

Spontaneous Polarization of Cryo-Deposited Films for Five Normal Saturated Monohydroxy Alcohols, $C_nH_{2n+1}OH$, $n = 1-5$

Alexandra N. Pilidi, Irini K. Gavra, and Athanassios A. Tsekouras*[✉]

Physical Chemistry Laboratory, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis, Zografos GR-15771, Greece

Supporting Information

ABSTRACT: Vapor-deposited films of neutral polar molecules on cold surfaces exhibit spontaneous electric polarization across the faces of the film. We deposited known amounts of the first five members of the normal monohydroxy alcohols at substrate temperatures in the range of 30–130 K. It is known that voltages measured are proportional to film thickness and that the effect is substrate-independent. The main trend observed was that the voltage per molecule surface density grows with molecule size and drops with deposition temperature. With the exception of some high-temperature methanol depositions, the films had a negative voltage on the vacuum side. Furthermore, the heavier members (1-butanol and 1-pentanol) showed reduced voltages for the lowest temperatures, suggesting that all members of the series could follow this pattern at temperatures below what was experimentally accessible. After deposition, film voltage was monitored during a temperature ramp showing first an increase in the voltage measured, then gradual decay before film evaporation. Initial film voltages are in general agreement with the concept of surface mobility of vapor-deposited molecules and indicate a negative correlation with dipole moment size.



INTRODUCTION

Molecules from the gas phase condense into a solid when they come in contact with a sufficiently cold substrate. If the molecules are polar, i.e., they have a dipole moment, and the substrate temperature is below a certain threshold, the condensate exhibits an electric potential difference between the side in contact with the substrate and that on the outside.^{1–13} This phenomenon was first reported 40 years ago^{1,2} but has not been studied extensively. Alcohols, in particular, have been examined on a few occasions.^{3–6,13}

The primary motivation for studying spontaneous polarization is a scientific curiosity, i.e., the desire to answer the question what makes neutral molecules pile up on a cold substrate in such a way that they exhibit a net voltage across the thickness of the layer. Which molecules will generate large voltages and which ones small? With which compounds and at what temperature do we get a positively or a negatively charged film? The phenomenon itself could have desired or undesired consequences in several circumstances. Charged particles approaching a polarized layer could be accelerated, decelerated, or even deflected from their intended target with unexpected results. Once well understood, the phenomenon could be used to our benefit as a simple, remotely accessed temperature-weighted integrator for sensitive products such as foodstuffs.

For vapor-deposited spontaneously polarized films, it is known that the voltages observed are proportional to the

thickness of the condensate films and that the nature of the substrate is immaterial, but the effect of other factors has not been established.¹¹ Some of these factors are expected to be the magnitude of the dipole moment, polarizability, substrate temperature and its value relative to characteristic temperatures of the condensing molecules (e.g., melting point, glass-transition temperature), rate of condensation, presence of other molecules (or absence thereof, i.e., vacuum), and collision energy of the impinging molecules. It is known that the observed voltages depend primarily on the identity of the condensing molecules and on the substrate temperature. Other factors are not easily controlled and have not been studied in any significant detail. Most importantly, the effect is associated with a metastable state of the condensate since heating the film eliminates the initial voltage and recooling the film does not reinstate the voltage.¹³ Hence, there is no doubt the films consist of molecules in an amorphous state. Some molecules have been reported to produce negative voltages^{2,6,7,13} (of the outer film surface with respect to the substrate side), others positive;^{8,9,11} a few are known to change voltage sign depending on substrate temperature.^{2,3}

We present here data for the first five members of the normal saturated monohydroxy alcohols. Comparable data on

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these compounds have been reported in the past.^{3,5,13} We deposited known gas amounts as a function of substrate temperature. We can thus show some trends and some variability in their behavior. For each compound, we have collected additional information regarding the evolution of the film voltage as its temperature is raised leading to the eventual elimination of the voltage and of the evaporation of the film itself. We conclude with a brief discussion on the emerging picture for spontaneous polarization of cryo-deposited films and its correlation with the magnitude of the molecular dipole moment.

EXPERIMENTAL SECTION

The experiments were conducted in an apparatus that has been described in detail in the past.¹³ Briefly, it is a triple-cross, high vacuum chamber equipped with a Kelvin probe (for measuring film voltages), a tube doser (for delivering known amounts of gas directly onto the substrate), a helium closed-cycle refrigerator cooling a polycrystalline platinum foil, and a quadrupole mass spectrometer for monitoring the gas-phase composition. In some cases, the mass spectrometer was turned off to avoid interference from leaking electrons and chamber pressure was used instead to monitor desorption.

Known amounts of a given gas at room temperature were delivered directly on the cold substrate, with a minuscule fraction escaping condensation. The number of molecules deposited was calculated based on the reduction of pressure in the gas reservoir of known volume and temperature.¹³ Deposition time was of the order of 60 s, while the total number of molecules was of the order of 10^{18} cm⁻². If we use the common definition 1 ML = 10^{-15} molecules cm⁻², deposition rates and total coverage are of the order of 10 ML s⁻¹ and 10^3 ML, respectively. We estimate the film thickness to be 1–3 μm (see ref 13 for calculation details). Within a couple of minutes after deposition, we measured the film voltage and started a temperature ramp at a rate of 0.25 K s⁻¹. During the ramp, we monitored film voltage and gas-phase composition. The maximum temperature reached was 260 or 300 K, which ensured complete removal of intact alcohol molecules, but possibly below the temperature required for complete removal of any decomposition products¹⁴ of the last monolayer. This was no cause for concern because, as already mentioned in [Introduction](#), the nature of the substrate does not affect the magnitude of spontaneous polarization.

RESULTS

Data were recorded for methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol. During the temperature ramp after the film deposition, the voltage (most often negative) was gradually eliminated; in many cases, it would first become more negative and then gradually approach zero. All compounds showed variation of the magnitude of the initial film voltage as a function of substrate temperature. Some maintained constant voltage sign for all temperatures studied, while others showed a change of initial voltage sign over the temperature range studied. The temperature range was limited on the low side by our apparatus, i.e., around 30 K, whereas on the high side, it depended on the compound itself, c.f., its desorption temperature and its ability to show nonzero voltage.

For each compound, we present a set of five figures. First, we show film voltage variation as a function of film temperature along with the mass spectrometer signal indicating film

desorption, although the phenomenon is more accurately described as sublimation and evaporation; on some occasions where the mass spectrometer was switched off, we display the chamber pressure as an adequate proxy for the mass spectrometer signal. These figures can be found in the [Supporting Information](#). One such example is given in [Figure 1](#) for an ethanol film. Preliminary treatment of the Kelvin probe signal, which is needed to subtract varying bias applied to the probe, has been described before.¹³

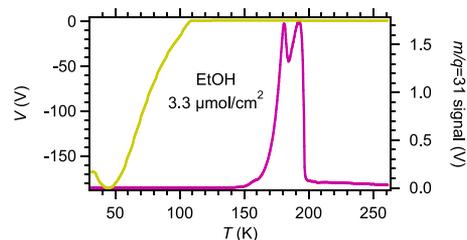


Figure 1. After deposition of 1.98×10^{18} molecules/cm² of ethanol at 32.2 K, the platinum foil temperature was ramped at 0.25 K s⁻¹. The initial positive film voltage, measured with a Kelvin probe as contact potential difference, is eliminated gradually and irreversibly. At around 170 K, the film molecules leave the substrate as determined with a quadrupole mass spectrometer. The mass spectrometer signal displays a split peak due to the close proximity of the Kelvin probe tip to the sample.

Then, for each compound, we show representative curves of film voltage scaled by the surface number density of deposited molecules as a function of film temperature, which is ramped up at a constant rate of 0.25 K s⁻¹. Each curve corresponds to different deposition (substrate) temperature, which is the starting temperature for every ramp. Note that, by using the definition 1 ML = 10^{-15} molecules cm⁻², the quantity 10^{-18} V cm²/molecule for scaled voltages is the same as mV/ML. The third figure for each compound (also included in the [Supporting Information](#)) summarizes the results by displaying average values of (initial) film voltage at the deposition temperature as a function of that temperature, along with an extremum (for alcohols, it is a minimum), which appeared at an intermediate temperature. Another figure shows the temperature where the extremum appears versus the deposition temperature. Following the analysis pattern set in ref 13, we also plot the difference between deposition temperature and temperature of the extremum against deposition temperature. The last figure of the set for each compound is the fractional increase in voltage reached at the extremum relative to the initial value of the film voltage,

$$f = \frac{V_{\min} - V_{\text{start}}}{V_{\text{start}}}$$

For a rudimentary analysis of the data, we used the degree of polarization, g , as derived in ref 13.

$$g = \frac{VA}{N} \frac{\epsilon_0 \epsilon_\infty}{\mu} \quad (1)$$

where V is the film voltage, N is the total number of molecules deposited, A is the area they were deposited, N/A is their surface number density, $\frac{VA}{N}$ is the film voltage scaled with the surface number density, ϵ_∞ is the relative dielectric constant at infinite frequency (used for very low-temperature dielectric response), μ is the dipole moment of the molecule, and $\frac{\mu}{\epsilon_0 \epsilon_\infty}$ is

the expected voltage for a single layer of molecules all oriented with their dipole moments parallel to the surface normal.

For a given compound, any scaled voltage can be interpreted as a degree of polarization using eq 1. This has been done on the figures that display initial and minimum scaled voltages, by using a right axis for the degree of polarization.

Pertinent Data for the Substances Studied are given in Table 1.

Table 1. Pertinent Data for the Substances Studied

#	compound (abbreviation)	formula	μ (D) ^a	ϵ_∞	T_g (K) ^d
1	methanol (MeOH)	CH ₃ OH	1.7	2.03 ^b	103
2	ethanol (EtOH)	CH ₃ CH ₂ OH	1.69	2.12 ^b	97
3	1-propanol (1-PrOH)	CH ₃ CH ₂ CH ₂ OH	1.55	2.10 ^b	100
4	1-butanol (1-BuOH)	CH ₃ (CH ₂) ₂ CH ₂ OH	1.66	1.92 ^b	112
5	1-pentanol (1-PeOH)	CH ₃ (CH ₂) ₃ CH ₂ OH	1.65	2.14 ^c	121

^aRef 15. ^bRef 16. ^cRef 17. ^dRef 18.

We present the results for the five alcohols in order of increasing molecule size.

Methanol films were studied for a detailed range of deposition temperatures. The voltage profile shows that the voltage is eliminated during the temperature ramp before the film is removed from the substrate (see Figure S1). The curves presented in Figure 2 and, more clearly, the initial film voltages

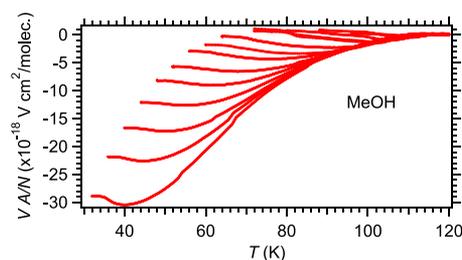


Figure 2. Scaled voltage of methanol films during temperature ramps for various deposition temperatures.

indicated in Figure S6a show that methanol films have mostly negative initial voltages, yet at the high side of the temperature range, the voltage turns positive. This is in agreement with earlier reports.³ All ramps cause the film voltage to go through an early minimum, i.e., the absolute value first increases during the temperature ramp. The locations of these minima are displayed in Figure S6b.

Ethanol films were deposited between 32 and 104 K. The corresponding voltage profiles during the temperature ramp are shown in Figure 3. Initial voltages and voltage at the minimum as well as corresponding degrees of polarization are given in Figure S7a. The correlation between temperature at the minimum and deposition temperature is depicted in Figure S7b. There is a great similarity between the curves for ethanol and methanol, although ethanol does not show positive voltages at any deposition temperature.

1-Propanol films were deposited at temperatures between 32 and 113 K, as shown in Figures S3 and S4. Propanol voltage profiles (Figure 4) as well as sequences of initial voltages, minimum voltages, and temperatures at the minima (Figure S8) resemble those of ethanol in every respect.

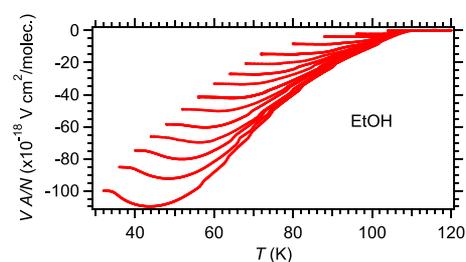


Figure 3. Scaled voltage profile for ethanol films deposited at various temperatures.

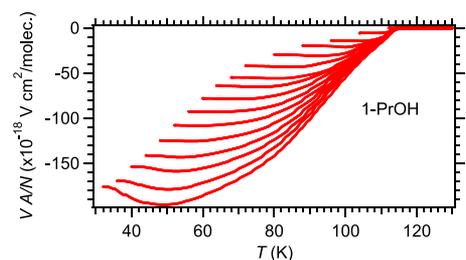


Figure 4. Scaled voltage profiles for 1-propanol films deposited at the low-temperature side of each ramp.

1-Butanol depositions were carried out in the temperature range of 32–120 K. A single run is shown in Figure S4. All curves shown in Figure 5 and their characteristic points

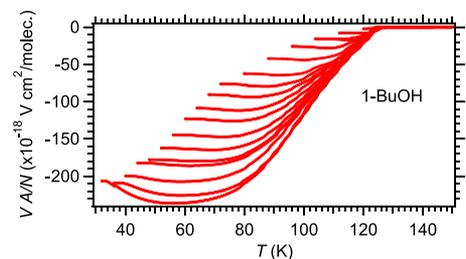


Figure 5. Scaled voltage profiles for 1-butanol films for various deposition temperatures.

presented in Figure S9 are similar to those of ethanol and 1-propanol with the notable change that at the two lowest deposition temperatures, the initial voltage measured is higher than that at 38 K.

1-Pentanol was deposited in the temperature range of 32–120 K. A single run is shown in Figure S5. Voltage curves for all temperatures shown in Figure 6 and their characteristic points shown in Figure S10 are similar to those of 1-butanol

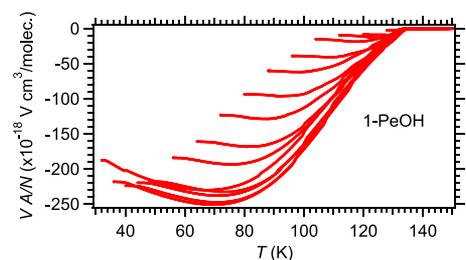


Figure 6. Scaled voltage profiles for 1-pentanol films deposited at the starting temperature of each ramp.

with the only difference being that the peak voltage occurs at 40 K rather than at 38 K, which is the case for 1-butanol.

DISCUSSION

The primary alcohols presented in this report appear to follow a simple trend of decreasing (absolute) film voltages with rising temperatures. Still, there is a strong indication that the initial film voltage is not monotonic and the first impression could simply be a consequence of the accessible temperatures on the low side. The heavier members of the series show a decrease in the absolute value of the initial voltage at the very low temperatures. It is possible that the lighter members could show the same trend at temperatures below 30 K. Such variations both in magnitude and sign have been reported for CO, NO, and acetone from the first systematic study of spontaneous polarization.²

The most significant results of this work are shown in Figure 7a; this figure summarizes the top panels of Figures S6–S10.

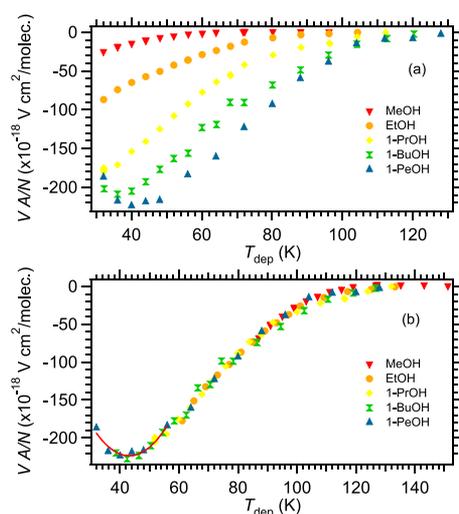


Figure 7. (a) Initial scaled voltage for *n*-alcohol films as a function of deposition temperature. (b) Same data scaled vertically and shifted horizontally for optimum overlap based on a least-squares fit. The solid line is a parabola fit for the determination of the coordinates of the minimum.

The initial film voltage for each alcohol studied is presented as a function of deposition temperature. It is very clear that the larger the molecule, the higher the effect of spontaneous polarization. All of the curves in Figure 7 seem to follow the same pattern. Since they correspond to similar compounds, it is conceivable that these curves could be made to overlap by vertical scaling and horizontal shifting. This has been achieved in Figure 7b. Since the 1-pentanol curve has the most complicated form, we used that curve as a template to

interpolate points at arbitrary temperatures. We then determined the required scaling factors and temperature shifts for the other four curves by the least-squares procedure. The result of the adjustment can be seen in Figure 7b. The fitting parameters (1σ uncertainties) are given in Table 2. The 1-pentanol curve needs to be multiplied by the factors in the second column, and its temperatures shifted by the values in the third column to match the curve of the compound listed in the first column.

Interpreting the fitting parameters, we can give an estimate of the maximum scaled voltage for each of the alcohols and the deposition temperature this voltage would be realized. These estimates are given in the 4th and 5th columns of Table 2, respectively. The estimated peak temperature for methanol being unphysical (-12 K) indicates that methanol deviates from the other compounds. The magnitude of the scaled voltage at the peak temperature can be used as a temperature-independent measure for the ability of each compound to form spontaneously polarized films. Furthermore, it can be used to determine a degree of polarization via eq 1.

Two less successful attempts for overlapping the initial scaled voltage curves are shown in the Supporting Information.

Figure 8 is another overlay of the data found in the top panels of Figures S6–S10; it shows the lowest scaled film

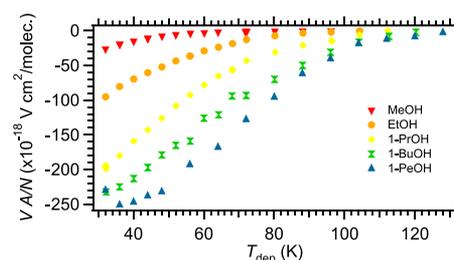


Figure 8. Minimum scaled voltage for *n*-alcohol films as a function of deposition temperature.

voltage measured for each compound during the temperature ramps at the corresponding deposition temperature. A fit similar to the one performed on the initial voltages of Figure 7 yielded parameter values that are essentially the same as those for the fit in Figure 7 (see the Supporting Information).

In all of the fits, methanol parameters are the ones with the highest uncertainties, indicating that methanol follows a somewhat different pattern from the other compounds. The results from the first two fits, which are based on the deposition temperatures, are substantially different from those of the fits based on the temperatures of the minima.

Figure 9 collects data from the middle panels of Figures S6–S10; Figure 9a shows the temperatures of the minima as a function of deposition temperature for the five alcohols. This picture has no distinct features. The differences between

Table 2. Results of the Fits Shown in Figure 7b

compound	fitting parameters		derived values		
	scale (1σ)	shift (1σ) (K)	$(VA/N)_{\max}$ (10^{-18} V cm ² /molec.)	T_{peak} (1σ) (K)	g_{\max} (1σ)
methanol	0.37 (0.11)	−55 (4.4)	−82 (24)	−12 (4.4)	−0.026 (0.0077)
ethanol	0.49 (0.03)	−29.0 (1.7)	−109 (7)	14 (1.7)	−0.034 (0.0021)
1-propanol	0.88 (0.02)	−19.8 (0.9)	−196 (5)	23 (1.0)	−0.067 (0.0016)
1-butanol	0.92 (0.01)	−6.4 (0.6)	−205 (3)	37 (0.7)	−0.072 (0.0010)
1-pentanol	1 (0)	0 (0)	−224 (2)	43.1 (0.4)	−0.072 (0.0006)

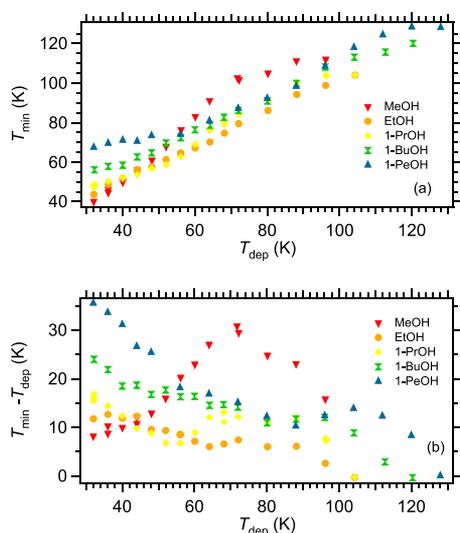


Figure 9. (a) Locations of the voltage minima during temperature scans as a function of deposition temperature for each film. (b) Difference between the temperature at which film voltage reaches minimum and deposition temperature as a function of deposition temperature.

deposition temperature and the location of the minimum are shown in Figure 9b for all compounds. Once again methanol stands out from the other alcohols.

The increase (in absolute value) of the film voltage expressed as a fraction of its value upon deposition is presented in Figure 10 as a collation of the bottom panels of

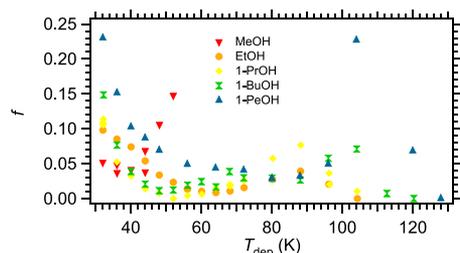


Figure 10. Fractional increase of film voltage at the minimum relative to the initial voltage, $f = \frac{V_{\min} - V_{\text{start}}}{V_{\text{start}}}$. Not all data for methanol are shown because they go off scale due to change in voltage sign during some of the ramps.

Figures S6–S10. Changes are largest for the lower temperatures, as well as show a local maximum around 100 K. Lacking a clear trend and given the irregularity of the data, no attempt was made to make the curves for different compounds to overlap by shifting and scaling. Again, methanol is strikingly different. Some of the methanol values are huge because they arise from curves that had near-zero voltage at the deposition temperature (positive on some occasions); during the temperature scan, that voltage dropped significantly yielding a change in voltage larger than the initial value (and of opposite sign).

One could expect that for deposition temperatures above the glass-transition temperature, no spontaneous polarization should be observed. This is more or less true for the five alcohols studied here. For the three heavier members, very small voltages were measured at deposition temperatures higher than the corresponding T_g . This phenomenon has been

reported elsewhere.^{7,9} It may be explained by recalling that the measured polarization is a macroscopic observation of all molecular orientations. The fact that the substrate temperature is above the glass transition does not imply that the impinging molecules can become fully equilibrated, otherwise they would have to form a crystal rather than an amorphous solid.

One can speculate on what causes the increase of the film voltage upon heating. It cannot be attributed to dielectric response because voltage variation is not reversible.¹³ It may be attributed to rearrangement of molecules in the amorphous solid. It is known that vapor-deposited solids may be porous and increasing the temperature makes them more compact.^{19,20} Complementary measurements could address this question in the future.

The main question this work is trying to address is why molecules form a nonisotropic film; a second one, yet undoubtedly intimately related to the first one, is why the film voltage varies with temperature. A few years ago, it appeared that the latter issue had been tackled successfully through a model⁹ proposed by the Aarhus group. As it turns out, although the starting point may seem reasonable, upon closer inspection, that model does not have one crucial qualitative feature: it does not have the necessary form to yield a maximum or a minimum in voltage as a function of deposition temperature. We will elaborate briefly because we had attempted to use the model for our data without success. The proposed expression was of the form $g = \coth x - x^{-1}$, where $x = \frac{E_s \mu}{T}$ and $E_z = E_s [1 + \zeta(1 + g^2)] - E_a g$, with E_s , ζ , and E_a the (positive) model parameters. Unfortunately, it is a strictly monotonic function of temperature. This can be shown by taking the approximation¹⁰

$\coth x - x^{-1} = \frac{x}{3} - \frac{x^3}{45} + \dots \approx \frac{x}{3}$, which is adequate for the values of x encountered in the data. Upon substitution, we get the second-degree equation $\mu E_s \zeta g^2 - (3T + \mu E_a)g + \mu E_s = 0$, which can be solved exactly for g :

$$g = \frac{(3T + \mu E_a) \pm \sqrt{(3T + \mu E_a)^2 - 4\mu^2 E_s^2 \zeta}}{2\mu E_s \zeta}$$

Both solutions are positive,

if the parameters are taken to be positive, so there is no physical reason why reject one solution or the other. If $g = f(T)$ has a maximum or a minimum at T_m , the expression $\frac{dg(T_m)}{dT} = 0$ should be true, which leads to $4\mu^2 E_s^2 \zeta = 0$. If either E_s or ζ were zero, the model would collapse. Hence, we are led to the conclusion that in the proposed model, g has no extremum for any nonzero parameter value. Consequently, it cannot describe data that exhibit a maximum or a minimum. Among other pitfalls in the fitting procedure followed, it was assumed⁹ that $\frac{dg}{dT} = f(T, g)$.

A nonzero dipole moment is needed for vapor-deposited molecules to form a polarized film. As seen in Table 1, the dipole moments of the five alcohols are nearly the same. On the other hand, the scaled voltages or the degrees of polarization at any given temperature or at the peak are not the same. It is clear, qualitatively from Figure 7 and quantitatively from Table 2, that the longer the carbon chain, the larger the absolute film voltage. Incidentally, it is intriguing to consider water as an alcohol with no carbon atoms²¹ and see that it follows the same trend; water gives small negative film voltages.⁷ Quantities that could correlate with the rise in film voltage are the number of carbon atoms per molecule, molecular mass, and molecular polarizability.

None seems to give an acceptable correlation; see the Supporting Information for details.

We considered other quantities to test simple correlations with the peak film voltages such as melting points, glass-transition temperatures, enthalpies of fusion or vaporization, and even some combination of the aforementioned. Since most are not monotonic functions of chain length, while the film voltages are, they fail from the start. Nonetheless, it is instructive to examine the variation of the peak voltage and the degree of polarization simply as a function of the length of the carbon chain of the alcohols. This is done in Figure 11. The

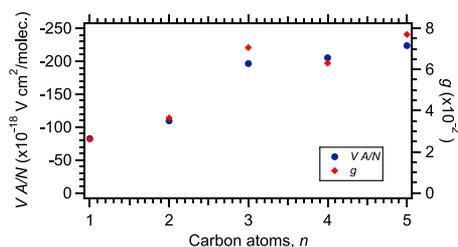


Figure 11. Expected peak scaled voltage and peak degree of polarization as a function of alcohol chain length.

curves are irregular and they do not seem to follow a simple form. Furthermore, the degree of polarization is not even monotonic. This is a consequence mostly of the nonmonotonic variation of the dipole moment, i.e., the exceptionally low value for the dipole moment of 1-propanol (see Table 1). This is yet another indication that the dipole moment is a necessary attribute of the deposited molecules, but it does not dictate the size of the extent of spontaneous polarization. In fact, as seen in Figure 11, 1-propanol with a lower dipole moment gives rise to a higher degree of polarization than the rest of the alcohols.

A very important fact regarding spontaneous polarization is that films acquire their voltage irrespective of the nature of the substrate on which they are grown. At the same time, the more molecules stick on the solid, the larger the observed voltage. This phenomenon is governed by the interaction between the incoming molecules while they are still mobile and the surface. It is a purely kinetic effect leading to a metastable structure. New molecules undergo the same procedure before becoming locked down on the cold surface and buried under the next impinging molecules. So, it makes good sense to consider an intermediate stage between the gas phase and the frozen phase where molecules have some limited mobility that guides them to their permanent location. During that stage, it is not clear whether the dipole moment affects the motion and the selection of the final molecule orientation. It is quite likely that incoming molecules are subject to stronger forces due to the contact interactions with nearby molecules than those caused by the presence of the dipole moment. Consequently, the spontaneously created voltage that we measure simply gives a macroscopic measurement of the collective orientation of the deposited molecules. That said, there is evidence (from published data² and unpublished results in our group) that a large dipole moment locks the molecules more strongly, thereby reducing the spontaneous polarization effect. This could coincide with strongly orienting intermolecular forces such as hydrogen bonds.

In recent years, a lot of research has been devoted to various properties of vapor-deposited glasses because of the great importance such materials have in the semiconductor industry.

The properties studied have provided information on the kinetic stability or the structure of these materials, although these conclusions were not based on voltage measurements. The consensus that emerged from such studies is that each deposited layer reaches local equilibrium on the surface and becomes immobilized, thus forming a layered structure with unique properties not seen in crystalline or frozen glasses.^{22–24} This formation mechanism is in very good agreement with our observations. It also agrees with the involvement of hydrogen bonds which seem to hinder the creation of such structures.²² Our alcohol data indicate that the increase of the size of the molecule, i.e., the dilution of potential hydrogen bond sites, causes the deposited molecules to move more freely and create polarized films more readily. What is not clear yet is why the measured voltages exhibit such gradual decrease with increasing substrate temperatures because higher temperatures would imply higher mobility before lockdown. It should be noted that polarized film formation is not limited to deposition temperatures below the known glass-transition temperatures. Incidentally, these latter temperatures are all clustered together and rise with molecule mass with the exception of methanol, which has a median T_g among the five alcohols (see Table 1).

One point we should not ignore is that molecular orientation and packing does not imply large film voltages. The main reason is that molecular axis and molecular dipole moment are not coaxial. This is seen clearly in Figures S14 and S15, which show projections of these vectors for methanol and 1-pentanol. A fully oriented layer may have all of the dipole moments pointing in the same direction, but that is not necessarily the surface normal (our measurements are along the surface normal). For different deposition temperatures, the average orientation may change gradually with respect to the surface causing either an increase or a decrease in film voltage. In the end, higher voltages do not necessarily mean that more molecules are oriented in the same direction. Furthermore, the angle between molecular axis and dipole moment and a gradual change of orientation could explain even a gradual change in voltage sign.

It is interesting that some simulations such as the one given in ref 24 show that the voltage sign may be predicted, with the degree of polarization (called order parameter in ref 24) at a chosen distance from the surface, indicating a very small average angle relative to the surface. Yet, there is no straightforward way for predicting what affects the voltage sign and the degree of polarization. Once more the need for more theoretical simulations becomes obvious.

SUMMARY AND CONCLUSIONS

In this paper, we report on negative voltage buildup across vapor-deposited alcohol films formed at cryogenic temperatures (30–130 K) on a platinum foil. The voltage is caused by nonisotropic layering of condensing polar molecules and is proportional to their number. We looked at methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol. Upon heating, the voltage at first becomes more negative and then gradually fades irreversibly at temperatures lower than the evaporation and desorption temperatures of the films. The most striking piece of information regarding these short-chain alcohols is that they share a similar size dipole moment, but they establish voltages that increase with chain length. The highest measured degrees of polarization range from 0.8% for methanol to 8% for 1-pentanol. Data from the heavier members of the series studied indicate that at some low deposition temperature (below 40

K), these films reach a maximum (absolute) voltage. Methanol seems to stand out in some respects from the other members of the series; at high deposition temperatures, the voltage buildup is positive, i.e., of opposite sign from the rest of the samples studied.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpccb.9b04978.

Detailed data regarding each alcohol separately as well as fits to data of minor success (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: thanost@chem.uoa.gr.

ORCID

Athanassios A. Tsekouras: 0000-0002-4757-324X

Notes

The authors declare no competing financial interest.

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