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Short Communications

Determination of Deuterium Contents in Small Samples of Water by a Drop Float Method

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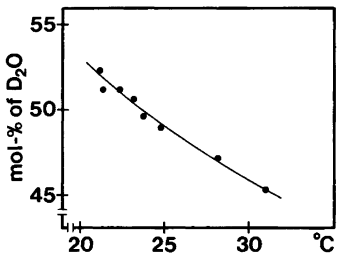

Fig. 1. Calibration curve for the reference liquid with 67.5 mol-% of xylene. Each point gives the temperature, where a drop just began to fall down.

In a recent adsorption study we needed a method to determine the deuterium content in a few drops of heavy water samples. As we had no access to suitable mass spectrometers we surveyed the literature[1,2] to find other practical means of analysis. The IR method proposed by Kimbrough and Askins[3] seemed to be ideal for our purposes. A water sample is first allowed to react with methyl orthoformate when methanol and deuteriomethanol are obtained in exactly the same ratio as there are protons and deuterons in the original sample. This ratio is measured from a near IR spectrum. We noticed that opposite to the claims of the authors, the deuterium fraction cannot be obtained directly from the intensities of the proper absorption peaks, but a calibration curve is necessary. Even then we did not achieve as good an accuracy and reproducibility as the authors suggested, and we began to try other methods.

The falling-drop method and float method have received a lot of attention[1,2,4,5] in the literature. However, nobody seems to have combined the ideas of these methods. We have now done it and the result is quite serviceable; a method where small water drops are used as floats. As in the usual falling-drop method, suitable organic reference liquids are needed. The conventional liquids,[6] mixtures of bromobenzene and xylene (containing three isomers), were found suitable. In order to prevent the change in density due to uneven evaporation[6] of the components, the reference liquids were closed in rubber-stoppered injection vials and water samples were added with a Hamilton needle through the stopper. Two modifications (A and B) of the method were used.

In modification A the density of a fixed reference liquid was changed by changing the temperature. The water drops began to fall down at certain temperatures depending on their densities. The calibration curve presented in Fig. 1 was composed with samples of known deuterium contents. The most suitable temperature range for our thermostat was 20 – 30 °C which corresponds to a range covering less than 10 mol-% in deuterium contents. To measure samples with deuterium contents outside this range a new suitable reference liquid must be taken and a new calibration curve composed.

In the more rapid modification B, the temperature was fixed and the density was changed by changing the mol ratios of the organic compounds. In practice this was done by preparing a set of liquids with regularly increasing densities; then the whole range of deuterium contents can be covered. By some exploratory trials it was relatively easy to find two liquids which were near the sample with respect to density and the deuterium contents could be derived from the calibration curve of Fig. 2.

There are some difficulties in using the methods. Aqueous drops tend to stick to the walls of glass vials and even to the surface of the organic liquid. The drops can be set hovering freely by injecting them slowly and carefully into the interior of the reference liquid. The two phases dissolve slightly in one another, which gradually changes their densities.

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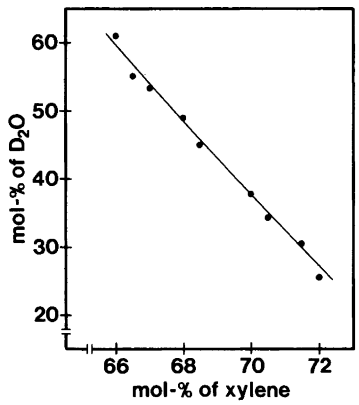

Fig. 2. Calibration curve for different bromobenzene/xylene mixtures.

Consequently, the best accuracy is obtained with fresh reference liquids and water drops. The largest difficulty in modification A is, however, connected with the convection streams within the reference liquid when the temperature is changed too rapidly. Thus, the temperature changing must be done rather slowly. To accelerate the measurements the correct temperature range should be known in advance. Modification B is much more convenient in this respect.

The precision of the described methods found from the calibration curves is about 1 – 2 mol-%. The largest deviations are probably due to the partial miscibility of the aqueous and organic phases. We think that our methods can be considered as good as spectrometric methods in analysis of heavy water samples when only moderate accuracy is needed.

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1. Kirshenbaum, I. *Physical Properties and Analysis of Heavy Water*, McGraw-Hill, New York 1951.
2. Vasaru, G., Ursu, D., Mihaila, A. and Szentgyörgyi, P. *Deuterium and Heavy Water – A Selected Bibliography*, Elsevier, New York 1975.
3. Kimbrough, R. D. and Askins, R. W. *Anal. Chem. 41* (1969) 1147.
4. Baertschi, P. and Thürkauf, M. *Helv. Chim. Acta 42* (1959) 282.
5. Brigoli, B., Cerrai, E. and Silvestri, M. *J. Sci. Instrum. 34* (1957) 292.
6. Frilette, V. J. and Hanle, J. *Anal. Chem. 19* (1947) 984.

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