

THE BUBBLE METHOD FOR MEASURING SURFACE TENSION OF LIQUIDS

Ladislav NOVOTNÝ

UNESCO Laboratory of Environmental Electrochemistry at The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, 118 40 Prague 1

Received December 28th, 1984

The principle of the bubble method for measuring surface tension of solutions and its changes is described. It is based on the determination of the volume or of the changes of the volume of a gas bubble at the orifice of a capillary in the moment of its detachment. One version of the bubble tensiometer is described.

For determination of surface tension of liquids, γ' , and of its changes many methods were suggested in the past^{1,2}. To the most frequently used ones belong the methods of capillary elevation, of maximum back pressure and the stalagmometric method¹⁻⁵. In the first two cases direct proportionality is assumed to exist between the surface tension γ' (*i.e.*, the interfacial tension liquid/air) and the back pressure of the phase boundary on the meniscus, in the third case the direct proportionality is assumed between the surface tension and the weight of the drop of the liquid forming at the front of a capillary of several millimeters in diameter.

In practice, however, various secondary factors complicate the assumed simple relationship between surface tension and the measured values^{1,2}. In the methods where meniscus is followed, *e.g.*, the effect of the inner walls of the capillary, changes of the contact angle or deformation of the meniscus by gravitational forces have to be taken into account; in stalagmometry the difference between the diameter of the neck of the drop at the moment of detachment and the external diameter of the capillary as well as mechanical vibrations or non-attainment of the vapour-liquid phase equilibrium at the interfacial boundary must be considered. A similar situation occurs also in further methods, like in determination of surface tension from the shape of a sessile drop or bubble¹, in the method of ring detachment^{1,6} and in others^{1,2}. The tensiometric methods are therefore used most frequently as relative methods. The measurements are carried out in comparison with a chemically similar reference sample and the results are corrected, according to needs, by means of correction factors tabulated as function of the radius of curvature of the meniscus or of the drop, of the parameters of the capillary, *etc.*

The development of the experimental techniques aims towards minimization of effects due to vibrations, to nonattainment of phase equilibrium liquid-vapour, to changes of constant angles, of temperature, *etc.*, in order to increase the sensitivity, reproducibility and rapidity of measurements. It is difficult to meet all these requirements simultaneously.

In practice, when changes of surface tension have to be determined or controlled within certain limits, simple, rapid and accessible methods are preferred in general of precision and sensitivity sufficient for the given purpose. From the viewpoint of the environmental, physical, analytical, organic *etc.* chemistry such methods are very desirable.

The aim of the present paper is to describe the principle of a new method^{7,8} for determination of the surface tension of liquids or for measurement of its changes, based on experience with the dropping mercury electrode^{8,9}.

EXPERIMENTAL

Apparatus and chemicals. The bubble tensiometer was set up of easily accessible components. The indication capillary was a laboratory made spindle-type capillary^{8,9} in vertical position with orifice pointing upwards (Fig. 1). It was made of a cylindrical polarographic capillary of inner diameter about 0.025 mm; the diameter of the orifice was about 0.3 mm. The time of the bubble was measured by means of a universal frequency counter BM 520 (Tesla Ústí nad Labem) or by stopwatch with precision of ± 0.05 s. The solutions to be measured were placed in an exchangeable part of a commercial polarographic cell connected to a fixed teflon head (produced by Laboratorní přístroje, Prague). If necessary, the cell was provided with a water jacket connected to a thermostat; for simple measurements instead of the cell an ordinary beaker could be used. The chemicals used were of analytical grade. Aqueous solutions were prepared with re-distilled water.

Instrumental arrangement and its function. The principle of the method is as follows: A gas (best chemically inert and dry) flows to the liquid the surface tension of which is to be measured through a capillary tube with inner diameter of the orifice d sufficiently wide (*e.g.*, $d \doteq 0.32$ mm) so that at the end of the tube separate bubbles form and detach themselves at an appropriate rate. From the volume of the spontaneously detached bubble or from the measured parameters which are connected with this volume, the values of surface tension γ' or of its change $\Delta\gamma'$ are determined.

One of possible instrumental arrangements consists of a receptacle of the compressed inert gas connected with the measuring capillary tube with its end oriented upwards in the liquid to be studied. The gas (*e.g.* air, N₂, O₂, H₂, Ar, *etc.*) can be pre-dried and its pressure in the receptacle can be controlled by a manometer. Exactly, the measured solution should be saturated with the inert gas at the beginning of the work, *e.g.*, by bubbling. It is usually unnecessary in water solutions because of negligible solubility of the mentioned inert gases. In case the inner diameter of the upper part of the capillary d_0 is sufficiently small (*e.g.*, $d_0 = 0.02-0.025$ mm), this part determines and maintains the constant rate of flow of gas through the capillary according to the Hagen-Poiseuille law¹¹ provided the gas pressure and other conditions are kept constant. The moisture of the gas should be such that no condensation of the liquid takes place inside the capillary.

If the diameter d is sufficiently large, if the end of the capillary is oriented upwards, if the front of the capillary is wetted by the liquid and if the rate of flow of gas is maintained constant, the periodic formation of gas bubbles is regular and reproducible and is not affected by the capillary front. A long period between two successive detachments of the bubbles, t_b , is favourable (e.g., about 30 s, depending on parameters of the capillary and on the pressure used) for the sake of establishment of the phase equilibrium liquid-gas at the interfacial boundary. Although the inner conicity of the capillary is not a necessary condition, it acts against rising of the liquid along the inner walls. When the gas pressure $\Delta p_r = p_r - p_{atm}$ of about 0.035 MPa is used, the effect of changes of the back pressure at the curved surface of the bubble is practically negligible. An exact temperature control of the liquid (with precision of ± 0.2 K), essential during long-time measurements, is usually not necessary when fast measurements are done, when reference liquids are often used or when the work is carried out at steady room temperature.

RESULTS AND DISCUSSION

RELATION BETWEEN THE SURFACE TENSION AND THE BUBBLE-TIME

The relation between the surface tension γ' and the time of the bubble t_b can be

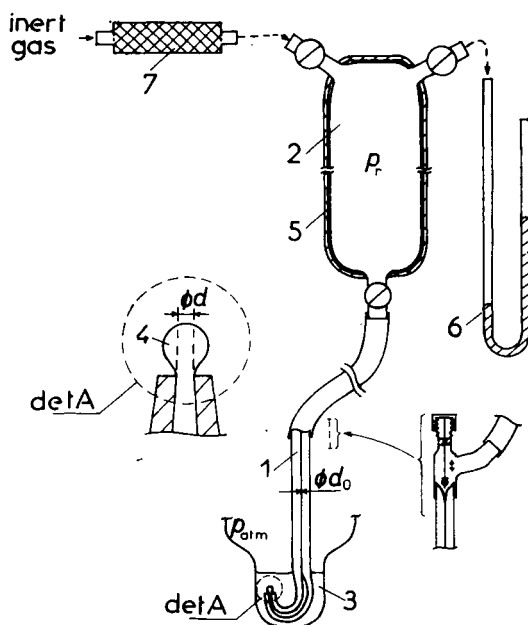


FIG. 1

Scheme of experimental arrangement of one version of the bubble tensiometer: 1 measuring spindle capillary; 2 receptacle of a compressed inert gas; 3 liquid to be studied; 4 gas bubbles; 5 heat insulator; 6 manometer; 7 drying element

derived on assumptions that the used gas is dry, that the equilibrium gas-vapour inside the bubble has been established, that the gas obeys ideal laws and that the above mentioned conditions for a reproducible formation of gas bubbles have been fulfilled. Then the equilibrium of forces at the neck of the bubble in the moment of its detachment is expressed by the equation (1)

$$2\pi r\gamma' = V_b \cdot \Delta\rho \cdot g, \quad (1)$$

where V_b is the volume of the bubble at detachment, $\Delta\rho = \rho_l - \rho_g$ is the difference of densities of the liquid and of the gas phase inside the bubble, r is the radius of the neck of the bubble and g is the acceleration due to gravity.

The volume V_b is given by Eq. (2)

$$\begin{aligned} V_b &= \bar{V}t_b + (p_1^0/p_{\text{atm}}) V_b, \quad [T] \\ V_b(p_1^0/p_{\text{atm}}) &= \Delta V, \end{aligned} \quad (2)$$

where \bar{V} is the volume rate of flow of gas through the capillary, ΔV the volume of volatile components of the liquid evaporated into the bubble during the time t_b , p_1^0 the saturated vapour pressure of the liquid and p_{atm} the pressure inside the bubble which under appropriate conditions practically equals to the atmospheric pressure.

Equation (2) presumes a negligible solubility of the gas in the given liquid. By its rearrangement we get the relation (3)

$$V_b = \bar{V}t_b \frac{p_{\text{atm}}}{p_{\text{atm}} - p_1^0} \quad (3)$$

from which in combination with (1) equations (4) and (5) result:

$$2\pi r\gamma' = g(\rho_l - \rho_g) \bar{V}t_b \frac{p_{\text{atm}}}{p_{\text{atm}} - p_1^0} \quad (4)$$

$$\gamma' = \frac{\bar{V}g}{2\pi r} (\rho_l - \rho_g) \frac{p_{\text{atm}}}{p_{\text{atm}} - p_1^0} t_b, \quad (5)$$

$$K_1 = \bar{V}g/2\pi r; \quad K_2 = \rho_l - \rho_g; \quad K_3 = p_{\text{atm}}/(p_{\text{atm}} - p_1^0).$$

Here $\rho_g = (1/RT) \sum_i p_i M_i$, p_i being partial pressures of individual components of the mixture of gases inside the bubble and M_i the molecular(atomic) weights of the gases.

In case of comparative measurements with a reference liquid K_1 is constant and

equation (5) acquires the form (6):

$$\frac{\gamma'}{\gamma'_0} = \frac{K_2 K_3}{(K_2)_0 (K_3)_0} \cdot \frac{t_b}{(t_b)_0}, \quad (6)$$

where the subscript "0" denotes the reference liquid.

EXPERIMENTAL VERIFICATION OF THE EQUATIONS

Table I gives the results of measurements carried out in acetone, toluene, n-heptane and benzene, with methanol as a reference. Because of different densities and vapour pressures the values K_i and $(K_i)_0$ in equations (5) and (6) differed so that their actual values had to be taken into account. The measurements were done at the temperature of 293.1 ± 0.2 K. The agreement of the experimental results with those published in literature is satisfactory. However, when compared with water as reference liquid the measured deviations amounted to about 2 mN/m.

For determining the surface tension of aqueous solutions of ethanol (Fig. 2) a 94% (volume) solution of ethanol was gradually added into the measured solution. The measurement was carried out without thermostating at room temperature

TABLE I

The surface tension of different organic solvents. Values of ρ_l , ρ_g and p_1^0 taken from published data¹²⁻¹⁵; methanol as a reference liquid: $\rho_l = 791.5 \text{ kg m}^{-3}$; $\rho_g = 1.2 \text{ kg m}^{-3}$; $p_1^0 = 12.8 \text{ kPa}$; $\gamma'_{\text{ref}} = 22.6 \text{ mN m}^{-1}$ (ref.¹⁴).

Substance	$10^{-3} \rho_l$, kg m^{-3}	$10^{-3} \rho_g$, kg m^{-3}	p_1^0 , kPa	t_b , s	$(t_b)_0$, s	γ'_{exp} , mN/m	γ'_{lit} , mN/m
Acetone	0.7906	0.0015	24.13	13.93	15.41	23.4	23.3 ¹³
				13.92	15.40		23.7 ^{14,15}
				13.93			
Toluene	0.8660	0.0013	2.80	19.82	15.66	28.2	28.4 ¹⁵
				19.84	15.65		28.5 ¹⁴
				19.82	15.67		
n-Heptane	0.6838	0.0013	4.73	17.65	15.68	20.1	20.3 ¹³
				17.64	15.69		
				17.63			
Benzene	0.8790	0.0014	9.88	18.87	15.70	29.1	28.9 ^{14,15}
				18.89	15.71		
				18.89			

of 298 K. After each addition of ethanol the solution was stirred and the time of the second or the third bubble was recorded (the first-bubble time measured immediately after each addition of ethanol could be affected in undesirable way by concentration and related equilibration processes in the solution). The measured bubble-times t_{exp} were corrected for the changes of density of the solution due to the additions of alcohol, according to Eqs (5), (6). As the gas pressure in the receptacle was not maintained constant, the reference bubble-time in pure water was corrected for the change of pressure, Δp_r , in the gas receptacle. Thus corrected values of surface tension, γ'_{exp} , are given in Table II. The differences between γ'_{exp} and the published data are acceptable.

An analogous comparison of experimental with published values of surface tension was done with the system NaCl-H₂O at various concentrations of the salt (Tab. III).

TABLE II

The measured values of surface tension γ'_{exp} of aqueous solutions of ethanol at 298 K. Concentration of ethanol c in weight %

$c, \% \text{ W}$	$t_b, \text{ s}$	$\Delta p_r, \text{ kPa}$	$(t_b)_0, \text{ s}$	$\rho_1 - \rho_2, \text{ g/ml}$	$\gamma'_{\text{exp}}, \text{ mN/m}$
0	31.79	32.66	31.79	0.9958	72.5
0.14	31.59	32.51	31.93	0.9956	71.7
0.40	31.01	32.46	31.98	0.9951	70.3
0.80	30.19	32.33	32.11	0.9944	68.1
1.57	28.73	32.28	32.17	0.9929	64.6
2.33	28.05	31.78	32.67	0.9915	62.0
3.08	27.10	31.68	32.77	0.9904	59.6
3.88	26.30	31.62	32.84	0.9889	57.7

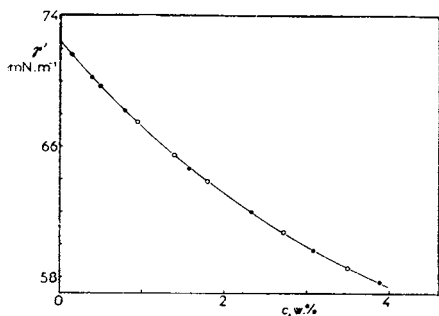


FIG. 2

The surface tension of water solutions containing ethanol in concentrations 0 to 4% (weight); the experimental (●) and the published (○)¹⁶ data

In that case the measurements were carried out relatively fast in reference to pure water after all solutions had been prepared and after each sample in a microbeaker had been dipped in a large beaker containing water at temperature of 293 K. The measured bubble-times were corrected only for the change of density of the solution by the added electrolyte.

Most successful was the application of the described method for measurements of changes of surface tension due to small additions of surface active substances, because in such cases it was not necessary to introduce corrections for changes of densities or of vapour pressures of the solutions. However, for the study of low concentrations (lower than about $5 \cdot 10^{-5} \text{ mol l}^{-1}$) the method of controlled convective adsorptive accumulation of surfactants⁸⁻¹⁰ had to be applied (the matter will be dealt with in more detail in a separate communication). This case is demon-

TABLE III

The surface tension of aqueous solutions of NaCl at 293 K; c concentration of salt; $\rho_g \doteq 0.0012 \text{ g/ml}$; γ'_{exp} measured surface tension; γ'_{lit} values of surface tension taken from literature; $(t_b)_0 = 72.8 \text{ mN/m}$

$c, \text{ mol/l}$	$t_b, \text{ s}$	$\rho_1, \text{ g/ml}$	$\rho_1 - \rho_g, \text{ g/ml}$	$\gamma'_{\text{exp}}, \text{ mN/m}$	$\gamma'_{\text{lit}}, \text{ mN/m}$
0	25.00	0.9982	0.9970	—	72.8
0.5	24.75	1.0187	1.0175	73.6	73.5
1	24.53	1.0399	1.0387	74.4	74.5
2	24.20	1.0775	1.0763	76.1	76.0
3	23.73	1.1147	1.1135	77.2	77.6
4	23.85	1.1500	1.1488	80.0	79.4

TABLE IV

Changes of bubble-time on additions of $\Delta V_1 \text{ ml}$ of saturated solution of motor oil to 10 ml of $0.5 \text{ mol l}^{-1} \text{ NaCl}$; $T = 293 \text{ K}$

$\Delta V_1, \text{ ml}$	$t_b, \text{ s}$	$\Delta t_b, \text{ s}$
0	34.06	—
0.6	32.65	1.41
1.2	31.47	2.59
1.8	30.73	3.33
2.4	30.26	3.80

strated in Table IV. Into 10 ml of 0.5 mol l^{-1} NaCl a saturated aqueous solution of motor oil (about 7 mg l^{-1})¹² was gradually added. Within the total bubble-time of 30–34 s the surface active hydrocarbon molecules were convectively accumulated for 25 s at the surface of the bubble. According to expectation the measured bubble-times were becoming shorter with additions of the saturated motor oil solution.

CONCLUSIONS

In the present paper the principle of the bubble method for measuring surface tension of solutions and its changes is reported. It is based on determination of the volume or of the changes of the volume of a gas bubble at the orifice of a capillary tube in the moment of its detachment. An experimental arrangement is described of one version of the bubble tensiometer where the gas is introduced to the bubble from a receptacle by means of a capillary of suitable geometrical parameters under a constant rate of flow. The functional properties of the described apparatus are demonstrated on selected examples. Under appropriate conditions the method is relatively fast and precise. Best suited appears its application to tensiometric measurements of solutions the densities and vapour pressures of which differ negligibly from those of the reference solutions. This application deserves further attention particularly as far as instrumental refinement of the method is concerned.

REFERENCES

1. Adamson A. K.: *Physical Chemistry of Surfaces*. 2nd Ed., Wiley, New York 1967.
2. Harkins K. D., Alexander A. E. in the book: *Determination of Surface and Interfacial Tension in Physical Methods* (A. Weissberger, Ed.). 3rd Ed., Vol. 1, p. 757–814. Wiley, New York 1963.
3. Hála E., Reiser A.: *Fyzikální chemie*. Published by Nakladatelství ČSAV, Prague 1960.
4. Miller T. E., Meyer K. C.: *Int. Lab.* 4, 28 (1984).
5. Voskresenskii A. A., Zhuravlev I. M.: *Zh. Fiz. Khim.* 52 (10), 2696 (1978).
6. Hey M. J., Schield D. W., Speight J. M., Will M. C.: *J. Chem. Soc., Faraday Trans.* 1, 77, 123 (1981).
7. Novotný L.: Czech. PV 7544–79, 7583–79, 5768–80; AO 210894, 220369, 220415, Prague 1979/80.
8. Novotný L.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1981.
9. Novotný L., Smoler I.: *J. Electroanal. Chem. Interfacial Electrochem.* 146, 183 (1983); *This Journal* 48, 964 (1983).
10. Kalvoda R.: *Anal. Chim. Acta* 138, 11 (1982).
11. Heyrovský J., Kůta J.: *Principles of Polarography*. Academia, Prague 1966.
12. Grünwald A.: *Vodní hospodářství* 4/B, 105 (1978).
13. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*. Brussels 1950.
14. Hodgman Ch. D.: *Handbook of Chemistry and Physics*. 36th Ed., Vol. II. New York 1954/55.
15. Habada M.: *Fyzikálně-chemické tabulky*. Published by SNTL, Prague 1954.
16. Koglin K.: *Kurzes Handbuch der Chemie*. Göttingen 1951.

Translated by M. Heyrovský.