Empirical Correlations of Partial Molar Volumes at Infinite Dilution of Organic Solutes and Transition States for S_N2 Hydrolysis and Ethanolysis of n-Alkyl Bromides

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Pseudo-first-order rate constants under pressures $\leqslant 98.1$ MPa have been measured for the hydrolysis of ethyl, n-propyl, and n-butyl bromides in water at 298.15 K and for the ethanolysis of methyl, n-propyl, and n-butyl bromides in ethanol at 333.15 K. Activation volumes (cm^3 mol^{-1}) were *ca.* -11 for the hydrolysis and about -25 for the ethanolysis. Partial molar volumes at infinite dilution were measured for n-butyl bromide in water at 298.15 K and for 66 organic solutes in ethanol at 333.15 K. Partial molar volumes of the transition states are shown to be adaptable to volumetric behaviour for common solutes, in which the partial molar volume of each solute is compared with that of the n-alkane having the same van der Waals volume.

The partial molar volume V^∞ of a solute at infinite dilution can be resolved into the van der Waals volume V_w and the void

$$V^\infty = V_w + V_{\mathrm{void}} \quad (1)$$

partial molar volume V_{void}.[1] Furthermore, the difference in V_{void} for a given solute from that of a hydrocarbon having the same V_w is defined as the solute–solvent interaction partial molar volume $V_{\mathrm{s-s}}^{(\mathrm{HC})}$. Thus, V^∞ is composed of three terms according to

$$V_{\mathrm{s-s}}^{(\mathrm{HC})} = V_{\mathrm{void}} - V_{\mathrm{void}}^{\mathrm{HC}} \quad (2)$$

equation (3). The values of $V_{\mathrm{s-s}}^{(\mathrm{HC})}$ obtained in water at 298.15 K

$$V^\infty = V_w + V_{\mathrm{void}}^{\mathrm{HC}} + V_{\mathrm{s-s}}^{(\mathrm{HC})} \quad (3)$$

reflect the hydrophilic properties of the solutes.[1] This treatment is expected to lead to useful correlations of V^∞ with solute molecular properties. From a different angle, the activation volume $\Delta V^\ddagger$ for a reaction is the difference in V^∞ between the transition state and the reactant(s) [equation (4) where ‡ in the parentheses denotes the transition state of the solute and the

$$\Delta V^\ddagger = V^\infty(\ddagger) - V^\infty(\mathrm{g}) \quad (4)$$

reactant(s)^g. Thus, $V^\infty(\ddagger)$ can be determined by the measurements of $\Delta V^\ddagger$ and $V^\ddagger(\mathrm{g})$.[2]

In this paper, this analytical method for V^∞ for common solutes is extended to $V^\infty(\ddagger)$ for the hydrolysis and ethanolysis of n-alkyl bromides. The temperature must be chosen so as to measure both $\Delta V^\ddagger$ and V^∞. Generally, the precise determination of $\Delta V^\ddagger$ requires moderate rate constants under pressure for a given reaction. On the other hand, rather low temperatures are favourable for the precise determination of V^∞ in order to minimize vaporization of the solvent in a dilatometer. Since V^∞ values in water at 298.15 K are already known for some common solutes including the reactants in the present hydrolysis,[1] this temperature was chosen for the hydrolysis. The ethanolysis of n-alkyl bromides is generally much slower than hydrolysis. From preliminary experiments, the highest temperature for V^∞ measurements in ethanol as solvent was *ca.* 333.15 K; this was then selected as the temperature for ethanolysis. Even for temperatures selected thus, both hydrolysis and ethanolysis were still slower than those for the usual $\Delta V^\ddagger$ measurements. Consequently, these requirements forced a sacrifice in the precision of $\Delta V^\ddagger$ rather than that of V^∞. Nevertheless, since solvent ethanol generally has high solubilities for both hydrophilic and hydrophobic solutes, more volumetric information is expected to be collected in ethanol than in water. The mechanism of these reactions has been well established as bimolecular attack of water or ethanol on the α-carbon atom of the n-alkyl bromide (S_N2)[3] [equation (5);

$$\mathrm{R^1OH + R^2CH_2Br \longrightarrow [R^1(H)O^{\delta+}\text{–}R^2CH_2\text{–}Br^{\delta-}]^\ddagger} \quad (5)$$

$\mathrm{R^1 = H}$ or $\mathrm{C_2H_5}$, $\mathrm{R^2 = H, CH_3, C_2H_5}$, or n-$\mathrm{C_3H_7}$)]. The purpose of this work is to find out how to adapt $V^\infty(\ddagger)$ to the molecular properties of the transition state in the activation process (5).

Results

Activation Volume.—The pseudo-first-order rate constants k_1 obtained for the hydrolysis of ethyl, n-propyl, and n-butyl bromides at 298.15 K for pressures $\leqslant 98.1$ MPa are given in Table 1. The values at 1 atm for hydrolysis of ethyl and n-propyl bromide are comparable to those given by Robertson, $10^7k_1/\mathrm{s^{-1}}$ 3.84 and 2.80, respectively, estimated by extrapolating his results at higher temperatures, 331 to 373 K.[4] The $\Delta V^\ddagger$ values at 1 atm were determined by fitting these results to the quadratic equation, $\ln k_1 = c_1 + c_2P + c_3P^2$. $\Delta V^\ddagger/\mathrm{cm^3\ mol^{-1}}$ for the hydrolysis, also listed in Table 1, are -9 to -12. Results obtained by electroconductimetry and by g.l.c. are consistent for both ethyl and n-propyl bromide. These $\Delta V^\ddagger$ values are comparable to the reported values for S_N2 hydrolysis of alkyl halides in water: $-14._5$ at 303 K,[5] $-17._0$ at 333 K, $-14._9$ at 343 K, and $-11._7$ at 353 K[6] for methyl bromide; $-10._5$ at 298 K and $-10._5$ at 303 K[5] for ethyl bromide; $-10._5$ at 328 K, $-10._5$ at 343 K,[7] and $-12._0$ at 338 K[5] for n-butyl chloride, and $-11._5$ at 323 K[8] for *p*-chlorobenzyl chloride.

The k_1 values for ethanolysis of methyl, n-propyl, and n-butyl bromides at 333.15 K under pressure are also listed in Table 1. The $\Delta V^\ddagger$ values at 1 atm, obtained by fitting to the quadratic equation, are -24 to -26. Although there are no reported values for direct comparison, the $\Delta V^\ddagger$ for S_N2 alcoholysis in the literature are in the region from -18 to -32.[9] The present values for ethanolysis and hydrolysis are reasonable and the

Table 1. First-order rate constants under pressures and activation volumes for the hydrolysis in water at 298.15 K and for the ethanolysis at 333.15 K of n-alkyl bromides.

Alkyl bromide	Method[a]	Pressure/MPa					$\Delta V^\ddagger$
		0.1	24.5	49.0	73.5	98.1	$cm^3\ mol^{-1}$
		$k_1/10^{-7}s^{-1}$					
Hydrolysis at 298.15 K							
Ethyl bromide	e	3.5_9	4.1_1	4.4_5		5.3_9	−12
	g	3.5_0	3.9_0	4.3_0		5.2_8	−11
n-Propyl bromide	e	2.3_2	2.5_6	2.8_4		3.3_8	−11
	g	2.3_9	2.7_0	2.9_4		3.4_5	−12
n-Butyl bromide	e	2.4_0	2.6_8	2.8_6		3.4_5	−9
Ethanolysis at 333.15 K							
Methyl bromide	g	$11._7$	$14._1$	$17._2$	$20._5$	$22._5$	−26
n-Propyl bromide	g	2.1_4	2.6_5	3.2_6		4.4_7	−26
n-Butyl bromide	g	1.9_5	2.3_1	2.9_7		4.2_3	−24

[a] Analytical method; e, electroconductometry; g, g.l.c. analysis.

maximum probable error in $\Delta V^\ddagger$ is 2. In other words, our k_1 values are not exact enough to examine the c_3 values in detail or any unusual dependence of ln k_1 on P as presented by Baliga and Whalley[6] and Kurz and Lu.[10]

Partial Molar Volumes at Infinite Dilution.—All values of V^∞ used in this work for non-electrolytes in water at 298.15 K are the same as those in the literature,[1] except that for n-butyl bromide which was determined as 97.8 $cm^3\ mol^{-1}$ in the present work. The molar volume of solvent water is 18.1 $cm^3\ mol^{-1}$.[11]

The solute species, for which the V^∞ values were measured in ethanol, were closely related to the reactants and the transition states in terms of molecular properties and structures. The V^∞ values in ethanol at 333.15 K are listed in Table 2 for linear and monofunctional solutes, *i.e.* alkanes, alcohols, bromides, and ethers. The results for linear and polyfunctional solutes, *i.e.* glycols, dibromides, glycol ethers, bromohydrins, bromoether, Cellosolves, and polyglycols, are summarized in Table 3 and those for the other solutes, *i.e.* alkenes and branched alkanes, alcohols, bromides, glycol, dibromide, and bromohydrins, in Table 4.

Partial Molar Volumes of Transition States.—The $V^\infty(\ddagger)$ for the hydrolysis and ethanolysis of n-alkyl bromides are given in Table 5, which are evaluated by equation (6), derived from equation (4) and $V^\infty(g) = V^\infty(R^1OH) + V^\infty(R^2Br)$. The V^∞

$$V^\infty(\ddagger) = \Delta V^\ddagger + V^\infty(R^1OH) + V^\infty(R^2OH) \quad (8)$$

value for methyl bromide in ethanol, which could not be measured because of its high volatility at 333.15 K, was estimated to be 61 by extending the curve for n-alkyl bromides downward to V_w (see Figure 1).

Discussion

Conventional Treatments of $\Delta V^\ddagger$.—The $\Delta V^\ddagger$ value has been thought to consist of the change in volume of reacting molecules $\Delta_1 V^\ddagger$ and that due to solvation $\Delta_2 V^\ddagger$.[9,2,13] The $\Delta_1 V^\ddagger$ term has frequently been evaluated by the cylindrical model, in which the volume change is calculated as the lengthening or shortening of a cylinder with a cross-section averaged for the reacting atoms. The bond distance in the transition state is usually approximated to be longer by 10–40% than the normal covalent bond length. The $\Delta_2 V^\ddagger$ value, obtained as $\Delta V^\ddagger - \Delta_1 V^\ddagger$, has been attributed mainly to the change of electrostriction V_{es} during the process.

In our activation process (5), the C–Br bond breaks and the C–O bond forms concurrently. By assuming that the bond lengths in the transition state are longer than normal covalent lengths by 10%, $\Delta_1 V^\ddagger - 7$ is derived. The numbers used in this calculation are the van der Waals radii of r_w/nm 0.152 for O, 0.170 for C, and 0.185 for Br, and the covalent bond lengths of r_b/nm 0.142 for O–C and 0.187 for C–Br.[14] Then, $\Delta_2 V^\ddagger$ are −2 to −5 for hydrolysis, and −17 to −19 for ethanolysis. Thus, rather small absolute values of $\Delta_2 V^\ddagger$ are estimated.

V_{es} has been evaluated by the Kirkwood equation differentiated with respect to pressure [equation (7) where μ is

$$V_{es} = -(N_A\mu^2/r^3)\{3/(2D+1)^2\}(\partial D/\partial P)_T \quad (7)$$

the dipole moment, r the radius of spherical dipole, and D dielectric constant of solvent]. However, $|V_{es}|$ does not exceed 0.4 for the transition state for hydrolysis even after assuming 40% longer bond lengths (dipole lengths, in order to evaluate the rather larger $|V_{es}|$), a charge of 0.2 e[15] [therefore, $\mu/(C\ m) = \delta_{el} = 0.2 \times 1.6 \times 10^{-19} \times (0.142 + 0.187) \times 10^{-9} \times 1.4 = 1.47 \times 10^{-29}$], and with r derived from $4N_A\pi r^3/3 = (V_w$ of the reaction centre in the transition state $H_2O^{+\delta}$–CH_2–$Br^{-\delta}$). For V_{es} for the initial state of the activation process, $|\Delta_{es}V^\ddagger|$ becomes <0.4. $|V_{es}|$ For the transition state, even for ethanolysis, never exceeds 3 in ethanol. Moreover, the addition of the theory of cavity compression, proposed by Whalley,[16] does not explain quantitatively the difference in $\Delta_2 V^\ddagger$ between hydrolysis and ethanolysis.

A somewhat different dissection of $\Delta V^\ddagger$ was proposed by Asano,[17] $\Delta V^\ddagger = \Delta_{int}V^\ddagger + \Delta_{therm}V^\ddagger$. Values of $\Delta_{int}V^\ddagger$ of −2.6 and −2.9 were derived from the experimental correlation between the rate constants and the modified compressions of solvent obtained under high pressures for S_N2 hydrolysis of benzyl chloride at 303 K and allyl chloride at 323 K, respectively.[17a] When these values are applied to the present hydrolysis, $\Delta_{therm}V^\ddagger$ is −6 to −9. Although this seems attributable to the compression of the solvent water molecules by the partial charges, it does not coincide with the V_{es} value expected by equation (7).

Thus, the existing approaches lead to the conclusion that some specific solvation such as hydrogen-bonding prevails during the activation process.

Table 2. V^{∞}, V_w, V_{void}, and $V_{s\text{-}s}^{(HC)}$/cm^3 mol^{-1} for linear and monofunctional solute at infinite dilution in ethanol at 333.15 K.

No.	Solute	Structure[a]	V^{∞}	V_w	V_{void}	$V_{s\text{-}s}^{(HC)}$
n-Alkanes						
1	n-Hexane	C_6	$140._5$	68.3	$72._7$	0
2	n-Heptane	C_7	$157._8$	78.5	$79._3$	0
3	n-Octane	C_8	$173._9$	88.7	$85._2$	0
4	n-Nonane	C_9	$191._3$	99.0	$92._3$	0
5	n-Decane	C_{10}	$209._3$	109.2	$100._1$	0
6	n-Undecane	C_{11}	$225._1$	119.4	$105._7$	0
7	n-Dodecane	C_{12}	$242._2$	129.6	$112._6$	0
8	n-Tetradecane	C_{14}	$275._9$	150.1	$125._8$	0
n-Alkyl alcohols						
9	Methyl alcohol	C_1OH	$42._8$	21.7	$21._1$	$-20._7$
10	Ethyl alcohol	C_2OH	$61._7$	31.9	$29._2$	$-19._2$
11	n-Propyl alcohol	C_3OH	$77._7$	42.2	$35._5$	$-19._7$
12	n-Butyl alcohol	C_4OH	$95._3$	52.4	$42._9$	$-19._0$
13	n-Pentyl alcohol	C_5OH	$112._7$	62.6	$50._1$	$-18._5$
14	n-Hexyl alcohol	C_6OH	$129._5$	72.9	$56._6$	$-18._8$
15	n-Heptyl alcohol	C_7OH	$146._4$	83.1	$63._3$	$-18._7$
16	n-Octyl alcohol	C_8OH	$163._5$	93.3	$70._2$	$-18._5$
n-Alkyl bromides						
17	n-Propyl bromide	C_3Br	$96._4$	48.5	$47._9$	$-11._4$
18	n-Butyl bromide	C_4Br	$113._3$	58.8	$54._5$	$-11._6$
19	n-Pentyl bromide	C_5Br	$130._7$	69.0	$61._7$	$-11._1$
20	n-Hexyl bromide	C_6Br	$147._5$	79.2	$68._3$	$-11._1$
21	n-Heptyl bromide	C_7Br	$164._7$	89.5	$75._2$	$-11._1$
22	n-Octyl bromide	C_8Br	$181._9$	99.7	$82._2$	$-10._7$
Di-n-alkyl ethers						
23	Ethyl n-propyl ether	C_3OC_2	$124._4$	61.7	$62._7$	$-5._3$
24	n-Butyl ethyl ether	C_4OC_2	$142._8$	72.0	$70._8$	$-4._0$
25	Ethyl n-hexyl ether	C_6OC_2	$177._2$	92.4	$84._8$	$-3._4$
26	Ethyl n-octyl ether	C_8OC_2	$212._1$	112.9	$99._2$	$-2._4$
27	n-Hexyl methyl ether	C_6OC_1	$159._3$	82.2	$77._1$	$-4._4$

[a] C_n means $CH_3(CH_2)_{n-2}CH_3$ for alkanes and $CH_3(CH_2)_{n-1}$ for the others.

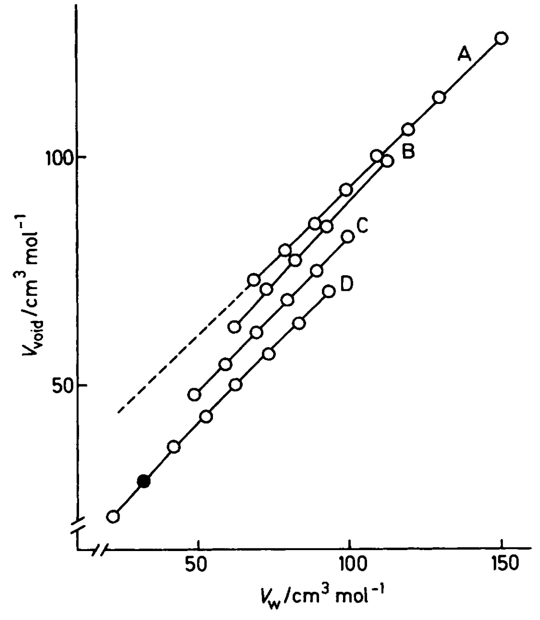


Figure 1. Plots of V_{void} against V_w for linear and monofunctional solutes in ethanol at 333.15 K. Filled circle corresponds to molar volume of pure ethanol: A, n-alkane; B, linear ether; C, n-alkyl bromide; D, n-alkyl alcohol.

Empirical Relation of V^{∞} for Common Solutes in Ethanol.—The V_{void} values are derived by subtracting V_w from V^{∞} according to equation (1). Those for all the solutes in ethanol at 333.15 K are also given in Tables 2–4 together with V^{∞} and V_w.

V_{void} for the linear and mono-functional solutes are plotted against V_w in Figure 1. V_{void} for n-alkanes, and therefore also V^{∞}, show a linear dependence on V_w [equation (8) where a^{HC}

$$V_{void}^{HC} = (a^{HC} - 1)V_w + b^{HC} \tag{8a}$$

$$V^{\infty HC} = a^{HC}V_w + b^{HC} \tag{8b}$$

and b^{HC} are constants]. The values determined by the least-squares method are: a^{HC} 1.65_6 and b^{HC} $27._5$ in ethanol at 333.15 K. Corresponding values in water were determined previously:[1] a^{HC} 1.53_4 and b^{HC} $9._9$ in water at 298.15 K. Thus, V^{∞} values for n-alkanes in ethanol are larger by at least $27._5 - 9._9 = 17._6$ than those in water. The V^{∞} values are not expected to increase to this extent due to the different thermal expansivity of water or ethanol at 333.15 and 298.15 K. However, V^{∞} for gaseous solutes of H_2, N_2, Ar, He, O_2, CH_4, C_2H_6, C_3H_8, CO, and CO_2 is already known to be much smaller in water than in nonaqueous solvents.[18] This behaviour was attributed to the abnormally high internal pressure of water by Masterton.[18c]

When V_{void} values for different series of solutes are compared at constant V_w in Figure 1, we obtain the sequence: alkane > ether > alkyl bromide > alcohol. Although a similar sequence is also found in water,[1] the differences between the homologous lines in ethanol are wider than those in water. For

Table 3. V^{∞}, V_w, V_{void}, and $V_{s-s}^{(HC)}$/cm^3 mol^{-1} for linear and polyfunctional solute at infinite dilution in ethanol at 333.15 K.

No.	Solute	Structure[a]	V^{∞}	V_w	V_{void}	$V_{s-s}^{(HC)}$	Deviation from additivity
Glycols							
28	Ethylene glycol	HOC_2OH	$54._0$	36.5	$17._5$	$-34._0$	$4._8$
29	Propane-1,3-diol	HOC_3OH	$69._6$	48.8	$22._8$	$-35._4$	$2._6$
30	Butane-1,4-diol	HOC_4OH	$85._8$	57.0	$28._8$	$-36._1$	$1._5$
31	Pentane-1,5-diol	HOC_5OH	$102._4$	67.2	$35._2$	$-36._4$	$0._8$
Dibromides							
32	1,2-Dibromoethane	BrC_2Br	$122._6$	69.7	$52._9$	$-20._4$	$1._6$
33	1,6-Dibromohexane	BrC_6Br	$155._8$	90.2	$65._6$	$-21._1$	$0._5$
Glycol ethers							
34	Ethlene glycol dimethyl ether	$C_1OC_2OC_1$	$108._8$	55.2	$53._6$	$-10._1$	$0._7$
35	Ethylene glycol diethyl ether	$C_2OC_2OC_2$	$145._3$	75.7	$69._6$	$-7._6$	$0._8$
36	Ethylene glycol di-n-butyl ether	$C_4OC_2OC_4$	$216._3$	116.6	$99._7$	$-4._3$	$0._1$
37	Diethylene glycol dimethyl ether	$C_1O(C_2O)_2C_1$	$147._1$	79.4	$67._7$	$-11._9$	$-0._1$
38	Diethylene glycol diethyl ether	$C_2O(C_2O)_2C_2$	$184._6$	99.8	$84._8$	$-8._2$	$0._5$
39	Diethylene glycol di-n-butyl ether	$C_4O(C_2O)_2C_4$	$255._3$	140.7	$114._6$	$-5._2$	$-0._1$
40	Triethylene glycol dimethyl ether	$C_1O(C_2O)_3C_1$	$185._9$	103.5	$82._4$	$-13._0$	$-1._2$
Bromohydrins							
41	2-Bromoethyl alcohol	BrC_2OH	$71._9$	42.9	$29._0$	$-26._7$	$4._1$
42	3-Bromopropyl alcohol	BrC_3OH	$86._9$	53.1	$33._8$	$-28._6$	$1._6$
Bromo ether							
43	2-Bromoethyl ethyl ether	BrC_2OC_2	$116._3$	62.5	$53._8$	$-14._7$	$1._7$
Cellosolves							
44	Ethylene glycol monomethyl ether	C_1OC_2OH	$80._8$	45.9	$34._9$	$-22._7$	$2._5$
45	Ethylene glycol monoethyl ether	C_2OC_2OH	$100._0$	56.1	$43._9$	$-20._4$	$3._8$
46	Ethylene glycol mono-n-butyl ether	C_4OC_2OH	$134._0$	76.6	$57._4$	$-20._4$	$2._0$
Polyglycols							
47	Diethylene glycol	$HO(C_2O)_2H$	$93._4$	60.7	$32._7$	$-34._6$	$7._8$
48	Triethylene glycol	$HO(C_2O)_3H$	$131._0$	84.9	$46._1$	$-37._1$	$6._9$

[a] C_n means $CH_3(CH_2)_{n-1}$ or $(CH_2)_n$.

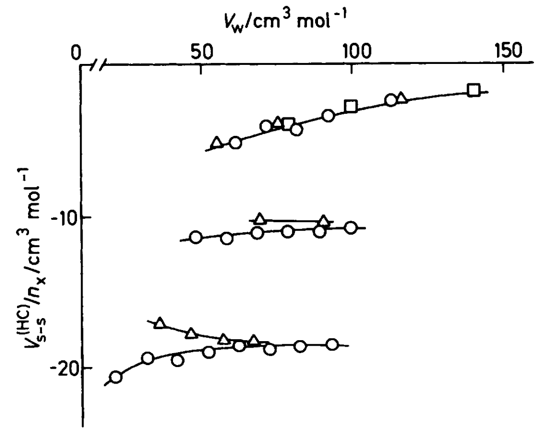


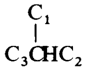
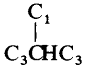
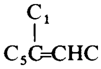
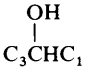
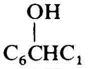
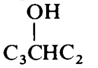
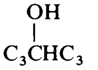
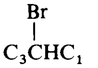
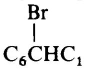
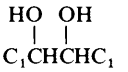
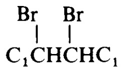
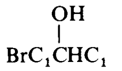
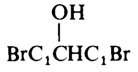
Figure 2. Plots of $V_{s-s}^{(HC)}/n_X$ against V_w for linear solute molecules in ethanol at 333.15 K. n_X = Functional number of solute. Circles, $n_X = 1$; triangles, $n_X = 2$; squares, $n_X = 3$.

example, the difference between the n-alkane and alcohol lines is *ca.* 19 in ethanol, while it is *ca.* 4 in water.[1]

The *above* comparison of V_{void} values at constant V_w can be quantified by introducing $V_{s-s}^{(HC)}$ defined in equation (2).[1] The values of $V_{s-s}^{(HC)}$ are also included in Tables 2–4. $V_{s-s}^{(HC)}$ values for the linear and mono-functional solutes are plotted against V_w values in Figure 2 (indicated by circles). The results for each of the homologous series of ethers, bromides, and alcohols show slight dependence on V_w and tend to converge to a fixed value at infinite V_w. In Figure 2, $V_{s-s}^{(HC)}$ values for the linear and homopolyfunctional solutes divided by functional numbers are also plotted (triangles for bifunctional and squares for trifunctional derivatives). Positive deviations from the corresponding monofunctional curves are found for the glycols and dibromides with relatively short chain lengths, but their curves tend to approach the corresponding monofunctional curves as V_w increases. The latter tendency denotes an additive property of the $V_{s-s}^{(HC)}$ term, and the former deviation from additivity. For the polyethers, additivity holds within experimental error.

For all the polyfunctional solutes studied, the additive values are estimated by reading off $V_{s-s}^{(HC)}$ of given functional groups at their V_w on the smoothed curves for corresponding monofunctional solutes drawn in Figure 2. The deviations from the additive values are also listed in the final columns of Tables 3 and 4. In Table 3, the deviations for the bromohydrins decrease when the chain length between OH and Br increases, similar to the behaviour of glycols and dibromides, and the magnitudes of the deviations are about halfway between those for the glycols and the dibromides. A similar comparison of the deviations for $X(CH_2)_2Y$ gives the sequence: glycol > bromohydrin > Cellosolve > bromo ether > diether. The deviations for the polyglycols are about twice the deviations of the Cellosolves, corresponding to approximate additivity for the polyethers.

Table 4. V^∞, V_w, V_{void}, and $V_{s-s}^{(HC)}$/cm^3 mol^{-1} for alkenes, and branched and polyfunctional solutes at infinite dilution in ethanol at 333.15 K.

No.	Solute	Structure[a]	V^∞	V_w	V_{void}	$V_{s-s}^{(HC)}$	Deviation from additivity
Branched alkanes							
49	3-Methylhexane	 $C_3\overset{C_1}{C}HC_2$	$157._3$	78.5	$78._8$	$-0._2$	$-0._2$
50	4-Methylheptane	 $C_3\overset{C_1}{C}HC_3$	$174._0$	88.7	$85._3$	$-0._4$	$-0._4$
Alkenes							
51	Hept-1-ene	$C_5CH{=}CH_2$	$151._0$	75.0	$76._0$	$-0._7$	$-0._7$
52	Oct-1-ene	$C_6CH{=}CH_2$	$168._1$	85.2	$82._9$	$-0._5$	$-0._5$
53	Non-1-ene	$C_7CH{=}CH_2$	$184._7$	95.5	$89._2$	$-1._0$	$-1._0$
54	Hex-2-ene	$C_3CH{=}CHC_1$	$131._0$	64.8	$66._3$	$-3._8$	$-3._8$
55	Oct-2-ene	$C_5CH{=}CHC_1$	$165._8$	85.2	$80._6$	$-2._8$	$-2._8$
56	3-Methyloct-2-ene	 $C_5\overset{C_1}{C}{=}CHC_1$	$146._8$	75.0	$71._8$	$-4._9$	$-4._9$
Branched alcohols							
57	2-Pentyl alcohol	 $C_3\overset{OH}{C}HC_1$	$131._7$	72.9	$58._8$	$-16._6$	$1._9$
58	2-Octyl alcohol	 $C_6\overset{OH}{C}HC_1$	$166._5$	93.3	73.2	$-15._5$	$3._0$
59	3-Hexyl alcohol	 $C_3\overset{OH}{C}HC_2$	$130._7$	72.9	$57._8$	$-17._6$	$0._9$
60	4-Heptyl alcohol	 $C_3\overset{OH}{C}HC_3$	$147._5$	83.1	$64._4$	$-17._6$	$0._9$
Branched bromides							
61	2-Bromopentane	 $C_3\overset{Br}{C}HC_1$	$131._9$	69.2	$62._7$	$-10._2$	$1._0$
62	2-Bromo-octane	 $C_6\overset{Br}{C}HC_1$	$183._9$	99.9	$84._0$	$-9._1$	$1._8$
Branched glycols							
63	Butane-2,3-diol	 $C_1\overset{HO}{C}H\overset{OH}{C}HC_1$	$89._6$	57.0	$32._6$	$-32._3$	$5._1$
Branched dibromide							
64	2,3-Dibromobutane	 $C_1\overset{Br}{C}H\overset{Br}{C}HC_1$	$124._8$	70.1	$54._7$	$-18._8$	$3._6$
Branched bromohydrins							
65	1-Bromomethylethyl alcohol	 $BrC_1\overset{OH}{C}HC_1$	$90._4$	53.1	$37._3$	$-25._1$	$5._3$
66	1-Bromomethyl-2-bromoethyl alcohol	 $BrC_1\overset{OH}{C}HC_1Br$	$101._6$	64.1	$37._5$	$-32._1$	$9._3$

[a] C_n means $CH_3(CH_2)_{n-1}$ or $(CH_2)_n$.

Thus, the deviations are closely related to the magnitudes of $|V_{s-s}^{(HC)}|$ of component groups.

In Table 4, $V_{s-s}^{(HC)}$ for the branched alkanes have the very small but negative value $-0._3$. Similar decrements in volume have already been pointed out in the field of petroleum chemistry.[19] The molar volumes of pure alkanes branched at the 3-, 4-, and higher positions are smaller than those of the corresponding n-alkanes, while those of 2-branched alkanes are somewhat greater than those of n-alkanes. This behaviour for the molar volumes of pure alkanes was explained in terms of internal rotation around the C–C bond axis.[19a]. $V_{s-s}^{(HC)}$ for alk-1-enes are also slightly negative: those for alk-2-enes are *ca.* -3, and that for 3-methyloct-2-ene is *ca.* -5. These values for the alkenes are of the same magnitudes as those found in the molar volumes of the pure alkenes. This behaviour was explained in terms of the obstruction of internal rotation by the double bond.[19a]

Deviations from additive values for the 2-alcohols are positive, *ca.* 2, and those for the 3- and 4-alcohols are *ca.* 1. These small differences can be rationalized if we refer to a common value of $1._0$ due to the secondary hydroxy group and the different deviations due to the branching forms, *i.e.* $1._0$ due to 2-branching and $-0._4$ due to 3- and higher position branching.

Table 5. V^{∞}, V_w, V_{void}, V^{HC}_{void}, and $V^{(HC)}_{s\text{–}s}$/cm^3 mol^{-1} of the transition states.[a]

Substrate	V^{∞}	V_w	V_{void}	V^{HC}_{void} [b]	$V^{(HC)}_{s\text{–}s}$ [c]
		Transition states for hydrolysis at 298.15 K			
Ethyl bromide	73	$49.7 + \Delta_w V^{\ddagger}$ (49.7/45.3)	$23 - \Delta_w V^{\ddagger}$ (23/27)	$36 + 0.53_4\Delta_w V^{\ddagger}$ (36/39)	$-13 - 1.53_4\Delta_w V^{\ddagger}$ $(-13/-6)$
n-Propyl bromide	89	$59.9 + \Delta_w V^{\ddagger}$ (59.9/55.5)	$29 - \Delta_w V^{\ddagger}$ (29/33)	$42 + 0.53_4\Delta_w V^{\ddagger}$ (47/40)	$-13 - 1.53_4\Delta_w V^{\ddagger}$ $(-13/-6)$
n-Butyl bromide	107	$70.1 + \Delta_w V^{\ddagger}$ (70.1/65.7)	$37 - \Delta_w V^{\ddagger}$ (37/41)	$47 + 0.53_4\Delta_w V^{\ddagger}$ (47/45)	$-10 - 1.53_4\Delta_w V^{\ddagger}$ $(-10/-3)$
		Transition states for ethanolysis at 333.15 K			
Methyl bromide	97[d]	$59.9 + \Delta_w V^{\ddagger}$ (59.9/55.5)	$37 - \Delta_w V^{\ddagger}$ (37/41)	$67 + 0.65_6\Delta_w V^{\ddagger}$ (67/64)	$-30 - 1.65_6\Delta_w V^{\ddagger}$ $(-30/-23)$
n-Propyl bromide	131	$80.4 + \Delta_w V^{\ddagger}$ (80.4/76.0)	$51 - \Delta_w V^{\ddagger}$ (51/55)	$80 + 0.65_6\Delta_w V^{\ddagger}$ (80/77)	$-29 - 1.65_6\Delta_w V^{\ddagger}$ $(-29/-22)$
n-Butyl bromide	150	$90.7 + \Delta_w V^{\ddagger}$ (90.7/86.3)	$59 - \Delta_w V^{\ddagger}$ (59/63)	$87 + 0.65_6\Delta_w V^{\ddagger}$ (87/84)	$-28 - 1.65_6\Delta_w V^{\ddagger}$ $(-28/-21)$

[a] Values in parentheses: (value for $\Delta_w V^{\ddagger} = 0$)/(value for $\Delta_w V^{\ddagger} = -4.4$). [b] Equations (9) and (10) or (10a). [c] Equation (2). [d] V^{∞} (methyl bromide) estimated by extrapolation of empirical correlation of V^{∞} against V_w for n-alkyl bromides.

Table 6. V^{∞}, V_w, V_{void}, and $V^{(HC)}_{s\text{–}s}$/cm^3 mol^{-1} of the reactants for the hydrolysis of n-alkyl bromides in water at 298.15 K.

Substrate	V^{∞}	V_w	V_{void}	$V^{(HC)}_{s\text{–}s}$
Ethyl bromide[a]	$66._7$	38.3	$28._4$	$-2._0$
n-Propyl bromide[a]	$82._2$	48.5	$35._8$	$-2._1$
n-Butyl bromide[b]	$97._8$	58.7	$39._1$	$-2._1$
Water[c]	$18._1$	11.4	6.7	$-9._3$

[a] Ref. 1. [b] This work. [c] Ref. 15.

Similarly, a value of *ca.* $1._4$ for the 2-bromides can be explained by $0._4$ due to the secondary bromo group and $1._0$ due to 2-branching. The deviation from the additive value for butane-2,3-diol is greater by $0._3$ than that for ethylene glycol, and that for 2,3-dibromobutane is also greater by $1._2$ than that for 1,2-dibromoethane. These results suggest that the volumes increase because of 2-branching and because of the approach of polar groups. The deviation for 1-bromomethylethyl alcohol is also greater by $1._2$ than that for ethylene bromohydrin. The result for 1-bromomethyl-2-bromoethyl alcohol is greater by $1._1$ than twice that for ethylene bromohydrin.

Thus, $V^{(HC)}_{s\text{–}s}$ for a complex solute molecule is found to be rationalized by the sum of the following contributions: (i) functional groups, (ii) molecular frame work or branching, (iii) grade (primary, secondary, and so on), (iv) distance between functional groups, (v) obstruction of internal rotation.

Application of Empirical Relation of V^{∞} *to* $V^{\infty}(\ddagger)$.—When the atomic geometry of a transition state is known or assumed, the van der Waals volume of activation $\Delta_w V^{\ddagger}$ can be evaluated. The calculation then necessary is to estimate only the change in overlapping volumes[12,14] of the van der Waals spheres of the reacting atoms. Thus, V_w of a given transition state can easily be derived from V_w for the reactants and $\Delta_w V^{\ddagger}$ [equation (9)]. V_w

$$V_w(\ddagger) = V_w(R^1OH) + V_w(R^2Br) + \Delta_w V^{\ddagger} \qquad (9)$$

for water was evaluated as 11.4 by using Bondi's calculation method[14] of V_w without consideration of hydrogen-bond formation.[1] $V^{(HC)}_{s\text{–}s}$ for water was estimated by referring to the extrapolation of the hydrocarbon line [equation (8a: *a* 1.53, *b* 9.9)] since its V_w value is smaller than that of methane. V^{∞}, V_w, V^{HC}_{void}, and $V^{(HC)}_{s\text{–}s}$ of the reactants for hydrolysis at 298.15 K are reviewed in Table 6, and those for ethanolysis are already included in Table 2. The values of $V_{void}(\ddagger)$ and $V^{(HC)}_{s\text{–}s}(\ddagger)$ corresponding to arbitrary $\Delta_w V^{\ddagger}$ values are listed in Table 5 for the present reactions.

By assuming 10% longer bond lengths, $\Delta_w V^{\ddagger}$ -4.4 is derived as a large absolute value. $V_{void}(\ddagger)$ and $V^{(HC)}_{s\text{–}s}(\ddagger)$ corresponding to the extreme cases of $\Delta_w V^{\ddagger}$ 0 and -4.4 are also given in parentheses in Table 5. $V^{(HC)}_{s\text{–}s}(\ddagger)$ for $\Delta_w V^{\ddagger}$ 0 is *ca.* -12 for hydrolysis and *ca.* -29 for ethanolysis. In the case of $\Delta_w V^{\ddagger}$ *ca.* -4.4, they are *ca.* -5 for hydrolysis and *ca.* -22 for ethanolysis. As already mentioned, $V^{(HC)}_{s\text{–}s}$ of n-alkyl alcohols in ethanol are *ca.* 5 times as negative as in water. The transition state for 'hydrolysis' in ethanol at 333.15 K is estimated to have a $V^{(HC)}_{s\text{–}s}$ value of about $5(-12 - 1.53\Delta_w V^{\ddagger})$. The molecular difference in the transition states of 'hydrolysis' and real ethanolysis is shown as HO(H)$\cdots$ and EtO(H)$\cdots$. The difference in $V^{(HC)}_{s\text{–}s}(\ddagger)$ $[= 5(-12 - 1.53\Delta_w V^{\ddagger}) - (-29 - 1.66\Delta_w V^{\ddagger})]$ is approximately equal to that between the alcohols and the ethers, *ca.* $(-19) - (-4) = -15$. This leads to $\Delta_w V^{\ddagger}$ -2.7, and accordingly corresponds to 18% stretching of the C–O and C–Br bonds from the normal covalent bond lengths. Although this is only a rough estimation of $\Delta_w V^{\ddagger}$, the results are sound.

V^{∞} for the majority of solute species have been measured in ethanol rather than water. $V^{\infty}(\ddagger)$ for ethanolysis is taken as a model for the behaviour of V^{∞} of common solutes. $V^{(HC)}_{s\text{–}s}(\ddagger)$ is also expected to be expressed as a linear combination of contributions from (i)–(v) (see earlier). When the transition state bears Br and OH, contribution (*i*) is *ca.* -11 and *ca.* -19, respectively. The OH part partially adds to the properties of an ether, the volumetric contribution of which is represented by Δ(OH). In the transition states of n-propyl and n-butyl bromides, branches at 3- and 4-position give contribution (ii) of $-0._4$. A secondary bromo group gives contribution (iii) of $0._5$. When Br and OH are separated by α-CH_2, contribution (iv) is $2._4$, estimated from the deviation for ethylene bromohydrin. When O, α-CH_2 and Br as well as β-CH_2 are fixed in given relative positions, contribution (v) is $-4._6$, for 3-methylhex-2-ene. The sum of contributions (ii)–(v) is $-2._1$. This approaches zero if contribution (iv) is more positive, which is expected from the slight curvature in Figure 2. In addition, contribution (vi), partial electric charges, may bring about some volume contraction [the contribution is expressed as $\Delta(\pm\delta)$]. The total sum of the contributions, $-32 + \Delta(OH) + \Delta(\pm\delta)$, corresponds to $V^{(HC)}_{s\text{–}s} = -29 - 1.66\Delta_w V^{\ddagger}$, averaged for the transition states. Therefore, $\Delta(OH) + \Delta(\pm\delta) = 3 - 1.66\Delta_w V^{\ddagger}$. Δ(OH) is not expected to exceed the difference in volume between the alcohols and ethers, *ca.* 15, and $\Delta(\pm\delta) < 0$. The limitation, $3 - 1.66\Delta_{\mathrm{w}}V^{\ddagger} < \Delta(\mathrm{OH}) < 15$, and the rewritten form $(3 - 1.66\Delta_{\mathrm{w}}V^{\ddagger})/15 < \Delta(\mathrm{OH})/15 < 1$ suggests that OH is converted into ether in the transition state by >20%.

Application of Empirical Relation of V^{∞} to $\Delta V^{\ddagger}$.—By substituting equation (1) into equation (4), $\Delta V^{\ddagger}$ can also be expressed by the three terms in equation (10) where relation-

$$\Delta V^{\ddagger} = \Delta_{\mathrm{w}}V^{\ddagger} + \Delta_{\mathrm{void}}^{\mathrm{HC}}V^{\ddagger} + \Delta_{\mathrm{s-s}}^{(\mathrm{HC})}V^{\ddagger} \qquad (10)$$

ships (10a–c) hold. $\Delta_{\mathrm{w}}V^{\ddagger}$ can be evaluated geometrically as

$$\Delta_{\mathrm{w}}V^{\ddagger} = V_{\mathrm{w}}(\ddagger) - [V_{\mathrm{w}}(\mathrm{R^1OH}) + V_{\mathrm{w}}(\mathrm{R^2Br})] \quad (10a)$$

$$\Delta_{\mathrm{void}}^{\mathrm{HC}}V^{\ddagger} = V_{\mathrm{void}}^{\mathrm{HC}}(\ddagger) - [V_{\mathrm{void}}^{\mathrm{HC}}(\mathrm{R^1OH}) + V_{\mathrm{void}}^{\mathrm{HC}}(\mathrm{R^2Br})] \quad (10b)$$

$$\Delta_{\mathrm{s-s}}^{(\mathrm{HC})}V^{\ddagger} = V_{\mathrm{s-s}}^{(\mathrm{HC})}(\ddagger) - [V_{\mathrm{s-s}}^{(\mathrm{HC})}(\mathrm{R^1OH}) + V_{\mathrm{s-s}}^{(\mathrm{HC})}(\mathrm{R^2Br})] \quad (10c)$$

described already. The $\Delta_{\mathrm{void}}^{\mathrm{HC}}V^{\ddagger}$ for each of the S_N2 reactions herein is evaluated by equation (11) obtained by substituting equation (8a) into equation (10b) and using equation (10a).

$$\Delta_{\mathrm{void}}^{\mathrm{HC}}V^{\ddagger} = (a^{\mathrm{HC}} - 1)\Delta_{\mathrm{w}}V^{\ddagger} - b^{\mathrm{HC}} \qquad (11)$$

Then, $\Delta_{\mathrm{s-s}}^{(\mathrm{HC})}V^{\ddagger}$ can be evaluated by subtracting $\Delta_{\mathrm{w}}V^{\ddagger}$ and $\Delta_{\mathrm{void}}^{\mathrm{HC}}V^{\ddagger}$, or the sum of these, $\Delta^{\mathrm{HC}}V^{\ddagger} = a^{\mathrm{HC}}\Delta_{\mathrm{w}}V^{\ddagger} - b_{\mathrm{HC}}$, from the observed $\Delta V^{\ddagger}$ value.

When $\Delta_{\mathrm{w}}V^{\ddagger}$ is negative, the $\Delta_{\mathrm{s-s}}^{(\mathrm{HC})}V^{\ddagger}$ is nearly zero or positive for both hydrolysis and ethanolysis (Table 7). From the viewpoint that the formation of partial charges involves some compression of the solvent, a zero or positive value may seem strange. In the case of hydrolysis, $V_{\mathrm{s-s}}^{(\mathrm{HC})}$ is *ca.* -2 for the bromides, *ca.* -9 for water, and *ca.* $-12 - 1.53\Delta_{\mathrm{w}}V^{\ddagger}$ for the transition states. The nearly zero or positive $\Delta_{\mathrm{s-s}}^{(\mathrm{HC})}V^{\ddagger}$ arises from the fact that negative value of the reactants $(-2) + (-9) = -11$ changes into a similar or less negative value of the transition state during the activation process. Thus, the negative value of water is found to play a significant part by relaxing the volume reduction when a H_2O molecule is incorporated in the transition state. This may be explained by the following qualitative characteristics of the activation process. $V_{\mathrm{s-s}}^{(\mathrm{HC})}$ for water is about twice that for the alcohols and comparable to that for the glycols. This seems reasonable because the H_2O molecule has two protons and two lone pairs of electrons which are able to form hydrogen bonds with other surrounding H_2O molecules, but OH in ROH or $\mathrm{HO(CH_2)}_n\mathrm{OH}$ has only one proton and two lone pairs of electrons. On the other hand, though the transition state also includes a H_2O molecule, one of its lone pairs is employed in half-bond formation with α-CH_2. Thus, $\Delta_{\mathrm{s-s}}^{(\mathrm{HC})}V^{\ddagger}$ for the present hydrolysis is attributable to the attenuation of the hydrophilic property, particularly the capacity for hydrogen-bond formation, in the reacting molecules. In other words, the molecular property of the very hydrophilic H_2O changes partially into that of the less hydrophilic OH group during the process.

The situation for ethanolysis is also very similar to that for hydrolysis. A positive $\Delta_{\mathrm{s-s}}^{(\mathrm{HC})}V^{\ddagger} = 3 - 1.65\Delta_{\mathrm{w}}V^{\ddagger}$ arises from the fact that the negative $V_{\mathrm{s-s}}^{(\mathrm{HC})}$ of the reactants $(-11._5)_{\mathrm{Br}} + (-19._2)_{\mathrm{OH}} = -31$ changes into a less negative value of the transition state $-28 - 1.65\Delta_{\mathrm{w}}V^{\ddagger}$. Thus, the negative value of ethanol in the ground state plays a significant part. The EtOH molecule certainly forms hydrogen bonds with other surrounding EtOH molecules, and one of the lone pairs of OH in the transition state is employed for half-bond formation in order to form the ether bond.

Thus, $V^{\infty}(\ddagger)$ and $\Delta V^{\ddagger}$ are related to the behaviour of V^{∞} for common solutes through the molecular properties of the initial and transition states symbolized in process (5).

Further Features of the Empirical Approach.—The n-alkane used for the evaluation of $V_{\mathrm{s-s}}^{(\mathrm{HC})}$ of n-hexyl bromide as a model solute is $\mathrm{CH_3(CH_2)_{6.071}CH_3}$, where the fraction 0.071 denotes $\{V_{\mathrm{w}}(\mathrm{Br}) - V_{\mathrm{w}}(\mathrm{CH_3})\}/V_{\mathrm{w}}(\mathrm{CH_2})$. Thus, $V_{\mathrm{s-s}}^{(\mathrm{HC})}$ is the volume change during the process where the terminal $\mathrm{CH_3(CH_2)_{0.071}}$ is exchanged by a bromo group with the same V_{w}. This is one of the essential characteristics of the $V_{\mathrm{s-s}}^{(\mathrm{HC})}$ term.[1] This is then applied to $\Delta_{\mathrm{s-s}}^{(\mathrm{HC})}V^{\ddagger}$ for ethanolysis of $\mathrm{C}_m\mathrm{Br}$ ($\mathrm{C}_m = \mathrm{C}_m\mathrm{H}_{2m+1}$). The definition of $\Delta_{\mathrm{s-s}}^{(\mathrm{HC})}V^{\ddagger}$ in equation (10c) can be rearranged as

$$\begin{aligned}\Delta_{\mathrm{s-s}}^{(\mathrm{HC})}V^{\ddagger} &= V_{\mathrm{s-s}}^{(\mathrm{HC})}(\ddagger) - (V_{\mathrm{s-s}}^{(\mathrm{HC})}(\mathrm{C}_m\mathrm{Br}) + V_{\mathrm{s-s}}^{(\mathrm{HC})}(\mathrm{C_2OH})\} \\ &= V_{\mathrm{void}}(\ddagger) - \\ &\quad \{V_{\mathrm{void}}^{\mathrm{HC}}(V_{\mathrm{w}}{}^{\ddagger}) + V_{\mathrm{s-s}}^{(\mathrm{HC})}(\mathrm{C}_m\mathrm{Br}) + V_{\mathrm{s-s}}^{(\mathrm{HC})}(\mathrm{C_2OH})\} \\ &= V_{\mathrm{void}}(\ddagger) - V_{\mathrm{void}}[\mathrm{Br(CH_2)}_{m+2+\Delta m}\mathrm{OH}] \qquad (12)\end{aligned}$$

equation (12) where Δn is $\Delta_{\mathrm{w}}V^{\ddagger}/V_{\mathrm{w}}(\mathrm{CH_2})$. Thus, $\Delta_{\mathrm{s-s}}^{(\mathrm{HC})}V^{\ddagger}$ denotes a comparison of V_{void} of the transition state with that of the hypothetical bromohydrin whose Br and OH have the same additive properties as Br and OH in the ground state. In this comparison, the contributions of Br and OH included in (i) are cancelled, while minor contributions caused by the lower V_{w} of the bromide and ethanol than of the transition state remain in (i) in addition to Δ(OH). The sum of (i)–(vi) is then $-2 + \Delta(\mathrm{OH}) + \Delta(\pm\delta)$, which is equal to the observed $\Delta_{\mathrm{s-s}}^{(\mathrm{HC})}V^{\ddagger}$ value. This leads to the conclusion already derived from $V_{\mathrm{s-s}}^{(\mathrm{HC})}(\ddagger)$. Further, the experimental approach from $V^{\infty}(\ddagger)$ to the molecular property of the transition state is not always restricted to a comparison with the hypothetical n-alkane in $V_{\mathrm{s-s}}^{(\mathrm{HC})}(\ddagger)$ or bromohydrin in $\Delta_{\mathrm{s-s}}^{(\mathrm{HC})}V^{\ddagger}$. $V^{\infty}(\ddagger)$ can be examined by comparison with V^{∞} of any solute in principle, if contributions such as (i)–(vi) for both states are estimated correctly.

Hyne and his co-workers determined $V^{\infty}(\ddagger)$ for the solvolysis of benzyl chloride in aqueous alcohols.[2,20,21] The solvent effect on $V^{\infty}(\ddagger)$ in aqueous ethyl alcohol was shown to be similar to those of various inorganic and organic salts.[21] The empirical approach applied in this work essentially resembles theirs, since we have also compared $V^{\infty}(\ddagger)$ *with* V^{∞} for real solutes. In addition, the present comparison of V^{∞} at the same V_{w} originates from classical evidence of the existence of hydrogen bonding given by the smaller molar volumes of water and alcohols than those of some other non-associating compounds of similar molecular size.[1,22]

The $\Delta_1V^{\ddagger}$ value estimated by the cylinder model also includes the volumetric change of the interstitial space between the van der Waals spheres of the relevant atoms in addition to $\Delta_{\mathrm{w}}V^{\ddagger}$. A solute molecule dissolved into solvent must create some space outside of such a cylinder[23] in order to equilibrate thermodynamically with the surrounding solvent molecules. The cylindrical space may be unsuitable for the estimation of the contraction due to the electrostriction as well as that due to the hydrogen-bond formation. A somewhat greater volume seems to be suitable. Theoretically, it is the partial molar volume that the solute molecule would create in the solvent if it had neither dipole moment nor hydrogen-bond formation. Realistically, we must pay attention to the behaviour of the observable V^{∞} of non-polar solutes such as hydrocarbons.[24]

Experimental

Kinetic Measurements under Pressure.—The high pressure apparatus used for electroconductivity measurements has been described elsewhere[25] and was essentially the same as that reported by Hyne.[26] Initial concentrations of alkyl bromides

Table 7. $\Delta_{s-s}^{(HC)}V^{\ddagger}/\text{cm}^3\ \text{mol}^{-1}$.[a]

	Hydrolysis at 298.15 K		
Substrate	Ethyl bromide	n-Propyl bromide	n-Butyl bromide
$\Delta_{s-s}^{(HC)}V^{\ddagger}$	$-2 - 1.53_4\Delta_wV^{\ddagger}$ $(-2/5)$	$-2 - 1.53_4\Delta_wV^{\ddagger}$ $(-2/5)$	$1 - 1.53_4\Delta_wV^{\ddagger}$ $(1/8)$
	Ethanolysis at 333.15 K		
Substrate	Methyl bromide	n-Propyl bromide	n-Butyl bromide
$\Delta_{s-s}^{(HC)}V^{\ddagger}$	$2 - 1.65_6\Delta_wV^{\ddagger}$ $(2/9)$	$-2 - 1.65_6\Delta_wV^{\ddagger}$ $(2/9)$	$4 - 1.65_6\Delta_wV^{\ddagger}$ $(4/11)$

[a] Values in parentheses = (value for $\Delta_wV^{\ddagger} = 0$)/(value for $\Delta_wV^{\ddagger} - =4.4$). $\Delta_{void}^{HC}V^{\ddagger} = -9._9 + 0.53_4\Delta_wV^{\ddagger} = (-9._9/-12._2)$ for hydrolysis and and $-27._5 + 0.65_6\Delta_wV^{\ddagger} = (-28/-30)$ for ethanolysis. See also equations (13) and (10) or (10a).

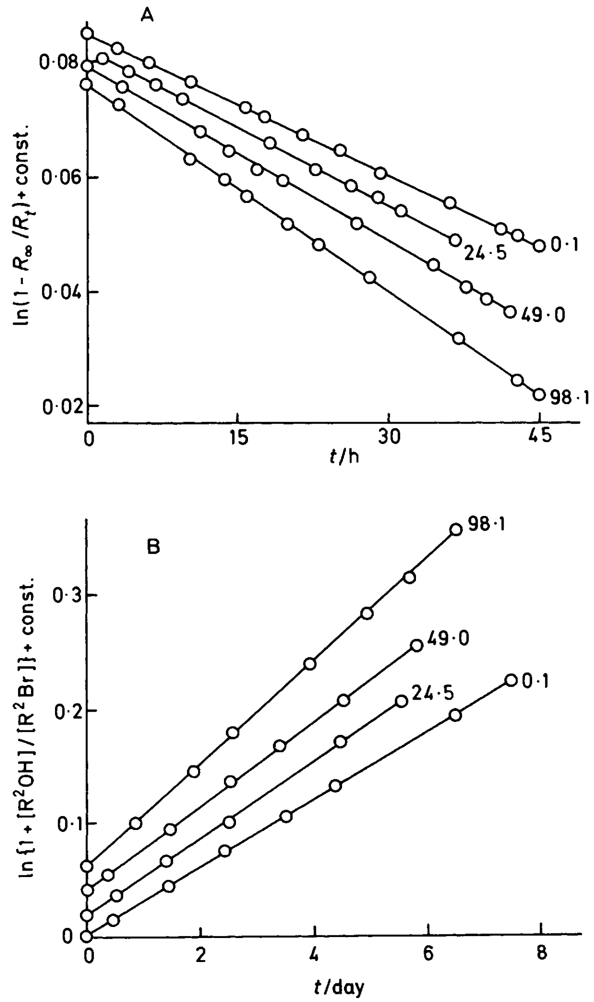


Figure 3. Pseudo-first-order plot for hydrolysis of n-alkyl bromide at 298.15 K. A, n-propyl bromide followed by electroconductimetry; B, ethyl bromide followed by g.l.c. analysis. Numbers, pressure in MPa.

were 0.0005–0.001 mol dm^{-3}. The aqueous solution of each bromide, stored at *ca.* 278 K, was used for measurements under different pressures. k_1 Values were determined by equation (13)

$$\ln(1 - R_\infty/R_t) = -k_1t + \text{constant} \qquad (13)$$

where R_t is the electrical resistance at time t and R_∞ that at infinite time. After measurements at 98.1 MPa, the bath temperature was raised to *ca.* 363 K and the reacting solution was left for *ca.* 50 h. The R_∞ value at each pressure was determined at 298.15 K by averaging the stationary values measured upon pressure raising and lowering. Although conductimetry could determine k_1 through measurements at rather low conversions, the reliability depends on R_∞. The determination just described was suspected to be prone to error. Thus a g.l.c. method was also used for two of the three bromides. The apparatus for g.l.c. analysis is described in detail elsewhere,[27] and was similar to that constructed by Whalley.[28] Initial concentrations were *ca.* 0.01 mol dm^{-3} for hydrolysis of ethyl and n-propyl bromides and for ethanolysis of methyl bromide. Those for ethanolysis of n-propyl and n-butyl bromides were 0.001–0.002 mol dm^{-3}. The ratio of the concentration of the alcohol or ether produced to that of the remaining alkyl bromide $[R^1OR^2]/[R^2Br]$ was evaluated from the ratio of the corresponding peak areas from f.i.d. chromatography. The analytical conditions for hydrolysis

$$\ln\{1 + [R^1OR^2]/[R^2Br]\} = k_1t + \text{const.} \qquad (14)$$

were column, PEG 1500, 15 mass % column temperature, 333 K; flow rate of nitrogen carrier gas *ca.* 0.8 cm^3 s^{-1}; flow rate of hydrogen for frame *ca.* 0.4 cm^3 s^{-1}; and flow rate of air *ca.* 8 cm^3 s^{-1}. Those for ethanolysis were column, PEG 200, 15 mass %, 4 m for methyl bromide, 2 m for n-propyl bromide; and PEG 400 15 mass %, 2 m for n-butyl bromide; flow rate of nitrogen *ca.* 0.4 cm^3 s^{-1}, flow rate of hydrogen *ca.* 0.3 cm^3 s^{-1}; flow rate of air *ca.* 8 cm^3 s^{-1}; column temperature, 328–333 K. Each of the stationary liquids was supported on 60–80 mesh Uniport-B and packed in tube of 4 mm i.d.

Plots of $\ln(1 - R_\infty/R_t)$ and $\ln(1 + [R^1OR^2]/[R^2Br])$ against t are given in Figure 3 for hydrolysis of n-propyl and ethyl bromides, as examples. Thus, the linear progress of the reactions is confirmed. Similar results were observed in the other kinetic measurements. k_1 Values were obtained from the slopes of the straight lines in these plots. Final conversions were up to *ca.* 7% for conductimetry, and up to *ca.* 30% for g.l.c. analysis. Thus k_1 is regarded as the initial-rate constant. In addition, the temperature of the thermostat was estimated by a thermometer reading to 0.1 K and regarded as accurate to ±0.05 K; it then was monitored by a Beckmann thermometer graduated in 0.01 K. Temperatures for a series of measurements of a given substrate under pressure were the same within 0.01 K. However, they were not rigorously consistent for different substrates and analytical methods, all were accurate only to within 0.1 K.

Partial Molar Volume Measurements.—The V^{∞} value of n-butyl bromide in water at 298.15 K was measured by a dilatometric method described previously.[1,27a] The apparent partial molar volume was found to decrease for a short time just after injection, and then it reached a constant value. This was similar to observations for ethyl and n-propyl bromide.[1] The constant value of the apparent partial molar volume was adopted as V^{∞}. The same techniques were also applied to V^{∞} measurements in ethanol at 333.15 K.

Reagents.—Ethyl and n-propyl bromides and water were the same as in V^{∞} measurements described previously.[1] Methyl and n-butyl bromide were purified by the same method as ethyl and n-propyl bromide. Ethanol used as solvent in kinetic measurements for ethanolysis was a commercial reagent grade sample dried by quicklime and aluminium amalgam generated from metal foil and mercury(I) chloride, and fractionally distilled under dry nitrogen. Ethanol used in V^{∞} measurements was the same reagent as above but dried over 3A molecular sieves. The water content of both ethanol samples was <0.01 mass % by Karl Fisher titration. n-Hexyl and n-octyl ethyl ether were synthesized from the corresponding bromides and excess of sodium ethoxide in ethanol. Other reagents were commercially guaranteed. All reagents for solutes were used after repeated distillation until g.l.c. analysis showed a single peak.

References

1 S. Terasawa, H. Itsuki, and S. Arakawa, *J. Phys. Chem.*, 1975, **79**, 2345.
2 H. S. Golinkin, I. Lee, and J. B. Hyne, *J. Am. Chem. Soc.*, 1967, **89**, 1307.
3 C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Cornell Univ. Press, Ithaca and London, 1963, 2nd edn., ch. VII.
4 R. E. Robertson, *Prog. Phys. Org. Chem.*, 1967, **4**, 213.
5 A. H. Ewald and D. J. Ottley, *Aust. J. Chem.*, 1967, **20**, 1335.
6 B. T. Baliga and E. Whalley, *J. Phys. Chem.*, 1969, **73**, 654.
7 M. J. Mackinnon and J. B. Hyne, *Can. J. Chem.*, 1971, **49**, 3840.
8 M. J. Mackinnon, A. B. Lateef, and J. B. Hyne, *Can. J. Chem.*, 1970, **48**, 2025.
9 W. J. le Noble, *Prog. Phys. Org. Chem.*, 1967, **5**, 207; T. Asano and W. J. le Noble, *Chem. Rev.*, 1978, 78, 407; W. J. le Noble and H. Kelm, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 841.
10 J. L. Kurz and J. Y.-W. Lu, *J. Phys. Chem.*, 1983, **87**, 1444.
11 For an example see J. A. Riddick and W. B. Bunger, 'Organic Solvents,' Wiley-Interscience, New York, 1970.
12 M. G. Gonikberg, 'Chemical Equilibria and Reaction Rates at High Pressures,' Khimiya, Moscow, 1969 (translated into Japanese by Y. Ogo, Nikkan Kogyo Shimbun, 1972).
13 S. D. Hamann, 'High Pressure Physics and Chemistry,' ed. R. S. Bradley, Academic Press, London, 1963, vol. II, ch. 8; E. Whalley, *Adv. Phys. Org. Chem.*, 1964, **2**, 92; K. E. Weale, 'Chemical Reactions at High Pressures,' Spon, London, 1967.
14 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
15 R. L. Showan, *Prog. Phys. Org. Chem.*, 1972, **9**, 275.
16 E. Whalley, *J. Chem. Phys.*, 1963, **38**, 1400.
17 (*a*) T. Asano, *Rev. Phys. Chem. Jpn.*, 1979, **49**, 109; (*b*) T. Asano and T. Okada, *J. Phys. Chem.*, 1984, **88**, 238.
18 (*a*) J. Horiuti, *Sci. Pap. Inst. Phys. Chem. Res* (*Tokyo*), 1931, 17, 125; (*b*) D. D. Elley, *Trans. Faraday Soc.*, 1939, **35**, 1421; (*c*) W. L. Masterton, *J. Chem. Phys.*, 1954, **22**, 1830; (*d*) T. Enns, P. F. Scholander, and E. D. Bradstreet, *J. Phys. Chem.*, 1965, **69**, 389.
19 (*a*) B. T. Brooks, C. E. Boord, S. S. Kurtz, and L. Schmerling, 'The Chemistry of Petroleum Hydrocarbons,' Reinhold, New York, 1954; (*b*) F. D. Rossini, B. J. Mair, and A. J. Streiff, 'Hydrocarbons from Petroleum,' Reinhold, New York, 1953.
20 D. D. Macdonald and J. B. Hyne, *Can. J. Chem.*, 1970, **48**, 2494.
21 I. Lee and J. B. Hyne, *Can. J. Chem.*, 1968, **46**, 2333; 1969, **47**, 1437; D. D. Macdonald and J. B. Hyne, *ibid.*, 1970, **48**, 2416.
22 G. C. Pimentel and A. L. McClellan, 'Hydrogen Bond,' Freeman, San Francisco, 1960, p. 53.
23 T. Asano and W. J. le Nobel, *Rev. Phys. Chem. Jpn.*, 1973, **43**, 82; Y. Yoshimura and M. Nakahara, *Ber. Bunsenges. Phys. Chem.*, 1985, **89**, 426.
24 H. Itsuki, S. Terasawa, K. Shinohara, and H. Ikezawa, *J. Chem. Thermodyn.*, 1987, **19**, 555.
25 S. Hariya and S. Terasawa, *Nippon Kagaku Zasshi*, 1969, **90**, 765.
26 J. B. Hyne, H. S. Golinkin, and W. G. Laidlaw, *J. Am. Chem. Soc.*, 1966, **88**, 2104.
27 (*a*) H. Itsuki, B. Matsuda, and S. Terasawa, *Nippon Kagaku Zasshi*, 1969, **90**, 1016; (*b*) H. Itsuki and S. Terasawa, *ibid.*, p. 1119.
28 J. Koskikallio and E. Whalley, *Trans. Faraday Soc.*, 1959, **55**, 809; A. R. Osborn and E. Whalley, *Can. J. Chem.*, 1961, **39**, 1094.

Received 5*th April* 1988; *Paper* 8/01317J