Volume Nonadditivity of Liquid Mixtures: Modifications to Classical Demonstrations

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Abstract: Departures from Raoult's law are often found in liquid mixtures resulting in volume nonadditivity. Modifications are proposed for experiments demonstrating volume contraction of water/ethanol and volume expansion of ethyl acetate/carbon disulfide liquid mixtures. A layer of paraffin oil or water is used to prevent mixing of the liquids at an earlier stage then desired. A demonstration of volume expansion in a CS_2/ethyl acetate system is proposed as well. The modifications significantly improve the ease of the demonstrations, which can be made even more impressive by coloring the liquids. A reaction vessel of simple construction is offered for a more vivid demonstration of the phenomenon.

Introduction

The volume contraction of water/ethanol mixtures with respect to the sum of volumes of the pure components is a well-known demonstration [1]. It also helps to illustrate, in an elegant way, the importance of microscopic quantities (intermolecular forces in this case) through the change of a macroscopic quantity (the volume). The volume contraction is a consequence of closer packing (on average) of the molecules in the mixture. The same phenomenon is expected in all cases of strong negative departures from Raoult's law [2].

In the case of a positive departure from Raoult's law, a volume expansion occurs. One known example [3] is the volume expansion of the ethyl acetate/carbon disulfide mixture as compared to the sum of the volumes of the pure components. In this case, the molecules are, on average, at larger distances than in the pure liquids [4].

In their original form [1, 3], however, these demonstrations may be somewhat tedious (and require some experience), because the ethanol (or ethyl acetate) is supposed to be carefully added on the top of the water (or carbon disulfide). No matter how cautiously this is done, mixing of the liquids always occurs to a certain extent. In the case of a water/ethanol system, this is particularly evident if the ethanol is first colored by few crystals of some indicator or other dye (methylene blue or napthol green work well). Those inexperienced with this type of experiment often have to make repeated attempts in order to perform a successful demonstration.

There is an elegant way to get rid of this inconvenience, which is caused by the inevitable and undesirable mixing of the liquids. If a layer of paraffin oil is placed over the water in the graduated cylinder (Instead of a graduated cylinder, we used a vessel designed to read accurately the change in the volume. See Figure 1.), the volume contraction demonstration is much more convincing. Paraffin oil is immiscible with either water or ethanol, and it has a density lower than water, but higher than ethanol. Similarly, for the volume expansion demonstration, a layer of water may be placed over the carbon disulfide to prevent early mixing with ethyl acetate.

Construction of the Vessel

The volume of the vessel may vary within certain limits. (The authors encourage the use of vessels with a volume of at least 100 cm^3.) It can be easily constructed by a glass blower. The vessel consists of two (joined) parts. The upper part is actually a graduated tube (a peace of broken buret may be used), and the bottom part is a large tube or a wide test tube. Care should be taken about the quality of the glass used. If the quality of the glass used for the lower part of the vessel differs appreciably from that of the upper part, it may be difficult to properly join the two parts. The joint may survive a few hours (or even days), but will eventually crack. We recommend the use of a good quality hard glass. At least two vessels should be built.

The Demonstrations

Volume Contraction. For the volume contraction demonstration, we recommend that a diluted solution of a dye in ethanol be prepared. Methylene blue was found to work well, although the possible choices are almost unlimited. Next, prepare a diluted solution of fluorescein in distilled or deionized water. (Coloring of the ethanol/water phases is not necessary, but the students can follow the volume change in the vessel more easily if, at least, the liquid with lower density, in this case ethanol, is colored.)

Before the demonstration, place ≈ 50 cm^3 of water at the bottom of the vessel using a long-neck funnel. (Keep the walls dry.) Then, add paraffin oil ($\rho \approx 0.84$ g cm^{-3}) to make a layer that is 3 to 4 mm in thickness. Using a clean, dry funnel, add carefully ≈ 50 cm^3 of the (colored) ethanol over the paraffin oil. You may avoid the use of the funnels if you pour the liquids *very carefully* down one side of the vessel. In this case, we recommend that you wait some time before pouring the next liquid. If the demonstration is set up like this prior to use, only the vessel (clamped on a stand with the liquids separated by paraffin oil) need be brought into the lecture hall. In such a case, the demonstration can be performed in 2 to 3 minutes.

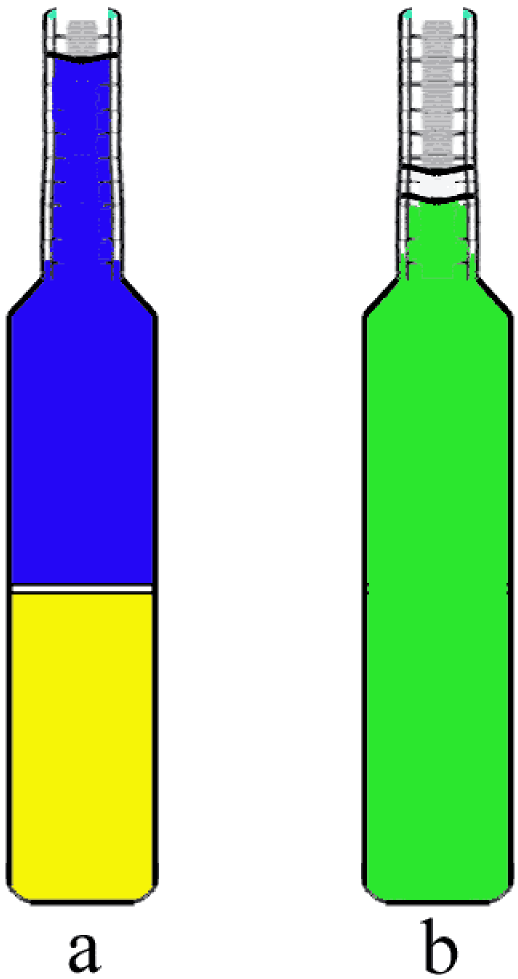

Figure 1. The initial volume of the liquid system (a) is reduced after mixing (b).

Start the demonstration by reading the total volume (or, if this is already known approximately, read only the ethanol level position). A long knitting needle may be clamped into position, pointing to the ethanol level. Then, use a rubber stopper to close the vessel mouth and invert it twice to mix the liquids. Clamp the vessel for about one minute, and then examine the total volume. The vessel will have two liquid phases: a mixture of water and ethanol (green) and paraffin oil (colorless, see Figure 1b). The total volume of the liquids will be, within a few milliliters, lower.

If more vessels are available, you can make a comparison with a carbon tetrachloride/ethanol system, in which no measurable volume change is detected. In this case, the volume reduction is found to be about 3 to 4% of the starting value. Acetone can be used successfully instead of ethanol [1]. The process of mixing of the two liquids is slightly exothermic. This can be measured by means of a thermocouple or a conventional thermometer; the typical temperature change that we measured (using a thermocouple thermometer), was 5.3 ± 0.1 K, using equal volumes of water and alcohol. The volume contraction read immediately after mixing was 3.2 mL. After the system reached thermal equilibrium (volume read after about 1 h), there was an additional volume decrease of about 0.3 mL (a total volume contraction of about 3.5 mL).

Point out the volume reduction (the nonadditivity of the volumes) to the students, and discuss the similarity of water and ethanol molecules. Mention that intermolecular forces are the reason for the volume contraction. Ask the students a question about their expectations for similar systems (e.g., water/methanol, water/acetone, water/dioxane). If possible, check their expectations by experiments.

The procedure described is a simple, yet effective demonstration of nonadditivity of volumes in a two-component liquid system. Being slightly exothermic, it also shows that the dissolution (which is always followed by solvation) is physicochemical and not just a simple physical process.

Volume Expansion. The necessary precondition for volume expansion to be observed is a large positive deviation from Raoult's law. Suitable liquids that shows measurable volume expansion upon mixing are carbon disulfide and ethyl acetate.

The procedure is similar to that for volume contraction. CS_2 is colored by blue eosin (the color is pale pink) and is placed first into the vessel. A layer of distilled water is added next; then the vessel is refilled with ethyl acetate, which is yellow when colored with a few crystals of cadion (*p*-nitrobenzenediazoaminoazobenzene).

The demonstration starts by reading the total volume (i.e., the ethyl acetate level position). A knitting needle is clamped pointing to the ethyl acetate level. The vessel is corked and inverted (twice) to mix the liquids. After a short time, examine the total volume. In this case, the vessel will have two liquid phases: a mixture of CS_2 and ethyl acetate (somewhat darker yellow) and water (orange). The total volume is larger by 1.2 mL. As would be expected, a temperature lowering occurs (ΔT = –4.6 K, measured with the same device as above). After thermal equilibrium is reached, the volume of the mixture increases by 0.6 mL (a total volume expansion of ≈ 1.8 mL).

Safety Tips and Disposal

Carbon disulfide is an easily flammable and highly toxic substance. Never inhale its vapors! If this part of the demonstration is to be used, it should be performed in a hood. In case of accident, call for a physician immediately. The waste containing CS_2 must be collected and stored in hermetically closed containers in a fire safety cabinet. Because of serious health and fire hazards, carbon disulfide should never be poured into a sink.

For those reluctant to perform this demonstration, the included video clip may be useful.

Conclusion

Minor modifications (such as addition of paraffin oil and color) to this well-known demonstration can make it significantly easier to perform and more vivid to the students.

Those reluctant to perform demonstrations with poisonous chemicals (e.g., CS_2) can safely use the enclosed video clip as a complement to the volume contraction demonstration described above.

Supporting Material. The supporting material described below are available as s00897010478b.zip (http://dx.doi.org/10.1007/s00897000478b).

Photos are included (FUJIFILM *FinePIX4700* digital camera, has been used), as well as two movies. Photos are in .JPG format. The movies are in .AVI format, playable using Quick Time Player.

Photo 1. Setup for the contraction demonstration before (left) and after (right) mixing. Expanded views of the buret part (upper rectangles) and of the liquid interfaces (lower left rectangle) are shown.

Photo 2. Setup for the expansion demonstration, before (left) and after mixing (right). Enlarged views of the buret part (upper middle rectangle, showing the expanded volume), and of the liquid interfaces (lower middle rectangle).

Movie 1. A 30-s movie of the volume contraction demonstration using the water/ethanol system.

Movie 2. A 19-s movie of the volume expansion demonstration using the ethyl acetate/carbon disulfide system.

References and Notes

1. Summerlin, L. R.; Borgford, C. L.; Ealy, J. B. *Chemical Demonstrations: A Sourcebook for Teachers;* American Chemical Society: Washington, DC, 1987; Vol. 2, p 15.
2. Atkins, P. W. *Physical Chemistry*, 3rd ed.; Oxford University Press: Oxford, England, 1986; p 180.
3. Shakhashiri, B.Z. *Chemical Demonstrations: A Handbook for Teachers of Chemistry;* The Wisconsin University Press: Madison, WI, 1989; Vol. 3, p 225–228.
4. Studies of partial molar volumes have also been performed [5]. These, however, are interesting as laboratory experiments, but are not suitable as chemical demonstrations.
5. Loucks, L. F. *J. Chem. Educ.* **1999,** *76,* 425–427.