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THE MEASUREMENT OF INTERFACIAL TENSION BY DROP-WEIGHT METHOD

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SUMMARY

Capillary rise, drop-weight, pendant-drop and ring methods which are originally developed for surface tensions have been adapted to the measurement of interfacial surface tensions. Dropweight method is, however, frequently employed for the purp se. Interfacial tensions usually lie between the individual surface tensions of the two liquids in question. Interfacial tensions are of extreme importance in connection with colloids, biological systems and separation processes such as liquid extraction, mixed vapour condensation with an immiscible condensate.

The interfacial tensions for the systems of toluene-water, benzene-water, n-heptane-water and cyclohexane-water have been determined over a temperature range of 20–80 °C by the drop-weight method. The method that is described by Harkins (3) has been slightly modified to eleborate better experimental measurements. The relationship between the interfacial tension and temperature has been correlated by the least square method for each of the systems.

ARAYÜZEY GERİLİMİNİN DAMLA AĞIRLIĞI YÖNTEMİ İLE ÖLÇÜLMESİ

ÖZET

Başlangıçta yüzey gerilim ölçümleri için geliştirilen kılcal boruda seviye yükselmesi, damla ağırlığı ve koparma yöntemleri arayüzey gerilimlerinin ölçülmesine adapte edilmiştir. Bununla birlikte damla ağırlığı yöntemi bu amaçla sıkça kullanılmaktadır. Arayüzey gerilimleri genellikle söz konusu iki sıvının bireysel yüzey gerilimleri arasında yer alır. Arayüzey gerilimleri kolloidler, biyolojik sistemler ve sıvı-sıvı ekstraksiyonu ve karışmıyan kondensat veren buhar karışımlarının yoğuşması ile ilgili olarak çok önemlidir.

Toluen-su, benzen-su, n-heptan-su ve çiklohekzan-su sistemlerinin yarayüzey gerilimleri 20–80 °C sıcaklık aralığında damla ağırlığı yöntemi ile belirlendi. Harkins (3) tarafından tanımlanan yöntem daha iyi deneysel ölçümler elde etmek üzere bu çalışmada modifiye edildi. Arayüzey gerilimi ile sıcaklık arasındaki bağıntı herbir sistem için "en küçük kareler metodu" ile elde edildi.

INTRODUCTION

The force, equivalent to surface tension, that is operative at the surface of separation between two insoluble, or sparingly soluble, li-

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quids is called the interfacial tension. The subject of interfacial tension is of considerable importance in connection with the properties of emulsions, detergents, foams and separation processes such as condensation, distillation and liquid extraction.

Antonoff (1,2) suggested a relationship, which holds in many instances, the tension γ_i at the interface between two liquids 1 and 2 with surface tensions γ_1 and γ_2, respectively, is given by

$$\gamma_i = \gamma_2 - \gamma_1 \qquad (1)$$

γ_1 and γ_3 are the surface tensions of the two mutually saturated phases under a common vapour or gas. The accuracy of interfacial tension calculated from this equation is not more than 15 per cent. If surface tensions of the pure components, not mutually saturated. were used in Antonoff's equation then the error on the interfacial tension could be as high as 100 per cent.

Since surface (and interfacial) tensions are always positive, it follows that the interfacial tension is less than that of the larger of the two surface tensions. This is because the attraction across the interface, between the molecules of one liquid and those of the other, tends to reduce the inward pull of the molecules in the surface by those of the same kind. The greater the molecular attraction between the two liquids the lower is the interfacial tension. Surface tensions almost invariably decrease with increasing temperature, it is, therefore, expected that interfacial tension should also behave in a similar way.

EXPERIMENTAL

Reagents and Apparatus:

All the chemicals used were of analytical grade, that is, benzene, toluene, n-heptane and cyclohexane being A.R. grade, supplied by BDH. Distilled water was used in all the experiments.

The apparatus is shown in Fig. 1. It consists of a ground syringe (A) which holds the heavier phase and a micrometer screw gauge (B) which measures the displacement of the syringe plunger (C). A rubber band (D) is used to keep the plunger in contact with the end of the micrometer screw. The tip of the syringe is immersed in the lighter phase liquid contained in the vertical vessel (E) The vessel (E) is immersed in a water-thermostat-bath (F) which may be adjusted to any temperature by means of the heater and temperature regulator (G). A mer-

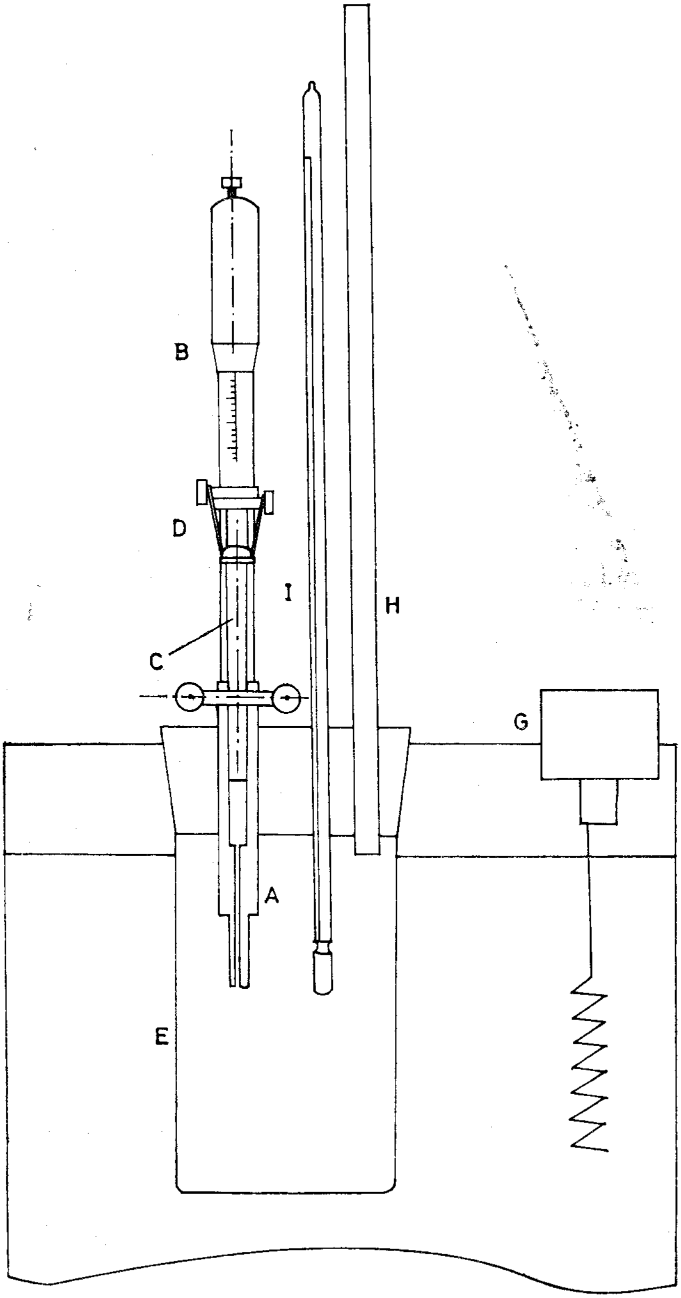

Figure 1. Determination of interfacial tension (Drop-weight Method)

cury-in glass thermometer (I) measures the temperature of the lighter phase liquid. A small diameter glass tube (H) is installed in the cover of the vessel (E) in order to maintain the atmospheric pressure in it.

Experimental Method:

The experimental technique is the drop-weight method described by (Harkins 3). This method is further modified by attaching a micrometer into the syringe in order to achieve an accurate displacement of a syringe plunger and thus measuring the volume of a drop correctly. In this method the vessel (E) is filled with lighter liquid phase and syringe (A), with the heavier liquid. Care is to be taken to move any air that might be present in the syringe. Next the tip of the syringe is submerged in the lighter liquid phase, so that it is at a distance of 3–4 cms from the bottom of the vessel (E). When the temperature reached a stable desired value, a drop of the heavy phase is generated by turning the micrometer screw. The drop is formed slowly in the lighter phase. The formation of the last 10 percent of the drop size should take at least 1–2 minutes. This can be achieved by manipulating the micrometer screw with extreme care. The final reading of the micrometer gauge should be taken when the drop of the heavier phase is about to break away from the syringe tip. The volume of the drop is found from the difference between the first and final readings on the micrometre screw.

The interfacial tension is calculated from the equation of force balance. Thus, just before the break-off of the drop, the drop weight is equal to the supporting force due to the interfacial tension. Thus we may write

$$v \, \Delta\rho g = 2\pi r \gamma_i \qquad (2)$$

Rewriting eq. (2) gives

$$\gamma_i = \frac{v \, \Delta\rho g}{2\pi r} \qquad (3)$$

The value of γ_i calculated from eq. (3) would be in error, since a fraction of the original drop remains at the tip of the syringe. The volume, v in eq.(3) has to be adjusted by a factor which is a function of v/r^3. Values of this factor have been determined empirically by Harkins and Brown (4,5) (Harkins and Brown 1919, Lando 1967). This factor is given elsewhere (6,7) (International critical Tables 1928, Weisberger 1949) and is presented if Figure 2. The relationship between the factor F inclu-

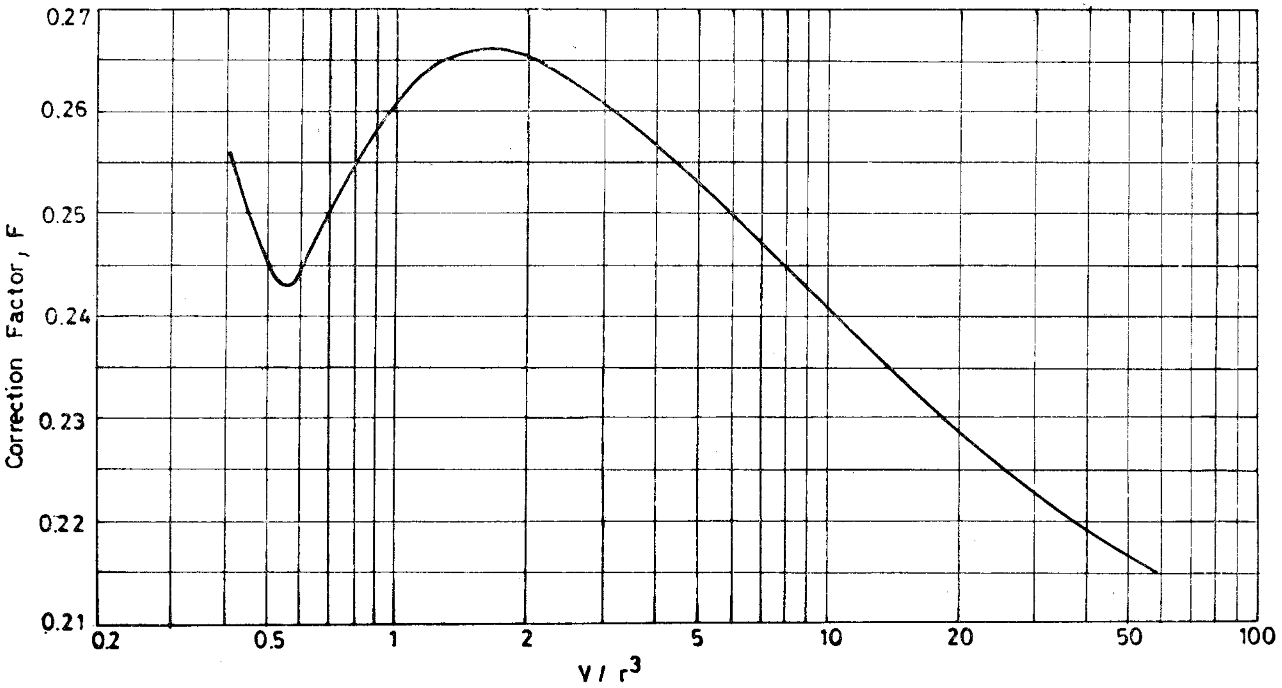

Figure 2. Correction factors for drop-weight method.

des also a value of $1/2\pi$ and the above equation finally assumes the following from.

$$\gamma_i = \frac{v \, \Delta\rho \, g \, F}{r} \tag{4}$$

RESULTS AND DICSUSSION

Measurements of interfacial tensions with temperature for the systems of toluene-water, benzene-water, n-heptane-water and cyclohexane-water, by the drop-weight method are shown, respectively, in Figs.3 to 6. From all these figures the interfacial tensions decrease with an increase in temperature, as should be expected. Five runs have been carried out at each temperature for all the systems studied. The average of five values were taken to represent the each point.

Experimental data on interfacial tension are rare and reported for some organic-water systems at room temperature, determined by

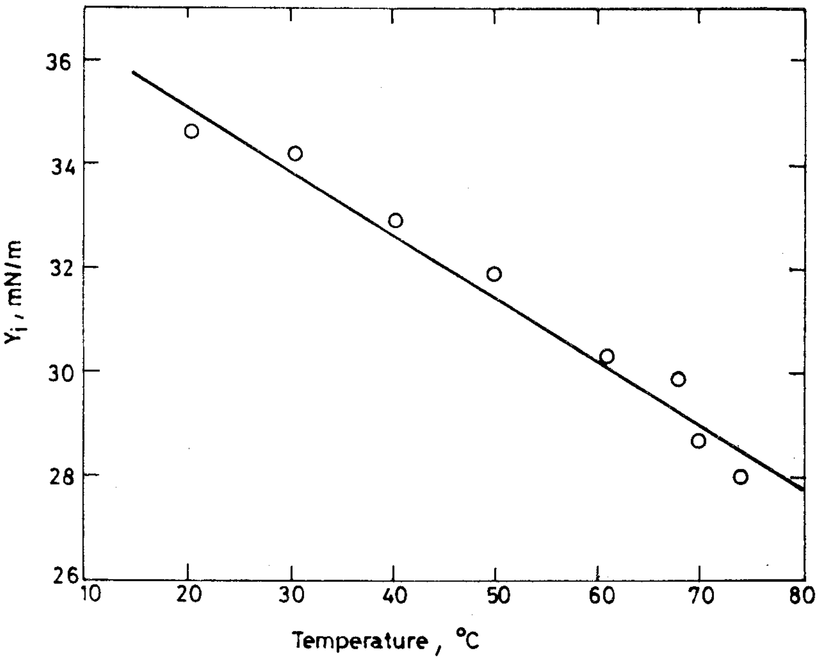

Figure 3. Variation of the interfacial tension with temperature for toluene-water.

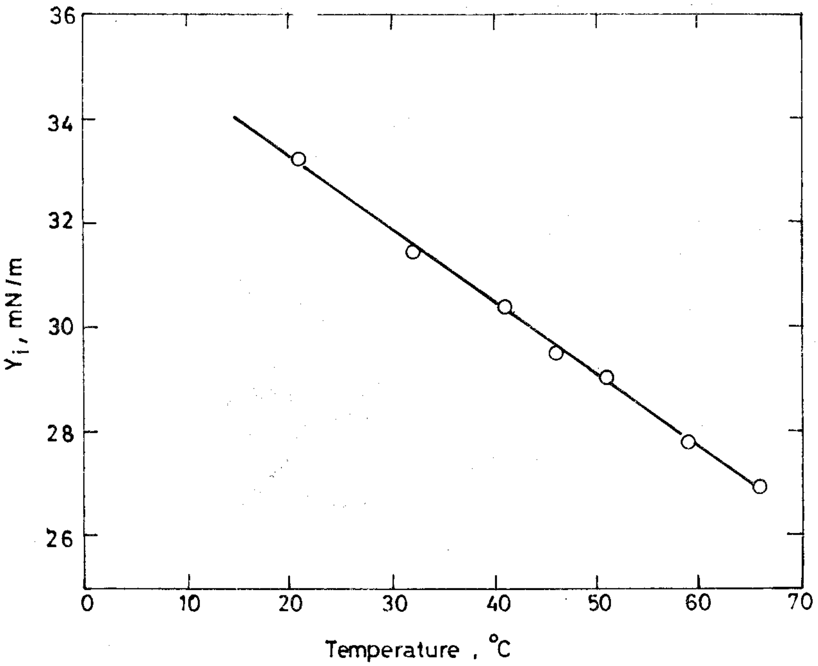

Figure 4. Variation of the interfacial tension with temperature for benzene-water.

drop-weight method (6,8) (International critical Tables 1928, Timmermans 1960). A few data also have been recorded by other methods, that is, pendant-drop or falling drop (9) (Harkins 1921). Comparison between these methods, for apparently same organic-water systems are shown in Table 1.

Table 1. Comparison of the interfacial tensions, determined by diffeerent methods, at 20°C.

System	Interfacial tension, mN/m		
	Drop-weight Method	Pendant-drop Medhot	Drop-weight M. (This study)
Benzene-water	35.0	30.1	33.2
Toluene-water	36.1	32.9	35.0
CCl_2-water	45.0	43.8	—
n-Hexane-water	51.0	—	—
n-Heptane-water	—	—	49.2
n-Octane-water	50.8	—	—

From Table 1 the interfacial tensions measured by the two methods at the same temperature are somewhat different. The interfacial ten-

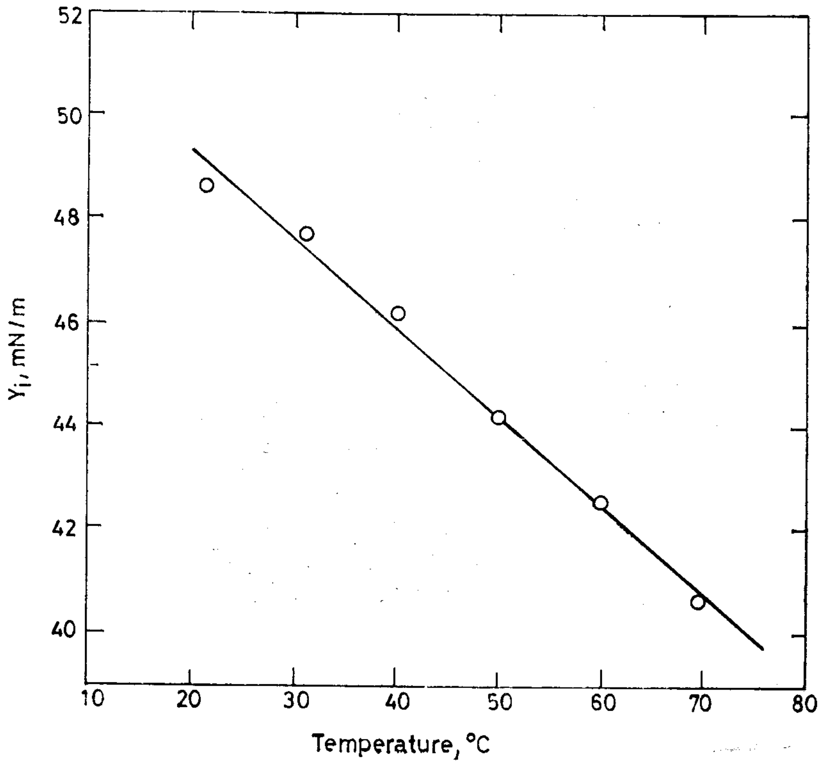

Figure 5. Variation of the interfacial tension with temperature for n-heptane-water.

sions determined by the drop-weight method in this work are invariably smaller than those reported by the same method, but falling in between the values obtained from different two methods (6,9) (International Critical Tables 1928, Harkins 1921) as shown in Table 1. A data for n-heptane-water system has not been reported. The validity of its experimental value, however, may be shown by comparing it to the data extracted for its homolog series, n-hexane and n-octane. with water. As can be seen from Table 1 the measured interfacial tension of n-heptane-water falls below the average values of these systems, the percentage error being —3.3%. The average percentage error between the experimental values and data reported is about —3.8%, on the basis of data recorded. Another reason for the discrepancy may be due to fact that the interfacial tension at the phase boundary liquid-liquid is in general varied much more by impurities than the surface tension at the gas-liquid interface (6).

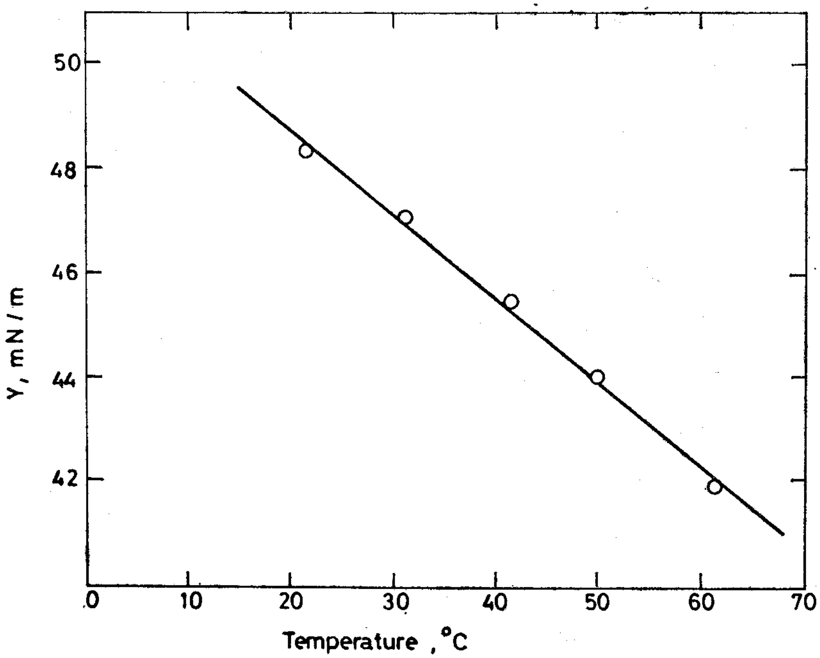

Figure 6. Variation of the interfacial tension with temperature for cyclohexane-water.

CONCLUSIONS

The interfacial surface tensions have been measured at the temperature range of 20 to 80 °C by the drop-weight method described by Harkins (3) (Harkins 1949). This method is modified for providing accurate results.

The interfacial tensions measured by this method compare well with the experimental data obtained with the same method as well as others.

The experimentally measured interfacial tensions have invariably decreased as the temperature is increased for all the systems. The relationship between these two values has been correlated by the least square method as follows:

Toluene-water : $\gamma_i = 37.7 - 0.123\ t$

Benzene-water : $\gamma_i = 36.0 - 0.139\ t$

n-Heptane-water : $\gamma_i = 52.7 - 0.171\ t$

Cyclohexane-water : $\gamma_i = 52.0 - 0.161\ t$

where γ_i is the interfacial tension in mNewton/m, and

t is the temperature in °C.

SYMBOLS USED

F	correction factor
g	acceleration of gravity
r	radius of the syringe tip
t	temperature
v	volume of drop
γ_i	interfacial tension
γ_1	surface tension of organic
γ_3	surface tension of water
$\Delta\rho$	density difference

REFERENCES

ANTONOFF, G.N., J. Russ. Phys. Chem. Soc., 39, 342, 1907.

HARKINS, W.D., Determination of Surface and Interfacial Tension, Chap. 14, "Physical Methods of Organic Chemistry (Ed. A. Weistberger)", Interscience, New York, 373, 1949.

HARKINS, W.D., BROWN, F.E., J. Amer. Chem. Soc., 41, 499, 1919.

HARKINS, W.D., CHENG, V.C., J. Amer. Chem. Soc., 43, 35, 1921.

International Critical Tables, Vol. 4, McGraw-Hill, New York, 436, 1928.

LANDO, J.L., OAKLEY, H.T., J. Colloid Interface Sci., 25, 526, 1967.

PERRY, R.H., CHILTON, C.H., Chemical Engineers' Handbook, 5th Ed., McGraw-Hill, New York, 3–238, 1973.

TIMMERMANS, J., Physico-chemical Constant of Binary Systems, Vol. 4. 2,, 1960.

WEISBERGER, A., Physical Methods of Organic Chemistry, Vol. 1– Part I, Interscience, New York, 373, 1949.