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Alternative Demonstrations of Slow Processes. III: A Demonstration and Video Clip Showing Effusion in Liquids

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Abstract

Effusion in liquids is much slower compared to that occurring in gases. It can be easily demonstrated using standard equipment based on a porous cup (full of colored glycerol), and immersed in a beaker with water. Water slowly enters the cup (despite its lower density, compared to that of glycerol). The effusion process can be monitored qualitatively through the change of the level of glycerol in the glass tube connected to the porous cup. A 44 s video clip containing 270 photographs (taken in a 90 minute period) has also been prepared, as a time saving demonstration of effusion in liquids and one more demonstration concerning relatively slow processes.

Key words: transport phenomena, effusion; liquids; glycerol; water; video clip

Introduction

Effusion is often defined as a process of leaking of a fluid through a narrow pinhole [1–3] or, alternatively, as a (hindered) diffusion through a porous wall [4]. The later process is sometimes referred to as a transfusion, although there is no principal difference between the two, since the process of transfusion can always be considered as multiple effusion (each pore of the porous wall being equivalent to a single narrow pinhole).

It is well known from physical chemistry textbooks [1] that the rate of effusion in a given gas is:

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{pA_0N_A}{\sqrt{2\pi MRT}} \qquad (1)$$

where N is the number of molecules, t is the time, p is the pressure of the gas, A_0 is the area of the hole through which the effusion process takes place, N_A is the Avogadro's constant, R is the universal gas constant, T is the thermodynamic temperature, and M is the molar mass of the gas. The above equation is derived from the kinetic theory of gases.

Knowing that for an ideal gas $pV = nRT$, it is easy to prove the following relation for the rate of effusion:

$$\frac{\mathrm{d}N}{\mathrm{d}t} \propto \sqrt{\frac{T}{M}} \qquad (2)$$

Thus it is obvious that the rate of effusion is higher the higher the temperature and the lower the mass of the gas molecules. If the rates of effusion of two different gases are compared, providing the temperature is the same, one easily comes to:

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \qquad (3)$$

where r denotes the rate of effusion, and indices 1 and 2 refer to the first and second gas, respectively. Eq. 3 actually gives the well-known Graham's law of effusion.

Demonstrations of effusion in gaseous state are numerous [4–7], albeit sometimes erroneously identified as diffusion [6,7]. The most striking of all of these is the hydrogen fountain [4–5], due to the fact that hydrogen is the lightest of all gases, so the rate of effusion (cf. Eq. 2) is the highest possible one (providing one demonstrates effusion of different gases against air as a standard). To the best of our knowledge, no demonstration of effusion in liquids has been offered so far. Having this in mind, we decided to develop such an experiment that will result in a demonstration, which is:

- effective
- fast enough
- cheap
- safe
- free of waste that contains environmental pollutants

Our attempts appeared to be successful and in agreement with all above requirements, as will be elaborated shortly.

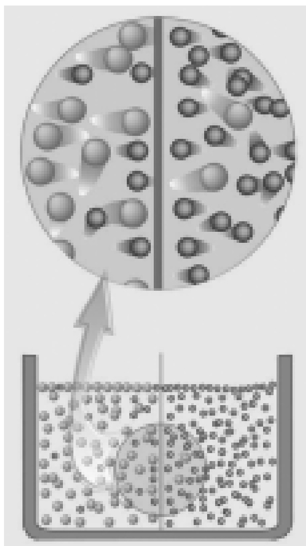

Figure 1:
Effusion in liquids – a schematic view: lighter molecules (water) move faster through the porous wall than the heavier ones (glycerol).

Experimental

Equipment and chemicals. The demonstration could be performed using simple and inexpensive equipment and chemicals, like:

- a porous cup (≈ 100 mL; one made of burned clay works fine)
- a beaker (≈ 400 mL)
- a glass bottle (≈ 200 mL)
- graduated glass tube (≈ 30 cm in length)
- 1-hole rubber stopper, to fit both the porous cup and the glass tube
- glycerol (cca 100 mL)
- deionized or distilled water
- methylene blue (cca 100 mg)

All equipment is presented in Fig. 2.

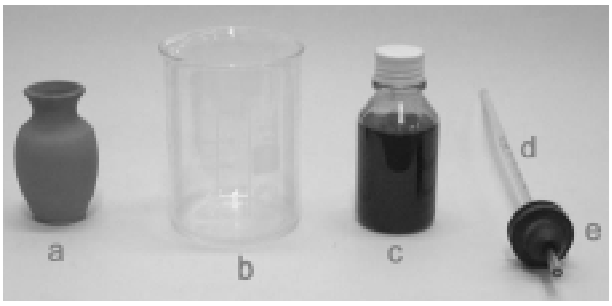

Figure 2. Equipment used for demonstration of effusion in liquids: porous cup (a); beaker (b); bottle filled with colored glycerol (c); graduated glass tube (d); one hole rubber stopper (e).

Preparation for the demonstration. The methylene blue (50–100 mg) is first dissolved in cca 100 mL of glycerol, in a glass bottle. In order to obtain homogenous solution it may be necessary to shake the bottle several times during about half an hour.

It is necessary to fill the porous cup with water, few hours before the demonstration (or, better, overnight). If a dry cup is used, some time will be wasted waiting for the liquids to fill the pores, during which process the system may show odd behavior (like the level of colored glycerol in the glass tube decreasing with time in the beginning of the demonstration, instead of increasing). An independent check proved that basically the same results are obtained if the porous cup is first soaked in glycerol.

The demonstration. The porous cup (previously filled with water, or kept under water) is filled to the top with the colored glycerol. After that the cup is stoppered with the rubber stopper (the graduated glass passes through the hole). The cup is stoppered tightly enough, to sustain a visible level of the colored glycerol in the tube. The beaker is filled with water by two thirds of its volume, and is placed on a suitable base in front of white screen.

The demonstration starts when the assembled equipment is placed in the beaker with water. In few minutes it becomes obvious that the level of the colored liquid in the tube increases. This means that, despite of its lower density, water enters the cup through the porous wall. After about 1 hour the level is much higher then it was in the beginning (cf. Figs. 3 a–d).

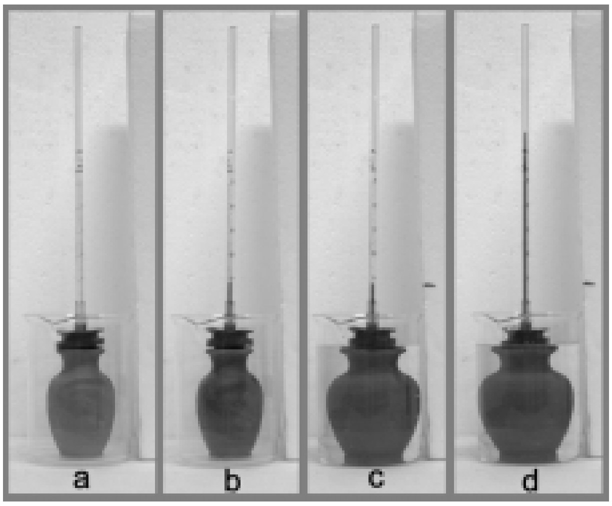

Figure 3: Effusion in liquids: experimental setup (a); glycerol is added to the porous cup (b); water is added to the beaker – start of demonstration (c); and end of demonstration (d). The initial level of glycerol is marked on the white styrofoam block next to the beaker (cf. Figs. 3 c–d) and serves as a point of reference. The porous cup has seemingly expanded in the latter two figures, as a consequence of the change of the optical properties of the medium (the refraction index of water is ≈ 1.33, and that of air is very close to 1).

At first sight the demonstration is similar to osmosis. However, there is a very important difference: osmosis is the movement of solvent particles from high solvent concentration to low solvent concentration through a semi-permeable membrane, which only allows the solvent molecules to move through. For example, if we used glycerol/water solution in contact with pure water, using semi-permeable membrane, the water molecules would move into the glycerol/water solution. However, when we use porous membrane, both water and glycerol molecules are now able to transfer and in this case the movement of the water molecules into the glycerol/water solution (or the pure glycerol, as in this case) is due to effusion. The water molecules are lighter than glycerol molecules and thus the rate of effusion of water molecules is faster than for glycerol molecules, assuming liquids obey Graham's law.

The porous walls of the used cup are transparent in both directions. After a longer period of time (about 5–6 hours), one could see that the water in the beaker has light blue color. This is due to the glycerol molecules (and the methylene blue dye) that traveled by effusion in the reversed direction. The process is from the very beginning (unlike osmosis) a 2-way process, albeit the rate of the reversed process is slower as it should be. Even more arguments that the demonstrated process is indeed a demonstration of effusion are given in the subheading Notes.

The process is much slower than is effusion in gases [4–7]. However, it is still possible to demonstrate it in a lesson period. For those that prefer to organize their lecture using classical demonstrations (i.e. experiments that last only few minutes), we offer a video clip of the process, employing the so-called fast-motion technique [8,9]. Snapshots were taken in 90 minutes period, during which the level of colored glycerol increases by more than 10 cm. The photos were linked to make a short movie (cf. Movie 1).

The demonstration is appropriate for both 1st year students within the general chemistry course, and for 2nd or 3rd year students within advanced physical chemistry courses. No particular background knowledge is required for the former (it is enough to understand the basics of diffusion, effusion and osmosis). The latter are expected to be familiar with the kinetic theory of gases, the properties and differences in behavior of both gasses and liquids. The purpose of the demonstration is to complement existing demonstrations on gas effusion, and to make a clear-cut distinction between effusion in liquids and osmosis. After this demo is performed, the importance of the existence of semipermeable membrane becomes obvious.

Safety tips and disposal

The glycerol, as any other alcohol, is somewhat toxic. If swallowed, by accident, call for physician immediately. If spilled just wash it with water. The waste may freely be disposed in the sink and flushed with water. When performing the demo, safety goggles should be worn (as always, when performing chemical demonstrations). Some care is also needed when inserting the glass tube into the rubber stopper (the tube may crack and hurt the instructor).

Notes

We checked that the demonstration might also be performed with different pairs of liquids, like ethanol–amyl alcohol or ethanol–carbon tetrachloride pairs. However, it is both slower (due to lower molar mass ratios, in the case of ethanol–amyl alcohol pair [10], and probably due to much higher density of CCl_4 in the case of C_2H_5OH–CCl_4 pair [11]), and it is environmentally unacceptable (particularly with CCl_4 or other halogen derivatives of hydrocarbons).

One could have doubts whether the process described is due to effusion, and not due to osmotic pressure gradient perhaps? However, the osmotic pressure is a colligative property. Therefore, if one fills the cup with solution of water in glycerol, against pure glycerol in the beaker, the glycerol should enter the cup. Actually, in reality the opposite happens! It is always the liquid with lower molecular mass that moves faster through the porous walls, so it is not due to osmosis.

In case of doubt whether perhaps viscosity differences might be at the origin of the phenomenon (thus expecting that the liquid with higher viscosity should run slower), one may argue that in the ethanol–CCl_4 pair it is ethanol that moves faster through the porous wall, despite its somewhat higher viscosity. Obviously, the role of the molecular mass is in all studied cases the dominant factor.

In line with what was said above, any pair of completely miscible solvents could in principle be used. However, for best results it is important that the ratio of molar masses of the two liquids should be as high as possible (cf. Eq. 3) [12]. From our experience, the pair water–glycerol is close to the ideal pair for this demonstration.

One may object that the ratio of the molar masses for monomers of water and glycerol does not give a correct estimate of the actual mass ratios, for oligomers are present in both water and glycerol. One would expect that this ratio might be used at least semiquantitatively, as a first guess value for the principal factor that governs the rate of effusion. Actually, some time ago a publication appeared that supports very strongly the notion of effusion in liquids, despite the very strong intermolecular interactions and molecular velocity distributions that deviate significantly from Maxwellian [13].

Conclusion

The offered demonstration may be performed easily. It uses some simple and cheap chemicals, and very common equipment. The effusion process becomes obvious after few minutes. Providing a large porous vessel is used (with a volume of at least 1 and preferably 2 L), it is possible to witness the transfer of liquid (water) in real time (up to one minute, a time period that might be compared with the duration of the offered video clip). This is both educational and a novel demonstration, since no similar experiment was found in the literature after a thorough search.

The offered video clip (employing the fast motion technique) may be used as time saving alternative. The students liked the demonstration (they seem to like all demos based on video clips that 'accelerate' the otherwise slow processes [8,9]).

In our next contribution attention will be paid to few demonstrations of diffusion processes (some new and some well known), in both gases and liquids, as well as to preparation of suitable video clips.

Supporting material

Figures 2 & 3 are photographs taken with FUJIFILM *FinePIX4700* digital camera. The movie (LiqEffus.mpg) is a collection of photographs that were taken by ToUcamXS (Phillips) digital camera, which was coupled to and software controlled by a PC. The movie LiqEffus.mpg was a result of linking 270 snapshots (each of 640×480 resolution) and is playable with the Windows Media Player. When playing the file, it is recommended to view it with the 'full screen' option. The added music is, of course, optional (one can always switch off the speakers).

Movie. A 44 seconds movie (LiqEffus.mpg) showing the change of the level of colored glycerol in the glass tube, due to effusion of water.

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Conclusion:

Historically, most chemistry terms are derived from Classical Greek and Latin word roots. The trend still continues as newer concepts are being developed and given names. There are about a dozen most frequently used affixes – *ortho*, *tropo*, *mer*, *meta*, *iso*, *para*, *hetero*, *syn*, *homo*, *topo*, *dia* and *pseudo*. For a starter, the knowledge of the etymology of chemistry terms can potentially remove their often intimidating appearance and help understand the concepts represented by them succinctly. And this can be a basis for further development. As one progresses, it may appear in few cases that due to the advancement in science the original concepts got refined though, they still retain the original terms coined for them, and that the etymology approach may be misleading. Not taking the etymology approach so far that it is an added burden; on the other hand, a means to take positively on the heavily loaded chemistry curriculum is expected to be one step in replacing sobriety with a pleasurable learning experience.

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10. Of course, if the molar masses are exactly the same, one would expect, to a first approximation, equal rates of effusion for both liquids and hence no changes of the liquid column in the glass tube.
11. The importance of the relative densities of the liquid pair will be explained briefly: one deals with a porous cup. Apart from the tendency that lighter molecules move faster (due to effusion or hindered diffusion), also the liquid with higher density will have (opposite) tendency to run through the pores and equalize its level in both parts (the porous cup and the beaker) of the system, as a consequence of gravity, i.e. the hydrostatic pressure.
12. It should be noted that Eq. 3 holds strictly for ideal gases. It is expected to be an excellent approximation for real gases as well, but only an approximation for liquids, due to significant intermolecular interactions.
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