Interfacial Tension between

Fluorinerts and Silicone Oils

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Abstract

The interfacial tension as a function of temperature between various fluorinerts and silicone oils was measured. These experimental values are compared to predictions by Antonow's rule and by a method proposed by Girifalco and Good. The quality of agreement between experiments and predictions is discussed for the two models.

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The variation of surface tension (*st*) and interface tension (*it*) with temperature is an important driving force for thermal flows known generally as thermocapillary flow. Most surface tensions decrease with increasing temperature. Accordingly, cooler surface areas pull molecules from the neighboring warmer regions thus creating flow at the surface of the liquid. The resulting flow is known as "thermocapillary convection," or "Marangoni convection" for temperature gradient applied orthogonally to the interface.

Besides buoyancy driven convective flow originating from density changes and the concurrent action of gravity, convective flow induced by the temperature dependence of the *st*-gradient plays an important role in many technologies, such as crystal growth. Buoyancy driven convection in a gravitational field, such as the Earth's, tends to mask thermocapillary convection. In a microgravity environment, however, the latter is found to be the major driver for thermal flows. As these thermal flows may lead to crystallographic defects in electronic material crystals, scientists devised the liquid encapsulated crystal growth processes. This creates a liquid-liquid interface between the encapsulant and the melt. Liquid encapsulated crystal growth has become a viable processing technique in Czochralski crystal growth and was proposed for space processing of GaAs [Barocela and Jalilevand,1987]. As thermocapillary flow becomes dominant in low-gravity a need arose to study the fluid mechanics of immiscible liquid layers.

Fundamental physics of buoyancy driven and thermocapillary convection in immiscible liquid layers are investigated experimentally, analytically and numerically by Prakash and Koster [1993]. The interface tension gradient (*itg*) is one of the parameters needed for these studies. Surface tension data on the employed fluids are scarce, which is even more true for interface tension data. The experimental determination of *itg* of the pertinent fluid combinations became necessary. The data are also in support of a thermocapillary space flight experiment, to be performed aboard the International Microgravity Laboratory IML-2 in June 1994.

As interfacial data taking is quite involved it would help to have a reliable predictive tool to evaluate interfacial tensions. Several theories have been developed to calculate the *it* for two liquids whose *st* is known. Two of these theories, Antonow's rule [Gibbs, 19] and the method after Girifalco and Good [1956], assume total immiscibility between the two fluids. Another theory proposed more recently by Boudh-Hir and Mansoori [1991] assumes partial miscibility between the liquids. Their formula requires the determination and knowledge of very minute density changes at molecular level and molecule dimensions of the fluids. For a practicable estimation this theory becomes rather involved as no reliable experimental means are available to provide some of the required data. For that reason this paper focuses on Antonow's rule and the method of Girifalco and Good.

2. *Theoretical Determination of Interface Tension and its Gradient*

Antonow's rule and the method after Girifalco and Good are two well-known methods for perfectly immiscible liquid-liquid systems. Though, various fluid-fluid interface systems prove the validity of these formulae **[.?Ref??.]**, both do not necessarily give exact values for interface tensions for any liquid-liquid combination.

The following equation is known as "Antonow's Rule:"

$$\gamma_{12} = | \sigma_1 - \sigma_2 | \tag{1}$$

Differentiation of Antonow's Rule with respect to temperature leads to the equation for the *itg* as function of the surface tension gradients (*stg*):

$$\frac{d\gamma_{12}}{dT} = \left| \frac{d\sigma_1}{dT} - \frac{d\sigma_2}{dT} \right| \tag{2}$$

Reported measurements [**REF????**] of interfacial tension give results in good agreement with those calculated according to Girifalco and Good's formula [Girifalco and Good, 1956]. Their equation reads:

$$\gamma_{12} = \sigma_1 + \sigma_2 - 2\,\Phi\,\sqrt{\sigma_1\,\sigma_2} \tag{3}$$

The differentiated equation for the *itg* is:

$$\frac{d\gamma_{12}}{dT} = \frac{d\sigma_1}{dT}\left(1 - \Phi\sqrt{\frac{\sigma_2}{\sigma_1}}\right) + \frac{d\sigma_2}{dT}\left(1 - \Phi\sqrt{\frac{\sigma_1}{\sigma_2}}\right) \tag{4}$$

The values for the *st* and *stg* as well as the *itg* will be measured. The constant Φ depends

on the diameter of single spherical molecules and on the molar volume for non-spherical molecules. In case of the long chain molecules, such as fluorinerts and silicone oils, the theoretical determination of this constant becomes more complicated. The values for Φ are calculated by means of equation (3), employing measured *st* and *it* data at a temperature of T = 25° C:

$$\Phi = \frac{\sigma_1 + \sigma_2 - \gamma_{12}}{2\sqrt{\sigma_1 \sigma_2}} \tag{5}$$

and by means of equation (4) employing measured *stg* and *itg* data:

$$\Phi = \frac{\frac{d\sigma_1}{dT} + \frac{d\sigma_2}{dT} - \frac{d\gamma_{12}}{dT}}{\frac{d\sigma_1}{dT}\sqrt{\frac{\sigma_2}{\sigma_1}} + \frac{d\sigma_2}{dT}\sqrt{\frac{\sigma_1}{\sigma_2}}} \tag{6}$$

3. Experimental Procedures

The *st* and *it* are measured by means of the ring method after du Noüy. This method has been chosen because of its simple handling, while giving a fair degree of accuracy. The manual tensiometer (Krüss, Interfacial Tensiometer K8) can measure *st* accurate to ± 0.1 dynes/cm. With a constant temperature bath the temperature was regulated to ± 0.1° C. The glass test vessels have a diameter of 45 mm and are kept in a large thermal mass which filters some of the temperature fluctuations. The du Noüy ring is made out of 90% platinum and 10% iridium; its dimensions are: (i) mean radius R =

9.545 mm, (ii) radius of the wire's cross-section r = 0.185 mm, and (iii) radius-ratio R/r = 51.6.

According to diverse standards [ASTM D 971-82, ASTM D 2285-85] the glass vessels are cleaned with petroleum naphtha, to remove any residual oil, methyl ethyl ketone, a solvent for silicone oils, **xxx%** chromic acid, a solvent for any other residues, **xxx%** phosphoric acid, to remove residual chromic acid, and finally followed by several washes with distilled water. Before every measurement the ring is cleaned by immersing it into tap water, distilled water, petroleum naphtha, and methyl ethyl ketone, and subsequent red glowing in a bunsen flame.

Three measurements were taken at four specific plateaus of constant isothermal temperature between 5° C and 45° C. Every measurement has been repeated several times and the repeatability did not differ by more than ± 0.1 dynes/cm, which represents the accuracy of the device itself. The values read from the scale were corrected with a correction factor proposed by Zuidema and Waters [1941] and additionally with a factor of 1.07 **[Ref???]** to take into account that the tensiometer has been linearly compensated.

The *st* is measured by pulling the ring from the bulk of the fluid to its surface after the device was zeroed with the weight of the dry ring in air. Measurements of *it* were taken in the pushing mode, which means that the ring was pushed from the lighter fluid in the upper layer into the heavier fluid in the bottom layer. The device was zeroed

with the ring immersed into the lighter liquid. The pushing mode was chosen because of the higher surface tension of the more polar silicone oil compared to the fluorinerts. During pulling tests from the fluorinert into the silicone oil it was observed that the ring "jumps" at one point in time from the fluorinert into the silicone oil with erratic tension readings. Measuring the interface tension with the pushing method led to a high repeatability of the measurements.

4. Results

The *st* of fluorinerts FC 40, FC 70, and FC 75 (3M Company) and silicone oils (Hüls) with a viscosity of 2 cSt, 10 cSt, and 100 cSt as well as the *it* for combinations of these immiscible liquids were gauged. The immiscibility was tested with coherent optical techniques which are very sensitive to refractive index changes caused by diffusion. All data points, corrected as discussed above, are shown in Fig. 1 and 2. *St* and *it* for the investigated liquids decrease linearly with increasing temperature. *St* of silicone oils (around 20 dynes/cm) and fluorinerts (around 17 dynes/cm) is found to be much stronger than *it* (around 5 dynes/ cm), *stg* of -0.06 dynes/(cm K) are about two times higher than *itg* around -0.03 dynes/(cm K).

Data taken at T = 25° Care listed in Tab. 1 and 2. As shown in Tab. 1, *st* data obtained with our experimental set-up match those values from other **[REF???]** source within an error of ±3.3%, FC 40 with an error of ±9.4% excepted. The measured *stg* are

up to 32% smaller than reference values.

The *it* measurements are compared to values calculated by Antonow's rule (eq. **1**) and Girifalco and Good (eq. **3**). For the latter method a Φ-value was calculated from the measurements of *stg* and *itg* (eq. **6**). Comparing *it* obtained with Antonow's rule to experimental data shows that for liquid combinations with nearly the same *st* of the single liquids, Antonow's rule predicts an *it* which is between 54% and 93% smaller than the measured value (Tab. 3). For two liquids of different *st*, as for FC 75 and any silicone oil, application of Antonow's rule leads to results in good agreement with the measured values, as errors of less than -4% are found (Tab. 3). Applying Girifalco and Good for *it* prediction results in values much higher than the measured ones (Tab. 2).

Comparing *itg* derived from measurement to those calculated with the differentiation of Antonow's rule (eq. **2**) show that Antonow predicts gradients too small for liquids of almost equal *st* (Tab. 3). *Itg* calculated with the differentiated method of Girifalco and Good (eq. **4**) employing a Φ value derived from *st* and *it* measurements (eq. **5**) show a smaller gradient than the measured one, yet, the error is smaller than for the *it* (Tab. 3).

Girifalco and Good's method leads to results in good agreement with experimental measurements when the Φ-values calculated from measured *it* (eq. **5**) and measured *itg* (eq. **6**) are the same (Tab. 3). Increasing divergence between these calculated Φ-values goes along with larger errors between theoretical model and

measurements. This is the case for relatively high values for measured *it* (FC 40/ 100 cSt, FC 70/ 10 cSt, FC 70/ 100 cSt).

5. Conclusion

Antonow's rule was found to lead to sufficiently good predictive results for interfacial tensions when the difference in surface tension of the single liquids is relatively high (3.2 - 5.7 dynes/cm in our case). The method after Girifalco and Good, with its prediction of the parameter Φ predicts the *it* well for higher *it*. In cases of higher, experimentally obtained *it*, the values calculated after Girifalco and Good, and even after Antonow's rule, are found to match well. This agreement was also reported by Harkins, *et al.* [1916]. The mismatch between *it* and *itg* values determined after Girifalco & Good and the measured values stem from the difficult determination of the Φ-value. However, if the interfacial tensions of one system, e.g. fluorinert/silicone oil, is measured and the parameter Φ determined based on these values, then the parameter Φ can be used with good confidence as a predictive tool for the estimate of interfacial tensions of other fluorinerts and silicone oils.

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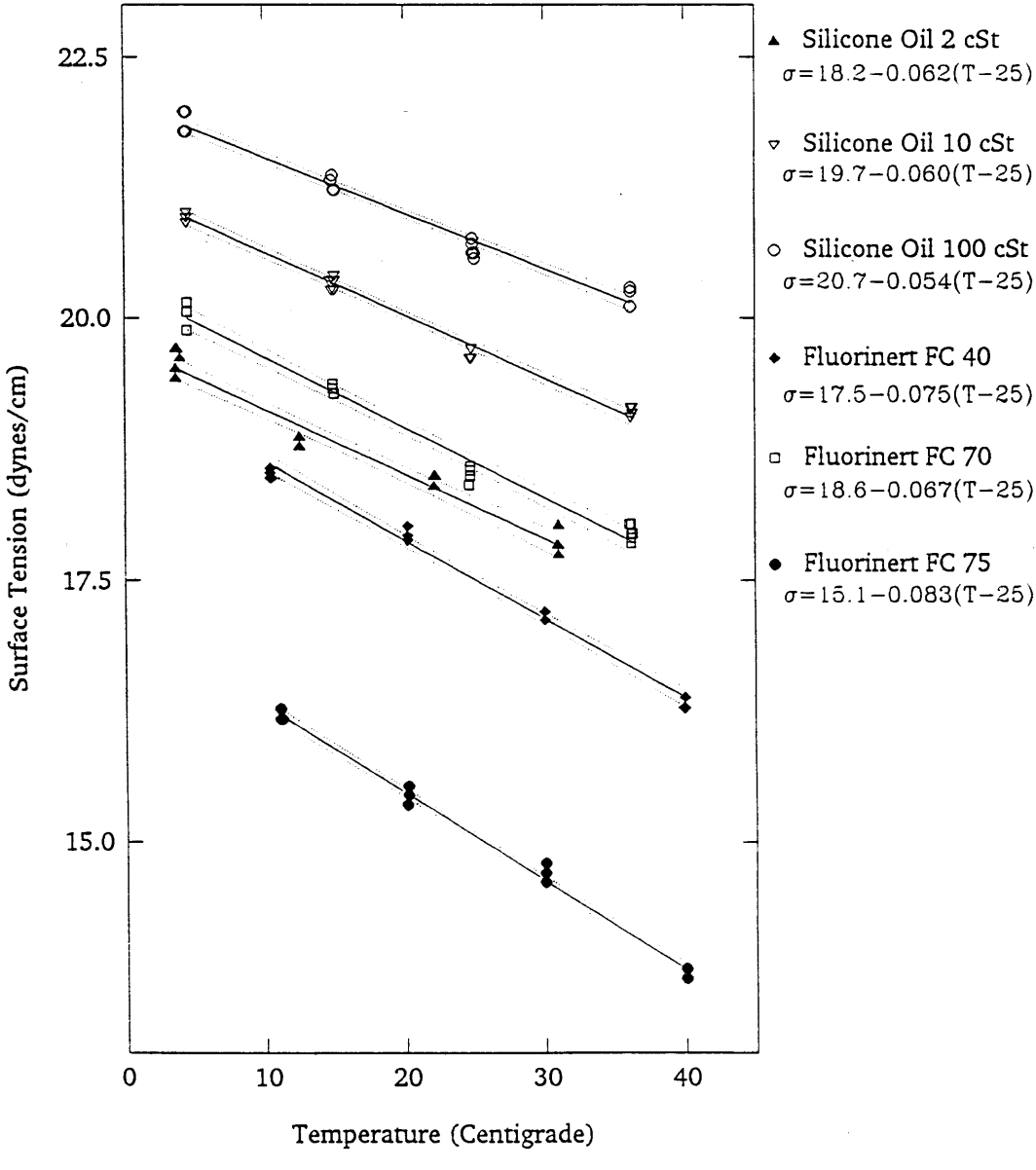
Surface Tension Measurements



Interface Tension Measurements

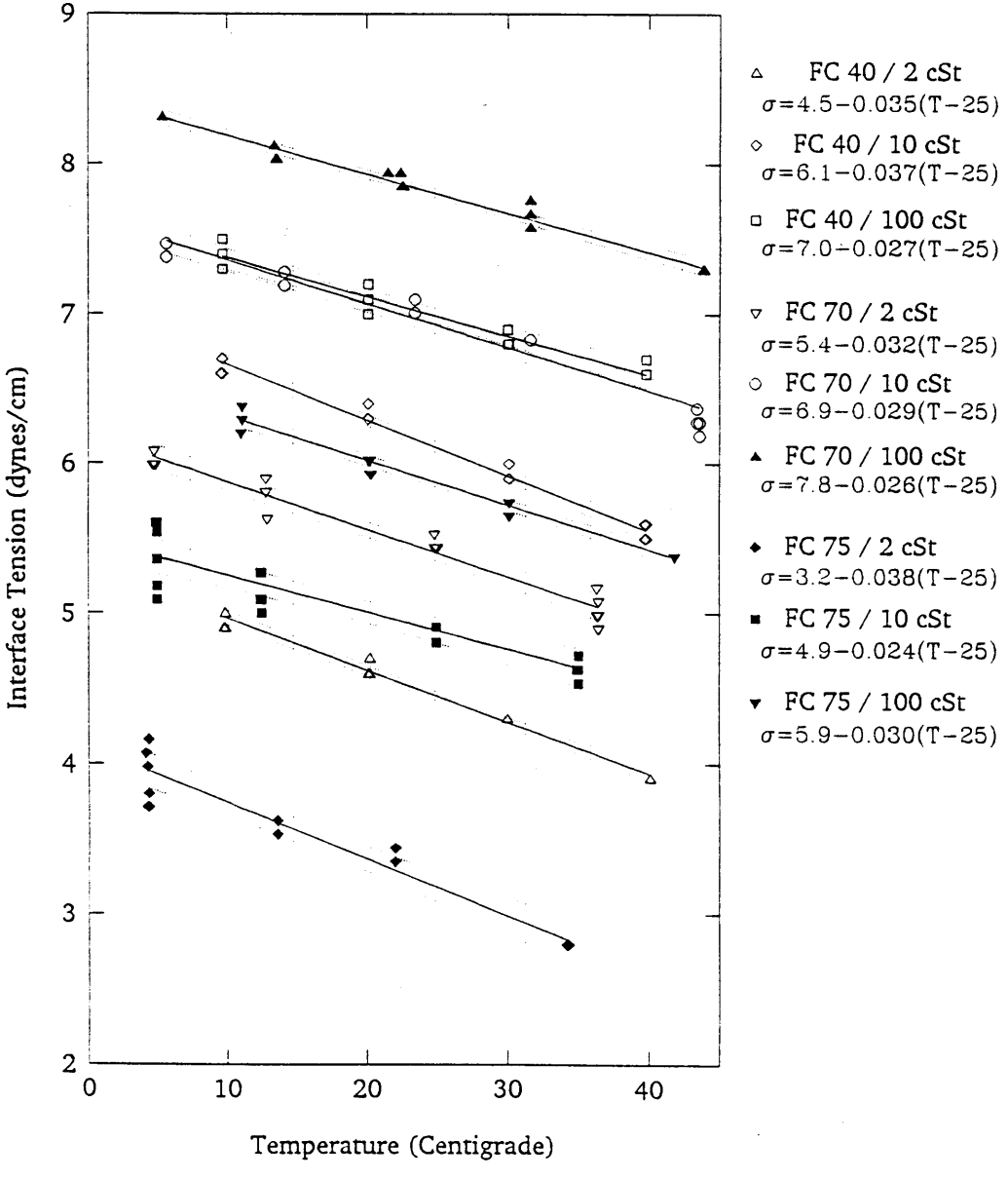


Table 1: Surface Tension Data (T = 25 C)

Fluid	p	D	F	Measurements		Reference		Error	
	scale reading	density	correct. factor	s.t.	s.t.g.	s.t.	s.t.g.	Meas./Ref., s.t.	Meas./Ref., s.t.g
	[dynes/cm]	[g/cm^3]	[-]	[dynes/cm]	[dynes/cm/K]	[dynes/cm]	[dynes/cm/K]	[%]	[%]
FC 40	19.1	1.870	0.855	17.5	-0.075	16 1)	-	+9.4	-
FC 70	20.3	1.940	0.856	18.6	-0.067	18 1)	-	+3.3	-
FC 75	16.5	1.760	0.854	15.1	-0.083	15 1)	-0.122 1)	+0.7	-32.0
2 cSt	19.5	0.871	0.873	18.2	-0.062	18.7 2)	-0.068 3)	-2.7	-8.8
10 cSt	21.1	0.935	0.873	19.7	-0.060	20.1 2)	-0.068 3)	+2.0	-11.8
100 cSt	22.2	0.964	0.874	20.7	-0.054	20.9 2)	-0.068 3)	-1.0	-20.6

1) Fluorinert 3M, Product Manual

2) DOW Corning Corporation

3) Burelbach, Bankoff, Davis, Phys.Fluids A, Vol.2, No.3, March 1990

Table 2: Interface Tension Data (T = 25 C)

Fluids	p	D-d	F	Measurements		Antonow		Girifalco phi: calculated from eq.6	Girifalco from eq.5
				i.t.	i.t.g.	i.t.	i.t.g.	i.t.	i.t.g.
	[dynes/cm]	[g/cm^3]	[-]	[dynes/cm]	[dynes/cm/K]	[dynes/cm]	[dynes/cm/K]	[dynes/cm/K]	[dynes/cm/K]
FC 40/ 2 cSt	4.9	0.999	0.845	4.5	-0.035	0.7	-0.014	10.7	-0.013
FC 40/ 10 cSt	6.7	0.935	0.851	6.1	-0.037	2.2	-0.015	11.2	-0.026
FC 40/ 100 cSt	7.7	0.906	0.850	7.0	-0.026	3.2	-0.022	7.7	-0.024
FC 70/ 2 cSt	6.0	1.069	0.848	5.4	-0.032	0.4	-0.005	7.4	-0.013
FC 70/ 10 cSt	7.6	1.005	0.851	6.9	-0.029	1.1	-0.007	7.7	-0.025
FC 70/ 100 cSt	8.6	0.976	0.853	7.8	-0.026	2.1	-0.013	7.9	-0.024
FC 75/ 2 cSt	3.5	0.889	0.845	3.2	-0.038	3.2	-0.022	10.1	-0.012
FC 75/ 10 cSt	5.4	0.825	0.849	4.9	-0.024	4.7	-0.023	7.2	-0.010
FC 75/ 100 cSt	6.4	0.796	0.852	5.9	-0.030	5.7	-0.030	11.0	-0.008

Table 3: Phi-Values and Errors

Fluids	phi calculated from eq.5 [-]	phi calculated from eq.6 [-]	Error Ant./ Meas. i.t [%]	Ant./ Meas. i.t.g [%]	Girif./ Meas. phi: calculated from eq.6 i.t. [%]	Girif./ Meas. from eq.5 i.t.g. [%]	phi (eq.5)/ phi (eq.6) [%]
FC 40/ 2 cSt	0.9	0.7	-84	-60	138	-63	-22
FC 40/ 10 cSt	0.8	0.7	-64	-59	84	-30	-13
FC 40/ 100 cSt	0.8	0.8	-54	-15	11	-8	0
FC 70/ 2 cSt	0.9	0.8	-93	-84	36	-59	-11
FC 70/ 10 cSt	0.8	0.8	-84	-76	11	-14	0
FC 70/ 100 cSt	0.8	0.8	-73	-50	1	-8	0
FC 75/ 2 cSt	0.9	0.7	0	-42	215	-68	-22
FC 75/ 10 cSt	0.9	0.8	-4	-4	47	-58	-11
FC 75/ 100 cSt	0.9	0.7	-3	0	87	-73	-22

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Lieber Hannes:
Ich bin nicht früher dazu gekommen mich mit der Veröffentlichung von Christians Messungen zu beschäftigen. Hier ist ein erster Draft. Wir machen noch eine bessere Fehleranalyse. Bitte überarbeite die Version und schicke mir Deine Verbesserungen.
Ich bin mir nicht sicher wo diese Arbeit zu publizieren. Vielleicht kannst Du mir eine Zeitschrift empfehlen.

Viele Grüße

Jan