

Partial Molal Volumes and Additivity of Group Partial Molal Volumes of Alcohols in Aqueous Solution at 25 and 35 °C

HARALD HØILAND and EINAR VIKINGSTAD

Department of Chemistry, University of Bergen, N-5000 Bergen, Norway

The densities in aqueous solution of homologous series of alcohols have been measured at 25 and 35 °C. The systems were primary alcohols from propanol to hexanol; secondary alcohols from 2-propanol to 2-heptanol, 3-pentanol and 3-heptanol; the diols 1,2-propanediol, 1,3-, 1,4-, and 2,3-butanediol, 1,5- and 2,4-pentanediol, 1,7-heptanediol, and also mannitol.

Group partial molal volumes have been calculated confirming the additivity relation. They have been compared with van der Waals group volumes and group partial molal volumes in pure liquids and discussed in relation to a clathrate-like solvation model.

The additive properties of group partial molal volumes in homologous series of organic solutes, electrolytes or non-electrolytes, are of interest in solution theory and as an aid in the construction of simple models for numerical simulation work.

The first investigation of such additivity relations in aqueous solution was made by Traube.¹ Recent measurements of partial molal volumes of alcohols,² carboxylic acids and their salts,³⁻⁵ and alkylamine hydrobromides⁶ have been utilized to calculate the group partial molal volume of the methylene group, average value 16.0 cm³ mol⁻¹, in agreement with Traube's results. This value is constant from series to series as long as the alkyl chain is straight.

The partial molal volumes of the carboxylic acids and their salts have been used to calculate the group partial molal volumes of the carboxyl and the methyl groups.⁴ In these series the group partial molal volumes are additive with a precision better than ± 1 %. The additive

nature of group partial molal volumes in pure organic liquids has also been demonstrated.⁷

EXPERIMENTAL

The alcohols were all supplied by Fluka. 2-Hexanol, 2-heptanol, 3-heptanol, and 1,7-heptanediol were *purum* grade, the rest *puriss.* grade. D-(-)-Mannitol was supplied by Merck.

The alcohols were all checked for impurities by gas-liquid chromatography. The impurity level was 1–2 parts per thousand for most alcohols. This was considered satisfactory and these alcohols were used without further purification. 1-Propanol and 2-propanol had a slightly higher impurity level, and they were distilled *in vacuo*, boiling points as given in the literature.⁸

D-(-)-Mannitol was dried *in vacuo* at 120 °C.

Water was passed through an ion exchange column, distilled and boiled. A portion of the water was doubly distilled as a check. No difference in density was observed.

The densities were measured by a Paar density meter (DMA O2C) as previously described.⁹ Temperature was measured by a Hewlett-Packard quartz thermometer.

The temperature was controlled to ± 0.007 °C with an oil thermostat. Estimated error in the density ± 5 × 10⁻⁶ g cm⁻³.

RESULTS

Infinite dilution values. For each alcohol solutions were made at 4–7 concentrations in the range 0.02–0.5 mol kg⁻¹. Densities were measured, apparent molal volumes were calculated and extrapolated to infinite dilution assuming a linear concentration dependence. Typical plots are shown in Fig. 1. The error in the partial molal volumes at infinite dilution has been estimated to ± 0.10 cm³ mol⁻¹.

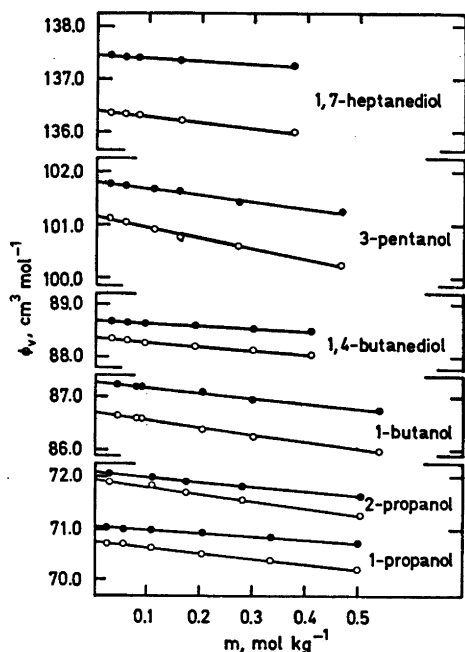


Fig. 1. Apparent molal volume versus concentration. The open circles are at 25°C, the closed at 35°C.

This linear extrapolation method has been critically investigated by Franks and Smith.¹⁰ It was pointed out that linear plots do not necessarily give correct values of the partial molal volumes at infinite dilution, mainly due to a point of inflection in density as a function of concentration at higher concentrations. However, it appears that in the concentration range covered in this work the linearity is very good, and the final result for 1- and 2-butanol is in excellent agreement with the values of Franks and Smith evaluated from a more elaborate method of extrapolation.

Literature values for the partial molal volumes at infinite dilution were found for 1-propanol, 1- and 2-butanol, 1- and 3-pentanol at 25°C.^{2,10,11} No data were found at 35°C. In all these cases the values at 25°C agree. Friedman and Scheraga¹² report values for some primary and secondary alcohols at 1, 20, 40, and 50°C. By interpolation of these data the two sets may be compared at 25 and 35°C. Apparently for 2-propanol and 2-butanol the agreement is excellent. However, for 1-

propanol, 1-butanol, and 1-pentanol the interpolated values from Friedman and Scheraga's work are 0.4–0.6 cm³ mol⁻¹ lower at 25°C and 0.6–1 cm³ mol⁻¹ lower at 35°C.

Calculations of group partial molal volumes. The group partial molal volume of the methylene group is easily determined by subtraction:

$$\bar{V}^{\circ}(\text{CH}_2) = \bar{V}^{\circ}(n+1) - \bar{V}^{\circ}(n) \quad (1)$$

$\bar{V}^{\circ}(n)$ represents the partial molal volume of the solute molecule containing n methylene groups.

The values calculated from eqn. (1) are given in Table 1, the average being 16.0 cm³ mol⁻¹ in excellent agreement with previous determinations.²⁻⁷

With a knowledge of the group partial molal volume of the methylene group it is possible to proceed and calculate the group partial molal volume of the hydroxymethyl group, CH₂OH, from the data for 1,4-butanediol, 1,5-pentanediol and 1,7-heptanediol. It is assumed that the two hydroxymethyl groups are equivalent with respect to group partial molal volumes. The result given in Table 1c shows that a remarkably constant value of 28.2 cm³ mol⁻¹ is found.

The group partial molal volume of the methyl group may then be calculated from the homologous series of primary alcohols. The sum of the group partial molal volumes of the hydroxymethyl and the methylene groups can be subtracted from the total partial molal volume. This yields an average value for the methyl group $\bar{V}^{\circ}(\text{CH}_3) = 26.5$ cm³ mol⁻¹. Previous calculations of this quantity based on carboxylic acid series gave $\bar{V}^{\circ}(\text{CH}_3) = 26.1$ cm³ mol⁻¹. Taking all series into account the average group partial molal volume turns out to be: $\bar{V}^{\circ}(\text{CH}_3) = 26.4 \pm 0.3$ cm³ mol⁻¹.

Since all the other group partial molal volumes have been determined, the value of the hydroxymethylene group may be calculated from the secondary alcohols, Table 1b. Apparently the group partial molal volume of the hydroxymethylene group depends on the position it occupies in the molecule. In 2-position the value is 1.4 cm³ mol⁻¹ higher than in 3- or 4-position, and in 2-position relative to a carboxyl group the value has been calculated to 17.2 cm³ mol⁻¹.⁴

Table 1. Partial molal volumes and group partial molal volumes at infinite dilution, $\text{cm}^3 \text{mol}^{-1}$.

	$\bar{V}^\circ (\pm 0.1)$	35°C	$\bar{V}^\circ (\text{CH}_2)$		$\bar{V}^\circ (\text{R})$	
	25°C		25°C	35°C	25°C	35°C
(a) Primary alcohols					R = CH_2	
1-Propanol	70.75	71.08			26.6	26.7
1-Butanol	86.62	87.28	15.9	16.2	26.4	26.7
1-Pentanol	102.62	103.46	16.0	16.2	26.4	26.5
1-Hexanol	118.65	119.64	16.0	16.2	26.5	26.6
(b) Secondary alcohols					R = CHOH	
2-Propanol	71.93	72.10			19.1	19.3
2-Butanol	86.64	87.04	14.7	14.9	17.9	18.0
2-Pentanol	102.55	103.33	15.9	16.3	17.8	18.1
2-Hexanol	118.49	119.40	15.9	16.1	17.8	18.0
2-Heptanol	134.39	135.65	15.9	16.2	17.7	18.1
3-Pentanol	101.16	101.81			16.4	16.6
3-Hexanol	117.14 ^a		16.0		16.3	
3-Heptanol	133.3	134.4	16.2	16.2	16.5	16.8
4-Heptanol	133.2 ^a		16.1		16.4	
(c) Diols					R = CH_2OH	
1,4-Butanediol	88.35	88.69			28.2	28.2
1,5-Pentanediol	104.35	104.95	16.0	16.1	28.2	28.2
1,7-Heptanediol	136.40	137.45	16.0	16.2	28.2	28.2
1,2-Propanediol	71.22	71.68				
1,3-Butanediol	88.32	88.66	17.1	16.9		
2,3-Butanediol	86.56	86.96				
2,4-Pentanediol	104.64	105.10	18.0	18.1		
(d) Mannitol	119.33	120.37				

^a Literature values from Ref. 2.

Table 2. Group partial molal volumes in aqueous solution and in pure liquids, van der Waals volumes and excess volumes, all in $\text{cm}^3 \text{mol}^{-1}$.

Groups	Aqueous	Solution	Pure liquids 20°C	Van der Waals volumes	Excess Volumes
	25°C	35°C			
CH_2	26.4	26.5	31.48	13.67	-5.1
CH_2	16.0	16.2	16.58	10.23	-0.6
COOH	25.8	26.1	27.24	19.74	-1.4
CH_2OH	28.2	28.2	26.83	18.27	1.4
CHOH	17.8 ^a	18.0 ^a		14.82	
	16.4 ^b	16.7 ^b			
	17.2 ^c				
CH_2COO^-	33.6 ^d				
CHOHCOO^-	34.9 ^d				

^a Hydroxymethylene group in 2-position, ^b in 3- or 4-position, and ^c in 2-position to a carboxyl group.
^d Ref. 3.

Since the group partial molal volume of the methyl group has been redetermined from a larger number of data, some recalculated group partial molal volumes in Table 2 differ slightly from those previously published.³ However, the differences are largely within the limits of experimental error.

DISCUSSION

The group partial molal volumes in aqueous solution may be compared with group partial molal volumes in pure liquid alcohols⁷ and also with van der Waals group volumes.¹³ The data for pure liquids compiled in Table 2

is at 20 °C. However, the densities of the pure liquids change but little with temperature in this region,⁹ and the difference of 5 °C does not seem significant for qualitative comparisons.

The difference between the partial molal volume in aqueous solution and in the pure liquid has been termed the excess volume of the solute.¹⁴ Excess group partial molal volumes are given in Table 2. However, the pure liquid is not satisfactory as a standard state and the excess volume may, it seems, just as well reflect specific volume effects in the pure liquid rather than solute-solvent interaction effects in water. For instance, the excess volume is negative for all the groups except the hydroxymethylene group. In pure primary alcohols extensive hydrogen-bonding takes place¹⁴ forming long chains of hydrogen-bonded alcohol molecules which could reduce the group volume of the hydroxymethyl group, and in consequence lead to a positive excess volume. However, a large negative excess volume may still be taken to reflect stabilization of solvent structure,¹⁵ and in this respect the methyl group is unique, having a much more negative excess volume than any other group. The methylene group has a small negative excess volume. Nevertheless it means that the excess volume of the solute as a whole decreases with the length of the molecule, suggesting increased stabilization of water structure with solute size.

The group partial molal volumes in aqueous solutions compared with van der Waals volumes, show that the void volume around the methyl group must be larger than the void around the other groups. NMR-data¹⁶ on dilute alcohol solutions have been interpreted in terms of the solute in a clathrate-like environment where the hydroxyl group hydrogen-bonds into the water lattice thus helping to form the cavity wall. In this model the methyl group seems to be rotating freely in a large void, and the larger group molal volume of the hydroxymethylene group in 2-position compared with 3- or 4-positions, is probably due to this large void around a rotating methyl group. Hydrogen-bonding between water and the hydroxy-methylene group in 2-position may also be made difficult.

The volume increment per methylene group deviates substantially from 16.0 cm³ mol⁻¹

in three instances: (1) from 2-propanol to 2-butanol, (2) from 1,2-propane-diol to 1,3-butanediol, and (3) from 2,3-butanediol to 2,4-pentanediol. The observed partial molal volumes of these alcohols may be compared with the partial molal volume calculated from the group partial molal volumes. The comparison reveals that 2-propanol has an observed partial molal volume that is 1.3 cm³ mol⁻¹ higher than expected from the additivity relation, and 1,2-propane-diol and 2,3-butanediol have observed partial molal volumes that are lower than expected, 1.2 and 1.8 cm³ mol⁻¹, respectively.

2-Propanol has two methyl groups separated only by a hydroxymethyl group. The large void volumes around the methyl group seem to interfere with each other and increase the total void by about 1 cm³ mol⁻¹. In 1,2-propane-diol and 2,3-butanediol two polar hydroxyl groups occupy neighbouring positions. The two polar groups apparently have a mutual effect on the surrounding water that reduces the partial molal volume, possibly through extensive hydrogen-bonding. This mutual interaction between neighbouring polar groups and water is also observed for a carboxyl and a hydroxymethylene group in neighbouring positions.⁴ Such reductions in the volume requirements are clearly demonstrated by the partial molal volume of mannitol. If the partial molal volume of mannitol is estimated from adding the group partial molal volumes in Table 2, the result is \bar{V}^0 (mannitol) = 124.8 cm³ mol⁻¹, more than 5 cm³ mol⁻¹ higher than the observed value. The many neighbouring polar groups reduce the partial molal volume.

Mannitol is essentially a hydrophilic molecule and no clathrates are known to exist for hydrophilic solutes.¹⁷ The group partial molal volumes in Table 2 are based on data for alcohol solutions where a clathrate-like structure is a possibility. Thus the difference between calculated and observed partial molal volume for mannitol may be related to different volume requirements between a clathrate-like structure on one hand, and a model where short-range solute-water interactions are dominating on the other.

The effect of temperature on the group partial molal volumes is small in the range 25–35 °C. The hydroxymethyl group is appar-

ently not affected at all, and the other group partial molal volumes increase by 0.1–0.3 cm³ mol⁻¹. This increase is of the same order of magnitude as the experimental error in the partial molal volume determinations, and consequently no great significance can be attached to these group molal expansibilities.

REFERENCES

1. Traube, J. *Samml. Chem. Vortr.* 4 (1899) 255.
2. Cabani, S. Conti, G. and Lepori, L. *J. Phys. Chem.* 78 (1974) 1030.
3. Høiland, H. *Acta Chem. Scand. A* 28 (1974) 699.
4. Høiland, H. and Vikingstad, E. *J. Chem. Soc. Faraday Trans. 1* 71 (1975) 2007.
5. Sakurai, M. *Bull. Chem. Soc. Jap.* 46 (1973) 1596.
6. Desnoyers, J. E. and Arel, M. *Can. J. Chem.* 45 (1967) 359.
7. Exner, O. *Collect. Czech. Chem. Commun.* 32 (1967) 1.
8. Timmermanns, J. *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier, New York 1950, p. 313.
9. Høiland, H. *J. Chem. Soc. Faraday Trans. 1* 71 (1975) 797.
10. Franks, F. and Smith, H. T. *Trans. Faraday Soc.* 64 (1968) 2962.
11. Alexander, O. M. *J. Chem. Eng. Data* 4 (1959) 252.
12. Friedman, M. E. and Scheraga, H. A. *J. Phys. Chem.* 69 (1964) 3795.
13. Bondi, A. *J. Phys. Chem.* 68 (1964) 441.
14. Franks, F. and Ives, D. J. G. *Quart. Rev. Chem. Soc.* 20 (1966) 1.
15. Franks, F. and Reid, D. S. In Franks, F., Ed., *Water, a Comprehensive Treatise*, Plenum Press, New York 1973, Vol. 2, p. 323.
16. Glew, D. N., Maks, H. D. and Rath, N. S. *Chem. Commun.* (1968) 264.
17. Franks, F. In Covington, A. K. and Jones, P., Eds., *Hydrogen Bonded Solvent Systems*, Taylor and Francis, London 1968, p. 31.

Received September 22, 1975.