Methanol, Ethanol and Propanol in EHD liquid bridging

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Abstract. When a high-voltage direct-current is applied to two beakers filled with water or polar liquid dielectrics, a horizontal bridge forms between the two beakers. In this work such bridges made of methanol, ethanol, 1-propanol and 2-propanol are investigated with polarimetry and thermography. Whereas methanol, ethanol and 1-propanol bridges become warm like a water bridge, a 2-propanol bridge cools down relative to the surroundings. It is shown how the different stability of the primary and secondary alcoholate ions and the resulting small difference in conductivity between 1-propanol and 2-propanol is responsible for this novel effect.

1. Introduction

In 1893 Sir William George Armstrong first reported the formation of a horizontal bridge of water forming between two wine glasses filled with chemically pure water when a direct-current (DC) high-voltage was applied [1]. Recently, a number of publications made the broader scientific community aware of this experiment [2-7].

The experiment is stable, easy to reproduce, and grants free experimental access to water inside the bridge under variable high voltage and atmospheric conditions in air, thus giving insights into basic features of dipole-dipole interaction in water [8]. Therefore a number of experiments in the horizontal bridge of water was performed including neutron scattering [4,5], visualization and optical measurement techniques [6], Raman scattering [9], Brillouin scattering [10], reduced gravity experiments [11], and was discussed in relation to molecular vibration coupling [12] and the influence of some electrolytes [13] and non-ionic solvents [14] on the water bridge.

Several authors discussed the electrohydrodynamics of this phenomenon. Widom \textit{et al.} [15] and Saija \textit{et al.} [16] claim that the high dielectric permittivity of water is the reason for a stable bridge forming and used the Maxwell stress tensor to calculate tensions within the bridge. A similar approach was used by Marin and Lohse [17]. It has been shown that a horizontal bridge forms also in methanol [8] and glycerol [17]. Aerov [18] pointed out that a stable equilibrium for the bridge’s surface is...
reached when the axial electric field is strong enough to counteract distortions caused by surface tension.

All electrohydrodynamic discussions of these experiments use previous literature on a phenomenon also named ‘liquid bridge’, but resembling a vertical column of liquid, pinned at each end between planar electrodes, and surrounded by a non-conducting, dielectric gas. These experiments were performed with both AC and DC fields and led to a detailed analysis of this vertical liquid bridge and its stability [19-23]. It has been shown that the longitudinal field along a liquid jet axis has a stabilizing effect on the liquid – gas interface [24] which was later also discussed for vertical liquid bridges [25]. In this sense the liquid bridge formation can be explained as action of the electrohydrodynamic stress tensor replenishing the liquid within the bridge against any drainage mechanism. Recently, the formation of bridges with acetone, dichloromethane (DCM), dimethylformamide, dimethylsulfoxide, ethanol, glycerol, methanol, 1-propanol, 2-propanol, and tetrahydrofuran have been reported and investigated [26].

In this work the Armstrong experiment is repeated with methanol, ethanol, 1-propanol and 2-propanol. The polarimetric and thermographic properties are reported and discussed.

2. Experimental

For the DC experiments we use two 40 ml glass beakers with spouts, 15 x 5 x 0.25 mm platinum electrodes, a DC high-voltage 0-25 kV power supply Phywe ‘Hochspannungs-Netzgerät 25kV’ (No 13671.93, Göttingen, Phywe Systeme GmbH, Germany) with a maximum current of 0.5 mA and a 42nF capacitor in parallel to the bridge. For imaging a Canon 300D with a Sigma 105mm 1:2.8 macro lens, a Panasonic 3CCD NV-DX100 camcorder with Raynox DCR-150 or Raynox DCR-250 conversion lenses, a Photron FASTCAM SA1 high-speed camera with a Nikkor 60 mm 1:2.8 macro lens, or a CASIO Exilim High Speed EX-F1 - were used. All liquids are common solvents and were used in a chemically pure grade. Deionized water was provided by a Barnstead NANOpure type I ultrapure water system (Thermo Fisher Scientific Inc., Waltham, MA) with an initial conductivity of 0.056 μS cm\(^{-1}\) recorded with the integrated conductivity meter of the system. This conductivity rose quickly to 0.8 μS cm\(^{-1}\) with a pH value of 5 due to CO\(_2\) saturation under atmospheric conditions (Kendall 1916). All images were scaled. Infrared imaging (thermal imaging) was done with a FLIR 620 camera (FLIR systems, MA, USA). The images of the bridges chosen for analysis were taken at a point in time when either a temperature equilibrium was reached, or, if that was not possible, during a time before the bridge broke down when temperature changes were minimal. An emissivity of 0.92 was assumed for all liquids. The lengths of the bridges were the maximum lengths attainable for stable bridges in case of the alcohols. The length of the water bridge was intentionally kept shorter for reasons of better comparison.

For polarometric visualisations a ceramic glass diffuser (50 x 50 cm, 5 mm thick) was placed behind the beakers, illuminated by a halogen lamp from behind with a linear polarizer put on top of the diffuser. A second polarising filter was placed in front of the imaging device and used as the analyzer.

For high voltage conductivity measurements, the set-up consisted of two platinum electrodes dipped 10mm deep into the liquid in a glass cuvette (Groß-Küvette 700.000, Hellma GmbH & Co. KG, Müllheim Germany) with 50 mm inner width, 50 mm inner height and 10 mm inner depth, with 50mm electrode distance under atmospheric conditions. With this set-up, voltage versus current diagrams of the different liquids were recorded.

3. Results

Fig. 1 shows the alcoholic bridges (b-e) in comparison to a water bridge (a) as well as polarimetric images of such bridges (f-j). Generally, the alcoholic bridges are thinner and shorter than the water bridge, more difficult to create and less stable [26]. The characteristic bright zones on the top and
bottom of the bridge initially discovered for aqueous bridges under polarized light [3,6] is present for all alcoholic bridges as well.

**Fig. 1:** (a)-(e): Horizontal bridges forming in different polar liquids under atmospheric conditions and DC voltage. The bars are 1 cm. (f)-(j): Liquid bridges between crossed linear polarisers. P indicates the direction of the polarizer, A the direction of the analyzer. (a,f) water 12 kV, (b,g) methanol 9.5 kV, (c,h) ethanol 9.5 kV, (d,i) 1-propanol 10 kV, (e,j) 2-propanol 8 kV

**Fig. 2:** Thermographic images of horizontal bridges forming in different polar liquids under atmospheric conditions and DC voltage. (a) water 12 kV, (b) methanol 9.5 kV, (c) ethanol 9.5 kV, (d) 1-propanol 10 kV, (e) 2-propanol 8 kV
Fig. 2 shows a thermographic analysis of the alcoholic bridges (b-e) in comparison to a water bridge (a). The scales of the images were adapted to match the observed temperature regions. For the sake of comparison, the same scale was chosen for 1- and 2-propanol, respectively.

The most prominent feature of this image is the fact that the water, methanol, ethanol and 1-propanol bridges are heating up whereas the 2-propanol is slightly cooling down. Next to that, the temperature of the methanol bridge was the highest, followed by ethanol, water, and 1-propanol. These trends are evaluated in Fig. 3.

In addition to the liquid bridge set-up, a single cuvette set-up was used to measure the high voltage conductivities of the liquids investigated under more stable conditions. The measurements showed that these properties are non-Ohmic under the conditions applied, and they are plotted in Fig. 4.

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**Fig. 3:** Relative surface temperature changes across the liquid bridge set-ups. The evaluated paths are shown in the insets on the left. Lengths are normalized for reasons of comparison. The borders between bridge and spout are an approximation.
4. Discussion

There are two mechanisms at work in all liquids investigated responsible for the temperature changes: Ohmic resistivity causes heating, whereas evaporation causes cooling. In all liquids except for 2-propanol, the Ohmic heating outweighs the evaporation. The following subsections will discuss and explain these facts in detail.

4.1. Alcoholate ion stabilities

It is basic knowledge of organic chemistry that secondary alcoholate anions are less stable than primary ones because a primary carbon atom carries more positive partial charge than a secondary one, thus the negative charge of the oxygen can be distributed more easily in case of a primary alcoholate. This molecular feature becomes measurable as a macroscopic property when looking at the conductivity of the alcohols. Thus, there are far less alcoholate ions in 2-propanol than in 1-propanol, resulting in a lower current (see Fig. 4), and, consequently, in lower Ohmic heating of the liquid.

4.2. Dipole moment and conductivities

The field strength applied in the present experiments does not cause a significant influence on the dipole moment of the single alcohol molecules. Calculations using optimized RHF/6-311++G** structures, which were verified to be local minima via frequency analysis, showed that at the field strengths up to 20kV/cm results do not differ from calculations without external fields. First significant changes of charge distribution and geometry required $10^4$ times higher field strengths. This result is in line with a similar calculation for water [27]. However, these calculations do not consider the dissociation of molecules into ion pairs. It is well known that the conductivity of dielectric liquids increases with permittivity due to an accompanying decrease of the electrostatic attraction between ion pairs [28]. Whenever a high-voltage DC field is applied to the fluid, an increasing number of ions
escape recombination, causing an increase in conductivity, as was discussed by Onsager and Brière [29,30]. While at low voltage Ohmic behavior is observed due to ions generated by dissociated molecules; at high voltage the dissociation rate is proportional to the electric field but the recombination rate is not and the current approaches saturation [31,32]. These effects are clearly visible for all alcohols in Fig. 4.

4.3. Evaporation
Of all alcohols, methanol has the lowest boiling point (65°C) followed by ethanol (78°C), 2-Propanol (82°C) and 1-Propanol (97°C). According to Hinds [33] a curved surface modifies the attractive forces between surface molecules facilitating diffusion from the liquid surface, and consequently favours evaporation. Thus, when compared to a flat air-liquid interface, an increase on the diffusion of molecules throughout this same interface is expected. Another important point is the presence of surface charge. According to Hartman et al. and Darabi et al. [34,35] the electrostatic stress created by the presence of these charges counter-acts the surface tension stress on the liquid surface. The net effect is the production of secondary motion that destabilizes the thermal boundary layer near the heat transfer surface, leading to higher effective heat transfer coefficients, and causing the production of vapour along the whole air-liquid interface of the set-up with most of the evaporation taking place where the electric field is highest – across the liquid bridge [26]. This is the reason why the 2-propanol bridge is cooler than the bulk liquid, as can be seen in Figs. 2 and 3.

4.4. Polarimetry
It has been suggested that either bubbles or density gradients [3,6] or birefringence [3,5] are possible sources of the bright zones visible when looking at a water bridge using a polarimetric set-up. Until now, this issue is still not resolved. We suggest that, since this effect is not intrinsic to water (see Fig. 1), what ever physics responsible may apply for the alcohols investigated as well, thereby ruling out water specific origins.

5. Conclusions
The infrared emission of alcoholic EHD bridges made of methanol, ethanol, 1-propanol and 2-propanol were compared to an aqueous EHD bridge. The temperature of the primary alcohol bridges is decreasing with their decreasing conductivity. Water is an exception because of its unusually high heat capacity (4.18 J / g·K) compared to methanol (2.59 J / g·K) and ethanol (2.44 J / g·K), thus aqueous bridges are cooler although the conductivity of water is higher than that of the alcohols. Furthermore, we found that a 2-propanol bridge cools down whereas all other bridges heat up. This effect can be explained by two mechanisms responsible for the temperature changes: Ohmic resistivity causing heating, and evaporation causing cooling. In all liquids except for 2-propanol, the ohmic heating outweighs the evaporation. Moreover, since evaporation is increased by electric fields [34,35] and surface curvatures [33], it is expected to be highest along the bridge, thus explaining why the 2-propanol bridge shows anomalous cooling.

In addition, the bright zones originally found in a polarimetric investigation of the water bridge [3] were reproduced for all liquids, thus showing that they are not a water-intrinsic effect.

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