indicates that the activation energy for the H atom displacement process is about equal to or slightly less than that of the H atom abstraction from crotonaldehyde. The value for the latter reaction is not known, but the similar reaction with acetaldehyde is reported to have an activation energy $\leq$ 6 kcal.[11] If, of course, chain A supplies a significant amount of propylene the kinetics become more complex and this treatment breaks down.

Summary

It now seems well established that displacement processes are important modes of reaction of methyl radicals with biacetyl,[12] *trans*-methyl propenyl ketone and crotonaldehyde. Recently other displacement processes have been reported to occur when methyl radicals react with propylene and 1-butene. Varnerin[13] states that at least 5% of the methyl radicals generated in the pyrrolysis of mixtures of CD_3CDO and propylene react by (22)

$$CD_3 + CH_2{=}CHCH_3 \longrightarrow CD_3CH{=}CH_2 + CH_3 \quad (22)$$

McNesby and Gordon photolyzed acetone-d_6 in the presence of 1-butene[14] at 375 and 500° and explain their results by a mechanism which includes the displacement process

$$CD_3 + CH_2{=}CHCH_2CH_3 \begin{cases} \longrightarrow CD_3CH_2CH{=}CH_2 + CH_3 \\ \longrightarrow CH_2{=}CHCD_3 + C_2H_5 \end{cases}$$

Within a few weeks the reverse reactions were reported by Kebarle and Bryce.[15] In both instances

$$CH_3 + CH_2{=}CHCH_2CD_3 \begin{cases} \longrightarrow CH_3CH_2CH{=}CH_2 + CD_3 \\ \longrightarrow CH_2{=}CHCH_3 + CH_2CD_3 \end{cases}$$

the investigators propose that methyl radicals first add to the double bond to form an intermediate radical which subsequently dissociates into a new olefin and another free radical. For example, McNesby and Gordon visualize the two step process

$$CD_3 + CH_2{=}CHCH_2CH_3 \longrightarrow [CD_3CH_2CHCH_2CH_3]$$
$$[CD_3CH_2CHCH_2CH_3] \longrightarrow CD_3CH_2CH{=}CH_2 + CH_3$$

A similar intermediate has been suggested in the methyl displacement of acetyl from methyl propenyl ketone[3] and may exist in the analogous process with crotonaldehyde. However, there is little if any direct evidence for these intermediates.

An interesting process, recently suggested by Kistiakowsky and Mahan[16] to explain their results from the photolysis of methyl ketene, is the attack of the ethylidene radical on methyl ketene to give butene and CO

$$CH_3CH + CH_3CH{=}C{=}O \longrightarrow C_4H_8 + CO$$

This process can be classified as a displacement of carbon monoxide by the ethylidene radical.

Two examples of what might be termed H atom displacements are proposed by Rabinovitch, Davis

$$H + CH_3CH{=}CH_2 \longrightarrow CH_2{=}CH_2 + CH_3$$

and Winkler[17] and reported by Forst and Winkler.[18]

$$H + CH_3CN \longrightarrow HCN + CH_3$$

The recent accumulation of this body of evidence for free radical displacement processes indicates that secondary reactions of this type may be of considerable importance in a number of other systems similar to those described. Current studies in this Laboratory include an investigation of the reactions of methyl radicals with the α,β-unsaturated ester, methyl crotonate.

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RIVERSIDE, CALIF.

[CONTRIBUTION FROM THE CHEMICAL INSTITUTE, FACULTY OF SCIENCE, NAGOYA UNIVERSITY]

Ultrasonic Interferometer Measurements of the Amount of Bound Water. Saccharides

BY HAZIME SHIIO

RECEIVED JUNE 19, 1957

Ultrasonic velocities in aqueous solutions of a number of saccharides have been measured with an ultrasonic interferometer, and the amounts of hydration have been determined at 25°. The following samples were studied: xylose, arabinose, fructose, glucose, α-methyl glucoside, sucrose, maltose, cellobiose and raffinose. The amount of bound water obtained is 0.28, 0.42, 0.38, 0.35, 0.23, 0.20, 0.22, 0.25 and 0.22 cc./g. solute, respectively. From these values, it is shown that 0.5–0.9 water molecules are hydrated to one OH radical of each saccharide. Further investigations were carried out on the hydrations of a few saccharides at various temperatures, and the enthalpy difference between hydrate water and non-hydrated has been estimated to be about 12–13 kcal./mole.

Introduction

The compressibility of the solution may be determined by the effects from solvent, solute and solvation. The effects of the solute are separated into two parts: the compressibility of the solute molecule and solute–solute interaction. If the concentration of the solution becomes sufficiently low, the second effect becomes negligible. The compressibility of low molecular weight solute molecules may be negligibly small compared with other effects. In the previous report,[1] we have shown by adding the ethanol to the solution that the compressibility of the sugar molecule was nearly zero. In such case, therefore, the effects of the solute should not be taken into account, and we can obtain the amount of hydration from measurements of the compressibility of solvent and solution.

Passynsky[2] estimated the hydration of sucrose by measuring the ultrasonic velocity, but his method was a little different from ours. Pryor and Roscoe[3] measured the ultrasonic velocity of the solutions of sucrose and a few other saccharides at temperatures from 20 to 80° and showed qualitatively that "solvation envelope" decreased with increasing temperature, provided the sugar molecules could be regarded as incompressible. But they did not extrapolate the measurement to zero concentration as we did, and the effects due to the interaction between solute molecules still existed at the concentrations of their experiments.

In this report, employing previous method, the hydrations are investigated for a number of saccharides over a wide temperature range.

Experimental

The ultrasonic velocities in solutions were measured with an interferometer using X-cut crystal of resonance frequency 1 mc. The materials were E.P. grade chemicals, and were dried in a vacuum desiccator for a week. The measurements were made at 25° for solutions of most of the saccharides, and for glucose, sucrose and maltose at 20, 25, 35 and 45°. The methods were described in a previous report.[4]

Results and Discussion

According to the previous report,[1] neglecting compressibility of the solute, we have

$$\lim_{c \to 0} \Delta/c \equiv (\beta/\beta_0 - V_0)/c = -v_0(1 - \beta_2/\beta_0)/c \quad (1)$$

The notations used are

β = adiabatic compressibility of soln.
β_0 = adiabatic compressibility of solvent
β_2 = adiabatic compressibility of bound water
v_0 = specific vol. fraction of bound water
V_0 = apparent specific vol. fraction of total solvent used *i.e.*, $V_0 = (d - c)/d_0$
d = density of solution
d_0 = density of solvent
c = concn. of solute, g./cc. of soln.

By the measurements of β, β_0, V_0 and c, we obtain Δ/c at various concentrations of saccharides. The results and their values extrapolated to zero concentration, $\lim_{c \to 0} \Delta/c$, are shown in Fig. 1 and Table I.

The experimental values of Δ/c for sucrose, Fig. 1, increase linearly with concentration, probably by reason of the solute–solute interaction depending on the square of concentration. Therefore, the values of $\lim_{c \to 0} \Delta/c$ in Table I were obtained graphically by the extrapolation.

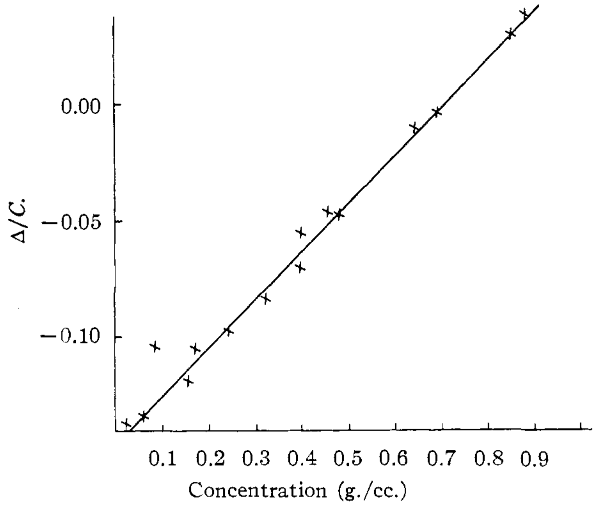

Fig. 1.—Sucrose solutions at 20°.

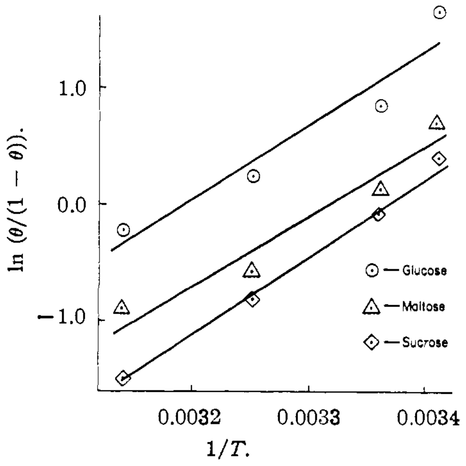

Fig. 2.—Temperature dependence of the hydration.

As is seen in equation 1, the value of $-\lim_{c \to 0} \Delta/c$ is proportional to the volume of bound water. The value of β_2 in the proportionality constant $(1 - \beta_2/\beta_0)$ has been arbitrarily assigned by various authors; some gave it zero value for both electrolytes[2,5] and non-electrolytes.[2,3] It may be justified in electrolytes owing to strong electric field surrounding ion. However for non-electrolytes, such as saccharides, the change of volume in dissolution process is negligibly small, so that the difference of the compressibility between hydrated water and normal water may be smaller than in the case of electrolytes. There are several methods to obtain the bound water[4,6]: that is, vapor pressure lowering or freezing point depression methods determining "non-solvent water," calorimetric or dilatometric methods of "non-freezing water," cobaltous chloride method, dielectric method, etc. In these methods, it is mentioned that the bound water is of solid-like structure to lose the freedom of mobility, and the free volume contained in the free water is decreased; then, the compressibility of bound water may be considerably smaller than in

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TABLE I

EXPERIMENTAL RESULTS AT 25°

	c (g./cc.)	d	β/β_0	V_0	$-\Delta/c$	$-\lim_{c\to 0} \Delta/c$
Xylose	0.1954	1.0679	0.8505	0.8751	0.126	0.17
	.1669	1.0574	.8728	.8931	.122	
	.1193	1.0404	.9064	.9238	.146	
	.1016	1.0339	.9203	.9350	.145	
	.0918	1.0306	.9271	.9416	.158	
	.0768	1.0249	.9397	.9509	.146	
Arabinose	.1979	1.0714	.8382	.8761	.192	.25
	.1573	1.0560	.8681	.9013	.211	
	.1260	1.0446	.8945	.9213	.213	
	.1052	1.0366	.9095	.9341	.234	
	.0883	1.0303	.9248	.9448	.226	
	.0672	1.0221	.9431	.9577	.217	
Fructose	.1835	1.0676	.8528	.8866	.184	.23
	.1390	1.0506	.8860	.9143	.204	
	.1349	1.0490	.8885	.9168	.210	
	.1199	1.0433	.9019	.9261	.202	
	.0865	1.0305	.9277	.9458	.209	
Glucose	.1971	1.0715	.8455	.8770	.160	.21
	.1726	1.0622	.8644	.8922	.161	
	.1226	1.0436	.9027	.9237	.181	
	.0597	1.0196	.9513	.9628	.194	
α-Methyl glucoside	.1421	1.0422	.8876	.9027	.106	.14
	.0994	1.0286	.9191	.9319	.128	
	.0787	1.0220	.9364	.9461	.123	
	.0724	1.0201	.9422	.9504	.113	
	.0640	1.0174	.9480	.9562	.128	
Sucrose	.1585	1.0577	.8883	.9018	.085	.12
	.1425	1.0516	.8987	.9118	.092	
	.1234	1.0443	.9127	.9237	.089	
	.0979	1.0346	.9302	.9395	.095	
	.0866	1.0303	.9379	.9465	.100	
Maltose	.1760	1.0646	.8738	.8912	.099	.13
	.1276	1.0463	.9072	.9214	.111	
	.1199	1.0433	.9129	.9261	.110	
	.0730	1.0252	.9463	.9550	.119	
	.0421	1.0133	9688	.9741	.125	
Cellobiose	.1652	1.0603	.8624	.8977	.115	.15
	.1260	1.0453	.9054	.9220	.140	
	.1002	1.0354	.9252	.9379	.127	
	.0855	1.0298	.9348	.9471	.144	
	.0765	1.0262	.9425	.9525	.131	
	.0677	1.0229	.9492	.9580	.130	
	.0467	1.0150	.9644	.9711	.143	
Raffinose	.1314	1.0486	.9050	.9199	.113	.13
	.1149	1.0417	.9169	.9296	.111	
	.1011	1.0364	.9269	.9380	.110	
	.0862	1.0305	.9367	.9471	.121	
	.0729	1.0254	.9466	.9553	.119	

normal state (the compressibility of water and ice are about 45 and 18×10^{-12} cm.²/dyne, respectively). Thus we have used 18/45 for the value of β_2/β_0, and a reasonable value has been obtained for the hydration of dextrin in a previous report.[1] Using this value for β_2/β_0, the hydrations of saccharides are found as in Table II.

TABLE II

BOUND WATER OF SACCHARIDES (25°)

	Cc./g.	Mole/mole	Mole/OH radical
Xylose	0.28	2.3	0.58
Arabinose	.42	3.5	.89
Fructose	.38	3.8	.76
Glucose	.35	3.5	.70
α-Methylglucoside	.23	2.5	.63
Sucrose	.20	3.8	.48
Maltose	.22	4.2	.53
Cellobiose	.25	4.8	.60
Raffinose	.22	6.2	.56

The hydrations of sugars in solution have been investigated by a few authors who used various methods. Roscoe[3] calculated the ratio of the fractional volume of solvated solute to the dry solute from viscosity data, finding that the value of the hydration of sucrose was 2.7 mole/mole solute at 20°. Miller[7] obtained the hydration of non-electrolytes from data of the molality activity coefficients, using the method of Stokes and Robinson.[8] He showed that the solution really consists of solvated particles, instead of bare particles, dissolved in the remaining free solvent. He obtained 9.7 mole/mole solute as the hydration of sucrose at 25°. It is seen from Table II and Fig. 1 that our results are 4.7 mole/mole at 20° and 3.8 mole/mole at 25°, respectively. A little deviation exists among these values, but this is to be expected due to the different methods used by the authors. Therefore, it has *only* a relative significance characteristic to each method, and we should compare the results of measurements by one and the same method. In this sense, the above results would be regarded to agree rather well with those of other authors.

As the effects of OH radicals are considered to be dominant in hydration, the amount of bound water per one OH radical in the solute molecule is shown in the last column of Table II. These values were 0.5–0.9 H_2O/OH radical for every saccharide, but small deviations are seen among the different molecular structures.

The hydrations of di- and tri-saccharides are generally smaller than those of mono-saccharides. This effect is particularly evident in sucrose, which contains one glucose and one fructose in its molecule. The molecular structure of di- or tri-saccharide is considered to decrease the number of the free OH radicals owing to intramolecular hydrogen bonding, or steric hindrance among two monomers.

The comparison of hydration between maltose and cellobiose shows us some indication concerning the difference of the α- or β-glucoside bonding in the three-dimensional arrangement of glucose rings. It is interesting to see that cellobiose has the more bound water molecules than maltose. Thus it may be reasonable to draw the following conclusion. In cellobiose, intermolecular forces may be greater, so that, forming a polymer, it becomes fiber structure of cellulose. On the contrary, however, maltose constructs globular dextrin molecule owing to their intramolecular attraction. Thus, as the result of greater outward force, a cellobiose molecule in solution may be more hydrated than maltose.

The hydration for α-methyl glucoside in which the OH radical of the first carbon in glucose is substituted for OCH_3 is decreased by the hydrophobic nature of methyl radical.

The deviation of the hydration between xylose and arabinose may be due to the difference between the three-dimensional arrangements of OH radicals in the molecules.

The results of the investigation for sucrose, maltose and glucose at various temperatures are shown in Table III.

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TABLE III

TEMPERATURE DEPENDENCE OF THE HYDRATION

	Sucrose hydration			Maltose hydration			Glucose hydration		
	$-\lim_{c\to 0} \Delta/c$	Cc./g.	Mole/OH	$-\lim_{c\to 0} \Delta/c$	Cc./g.	Mole/OH	$-\lim_{c\to 0} \Delta/c$	Cc./g.	Mole/OH
20°	0.15	0.25	0.60	0.17	0.28	0.67	0.25	0.42	0.84
25°	.12	.20	.48	.13	.22	.53	.21	.35	.70
35°	.08	.13	.31	.09	.15	.36	.17	.28	.56
45°	.05	.08	.19	.07	.12	.29	.13	.22	.44
ΔH, kcal./mole		13			12			13	

From Table III, it is found that the hydration of sucrose decreases from 0.25 to 0.08 cc./g. as the temperature rises from 20 to 45°.

Pryor and Roscoe[3] calculated the fractional volume occupied by the solute as a solvated sugar molecule, c_2, from viscosity data. Such values of c_2 were larger than the values of the fractional volume c_1 derived from that of dry sugar. The value of ratio c_2/c_1 for sucrose decreased from 1.23 to 1.06 as the temperature rises from 20 to 70°. This change corresponds to the fact that bound water decreases from 0.15 to 0.04 cc./g. as the temperatures rises from 20 to 70°. In the case of glucose, the results of Roscoe gave the values of hydration decreasing from 0.10 to 0.02 (cc./g.) with the temperature rise from 25 to 50°. Our results differ a little from these values. But considering the fact that different assumptions have been used in these methods, the agreement of the values may be satisfactory.

If we apply the theory of Langmuir's adsorption isotherm[9] in the present case, the enthalpy change of hydration could be obtained by the equation

$$\ln \frac{\theta}{1 - \theta} = \Delta H/RT + \text{const.} \qquad (2)$$

in which

θ = amount of hydration in mole number per OH radical

ΔH = enthalpy difference between the state of hydrated water and non-hydrated one

From those curves, we obtained the values of ΔH given in Table III. These values of ΔH involve several other effects than the hydration: intramolecule structural changes of solute, breaking of the hydrogen bond between water molecules, etc. Therefore, the values of Table III cannot be discussed in more detail, but it may be mentioned that these values are of the correct order of magnitude as the energy of hydrogen bonding in all saccharides examined, and it is evident that hydrogen bonding plays an important role in these changes.

The author wishes to express his thanks to Prof. I. Sano and Assist. Prof. Y. Miyahara for their kind advice and encouragement.

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NAGOYA, JAPAN

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Determination of Atomic Polarizations and Dipole Moments for Slightly Polar Liquid Hydrocarbons[1,2]

BY ANTHONY J. PETRO[3] AND CHARLES P. SMYTH

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Dielectric constants, densities and indices of refraction at five wave lengths have been measured for the pure liquids benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, ethylbenzene, styrene and isopropylbenzene at 20, 40 and 60°. The electronic polarizations have been calculated by the Lorentz–Lorenz and Cauchy relationships and the total polarizations by the Clausius–Mosotti equation. The electronic polarizations have been found to be density dependent but a plot of the difference between total and electronic polarizations against the reciprocal of absolute temperature has been found to yield a straight line whose intercept is the atomic polarization and whose slope is proportional to the dipole moment. Values obtained by this method using the Debye equation agree well with those obtained by microwave dielectric constant measurements for all except *o*-xylene and compounds of higher moments. The liquid and vapor dipole moments have been correlated with the asymmetry of the molecules.

The determination of atomic polarization (P_A) for slightly polar compounds has, heretofore, been possible only by methods which are either indirect or difficult to apply experimentally or which give rather uncertain results.[4] Altshuller[5] recently has determined this quantity for several liquid nonpolar aromatic hydrocarbons but does not give values for the slightly polar compounds used in his work. It is the purpose of this paper to describe a simple method for measuring P_A for compounds whose dipole moments are less than about 0.5×10^{-18}. Furthermore, the dipole moments may simultaneously be determined with good precision, especially for compounds whose moments are so small that they are not amenable to accurate measurement in the gaseous state or in solution.

Experimental

The aromatic compounds studied were obtained from the Brothers Chemical Company, with the exception of benzene and toluene. The benzene used was the analytical reagent grade product of Merck and Company and the toluene was obtained from the Barrett Division of the Allied Chemical and Dye Corporation. The benzene and *p*-xylene were initially purified by fractional crystallization. *o*-Xylene

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[1] This research was supported by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command under contract No. AF18(600)1331. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

[2] This paper represents a part of the work to be submitted by Mr. A. J. Petro to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Monsanto Fellow in Chemistry, 1956–1957.

[4] A detailed summary of the various methods is given by J. W. Smith, "Electric Dipole Moments," Butterworth's Scientific Publications, London, 1955, Chapter 9.

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