Part II

PHYSICAL PROPERTIES

EVALUATION OF COMPOUNDS AND MATERIALS

Apparent Molar Volumes of Alcohols in Dilute Aqueous Solution

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In the course of an investigation into the nature of solutions of nonelectrolytes in water it was observed that the temperature dependence of the apparent molar volume of ethanol in water in very dilute solution showed interesting features. In particular, at about 10° C. there was no observable variation with temperature. For comparison the densities of dilute solutions of other alcohols were measured over a range of temperature, the apparent molar volume was calculated at each concentration, and the results were extrapolated to give the apparent molar volume in infinitely dilute solution.

EXPERIMENTAL

Methanol was purified by fractional distillation, dried with anhydrous calcium sulfate, and refractionated. $d_4^{25} = 0.7867$ [(*13*) 0.78655.]

1-Propanol was purified by the method of Kretschmer (*8*) $d_4^{25} = 0.8002$ [(*15*) 0.7999] $n_D^{23.6} = 1.3842$ [(*1*) 1.3840].

1-Butanol was purified by the method of Clark, Robinson, and Smith (*2*). $n_D^{20} = 1.39918$ [(*19*) 1.39922], $d_4^{30} = 0.8022$ [(*19*) 0.80206].

1-Pentanol was purified by extraction with water to remove water insoluble impurities, and extracted from aqueous solution with ether. The ether was evaporated and the product dried by refluxing with freshly ignited calcium oxide. The product was then fractionated, redried, and redistilled. $d_4^{25} = 0.8121$ [(*18*) 0.8112].

Dichloromethane was washed and concentrated sulfuric acid, dilute sodium hydroxide and water, dried with sodium hydroxide and fractionally distilled. $n_D^{20} = 1.4241$ [(*20*) 1.4246].

1,3-Propanediol was dried over calcium sulfate and distilled under vacuum. $d_4^{20} = 1.052$ [(*12*) 1.053].

Measurement of Apparent Molar Volumes. Densities of solutions were measured in a pycnometer of 20-ml. capacity. Solutions were made up by weight, allowance being made for the weight of vapor in the small vapor space in the weighing bottle. The solution was cooled to 0° C. to reduce the vapor pressure of solute, and displaced by mercury into the pycnometer, which had previously been filled with solute vapor at the equilibrium vapor pressure.

Vacuum corrections were applied and a double pan method of weighing used. At least two measurements were made at each concentration. Density measurements were correct to one part in 5×10^4. Apparent molar volumes were calculated from the densities in the usual way (*6*).

RESULTS

In the case of dichloromethane and 1-pentanol, measurements were made at one concentration only (1 gram %), since these are too insoluble for any variation of apparent molar volume with concentration to be determined. In the case of other alcohols and 1,3-propanediol measurements were made at four or five concentrations from 1 to 5 gram %. In all these cases the decrease of apparent molar volume with increasing concentration was linear within experimental error. Hence at each temperature the results can be expressed by the equation:

$$\phi V = \phi^\circ V + ac$$

where $\phi^\circ V$ is the value of the apparent molar volume at infinite dilution, and is equal to $\overline{V}_2^\circ$, the partial molar volume of the solute at infinite dilution. The molarity is given by c and the slope of the line by a.

For 1-pentanol values of a have been estimated from the values for other alcohols and these have been used to calculate $\overline{V}_2^\circ$ for 1-pentanol.

For ethanol, using the density data of Osborne, McKelvy, and Bearce (*14*) at 25° C., and the compilation of Thorpe (*17*) of data at 15.56° C., plots of ϕV against c were found linear below 6 grams %. At other temperatures, ϕV values were calculated from the data of Osborne, McKelvy, and Bearce from 20 to 5 gram %. Curves fitted to these values showed only a slight change of slope between 10 and 5 gram % and were linearly extrapolated to infinite dilution.

The results for the five alcohols are plotted in Figure 1. Values of V_2°, the molar volume of the pure liquid, are given for comparison in Table I.

Where suitable density measurements have been recorded in the literature, apparent molar volumes have been calculated from them. The data of Drucker (*4*) agree well with the present work, while those of Griffiths (*5*) do not.

The experimental error in $\overline{V}_2^\circ$ for methanol is of the order of 0.02 ml.; for ethanol, 1-propanol, and 1,3-propanediol, 0.03 ml.; and for 1-butanol and 1-pentanol, 0.05 ml.

The apparent molar volumes of dichloromethane at a molarity of 0.12 are given in Table II. A plot of ϕV against tem-

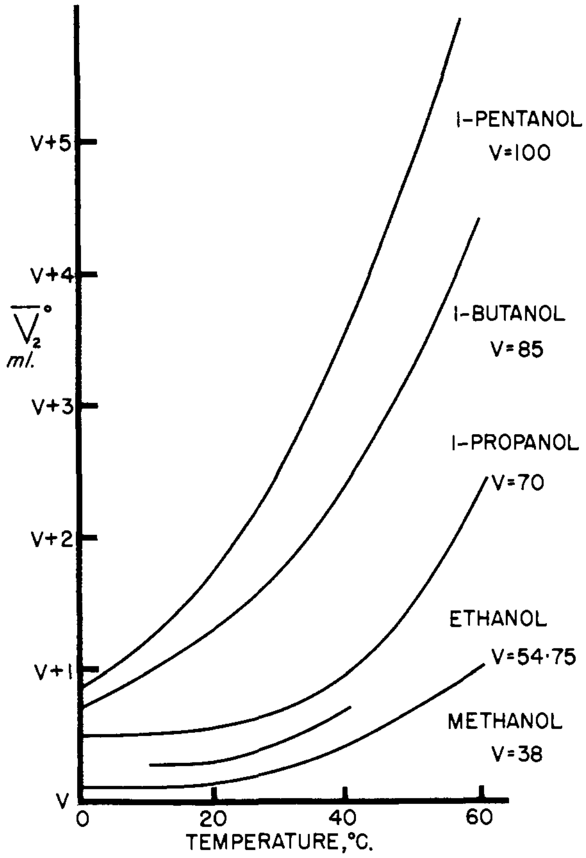

Figure 1. Partial molar volumes of alcohols in water at infinite dilution.

perature is linear over the range, with a slope corresponding to a value of the coefficient of expansion of dichloromethane in water of 1.42 × 10^{-3} per degree. For the pure liquid the coefficient of expansion is 1.37 × 10^{-3} per degree.

Other Measurements of Apparent Molar Volumes. There are few measurements of apparent molar volumes of nonelectrolytes in dilute aqueous solution and their variation with temperature recorded in the literature. Masterton (*10*) has studied solutions of benzene, methane, ethane, and propane. The results for benzene are similar to those recorded here for dichloromethane. At 20° C. the value of $V_2^{\circ} - \phi V_2$ = 89.5-83.1 ml. = 6.4 ml. The plot of ϕV_2 against temperature is linear, with the value of the coefficient of expansion of benzene in water being 1.16 × 10^{-3} per degree. For the pure liquid the value is 1.176 × 10^{-3} per degree. Masterton's work on the paraffins shows a marked lowering of ϕV values as the temperature is decreased. This effect was not observed by Krtichevskiĭ and Ilinskaya (*9*), who measured the apparent molar volume of methane and some other gases in water. Values for urea (*6*) and the four methyl halides (*7*) have also been measured.

DISCUSSION

The most striking feature of the present results is the curvature of the plots in Figure 1, especially at lower temperatures.

It is of interest to test the additivity of the volumes of groups making up the molecule. Increments of $\overline{V}_2^{\circ}$ per methylene unit were plotted against temperature. For increments between 1-pentanol and 1-butanol and between 1-butanol and 1-propanol fairly straight lines result, and these two lines nearly coincide. The line may be represented thus (*t* in degrees C.):

$$\overline{V^{\circ}}_{\text{—CH}_2\text{—}} = 15.0\,(1 + 2.12 \times 10^{-3}t)$$

$\overline{V^{\circ}}_{\text{—CH}_2\text{—}}$ represents the volume increment per methylene unit, between 1-propanol and 1-pentanol. Hence, there is some evidence that for alcohols at any temperature there is a certain

Table I. Partial Molar Volumes of Alcohols in Infinitely Dilute Solution ($\overline{V}_2^{\circ}$), and Decrease in Apparent Molar Volume per Unit Increase in Molarity (−a).

Solute	Temp., °C.	$\overline{V}_2^{\circ}$	$-a$	$V_2^{\circ\,a}$
CH_3OH	0.00	38.12	0.346	39.55
	15	38.13 (*3*)	0.212 (*3*)	40.25
	20.00	38.13	0.167	40.48
	25	38.68 (*5*)	0.432 (*5*)	40.73
	40.0	38.42	0.068	41.46
	59.9	38.92	0.013	42.48
C_2H_5OH	10.00	55.05	0.736	57.75
	15.56	54.98	0.636	58.07
	20.00	55.08	0.608	58.37
	25.00	55.08	0.507	58.68
	30.00	55.22	0.454	59.01
	40.00	55.42	0.070	59.69
C_3H_7OH	0.00	70.52	2.04	73.31
	15	70.58 (*3*)	1.30 (*3*)	74.38
	19.98	70.52	1.15	74.76
	25	70.66 (*4*)	0.96 (*4*)	75.12
	40.1	70.95	0	76.27
	59.8	72.39	0	77.96
C_4H_9OH	0.00	85.7	2.73	89.97
	20.00	86.3	1.41	91.53
	39.8	87.4	0.45	93.18
	60.0	89.4	0.3	94.93
$C_5H_{11}OH$	0.00	100.80	(3.4)	106.35
	20.00	101.80	(1.8)	108.20
	40.0	103.55	(0)	110.15
	59.9	106.35	(0)	112.22
$C_3H_6(OH)_2$	0.0	71.01	0.93	. . .
	20.0	71.44	0.26	72.3
	40.0	72.29	0.35	. . .
	60.0	73.00	0	. . .

[a] Molar volume of pure liquid (V_2°) is given for comparison. All values in ml.

Table II. Apparent Molar Volumes of Dichloromethane in Water

(Milliliters)

Temp., °C.	$\phi V (c = 0.12)$	V_2°
0.00	56.20 ± 0.02	62.46
10.06	56.96 ± 0.02	63.32
15.0	57.46 ± 0.04	63.71
25.2	58.06 ± 0.07	64.61
30.0	58.59 ± 0.10	65.00
34.7	58.97 ± 0.05	65.46

Table III. Volumes Associated with Constituent Groups in the Higher Alcohols

(Milliliters)

	Total Volume of End Groups				Volume of Each End Group	
Temp., °C.	$C_5H_{11}OH$	C_4H_9OH	C_3H_7OH	Average	$—CH_2OH$	$—CH_3$
0	55.8	55.7	55.5	55.7	28.0	27.7
20	55.0	55.1	54.9	55.0	27.9	27.1
40	54.7	54.8	54.7	54.7	28.0	26.7
60	55.7	55.6	55.5	55.6	28.0	27.6

volume associated with each group in the molecule so that $\overline{V_2}^\circ$ could be calculated by summing these volumes, in a way similar to that of Traube (*16*).

At temperatures of 0°, 20°, 40°, and 60° C., the volumes per methylene unit are 15.0, 15.6, 16.3, and 16.9 ml., respectively. For each alcohol, the volume associated with the end groups, $—CH_3$ and $—CH_2OH$, is calculated.

Again assuming additive volumes of groups, the $\overline{V_2}^\circ$ values for 1,3-propanediol may be used to calculate the volume associated with the $—CH_2OH$ group. Subtraction then gives the volume associated with the $—CH_3$ group.

These results suggest that water molecules are able to pack around both end groups, but especially the methyl group in a more open structure at lower temperatures.

A similar contraction with temperature has been reported by Holland and Moelwyn-Hughes (*7*) for methyl fluoride in water at low temperatures, and by Michels, Gerver, and Bijl (*11*) and Kritchevskiĭ and Ilinskaya (*9*) for several gases in water.

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Estimation of Interfacial Energy Factors of Surfactants

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Girifalco and Good (*1*) recently proposed a theory for estimating the interfacial energy of liquid-liquid systems using a function, Φ, equal to the ratio of the free energy of adhesion for the interface between phases and the geometric mean of the free energies of cohesion of the separate phases. When applied to several groups of "nonregular" systems of water-organic liquid interfaces, the accuracy of calculated interfacial tensions was 3 to 5 ergs per sq. cm. (*1*).

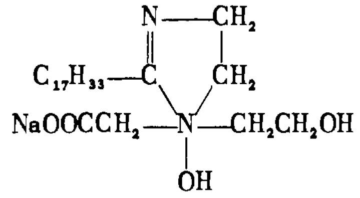
This article extends the proposed method to interfacial systems of aqueous surfactant solutions and organic liquids, the surfactant concentration level being that obtained in practical detergency.

EXPERIMENTAL

Materials. Surfactants. The following surfactants, all commercial preparations of 100% active content except where noted and all of different types, were used as received:

Surfactant	Symbol	Molecular Weight	% Active
Octyl phenyl nonaethylene glycol ether	IOPNG	602	100
tert-Dodecyl nonaethylene glycol thioether	TDNG	598	95
Tridecyl dodecaethylene glycol ether	TDG	728	100
Nonaethylene glycol monolaurate	NGML	613	100
Polyoxylethylene tall oil ester	PGTO	1050	100
Polyoxyethylene sorbitan monolaurate	PSML	1230	100
Dioctyl sodium sulfosuccinate	DOSS	444	100
Sodium *p*-dodecylbenzenesulfonate	SDBS	346	100
Lauric diethanolamide	LDA	287	100
Amphoteric agent	OMSF	1280	35

The amphoteric agent was 1-(2-sodium acetato),1-ethanol,2-heptadecenyl,4,5-dihydroimidazolium hydroxide, and possessed the following structural formula:



Since commercial surfactants usually consist of a homologous series of compounds, the molecular weights given above are mean theoretical values, in some instances supplied by the manufacturers.

Organic Liquids. The organic liquids used were as follows:

Paraffin oil. National Formulary, 28.74 centistokes at 100° F., viscosity index = 89.5, density 0.851, surface tension 29.9.

Glyceryl trioleate. Free fatty acid = 2.5%, free glycerol = 0; iodine No. = 78; saponification No. = 198; density 0.916; surface tension 31.6.

n-Octyl alcohol. Free fatty acid = 0.05%; B.P. = 194–5° C.; density 0.822; surface tension 26.9.

n-Octanoic acid. M.P. = 0–5° C.; density 0.906; surface tension 28.3.

n-Heptane. B.P. = 96–7° C.; density 0.680; surface tension 18.8.

Castor oil. C.P.; density 0.957; surface tension 34.4.

Iso-octane. 2,2,4-Trimethylpentane; 99 + %; density 0.689; surface tension 18.0.