Excess Volumes for $H_2O + D_2O$ Liquid Mixtures

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Abstract

The volume changes on mixing D_2O with H_2O have been measured with a new tilting-type dilatometer. The molar volumes are very nearly additive, but not exactly so. At 25°C, the excess molar volume V_m^E is positive, having a maximum value of about $1\cdot8\times10^{-4}$ cm^3 mol^{-1}, while at 4°C it is negative, with a minimum of about $-1\cdot2\times10^{-4}$ cm^3 mol^{-1}.

The 10% density difference between liquid H_2O and D_2O has been widely used[1,2] to determine the isotopic composition of mixtures, often by the 'floating drop' or the 'temperature float' method for H_2O-rich samples. Exact additivity of the molar volumes has been universally assumed, either explicitly or implicitly, yet there seems available no more recent supporting experimental evidence than the mixture density studies of Longsworth[3] and Swift.[4]
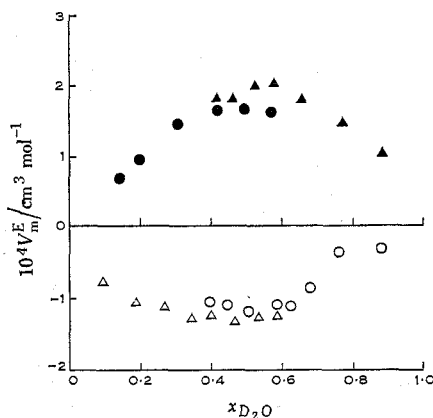

Fig. 1. Excess molar volume for mixtures of H_2O and D_2O at 25°C and at 4°C as determined by the dilatometer.
▲,● 25°C;
△,○ 4°C.

Having available a tilting-type continuous dilution dilatometer[5] we have briefly examined the $H_2O + D_2O$ system at 25°C and at 4°C with the results shown in

[1] Kirshenbaum, I., 'Physical Properties and Analysis of Heavy Water' (McGraw–Hill: New York 1951).
[2] Bauer, N., and Lewin, S. Z., in 'Techniques of Chemistry' (Eds A. Weissberger and B. W. Rossiter) Vol. 1, Part 4, p. 73 (Wiley–Interscience: New York 1972).
[3] Longsworth, L. G., *J. Am. Chem. Soc.*, 1937, **59**, 1483.
[4] Swift, E., *J. Am. Chem. Soc.*, 1939, **61**, 198.
[5] Bottomley, G. A., and Scott, R. L., *J. Chem. Thermodyn.*, 1974, **6**, 973.

Fig. 1. The deuterium oxide was obtained from Thompson–Packard Ltd, New Jersey, nominally $99 \cdot 8 \%$ D_2O by weight: both fluids were 'degassed' immediately prior to use. In this dilatometer about $1 \cdot 35$ mol of either H_2O or D_2O is progressively mixed with about $0 \cdot 9$ mol of the other component. At each temperature two dilution experiments start separately from either pure H_2O or pure D_2O and overlap between $x_{D_2O} = 0 \cdot 4$ and $0 \cdot 6$. The precision of the directly observed volume change is about 10×10^{-6} cm^3 in a total volume of between 15 and 45 cm^3, equivalent to sixth-place precision in the density. All necessary corrections have been made for the changing hydrostatic head during the experiment and for the mechanical distortion of the dilatometer consequent on mercury transfer (this necessitates a dummy run of H_2O into H_2O). Care is also necessary to allow the considerable heat of mixing to be dissipated. Taking these potential errors into consideration, the junction of the two halves of each V_m^E against composition curve seems acceptable for this type of dilatometer operating with about 1 mK temperature control. This evidence we believe defines the V_m^E values to within $0 \cdot 4 \times 10^{-4}$ cm^3 mol^{-1}. (Any effect of residual air in the samples will be less than this.) At 25°C the excess volumes are positive with a maximum of $+1 \cdot 8 \times 10^{-4}$ cm^3 mol^{-1} near $x = 0 \cdot 5$. Negative, numerically smaller, values are obtained at 4°C, possibly with some asymmetry. It is suggestive that the temperature of maximum density for H_2O is $4 \cdot 0$°C, while that for D_2O is $11 \cdot 6$°C.

Useful comparison with earlier work at 25°C is perforce limited, chiefly because both Longsworth and Swift claim only fifth-figure accuracy on their densities, equivalent to $\pm 2 \times 10^{-4}$ cm^3 mol^{-1} in V_m^E. They prepared their mixtures by progressive dilution of D_2O, thereby risking accumulation of error in composition—which must be known precisely in the density work but which is far less critical with this dilatometer. Longsworth's data for four intermediate compositions roughly equally spaced in mole fraction lead to V_m^E values of $+4 \cdot 9$, $+2 \cdot 8$, $+1 \cdot 2$, and $0 \cdot 3 \times 10^{-4}$ cm^3 mol^{-1}. Perhaps influenced by these asymmetric values, Swift substituted a more recent value of the density of D_2O into Longsworth's calculations. The V_m^E values recoverable from Longsworth's data then become 0, 0, $-0 \cdot 8$, $-2 \cdot 0 \times 10^{-4}$ cm^3 mol^{-1} and from Swift's measurements on five dilutions become 0, 0, $+6 \cdot 0$, $+4 \cdot 0$, $+4 \cdot 0 \times 10^{-4}$ cm^3 mol^{-1}; we cite Swift's own comment, 'the deviations of the two sets of data from ideality are in opposite direction, and it would be inferred that the true value lies between them'. Swift also took measurements at 5°C which correspond to 0, 0, $-3 \cdot 8$, $-1 \cdot 85$ and 0×10^{-4} cm^3 mol^{-1} for the same dilution sequence. (One mixture density reported by Swift as $1 \cdot 08243$ appears grossly incorrect.)

The more precise dilatometer results confirm the practical ideality in this system for the customary analytical purposes, but bearing in mind the current interest in the structure of these liquids, we suggest that further investigation at even higher precision and over a wider range of temperature is desirable.