

EFFECT OF SOLVENT VAPOURS ON TEWL MEASUREMENTS

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Introduction

The importance of TEWL measurements in product testing and claims support is well recognised. However, some formulations applied to the skin may contain volatile solvents whose vapours may interfere with the TEWL measurement process. The TEWL guidelines [1, 2] do not discuss this problem and we therefore present a study of the effects of a number of common solvents on TEWL measurements.

Modern TEWL instruments all use the same type of electronic sensor for humidity measurement. It is in the form of a thin-film capacitor, designed to allow vapours in the surrounding air to permeate its porous dielectric. The sorbed vapour causes the capacitance of the sensor to increase in proportion to its quantity and dielectric constant. Such sensors are specific to water vapour only to the extent that water has a higher dielectric constant than other common vapours. Interference from other vapours therefore affects all modern TEWL instruments.

The study used a condenser-chamber instrument [3] (Biox Systems Ltd, UK) whose closed chamber allows the humidity sensor to be exposed to high concentrations of the solvent vapours for prolonged periods of time. The condenser temperature is electronically stabilised to -13.4°C and this causes solvent vapours with higher boiling or freezing temperatures to condense.

Materials and Methods

The measurement method used is similar to the recently developed droplet calibration technique for TEWL [4], as illustrated in Figure 1.



Figure 1: Droplet method for testing solvent effects on TEWL measurement.

A micro-syringe (SGE Type GC) was used to dispense a 500nL droplet of solvent into a calibration cap that can be tightly coupled to the AquaFlux measurement chamber. The TEWL instrument was then set to record a time-series of flux density readings as volatile components of the droplet evaporate. Standard-grade chemicals as listed in Table I were used.

Table I: Solvent Properties.

| Solvent | Melting Temp C | Boiling Temp C | Dielectric Constant | Vapour Pressure kPa @ 20C |
|--------------------|----------------|----------------|---------------------|---------------------------|
| Glycerol | 18 | 290 | 43 | < 0.01 |
| Transcutol | -76 | 198 | | 0.01 |
| Propylene Glycol | -59 | 187 | 32 | 0.01 |
| Dimethyl Sulfoxide | 18.5 | 189 | 48 | 0.06 |
| Water | 0 | 100 | 78 | 2.3 |
| Isopropanol | -88 | 83 | 20 | 4.3 |
| Ethanol | -117 | 78 | 25 | 5.8 |
| Methanol | -94 | 65 | 33 | 12.8 |

Results

In each experiment, the TEWL measurement chamber was closed and empty during the first few seconds of measurement, with the signal settled to zero flux density. The empty cap was then quickly replaced with one containing the solvent droplet in its base, at the centre. The changeover gives rise to a signal peak centred at ~20 seconds, as the measurement chamber is briefly exposed to ambient humidity. Thereafter, the graphs show the response of the instrument to the solvent vapours.

Low Volatility Solvents

Of the four solvents with the lowest vapour pressures (Glycerol, Transcutol, Propylene Glycol, and DMSO),

Glycerol and Transcutol were found not to interfere with water vapour flux measurement at all. Their only observable effect was the release of a small quantity of dissolved water (5.8nL and 13.5nL respectively), as shown in Figure 2.

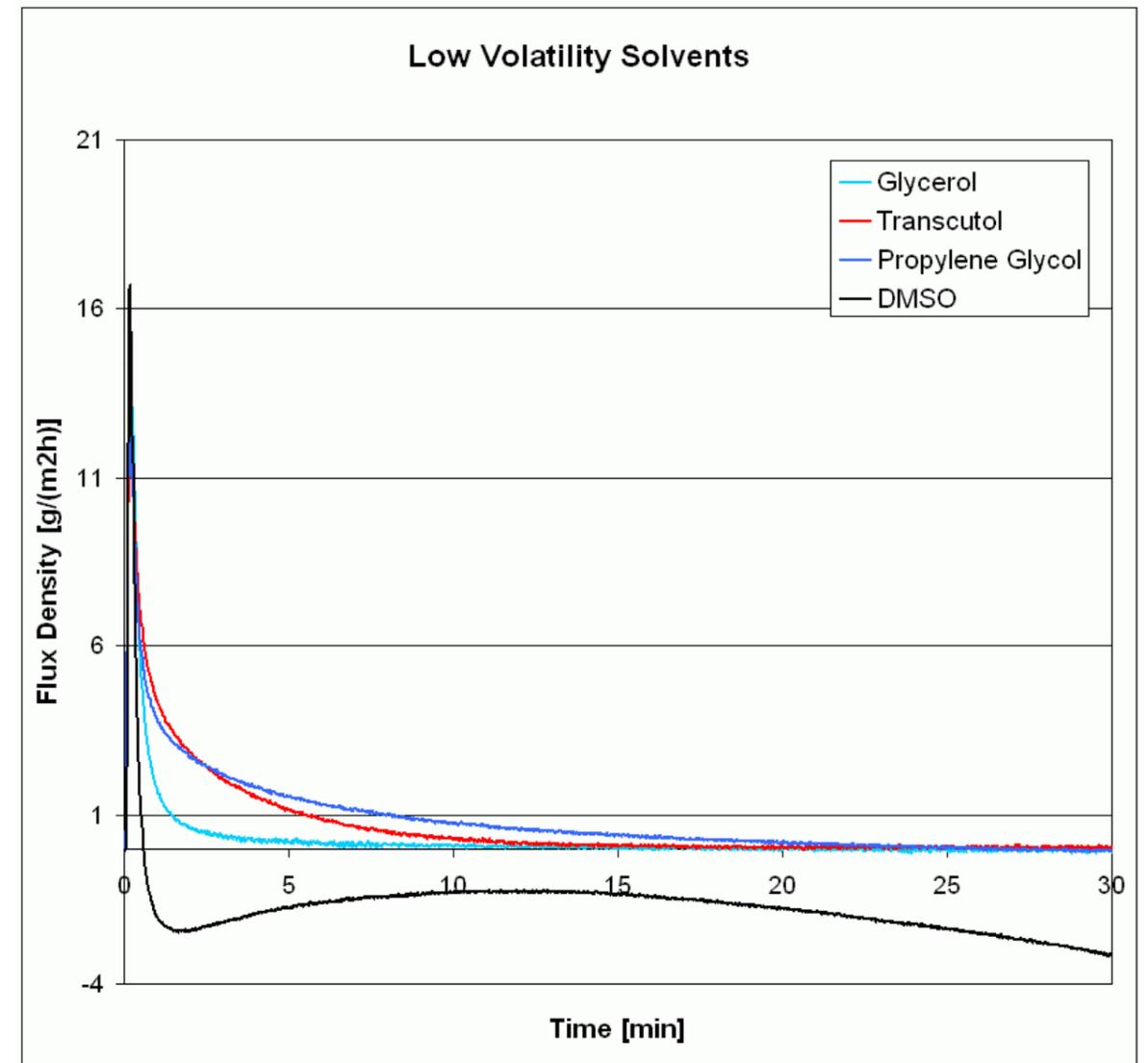


Figure 2: Droplet response from low volatility solvents.

A similar response was observed during the first 30 minutes with Propylene Glycol. However, the indicated flux density was found to decrease below the zero level

with prolonged exposure, reaching a value of $-4.6 \text{ gm}^{-2}\text{h}^{-1}$ after eight hours.

DMSO had a similar effect, but its action was immediate. This is thought to be caused by a lowering of water vapour pressure in the measurement chamber through the hygroscopic action of DMSO.

Alcohols

Response curves for three alcohols of higher vapour pressure than water are presented in Figure 3.

Isopropanol was found to have little effect. Once the dissolved water had evaporated, flux density reading was found to reach a minimum of $\approx -1.2 \text{ gm}^{-2}\text{h}^{-1}$ after about 3 minutes, but this was followed almost immediately by a slow upward trend, which peaked at $0.6 \text{ gm}^{-2}\text{h}^{-1}$ about one hour later. It subsequently reversed again, reaching a reading of $-0.9 \text{ gm}^{-2}\text{h}^{-1}$ after about two hours, after which it remained steady.

Ethanol was found to cause a significantly larger baseline shift, reaching a steady value of $-3.9 \text{ gm}^{-2}\text{h}^{-1}$ once the dissolved water had evaporated.

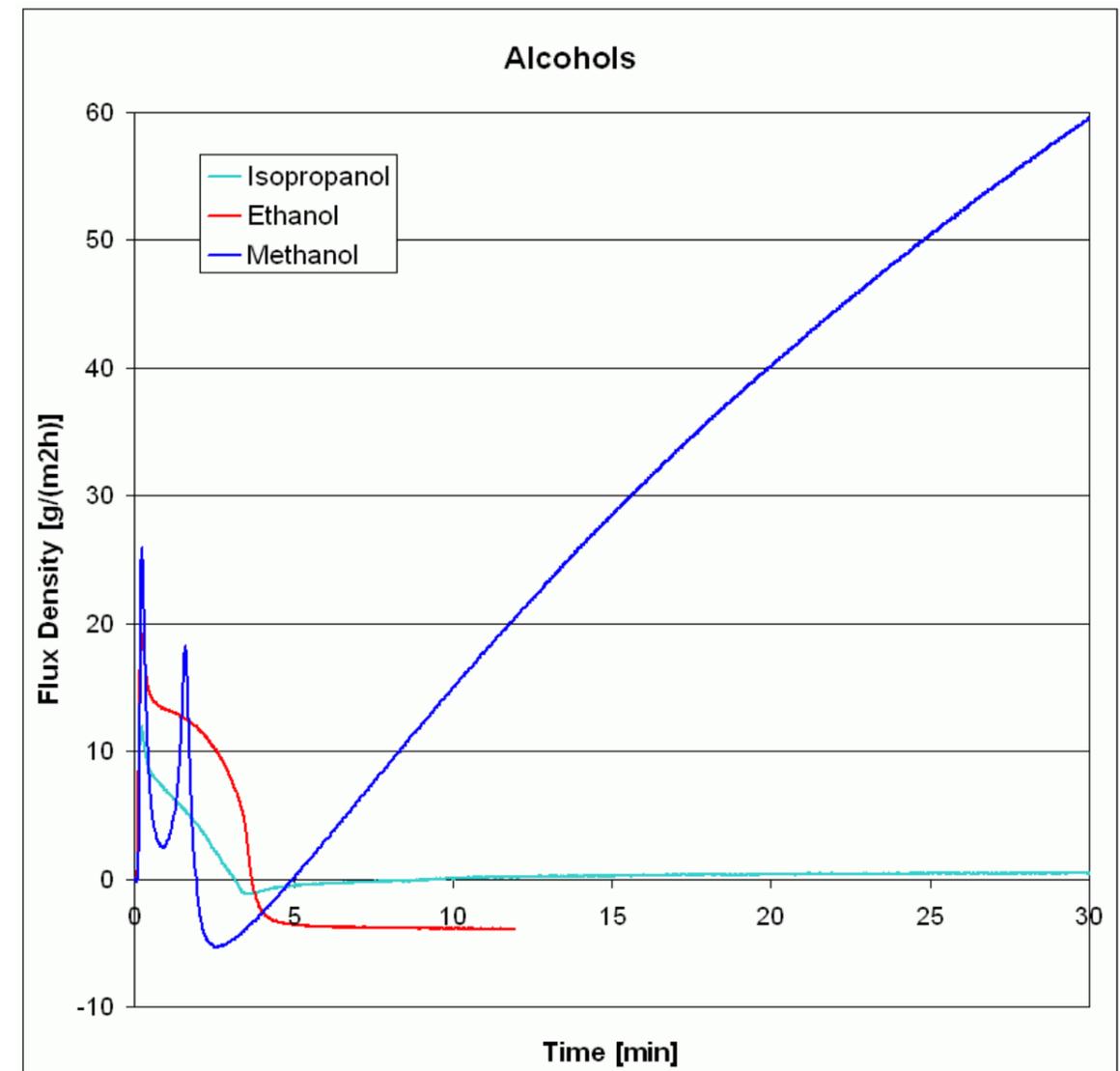


Figure 3: Droplet response from three alcohols of higher vapour pressure than water.

Methanol was found to have the biggest effect, with a secondary peak ~ 78 seconds after the first (water-loss) peak. The indicated flux density was then found to decrease, reaching a minimum of $\approx -5.3 \text{ gm}^{-2}\text{h}^{-1}$ approximately 65 seconds after the secondary peak. Thereafter it was found to rise quite rapidly, levelling out at $\approx 90 \text{ gm}^{-2}\text{h}^{-1}$ after about an hour.

Ethanol - Water Mixtures

The above tests may be somewhat unrealistic in that the solvents were trapped in the measurement chamber in undiluted form, with little or no water present. Any realistic formulation for use on skin would contain significant quantities of water and this would undoubtedly reduce the solvent interference effects on the measurements. This was tested with a number of commonly available ethanol - water mixtures, as shown in Figure 4.

In this case, the time-integral of the flux density (Q-Plot) is displayed rather than the flux density itself, to give a measure of the quantity of water released from the droplets. Presented in this way, it becomes immediately apparent that Beck's Alcohol-free Lager releases considerably more water than Glenfiddich. Although an accurate quantitative analysis is not possible, given the impurity content of these mixtures, it is nevertheless worthwhile to correlate the measured water content with the declared alcohol content, as in Figure 5.

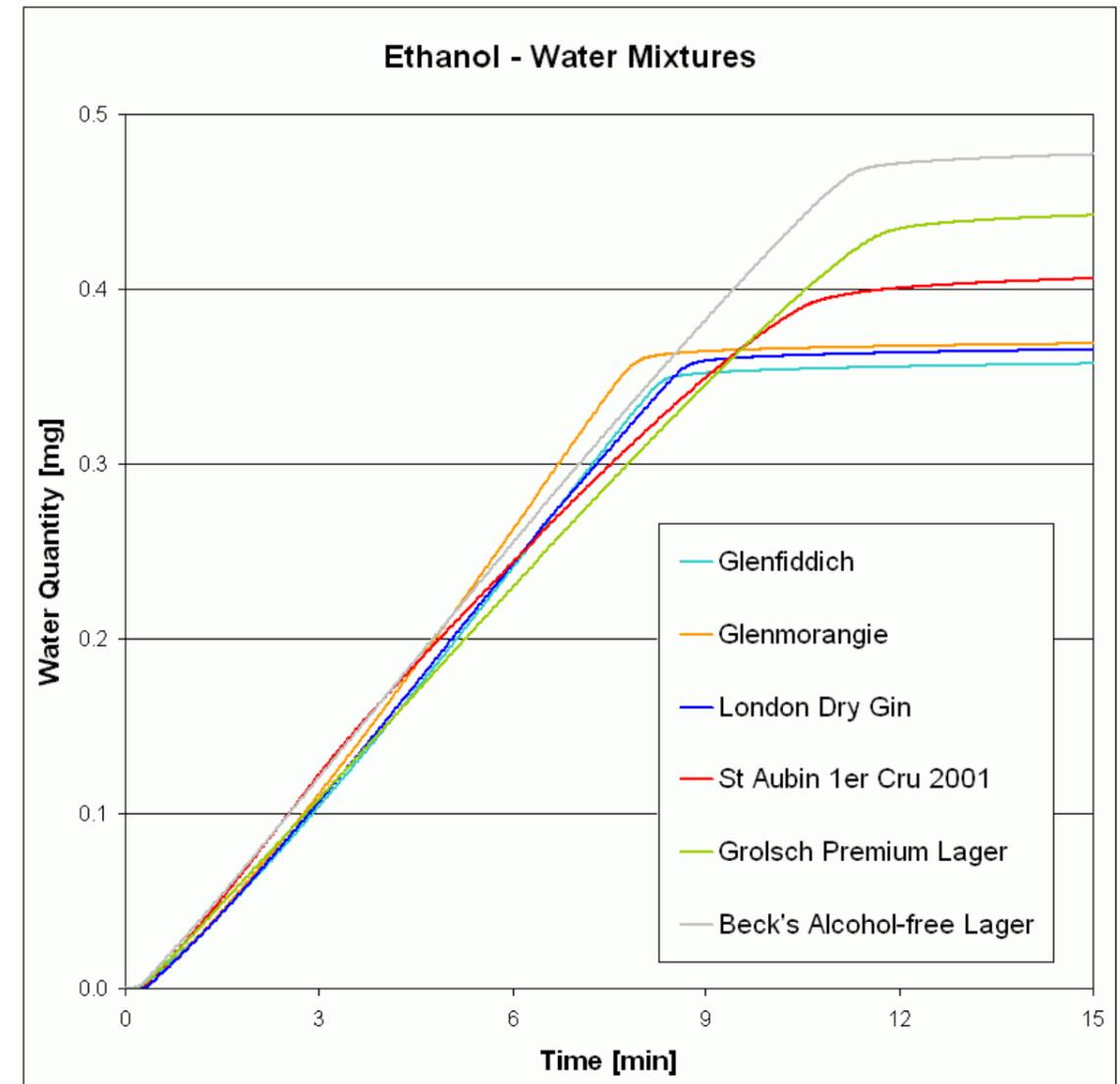


Figure 4: Q-plot of droplet response to Ethanol-Water mixtures.

Solvent Effect on Calibration

Capacitive humidity sensors used in all TEWL instruments discriminate only weakly between different vapours through the dielectric constants of the solvents. Solvent vapours are sorbed into the dielectric during exposure and traces may persist after exposure. Only Methanol exposure was found to cause a persistent change of sensor characteristics, where it took about 24

hours for the high flux density reading at the end of the exposure to this vapour to decay back to a zero baseline. Flux density calibrations after baseline recovery confirmed that the sensor had not been damaged by this exposure.

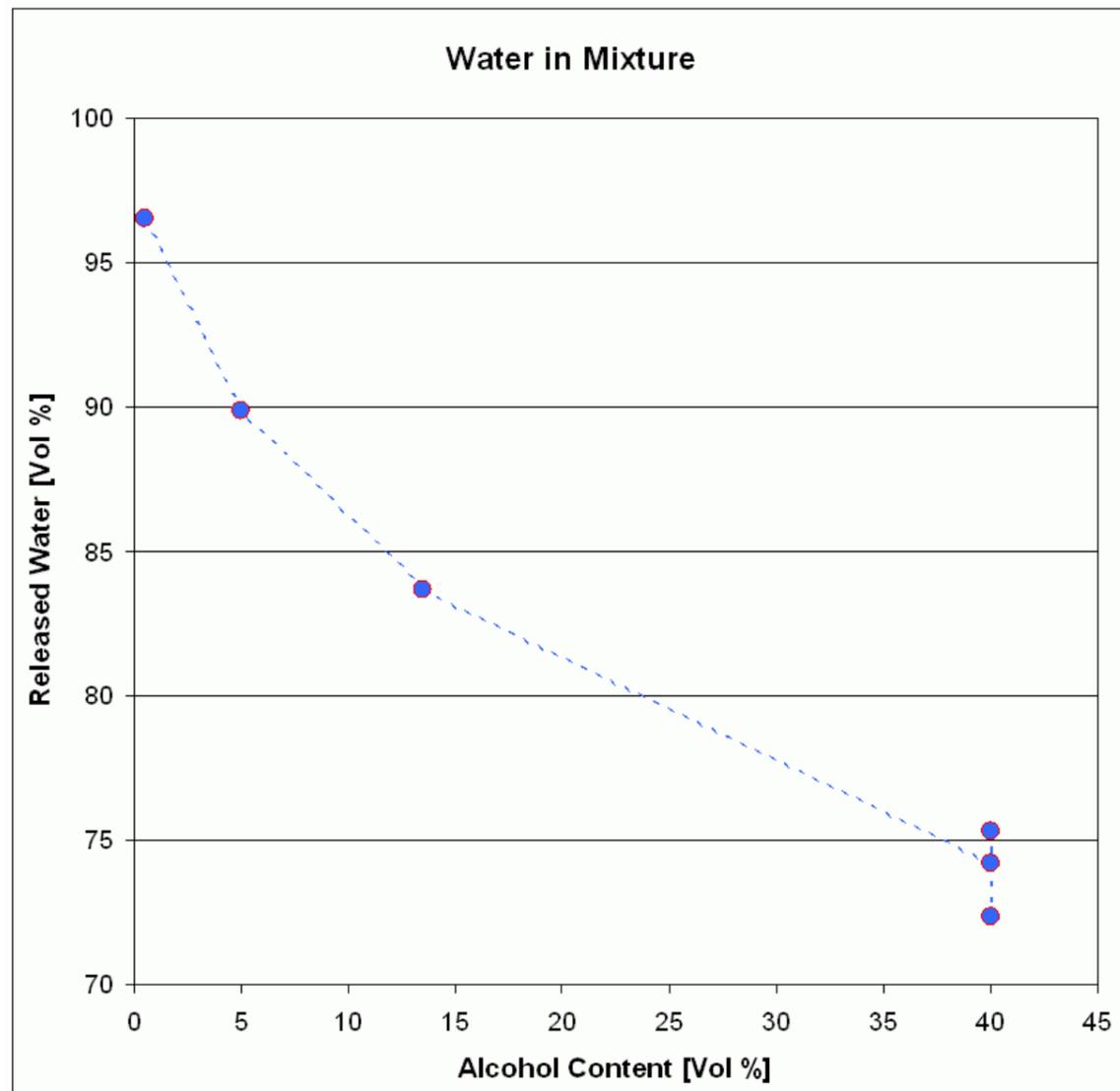


Figure 5: Correlation of the declared alcohol content with the water released from the droplets.

Conclusions

Solvents can interfere with TEWL measurement. Observed effects include (i) a component of flux from dissolved water, (ii) a response of the humidity sensor to non-aqueous vapours and (iii) a post-exposure change of calibration that could persist for several days. We therefore recommend the separate testing of any preparation to aid the interpretation of TEWL measurements in its presence, followed by a re-calibration to ensure that subsequent measurements remain valid.

References

1. J Pinnagoda, RA Tupker, J Agner and J Serup, *Guidelines for transepidermal water loss (TEWL) measurement*. A Report from the Standardization Group of the European Society of Contact Dermatitis, *Contact Dermatitis* **22** (1990) pp164-78.
2. V Rogiers and the EEMCO Group, *EEMCO Guidance for the Assessment of Transepidermal Water Loss in Cosmetic Sciences*. *Skin Pharmacol Appl Skin Physiol* **14** (2001) pp117-28.
3. Imhof RE, Berg EP, Chilcott RP, Ciortea LI, Pascut FC and Xiao P, *New Instrument for measuring water vapor flux density from arbitrary surfaces*, *IFSCC Magazine*, **5** (2002) 297-301.
4. Xiao P, Imhof RE, de Jesus MEP, Cui Y and the TEWL Calibration Consortium, *A new calibration method for TEWL with traceability to measurement standards*, *Skin Research & Technology (Abstracts)*, **10** (2004) 3.