

# Results of Interfacial Tension Tests between Pre-Equilibrated Ethyl Acetate and Water, Using a Kruss Drop Volume Tensiometer DVT10/DVT30 with Two Types of Orifices

Technical Note # 309e

by

Christopher Rulison, Ph.D., Kruss USA

## Background

The Kruss Drop Volume Tensiometer (DVT10 or DVT30) is a precise and accurate tool for determination of equilibrium and non-equilibrium interfacial tensions. It is, therefore, used in a variety of industries (including pharmaceuticals, personal care, oil, detergents, and food) to characterize the rate of adsorption of interfacial materials to newly formed interfaces (i.e. to study the processes of emulsion stabilization).

We are often asked by our DVT10/DVT30 users to define a set of standard liquids, having a well defined interfacial tension over a variety of flow rates, which they, themselves, can use as a "standard" for testing the operation of their DVT10/DVT30, as well as their own skills at using the instrument.

A good set of liquids for that purpose is ethyl acetate and water.

Ethyl acetate and water (when pre-equilibrated, by means of having been mixed together in the same container and left to sit overnight, before being separated, and used for testing) are reported to have an interfacial tension of 6.5 mN/m ... and they do when tested with a DVT10/DVT30 at a variety of flow rates.



Drop Volume Tensiometer DVT30

## Our Experimental Data

We have generated the following data with the two different types of orifices that are generally used with a DVT10:

Our standard thin-walled tungsten carbide tip (Kruss part # SH2301 – metallic gray in color), 0.254 mm I.D. = 0.254 mm effective diameter

Our chemically resistant alumina tip (Kruss part # SH2302 – white colored alumina), 0.254 mm I.D. = 0.264 mm effective diameter

Interfacial tension data obtained using the **standard thin-walled tungsten carbide tip** (Kruss part # SH2301 – metallic gray, tungsten carbide).

Five-drop experiments performed at various pump flow rates with pre-equilibrated ethyl acetate (density = 0.902 g/cm<sup>3</sup>) as the drop phase, and water (density = 0.998 g/cm<sup>3</sup>) as the continuous phase, at room temperature.

**Effective Diameter = 0.254 mm**

| Drop #    | Tension<br>at 2.0 ml/hr<br>(mN/m) | Tension<br>at 1.0 ml/hr<br>(mN/m) | Tension<br>at 0.5 ml/hr<br>(mN/m) | Tension<br>at 0.1 ml/hr<br>(mN/m) | Tension<br>at 0.05 ml/hr<br>(mN/m) |
|-----------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|------------------------------------|
| 1         | 6.51                              | 6.48                              | 6.53                              | 6.55                              | 6.50                               |
| 2         | 6.45                              | 6.49                              | 6.52                              | 6.52                              | 6.48                               |
| 3         | 6.47                              | 6.48                              | 6.56                              | 6.54                              | 6.49                               |
| 4         | 6.49                              | 6.45                              | 6.52                              | 6.52                              | 6.53                               |
| 5         | 6.48                              | 6.50                              | 6.52                              | 6.52                              | 6.50                               |
| Average   | <b>6.48</b>                       | <b>6.48</b>                       | <b>6.53</b>                       | <b>6.53</b>                       | <b>6.50</b>                        |
| Std. Dev. | 0.022                             | 0.019                             | 0.017                             | 0.014                             | 0.019                              |

**Overall Average = 6.50 mN/m**

**Overall Std. Dev. = 0.028 mN/m (0.4%)**

Interfacial tension data obtained using the **chemically resistant alumina tip** (Kruss part # SH2302 – white colored alumina)

Five-drop experiments performed at various pump flow rates with pre-equilibrated ethyl acetate (density = 0.902 g/cm<sup>3</sup>) as the drop phase and water (density = 0.998 g/cm<sup>3</sup>) as the continuous phase, at room temperature.

**Effective Diameter = 0.264 mm**

| Drop #    | Tension<br>at 2.0 ml/hr<br>(mN/m) | Tension<br>at 1.0 ml/hr<br>(mN/m) | Tension<br>at 0.5 ml/hr<br>(mN/m) | Tension<br>at 0.1 ml/hr<br>(mN/m) | Tension<br>at 0.05 ml/hr<br>(mN/m) |
|-----------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|------------------------------------|
| 1         | 6.55                              | 6.49                              | 6.53                              | 6.54                              | 6.53                               |
| 2         | 6.53                              | 6.49                              | 6.50                              | 6.53                              | 6.58                               |
| 3         | 6.54                              | 6.48                              | 6.53                              | 6.49                              | 6.53                               |
| 4         | 6.51                              | 6.49                              | 6.52                              | 6.54                              | 6.56                               |
| 5         | 6.57                              | 6.55                              | 6.57                              | 6.50                              | 6.55                               |
| Average   | <b>6.54</b>                       | <b>6.50</b>                       | <b>6.53</b>                       | <b>6.52</b>                       | <b>6.55</b>                        |
| Std. Dev. | 0.022                             | 0.028                             | 0.025                             | 0.023                             | 0.021                              |

**Overall Average = 6.53 mN/m**

**Overall Std. Dev. = 0.028 mN/m (0.4%)**

As you can see from the data, the DVT10/DVT30 does provide accurate interfacial tension data, over a variety of flow rates for pre-equilibrated systems.

In viewing the data with focus on the different tips, you will note that the recommended effective diameter for drop volume work does differ between the two tips, despite the fact that both have inside diameters of 0.254 mm. There is a simple explanation for this.

The design of the standard tungsten carbide tip was developed first. The design is quite unique. It took several years of research, and it is proprietary. Its major unique feature is that the walls of the tip, are machine ground to be extremely thin at the opening (much like a knife edge) so that the drop detaches completely from the interior diameter. Therefore, the effective diameter = the interior diameter, with no corrections for possible wetting to the outside diameter of the capillary.

When it was realized that tungsten carbide tips did not serve the needs of all of our customers, we subsequently designed a similar alumina tip with an I.D. of 0.254 mm for their use. However, ceramics cannot be ground to have as fine of edges as metals. And, experiments, including the one above, have shown that the effective diameter of our standard ceramic tip is 0.264 mm – 10 microns larger than it's inside diameter of 0.254 mm.

Since we know this effective diameter discrepancy for the ceramic tip is due to wetting of the edges of the capillary, and that the extent of wetting may vary for different pairs of liquids, one could also argue that the effective diameter of our alumina tip is not really a fixed value. Rather, it may vary from system to system. This is certainly true. And, it is a reason to use the standard tip, whenever possible. However, even in the worst possible case (which is never truly realized in practice), in which wetting does not occur with the alumina tip, and we have assumed 0.264 mm as the effective diameter, our interfacial tension value would only be inaccurate by 3.9%. That's just the price of having to work with a corrosive systems – and should not be limiting for comparative work.

### **Duplicating the Experiments Yourself**

Obviously, since the point of this note is to provide a standard system for checking the "standard" operation of a DVT10/DVT30, as user skills, you may wish to duplicate these experiments yourself.

When you do, here are some tips.....

BE SURE TO USE PURE HPLC GRADE ETHYL ACETATE, AND PURE DISTILLED WATER (deionized water is not acceptable for exacting work, as it often still contains interfacially active organics).

DO NOT SKIP THE PRE-EQUILIBRATION STEP. The DVT10 is a dynamic instrument, and is often used to measure how quickly surfactants and polymers diffuse to interfaces. However, it will also measure two liquids equilibrating with one another (in the sense that a trace amount of liquid 1 is soluble in liquid 2, no matter what two liquids you study), if the liquids are not pre-equilibrated.

So, PUT THE ETHYL ACETATE AND THE WATER TOGETHER IN THE SAME CLEAN GLASS CONTAINER, SHAKE, AND LET STAND FOR 24 HOURS, then separate the phases for use in this experiment.

FAILURE TO PROPERLY EQUILIBRATE THE PHASES WILL RESULT IN HIGHER THAN EXPECTED INTERFACIAL TENSION VALUES WHICH DECREASE WITH DECREASING FLOW RATE.

Good Luck.

2001 / Rev. 2004