



Understanding the role of monolayers in retarding evaporation from water storage bodies



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ABSTRACT

Retardation of evaporation by monomolecular films by a 'barrier model' does not explain the effect of air velocity on relative evaporation rates in the presence and absence of such films. An alternative mechanism for retardation of evaporation attributes reduced evaporation to a reduction of surface roughness, which in turn increases the effective vapour pressure of water above the surface. Evaporation suppression effectiveness under field conditions should be predictable from measurements of the surface dilational modulus of monolayers and research directed to optimising this mechanism should be more fruitful than research aimed at optimising a monolayer to provide an impermeable barrier.

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Introduction

For many decades it has been known that the application of certain surface active molecules in a layer no more than a single molecule thick can have a significant impact in reducing evaporation from water storages, including reservoirs of significant size [1,2]. These compounds which form monomolecular layers, or 'monolayers', should be contrasted with compounds (e.g., hydrocarbon or siloxane oils) which may be applied in layers of the order of microns thick in order to retain heat and retard evaporation from small bodies such as swimming pools [3].

The principal compounds that have been shown to be effective in monomolecular layers are hexadecanol, octadecanol, and ethylene glycol mono-octadecyl ether [4,5]. The first of these were demonstrated to be effective in the laboratory as long ago as the 1920s, while the last was patented for this application in the 1960s [6]. Laboratory interest in this phenomenon has waxed and waned since it was first observed, with many recent reports in the chemical literature on the development of materials for improving the durability and performance of these monolayers [7].

Performance of monolayers under field conditions has proven to be highly variable, with some field trials leading to significant water savings and others showing little benefit from these compounds [4]. This variability is probably the main reason that this effect, which has been known for the better part of a century, has

not yet been exploited commercially on a significant basis. In turn, the factors behind this variability have not been quantified. This is doubtless partly due to the difficulties of making experimental measurements on relevant parameters at the water/air interface, but arises from a lack of fundamental understanding of the mechanism of operation of these monolayers under field conditions. Recent work continues to interpret behaviour overwhelmingly in terms of an empirical 'evaporation coefficient' which is correlated with properties, independent of a clear physical mechanism [8].

Barrier Mechanism

It has frequently been suggested that a monolayer may provide an impermeable surface or 'barrier' on the water/air interface, retarding evaporation in this way, and the experimental results can certainly be interpreted in terms of a three-phase system with a diffusion coefficient for the transport of water through an intermediate hydrophobic phase. Indeed, a very good correlation has been observed between the capacity to reduce evaporation and the length of the hydrophobic chain in simple alcohols [1,9,10]. But, to paraphrase a highly-regarded physical chemist of our acquaintance: 'While it is true that a theoretical result should not be accepted until it is confirmed by experiment, it is equally true that an experimental result should not be accepted until it is confirmed by theory' [11].

While a model of a hydrophobic barrier is valid for much thicker layers of hydrophobic liquids, it is implausible that it could be applicable for a layer one molecule thick. To understand why, it is

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necessary to consider the fundamental molecular process of evaporation.

In general, evaporation from a surface that is flat on the scale of the mean-free-path of a diffusing molecule can be described by the Hertz–Knudsen equation, which can be derived from reasonable assumptions about the diffusion of an ideal gas [12], or using statistical rate theory [13]. This equation has been found to be generally applicable for a very wide range of substances and geometries and gives a rate of flux that arises from the competing diffusion of molecules from gas to liquid and from liquid to gas

$$J = \eta_e \sqrt{\frac{M}{2\pi R}} \left(\frac{P_{\text{Sat}}}{\sqrt{T_L}} - \frac{P_V}{\sqrt{T_V}} \right). \quad (1)$$

Here J is the mass flux of evaporating substance ($\text{kg s}^{-1} \text{m}^{-2}$), M is the molar mass of the substance (kg mol^{-1}), R is the ideal gas constant, T_L is the surface temperature of the liquid, T_V is the vapour temperature of the vapour in contact with the surface, P_{Sat} is the saturated pressure of liquid at T_L , and P_V is the vapour pressure of the vapour in contact with the surface. In the classical derivation, η_e is an empirical evaporation coefficient with values between 0 and 1, for which experimental values for the evaporation of water range over almost three orders of magnitude [14]. One recent review of the wide range of experimental values proposed for this coefficient concluded that for pure water evaporating into a gas phase containing only water vapour, η_e was unity at all temperatures and pressures [14]. More recently, η_e was measured at 0.62 ± 0.09 [15], a discrepancy which can readily be rationalised by considering that the derivation of the Hertz–Knudsen model assumes spherical gas molecules behaving ideally, without directed hydrogen-bonding effects. One possibility is that an inability to measure the local P_V at the interface with sufficient accuracy is largely responsible for the wide variation in reported values of this empirical fitting factor.

In the derivation of the Hertz–Knudsen equation using statistical rate theory, η_e is given by a vapour pressure- and temperature-dependent expression which is dominated by the entropy change on evaporation per mole, ΔS [13]

$$\eta_e = \frac{e^{\Delta S/R} - e^{-\Delta S/R}}{1 - (P_V/P_{\text{Sat}})\sqrt{T_L/T_V}}. \quad (2)$$

This model has shown a good fit to experimental data in the absence of monolayers and contains no diffusion-related terms [13]. Note that the driving force for evaporation in Eq. (1) is always the difference between P_V and P_{Sat} . In the limit of $P_V = 0$, this expression gives an extremely high value. This rate of outward flux is not reduced at all by increasing P_V : instead, it is balanced by a large inward flux. An observed evaporation rate under real conditions below the boiling point of water is thus always the difference between two large numbers. A moment's thought will show that a barrier to the diffusion of water on the surface of the water will operate equally in both directions: if it reduces the flux of exiting molecules, it should also reduce the flux of entering molecules. The net flux, however, will remain thermodynamically rather than kinetically controlled as long as the inward flux and outward flux remain large compared to the net flux. The outward flux at 20°C has been estimated to be equivalent to an evaporation rate of 9 m h^{-1} [16]. Thus, a reduction of diffusion rate of many orders of magnitude would be required to move from thermodynamically to kinetically controlled conditions.

An indication of the magnitude of the reduction required to achieve kinetically rather than thermodynamically controlled conditions may be estimated by considering evaporation of spherical droplets. The transition from evaporation controlled by diffusion in the liquid phase to evaporation controlled by diffusion in the gas phase has been well-studied for droplets, as shown below

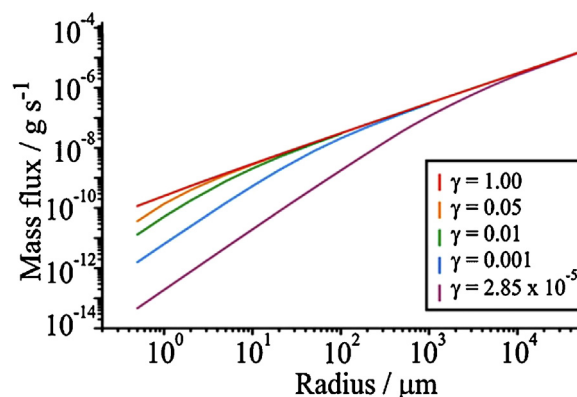


Figure 1. Variation of mass flux with empirical surface barrier constant γ [17], reproduced with permission.

in a figure reproduced from Davies et al. [17] (Figure 1). The evaporation of droplets is well described by the Maxwell model [18], where r is the diameter of the droplet, and D is the diffusion coefficient of water vapour in still air

$$J = \frac{D}{rRT} (P_{\text{Sat}} - P_V). \quad (3)$$

As droplets become smaller, they enter a diffusive regime where flux is no longer dependent on droplet size, but does depend on mass transport through the liquid phase, taken into account via an empirical constant γ .

$$J = \gamma \frac{P_{\text{Sat}}}{\sqrt{2\pi MRT}}. \quad (4)$$

In Figure 1, the experimental quantity $J4\pi r^2$ is plotted as a function of r .

It can be seen that under these conditions that once evaporation can no longer be described accurately in terms of effusion from a point source, even a change in surface impermeability of many orders of magnitude is insufficient to significantly change the flux across the interface, and that this change occurs at droplet radii on the millimetre scale even for γ values of order 10^{-4} .

The solubility of water in bulk hydrocarbons and its rate of diffusion in hydrophobic materials suggest that empirical 'diffusion coefficients' of water in a monolayer film sufficient to induce deviations from the models above are not physically credible [19]. The saturated molar solubilities of water in hexadecane ($\sim 5 \times 10^{-5} \text{ M}$) [20] and dry air ($\sim 10^{-3} \text{ M}$) at 25°C are not greatly different. The relative magnitudes of the diffusion coefficient of water vapour in hexadecane ($\sim 4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) [21] and air ($\sim 3 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$) [22] therefore suggest the diffusion of water through a hexadecane monolayer a few nanometres thick should take approximately the same time as diffusion through a layer of 'still air' a few millimetres in thickness. This thickness is the same order of magnitude as the predicted thickness of the boundary layer above a water surface where transport should be diffusive [23,24]. Approximating the monolayer as a polymer film, the flux through the film can be estimated using Eq. (5) [25]

$$J = D \times S \times \frac{dC}{dx} \quad (5)$$

where D is the diffusion coefficient through the monolayer ($4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$), S is the solubility coefficient (the relative solubility of water in the monolayer and air, 5×10^{-2}) and dC/dx is the 'concentration gradient' across the monolayer. This idealised Fickian model suggests a flux equivalent to 18 cm h^{-1} across the interface, well in excess of experimentally observed evaporation rates and well within the range of thermodynamic control. A highly

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