

can be reversed, however, by the addition of sodium sulfate, sodium citrate, or dipotassium hydrogen phosphate, as shown by ORD measurements. It was also shown by ultracentrifugation that the addition of these salts counteracts the dispersing forces of I and the subunits are reassociated to the 136,000-molecular weight form. The ionic environment significantly influences the dissociation of the heat-treated enzyme into its subunits, concomitantly with changes in activity *in vitro*.

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Calculation of Partial Molal Volume in Micellar Systems

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Abstract □ The partial molal volume of a large number of surfactants in the micellar state was calculated by the addition of partial atomic values and the inclusion of a term to account for the hydrocarbon liquid-like nature of the micelle interior. With micellar systems, such numbers often are difficult to obtain experimentally and this approach provides a means of determining relatively accurate values by simple calculation.

Keyphrases □ Partial molal volume—calculation, surfactants in the micellar state □ Surfactants in the micellar state—calculation of partial molal volume □ Micellar systems—calculation of partial molal volume of surfactants

The molecular volume of a surfactant in a micelle is a useful parameter for the study of properties of micelles. For example, it can be used, along with hydrodynamic and light-scattering data, to determine the amount of solvent associated with the micelle (1, 2), to determine the surface charge density and the surface potential of a micelle from its size (3), or, conversely, to determine its size from potentiometric titration data (4). The key to the usefulness of the molecular volume is that it does not change significantly with changes in the solution, such as pH, temperature, and ionic strength (5). Therefore, it can be used to relate the micelle radius and aggregation number, both of which are influenced by the stated conditions.

Table I—Partial Molal Volumes of Some Common Atoms and Groups

Atom	Partial Molal Volume, cm. ³ /mole ^a	Group	Partial Molal Volume, cm. ³ /mole ^a
C	9.9	CH ₃	19.3
H	3.1	CH ₂	16.2
H ⁺	-4.5	NH ₂	7.7
N	1.5	N(CH ₃) ₃ ⁺	66.3
N ⁺	8.4	COOH	19.0
O (=O or -O-)	5.5	COO ⁻	11.5
O (-OH)	2.3	C ₂ H ₅	35.3
O (diol)	0.4	C ₃ H ₇	51.7
S	15.5	C ₄ H ₉	67.9
P	17.0	C ₆ H ₁₃	100.3
P ⁺	28.5	C ₈ H ₁₅	132.7
Li ⁺	-5.2	C ₁₀ H ₂₁	165.1
Na ⁺	-5.7	C ₁₂ H ₂₅	197.5
K ⁺	4.5	C ₁₄ H ₂₉	229.9
Cl ⁻	22.3	OCH ₂ CH ₂	37.9
Br ⁻	29.2	One ring	-8.1
I ⁻	40.8	Two fused rings	-26.4

^a To convert to Å³/molecule, divide by 0.6023.

DISCUSSION

The molecular or molar volume of a solute cannot be measured, but the experimentally measured partial molal volume (p.m.v.) is a

Table II—Comparison of Estimated and Literature Values of the Partial Volume of the Polar Groups of Monomeric Surfactants

Polar Group	—Partial Molal Volume—		Number of Carbons in the Alkyl Portion of the Compounds Studied	Reference
	Traube (15)	Literature		
NH ₃ Br	45	42 ± 1	1, 2, 3, 4, 5, 6, 7, 8	17
N(CH ₃) ₃ Br	96	92 ± 1	8, 10, 12, 14	18
N(CH ₃) ₂ O	52	50 ± 5	7, 8, 9, 10, 11, 12	19
P(CH ₃) ₃ O	73	75 ± 5	8, 12	19
N(CH ₃) ₂ (CH ₂) ₈ SO ₃ H	123	113 ± 3	8, 10, 12	19
SO ₄ Na	32	39 ± 1	10, 12, 14	18, 19, 20
SO ₃ H	27	32	12	19, 20
SO ₃ Na	26	35 ± 2	12, 14	19, 20
C ₈ H ₄ SO ₄ Na	98	98 ± 8	4, 8	19, 20
SO(CH ₂) ₂ OH	61	64	6, 8	18
SO(CH ₂) ₃ OH	77	82	6, 8	18
SO(CH ₂) ₄ OH	94	98	6, 8	18
COOK	26	26	7, 11	19, 20
OOC CHSO ₃ Na CH ₂ OOC (CH ₂ CH ₂ O) ₄ OH	98	84	6 ^a	21
	234	234 ± 3	0, 4, 4 ^b , 6, 6 ^b , 8	22

^a Aerosol MA contains two chains. ^b Branched chain.

reasonable approximation of the true value (5). To determine the partial molal volume of a surfactant, it is necessary to measure the density difference between a solution of the surfactant and the solvent. Since the density of many surfactants, especially the nonionics, is close to that of water, it is often difficult to determine their partial molal volumes experimentally. To avoid this difficulty, many workers have attempted to calculate the volume or density of the surfactant by only considering the weight and volume of the saturated hydrocarbon portion of the surfactant. Poland and Scheraga (6) estimated the volume of CH₂ and CH₃ groups from molecular

models, while Tartar (7, 8) utilized the volume that these groups have in the liquid state. The latter choice seems somewhat more valid in view of the liquid nature of the micelle interior (9).

The error introduced in these treatments by ignoring the polar groups depends, of course, on the size and density of the polar groups. In general, the error is greater with a large polar group such as is found with most zwitterionic and nonionic surfactants. Furthermore, some surfactants have nonaliphatic groups in their nonpolar portions and these cannot be accounted for by this procedure. It is difficult also to draw a sharp distinction between the

Table III—Comparison of Estimated and Literature Values of the Partial Volume of the Polar Groups of Micellar Surfactants

Polar Group	—Partial Molal Volume—		Number of Carbons in the Alkyl Portion of the Compounds Studied	Reference
	Traube (15)	Literature		
—NH ₃ Br	45	33	7, 8	17
—NH ₃ Cl	40	30	12	19
—N(CH ₃) ₃ Br	94	88 ± 7	8, 10, 12, 14, 16	18, 21
—N(CH ₃) ₃ Cl	88	80 ± 3	12, 14, 16	19, 21
—N(CH ₃) ₂ O	52	44 ± 3	8, 9, 10, 11, 12	19
—P(CH ₃) ₃ O	73	62 ± 1	8, 10, 12	19
—N(CH ₃) ₂ (CH ₂) ₈ SO ₃ H	123	114 ± 2	10, 12, 16	19
—SO ₄ Na	32	36 ± 3	10, 12, 14	18, 19, 20, 23, 24, 25
—SO ₃ H	27	28	12	19, 20
—SO ₃ Na	26	31 ± 3	12, 14	19, 20
—C ₈ H ₄ SO ₄ Na	98	97 ± 5	4, 8, 10, 11, 12, 14, 15	2, 19, 20
—SO(CH ₂) ₂ OH	61	57 ± 1	6, 8	18, 19
—SO(CH ₂) ₃ OH	77	73 ± 1	6, 8	18, 19
—SO(CH ₂) ₄ OH	94	88 ± 1	6, 8	18, 19
—COONa	15	15	12, 14, 16, Oleyl	23, 26
—COOK	26	24 ± 1	8, 12	19, 20, 25
—OOCCHSO ₃ Na	98	103 ± 10	6 ^a , 8 ^a	21, 27
—OOCCH ₂				
—CH(CH ₂ COOH)CH ₂ N(CH ₃) ₃	134	120 ± 10	12, 14, 16	28
—(OE)OSO ₃ Na	76	80	12	29
—(OE) ₂ OSO ₃ Na	113	118	12	29
—(OE) ₃ OSO ₃ Na	148	155	12	29
—(OE) ₄ OSO ₃ Na	184	193	12	29
—(OE) ₅ OSO ₃ Na	220	231	12	29
—(OE) ₁₀ OSO ₃ Na	404	402	12	29
—(OE) ₈ OH	234	231 ± 4	4, 4 ^b , 6, 6 ^b , 8	22
—(OE) ₈ OH	312	310 ± 3	12, 16 ^c	30, 31
—(OE) ₁₂ OH	463	475 ± 10	12, 16 ^c	30, 32
—(OE) ₁₅ OH	577	556	16 ^c	33
—(OE) ₂₁ OH	804	745	16 ^c	33
—(OE) ₂₃ OH	880	887	12	30
—(OE) ₂₅ OH	1070	1079	12	34

^a Contains two chains. ^b Branched chain. ^c Partial molal volume determined in hexane.

polar and nonpolar portions of some molecules such as the alkyl benzene sulfonates, the alkyl pyridinium halides, and many surface-active drugs (10).

Another method which has been used successfully to estimate the partial molal volume of proteins (11, 12) and small organic solutes (13, 14), but which (to the authors' knowledge) has not been applied to surfactants, is that of Traube (15). In 1899, Traube found that pairs of organic compounds that differ in structure by a single atom or group differ in their experimentally measured partial molal volumes by nearly a constant value. For example, the differences in partial molal volume between ethanol and *n*-propanol, between butyric and pentanoic acids, or between benzene and toluene are all about 16.2 cm.³/mole at 15°. These values change only slightly with temperature; e.g., the given value is 16.0 at 0°, 16.3 at 25°, and 17.1 at 100°. By measuring the partial molal volume of a large number of organic compounds, Traube developed a list of apparent atomic and group volumes from which the partial molal volume of organic compounds could be estimated. The atomic and group volumes of some of the more common components of surfactants are shown in Table I. Some of these values were adjusted to account for recent, more accurate measurements (16).

In estimating the partial molal volume of monomeric surfactants, Table I can be used directly. For example, the volume of monomeric sodium lauryl sulfate (C₁₂H₂₅NaO₄S is 12 × (10.0) + 25 × (3.1) + 1 × (15.5) + 4 × (5.5) + 1 × (-5.7) = 229.3, which is within a few percent of the literature value of 235.0. Some comparisons between estimated and experimentally measured partial molal volumes of monomeric surfactants are shown in Table II¹. To keep both Tables II and III down to a reasonable length, only the volume of the polar group of a homologous series of surfactants is shown along with the alkyl chain lengths of the surfactants compared. These volumes were determined by subtracting the volume of the alkyl chain (i.e., 10 cm.³/mole for carbon and 3.1 cm.³/mole for hydrogen) from each experimental and calculated value.

Traube (15) found that the terminal group of liquid hydrocarbons appears to have a larger molar volume than partial molal volume. The difference was found to be about 13.4 cm.³/terminal methyl group. This value was termed the covolume by Traube, who explained it as being due to intramolecular space or the fact that carbon atoms on the same molecule are closer to each other than are carbons on adjacent molecules.

The nonpolar portion of a micellar surfactant, especially the terminal methyl group, is located in the interior portion of the micelle. This interior region has been shown by a number of workers to resemble a liquid hydrocarbon phase. The volume of the terminal methyl group of a surfactant in a micelle could be expected to be similar to the volume of that group in a liquid hydrocarbon environment. Consequently, the covolume must be included in the calculation of the partial molal volume. Thus, the calculated volume of sodium lauryl sulfate in the micellar state is 229.3, as calculated from Table I, plus 13.4 or 242.7, which is again in good agreement with the literature values which range from 246.4 to 253.0. Table III compares the calculated partial molal volume of the polar group of micellar surfactants with values determined by subtracting the 10 cm.³/mole for each carbon, 3.1 cm.³/mole for each hydrogen, and 13 cm.³/mole for the covolume from the literature values.

In Tables II and III the use of the volume of the polar group instead of the total surfactant has the effect of making the discrepancy between Traube's method and the literature appear larger than it actually is. For example, the volumes of the -SO₃Na group in Tables II and III differ from the literature values by about 20%, while the volumes of monomeric and micellar sodium lauryl sulfate are within 3% of their respective literature values, as already indicated.

The volume of the polar portion does not change significantly on micellization, which supports the conclusions of Corkill *et al.* (18)

¹ If one is interested in obtaining the volume of the surfactant ion exclusive of its counterions, one must subtract the volume of the counterion from the experimentally measured volume of the surfactant or ignore it in estimating the volume by Traube's method.

and Mukerjee (35) that there is little difference in hydration between surfactants in a monomeric and micellar state.

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