffusion coefficient would be *much* less in water, perhaps by one or two orders of magnitude, than it is in CCl_4. Although the clathrate cage model has been widely accepted by most physical chemists and biochemists (*12–18*, *28*), in fact, experimental evidence for the induction of icelike structure by the addition of nonpolar solutes to water is equivocal (*20*, *21*), and some researchers have presented data that argue against the existence of highly ordered clathrate structures (*11*, *19–21*). Several authors have developed an alternative statistical mechanical approach called the "scaled particle cavity theory" (*22*). Simulations using this theory suggest that the hydrophobic effect stems mostly from the small size of the water molecule, rather than from hydrogen-bonded clathrate structures (*23–27*). According to these results, the probability of finding an appropriate void in the fluid that will accommodate a solute is low because water is such a small molecule, *not* because of its hydrogen-bonding capacity. Entropy loss stems from the exclusion of water from these relatively large solute cavities, decreasing rotational and translational freedom (*25–27*) of the solvent (and solute). It is important to point out that both the cavity-based model and the clathrate cage model rest upon the fact that the hydrophobic effect is entropy, not enthalpy driven. The models differ only in how they explain the source of the entropy loss.

Finally, recent news reports featuring "flaming ice" retrieved from the ocean depths merit a mention here. The arguments discussed above explain why oil and water don't mix at standard temperature and pressure. But they also explain why oil and water *do* mix below the surface of the ocean or the arctic permafrost. In these regions of the earth, temperature is low (often significantly less than 0 °C), and pressure is quite high. Both of these conditions mitigate in favor of the aqueous solubility of nonpolar solutes. Recall that for most nonpolar solutes, both ΔS and ΔH are negative; therefore as T decreases, solubility increases. And because the average density of the two unmixed phases is significantly less than the density of the aqueous solution, as pressure increases, solubility increases. Finally, when these solutions freeze under high pressure, the hydrocarbon solutes remain stably trapped in tight pockets in the frozen hydrate. A recent report (*29*) stated that frozen clathrate hydrates "trapped beneath oceans and arctic permafrost may contain up to 53% of the world's organic carbon reserves." Methane is the most common gas found in frozen hydrates, "and the amount of methane in these frozen reserves in the U.S. alone may exceed [by more than 30-fold] the estimated total remaining conventional methane resources in the entire world." If effectively mined, these enormous reservoirs of frozen gas hydrates could easily "transform our energy economy from one based on oil to one based on gas…". All this from clathrate hydrates!

Conclusion

Although data and theory have been available for more than half a century to explain correctly why oil and water don't mix, this knowledge has not yet found its way into many introductory and organic chemistry textbooks in the United States. It seems curious that after such a long period of time this error remains uncorrected in introductory texts; apparently, the simplicity of the hydrogen-bonding explanation makes it a powerful and attractive model. Interestingly enough, some of the blame for the widespread acceptance of this explanation may lie with pioneering membrane biochemists who, even as they developed a robust new entropic model, confusingly held onto aspects of the old enthalpic explanation. Several examples of this are evident in the literature—for instance, in his introduction, Tanford (*16*, p 3) refers to "the dominant role of water self-attraction in the hydrocarbon-water system" and states that "the cause of the [immiscibility] effect must lie solely in a lack of affinity between hydrocarbon and water". By using terms like "water self-attraction" and "lack of affinity", Tanford seems to retain vestiges of the very enthalpic model that he proceeds to demolish several pages later.

The final question that must be addressed here is what type of physical explanation for the hydrophobic effect is appropriate at the beginning undergraduate level. Should textbook authors continue to offer the age-old simple, familiar, but incorrect enthalpic/hydrogen-bonding explanation? Most emphatically not. Should authors offer in its place details of the correct entropic explanation? Perhaps not. This explanation may lie beyond the scope of either first-year introductory chemistry or second-year organic chemistry. There may not be any need for these students to know about clathrate hydrate "cages" or scaled particle cavity theory. A discussion of the importance of solvation entropy effects could fit nicely in the section on the hydrophobic effect, but only if the format of the text allows such a discussion (i.e., if entropy and enthalpy have both already been introduced). Otherwise, the simple rule "like dissolves like", in the context of a discussion of different types of intermolecular forces, seems quite sufficient.

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Notes

1. Interestingly, my brief and anecdotal survey of European (British, French, German, and Swedish) introductory chemistry texts showed that these authors do stress the importance of entropy in explaining the hydrophobic effect. Perhaps this is because European introductory chemistry courses generally introduce the concepts of enthalpy, entropy, and free energy all together, in advance of their discussion of solubility.

2. Seidell's monograph tabulated solubilities of organic liquids in water at various temperatures. From the decrease in solubility with temperature it was clear that the solution process was exothermic. By plotting $-\ln K_{eq}$ vs. $1/T$ it was possible to determine $\Delta H_{solution}$ from these data.

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