

Formation and properties of association colloids

Theoretical background: J.C. Berg: An Introduction to Interfaces and Colloids – The Bridge to Nanoscience, World Scientific Publishing, Singapore, 2010.

Type of practice: Single.

Aim of practice: Comparison of the critical micelle concentrations determined by different methods.

1 Introduction

Amphiphilic (a.k.a. amphipatic) compounds constitute a special class of molecules, which contain both an apolar and a polar part in an asymmetric arrangement. One of their unique characteristics is that they have an inherent tendency to self-assemble in liquid (mostly in aqueous) solutions. This self-assembly may happen both in the interior of the solution (leading to formation of micelles) and at the L/G, L/L, or the L/S interface. As a result, amphiphilic molecules tend to adopt an orientation at any interfaces at which the polar head group of the molecule faces the polar solvent (typically water) and the apolar part (usually a hydrocarbon chain) is excluded from water. This part of molecule is preferentially located in the other phase (gas) or situated closer to it (polar liquid or adsorbed on the solid surface). These different arrangements of the amphipatic molecules are depicted in Figure 1 / I. The orientation of the molecules results in the decrease of the surface tension, hence they are also termed as surfactants (an acronym for “surface active agent”).

By increasing the analytical concentration of the surfactants, successively larger amounts of molecules are accumulated at the interface, and this means that their equilibrium concentration (in the “bulk”, i.e. in the interior of the liquid phase) becomes less and less in comparison with the respective analytical concentrations, which represent the total amount of surfactants added into the solution. For ionic surfactants, due to electroneutrality, the concentration of the counterions (charge-compensating ions, e.g. Na^+ ions for negatively charged dodecyl sulphate anions) will also be inhomogeneous. At a certain amount, however, the interface becomes saturated with the adsorbed molecules, as depicted in Figure 1 / II.

Parallel to the onset of saturation adsorption, individual amphiphilic molecules start to form aggregates termed as surfactant micelles. These are clusters of amphiphilic monomers, which are composed by “associating” a certain number of molecules. The average number of molecules building up the micelle is called the aggregation number, which ranges from ca. 30 to 120 for most of the different types of surfactants. Micelles are spherical objects (in the simplest case, see Figure 1 / III) at moderate concentrations, in which the

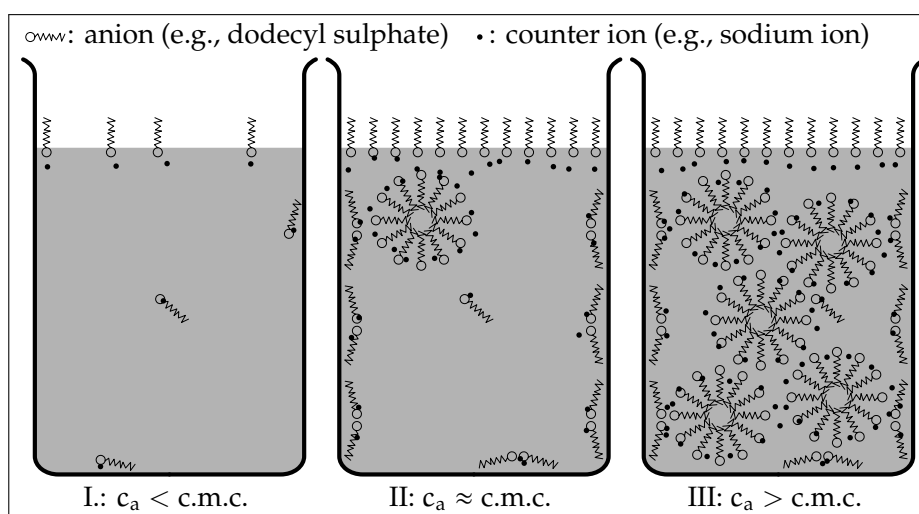


Figure 1: Sketchy representation of the change of the surface excess concentration and the micellization process for the salt of a long-chain amphipatic anion at increasing analytical concentrations (c_a). c.m.c. is the critical micelle concentration.

polar headgroups for an outer shell, which is contacted with the (polar) solvent¹, and the apolar tails arrange themselves to form an interior part, which is the “hydrophobic core” of the micelle.

The (lowest) concentration at which the micelles can be self-assembled from the dissolved monomers in solution is termed as the *critical micelle concentration*. This quantity is characteristic of the chemical entity of the solute, and quite a few abbreviations are used in the scientific literature in regard to it apart from the official c_M notation, such as c.m.c., C.M.C., cmc or CMC.

Most handbooks uses the sentence above as the definition of the c.m.c., but some of the most frequently used methods rely on the measurement of surface tension, which is associated with the saturation of the L/G interface and not directly with the formation of a colloidal assembly inside the bulk of the liquid phase. Therefore, we need to take into account to following two considerations for the precise determination of the c.m.c.:

1. The saturation of the surface by surfactant should occur at the same analytical concentration at which the formation of micelles starts. This condition is not necessary fulfilled. The concentration ranges of surface saturation and the micellization may partially overlap, but in some cases larger equilibrium concentration is needed for the formation of micelles. In these cases the experimentally determined c.m.c. values may be different from the real ones.
2. The surface area of samples of identical volume and concentration can be substantially different for the various experimental methods and setups. For each experiments there is a characteristic area / volume ratio (A/V), which can influence the the measured c.m.c.. However, this “surface effect” is often not taken into account.

Due to these discrepancies, the technical definition of c.m.c. is formulated by IUPAC as follows^[1]:

„There is a relatively small range of concentrations separating the limit below which virtually no micelle are detected and the limit above which virtually all additional surfactant molecules form micelles. Many properties of surfactant solutions, if plotted against the concentration, appear to change at a different rate above and below this range. By extrapolating the loci of such a property above and below this range until they intersect, a value may be obtained known as the critical micellization concentration (critical micelle concentration), symbol c_M , abbreviation cmc (or c.m.c.). As values obtained using different properties are not quite identical, the method by which the cmc is determined should be clearly stated.”

Based on this definition, a single measurement provides a definite concentration value. The consideration of multiple measurements, however, does not make this value more precise, but enables to describe the narrow concentration range of c.m.c..

2 Experimental methods for the determination of c.m.c.

The characteristic features of the graphs used to evaluate the c.m.c. are demonstrated in Figure 2. They look very different because the actual shape depends on the specific method employed. These methods are conveniently grouped into two categories: the first one involves methods in which (above the c.m.c.) the measured data are proportional to the molar amount of micelles.

Conductometry:

This method exploits the fact that the conductivity of solutions of ionically dissociating amphipatic compounds greatly change during micellization. When the measured conductance, specific conductivity or molar conductivity (or their logarithm) are plotted against the (logarithm) of the analytical concentration of the surfactant, we can get a curve which exhibits a break point at the c.m.c. (see Figure 2). Although this is one of the most frequently used methods, its disadvantage is that it can only be

¹If the solvent is apolar (or at least less polar), the structure of the micelle is “reversed”: polar headgroups will constitute a polar core, coated by an apolar layer that extends into the polar solvent. This colloidal assembly is termed as an “inverse micelle” or “reverse” micelle.

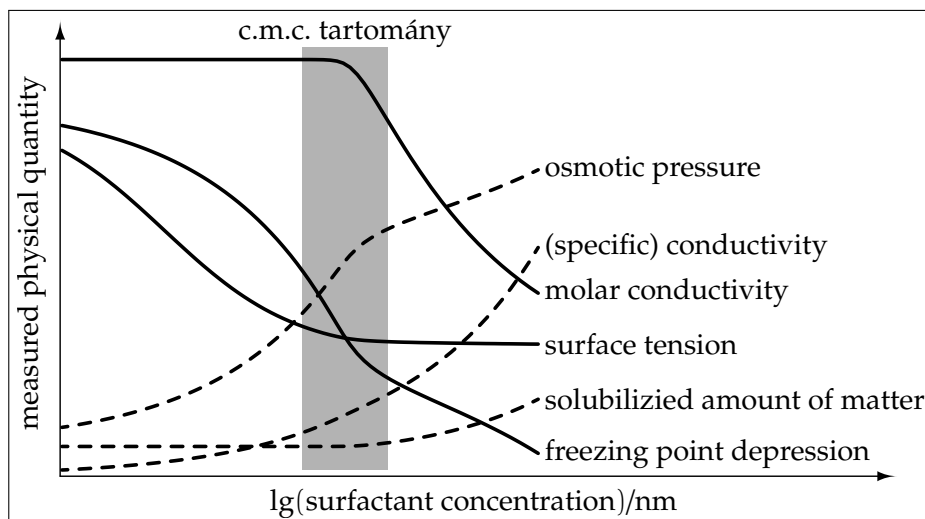


Figure 2: Typical profiles of curves obtained for the relevant c.m.c. determination methods.

applied for ionic surfactants. Its important advantage is, however, is the precision and it is also easily performed.

Measurement of colligative properties:

The number of dissolved species does not change linearly with the analytical concentration above the c.m.c., unlike for “ideal” solutions of fully dissociable salts. When micelles are formed from the respective monomers (individual amphiphiles), the number of species (= micelles) will be N times less than the total number of monomers, where N is the aggregation number. Since the colligative properties are linearly proportional to the concentration of species in the solution, any methods based on the measurement of a colligative property can be used for the c.m.c. determination. However, in practice, only the method of osmometry has practical significance because only this one is sensitive enough under normal laboratory conditions using regular laboratory equipment.

Solubilization:

Large amounts of insoluble or sparingly soluble compounds can be brought into the solvent by a process termed as solubilization. This means the incorporation of these guest molecules into the interior (formal micelles, into the apolar core) of the micelles. The increase in the number of micelles results in the linear increase of the solubilized concentration of the compound. This concentration is different from the total concentration of the compound, because a certain amount of it is still present in the solution (outside the micelles) as limited by its solubility.

The second category of methods include those which produce a “signal” which is proportional with the surface excess concentration of the surfactant. This signal is the surface (or interfacial) tension, which is usually noted as γ (in some sources, σ) and its unit is J/m^2 or N/m . When the surface concentration of surfactants becomes maximal, the surface tension no longer decreases with the bulk concentration of surfactant (in other words, added surfactants cannot lower the surface tension to a larger extent). Since saturation of the surface usually occurs at around the c.m.c., the latter can be determined as the intersections of the two lines in Figure 2, representing the (virtually) horizontal line above the c.m.c. and the line with the negative slope just below the c.m.c.. The following methods can be used to quantify the surface tension of a solution:

Direct measurement of the surface tension:

Tensiometers are instruments capable for the direct measurement of the force acting on an object, which is positioned into the interface (Figure 3). The shape of the object can vary; for example, the du Noüy (ring) method applies a (typically Pt – Ir) ring with a known perimeter. This ring is then detached

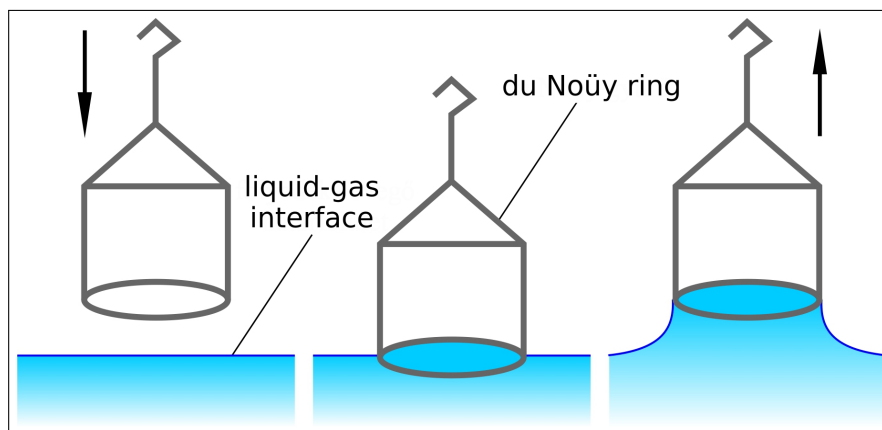


Figure 3: Measurement of surface tension by du Noüy ring method. Left-hand-side picture: approaching the ring to the liquid – gas interface. Middle image: ring attached to the interface. Right-hand-side image: location ring and shape of meniscus before detachment.

from the surface and the maximal force exerted on the ring during this process will be converted to the surface tension.

Drop volume method:

Droplets formed at the perimeters of open liquid tubes (tap, pipette, capillaries, etc.) do not fall down until the gravitational force is smaller than the combined forces originating from buoyancy and the surface tension. Consequently, (because gravitational force is $m \times g$), the “m” mass of the droplet is linearly proportional to γ surface tension:

$$\frac{\gamma_{\text{solution}}}{\gamma_{\text{solvent}}} = \frac{m_{\text{one drop of solution}}}{m_{\text{one drop of solvent}}} \quad (1)$$

Accordingly, if we know the surface tension of the solvent, a simple mass measurement provides the surface tension in a wide concentration range of solutions.

Various equipment can be used for the drop-by-drop release of liquids; the most important ones are depicted in Figure 4. Part (a) shows the simplest one, a regular pipette. Precise determination of γ by this is limited by two factors. One is that the frequency of dripping is influenced by the hydrostatic pressure, and the other is that, owing to the relatively small droplet size, a large number of droplets must be released in order to obtain a precisely measurable mass of liquid. In part (b), a sketchy drawing of an equipment specifically designed for dripping, the so-called Traube’s stalagmometer can

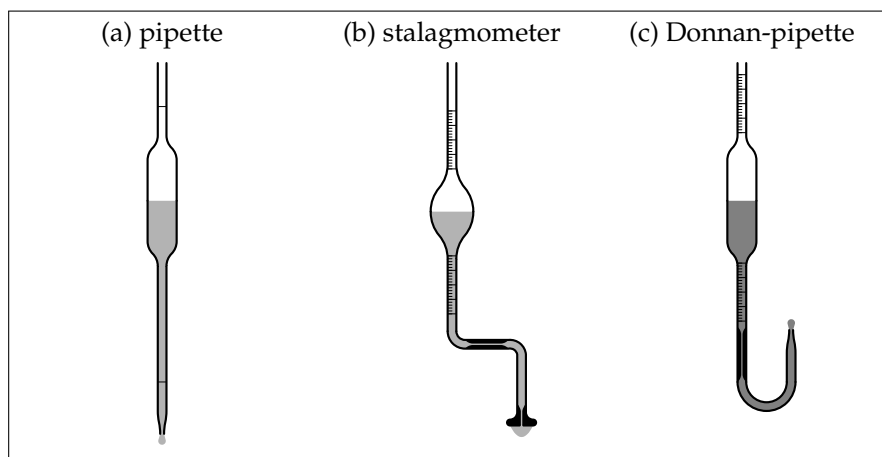


Figure 4: Glass wares used to determine surface tension through drop formation.

be seen. This contains an internal, horizontal capillary, the diameter of which determines the flow rate inside the device, so the effect of hydrostatic pressure on the flow rate is efficiently cancelled. The other advantage of the stalagmometer is that its dripping head was fabricated in order to enable the formation of large droplets, so a small number of droplets is enough for mass measurement.

Part (c) of Figure 4 shows another device, the Donnan pipette. This one is used for the measurement of the liquid/liquid (L/L) interfacial tension (note: γ for two contacting liquid phases is termed as interfacial tension, and “surface tension” is only reserved for L/G interfaces). In this case, the liquid with the lower density are filled into the pipette, and droplets detached from the pipette tip are moving upwards due to buoyancy effects.

3 Instructions

The student will perform two tasks in this practice for the determination of the c.m.c. of a surfactant in water. *If the instructor does not state otherwise*, these are the tensiometry and the conductometry. In the first case, surface tension will be measured, and in the second one, the specific conductivity of the solution.

The student will need to prepare a series of solutions by one of the two following options: 2.0–4.0 g sodium dodecyl sulphate (NaDS, $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4\text{Na}$) or 0.5–1.0 g sodium dodecyl benzene sulphonate (NaDBS, $\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_4\text{Na}$). Unless the teacher requires otherwise, you will need to use 2 g of NaDS and prepare solutions according to the “c” line of Table 1 in the following way:

1. The solutions are prepared by using two 100 cm³ volumetric flasks. Both flasks (**A** and **B**) must be clean but can contain traces of water.
2. Prepare 100 cm³ solution into Flask **A**, by measuring the required weight into it (as per default: 1 g NaDS). Try to avoid intense foaming associated with the filling of the flask. It helps a lot if you add water slowly and avoid intense jets of water, but better flow them down on the wall of the flask, and shake the bottle only gently and always right abeam².
3. Measure a “V₁” volume from Flask **A** into Flask **B** by a pipette (see Table 1).
4. Fill up Flask **B** to level.
5. The solution remained in Flask **A** is poured into a dry, clean Erlenmeyer flask for the measurements (a minimum volume of 45 cm³ is necessary), then Flask **A** should be washed (6–8 times) with water.

²“Secret” tip: when the flask is filled just up to the narrow neck of the volumetric flask, adjust your hand to add the water jet so slowly that it is separated into a flow of droplets. It is not that easy to perform, but a feasible addition of this droplet series will destroy the foam in the neck almost completely.

Table 1: Volumes of the solution series to be diluted to 100 cm³.

sorozatjel	a.	b.	c.	d.	e.
V ₁ /cm ³	60	60	60	50	60
V ₂ /cm ³	60	60	60	50	60
V ₃ /cm ³	60	60	60	60	50
V ₄ /cm ³	60	50	50	60	40
V ₅ /cm ³	60	50	50	60	40
V ₆ /cm ³	60	50	40	60	40
V ₇ /cm ³	60	50	40	60	60
V ₈ /cm ³	60	50	40	40	60

- The points 3–5 must be repeated, so that Flasks **A** and **B** have a reverse role, and the forthcoming cycles should involve the addition of V_2, V_3, \dots etc. volumes of taken out from the respective flasks (instead of V_1 from Flask **A**) according to the rows of Table 1.
- The above procedure should be repeated as many times as it is needed to collect a series of solutions with 10 different concentrations (including the stock solution, c_{\max} ; and water, $c_0 = 0 \text{ mM}$, as well).

Final note: when you measure the surface tension or the conductivity, the first sample to take should be always the purified water. Then, the solutions should be measured in the order of increasing concentrations.

Measurement of drop masses:

The stalagmometer (or pipette, if a stalagmometer is not available) is washed with several cm^3 volumes of the solution, and the solution is sucked into the device until its wider liquid container is filled until 70–90%.³ Next, release 8–13 droplets (for pipette 25–40 droplets) of solution by an infusion clamp slowly (with a rate no greater than 1 droplet per second) into a beaker, the weight of which was measured before. After dripping, measure the total mass (beaker + water) and calculate the mass of one droplet. Since mass is an additive property, note that you don't need to wash and dry the beaker each time between the measurements. Once the mass of the system (i.e., the beaker and the solution inside) is known, you can use it for dripping the next solution. Unless the teachers say otherwise, the drop number should be 10 for the stalagmometer and 30 for the pipette.

Direct measurement of the surface tension:

Measure the surface tension of the solutions by the tensiometer. Before each measurements, the sample holder should be rinsed 2–3 times with 1–2 cm^3 volumes of the solution and then should be filled with exactly 20.0 cm^3 solution. Later, the diameter (d_{tm}) of the sample holder should also be measured.

The detailed instructions about the use of the tensiometer are found as attached. Ask the teacher to help you if you are in need!

Conductometry:

Specific conductivities are directly measured by the device due to the internal calibration. However, the conductivity of pure water (which is to be measured first) must be subtracted from the measure values of solution conductivities. Taking ca. 10 cm^3 of samples is enough.

To ensure that the amount of solutions is appropriate for performing the measurements, rinse all equipment with a small volume of the targeted solution. Then, after the measurement, the remaining solution shall be used along the next measurement. Note down the temperature of the laboratory!

4 Evaluation of the measured data

If no measurement was performed with the drop volume method, the related instructions shall be skipped.

- Calculate the surface tensions from the results of the mass measurements using the known surface tension of water (γ_{W}) at the laboratory temperature. The latter can be calculated (in mN/m units) by the following empirical formula: $\gamma_{\text{v}}(t) = -2,7 \times 10^{-4} \cdot t^2 - 0,1406 \cdot t + 75,657$.
- If the tensiometer is not precisely calibrated⁴, the measured vales can be also recalculated by the above, taking into account the literature value. For example, if we get 70 mN/m for pure water instead of the literature value of 72 mN/m , the all of the other values of surface tension should be multiplied by the 72/70 correction factor.

³If you use a pipette, it is important that the dripping should start exactly from the same height of the liquid meniscus. To maintain this condition, you should put a mark by a permanent pen on the pipette.

⁴When the data measured for deionized water differs from that of the literature value by more than 0.5 mN/m .

Table 2: Summary of the experimental results.

$m_{\text{surfactant}} = \dots \text{ g}$, $t = \dots \text{ }^\circ\text{C}$,

c (M)	lg (c/M)	...	m_{bk} (g)	drop number	$m_{\text{bk+drp}}$ (g)	$m_{\text{l drp}}$ (g)	γ_{drp} $\left(\frac{\text{mN}}{\text{m}}\right)$	$(A/V)_{\text{drp}}$ $\left(\frac{1}{\text{cm}}\right)$...
	

$d_{\text{tm}} = \dots \text{ m}$,

$(A/V)_{\text{tm}} = \dots \text{ 1/m}$, $\kappa_0 = \dots \text{ S/m}$,

...	γ_{tm} $\left(\frac{\text{mN}}{\text{m}}\right)$	$\gamma_{\text{tm,corr}}$ $\left(\frac{\text{mN}}{\text{m}}\right)$...	κ (S/m)	κ_{corr} (S/m)	Λ_{c} (S·m ² /mol)	lg κ_{corr}	lg Λ_{c}
...			...					

3. The measured and the calculated data should be summarized according to Table 2, where the following abbreviations are defined as: c – molar concentration, bk – beaker, drp – droplet(s), bk+drp – beaker and droplets, corr – corrected, A/V – surface to volume ratio, tm – tensiometer, κ – specific conductivity, κ_0 – value corresponding to the pure solvent, Λ_{c} – molar conductivity.

For the calculation of the A/V values, we need to assume that the droplets are spherical, and the density of the liquid is 1.00 g/cm³.

4. Plot the experimental data obtained for the drop mass and for the tensiometry measurements on a γ vs. lg c diagram, and determine the c.m.c. value / range expressed in molar concentration for both curves. For the conductivity experiment, the lg κ vs. lg c and lg Λ_{c} vs. lg c values should be plotted on the same graph, using two different y-axes.
5. Compare the curves and c.m.c. values obtained by the different methods, and try to explain the possible differences. In case of the drop mass measurements, consider the difference in surface-to-volume ratios as well.

References

- [1] IUPAC. Compendium of Chemical Terminology, 2nd ed. (the “Gold Book”). Compiled by A.D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: <http://goldbook.iupac.org> (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. ISBN 0-9678550-9-8. doi:10.1351/goldbook.

Questions

1. What are amphipatic (amphiphilic) compounds?
2. What are surfactants?
3. Describe briefly (in a few sentences) the mechanism of the formation of micelles!
4. What kind of conditions must be fulfilled when we want to relate the saturation of the surface with the micelle formation?
5. Define the critical micelle concentration!
6. Describe briefly (in 2–2 sentences) those c.m.c. determination methods in which the measured signal is proportional to the amount of micelles!
7. Describe briefly (in 2–2 sentences) those c.m.c. determination methods in which the measured signal is proportional to the surface excess of the the surfactant!
8. Which equipment are known to you, based on counting droplets? Describe their most important characteristics in 1–1 sentence!
9. Note down in 4–5 sentences, how you are going to prepare the solution series!
10. To prepare a surfactant stock solution, we dissolve 2.3 g NaDS in a 100 cm³ volumetric flask (**A**) and then we fill it up with water. During the first dilution, we pipette out 60 cm³ of this solution into a second flask (100 cm³, **B**), which we fill up with water again. What is the molarity of the stock solution left in flask **A**, and that of the diluted solution in flask **B**? $M_r(\text{NaDS}) = 288.4$
11. To prepare a surfactant stock solution, we dissolve 2.3 g NaDS in a 100 cm³ volumetric flask and then fill it up with water. During the first dilution, we pipette out 50 cm³ of this solution into a second 100 cm³ flask, then we fill up with water again (i.e., a two-fold dilution is prepared). From this solution we again pipette out 50 cm³ into a next 100 cm³, which we fill up again with water, and so forth. What fraction is the molarity of the solution obtained upon the 6th dilution of molarity of the stock solution, and what is its value? $M_r(\text{NaDS}) = 288.4$
12. Note down in 4–5 sentences, how you are going to make graphs from your data!
13. What is the surface-to-volume ratio for a spherical liquid droplet, with mass of 0.08708 g and density of 1.00 g/cm³?