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ACIDITY IN AQUEOUS MIXED SOLVENT SYSTEMS—III

INFLUENCE OF THE ORGANIC SOLVENT MOLECULAR STRUCTURE ON THE ACIDITY OF AQUO-ORGANIC MIXTURES (ACIDITY FUNCTION, WATER STRUCTURE, HYDROPHILIC AND HYDROPHOBIC EFFECTS)

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Abstract—The acidity functions Ho and H_R have been determined for different aqueous organic mixtures (diols, carbohydrates) at constant acid concentration. We have checked, with a reaction involving a slow proton transfer, that Ho and H_R vary in direct proportion to the acidity of the systems.

The results are interpreted in terms of the variations of the proton activity which is dependent on the modifications of the water structure by the organic cosolvent.

In a preceeding paper,[1] we studied the acidity of different aqueous mixed solvents at constant acid concentration. We attributed the observed decrease in acidity to the increase in proton solvation. The organic solvent, when added to the water, broke the H-bonds and freed the water molecules which in turn became available to solvate the proton.

It was apparent that the basicity of these mixtures was a function of the hydrocarbon group of the organic solvent.

We intend to clarify the influence of the hydrophobic and hydrophilic groups on the water structure.

As evidence of the role of a long carbon chain on the structure of water, we chose a series of diols, since the diols are more miscible in water than the corresponding alcohols.

Then we studied the acidic properties of aqueous solutions of polyols and carbohydrates. If the basic character of the binary aqueous mixtures depends on the hydrophobic part of the organic product, then one should expect the reverse to be true (i.e. the aqueous system will have a more acidic character when the organic product is hydrophilic).

We determined the functions Ho and H_R at constant acid concentration with these different aqueous mixed solvent systems. Under the same conditions, we checked that the reaction involving the proton activity in the slow step is modified by the relative proportions of the reactants.

Finally, we determined by the isopiestic method, the variations of the activity coefficient of water in the aqueous mixed solvents.

EXPERIMENTAL RESULTS

Measurement of Ho. We have determined the function Ho[2] with constant acid concentration ($HCl = 0{\cdot}1\ Ml^{-1}$) in the following aqueous mixtures (Fig. 1): ethane diol-1,3 propane diol-1,4 butane

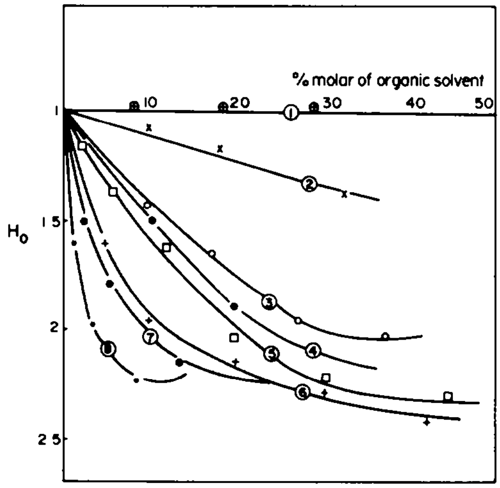
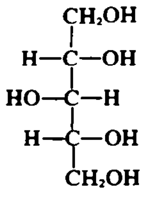
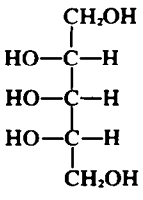


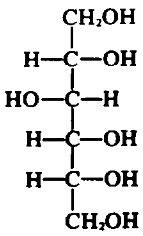
Fig. 1. Values of the acidity function Ho in the following mixtures: 1, H_2O-glycerol; 2, H_2O-ethane diol; 3, H_2O-1,3 propane diol; 4, H_2O-1,2,6 hexane triol; 5, H_2O-1,4 butane diol; 6, H_2O-1,5 pentane diol; 7, H_2O-1,6 hexane diol; 8, H_2O-1,7 heptane diol.



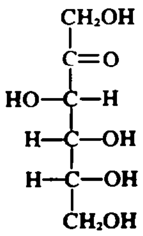
Xylitol



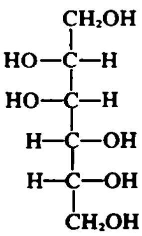
Adonitol



Sorbitol



Fructose



Mannitol

diol-1,5 pentane diol-1,6 hexane diol-1,7 heptane diol-glycerol and 1,2,6 hexane triol.

Ho was also measured in aqueous solutions of the indicated carbohydrates (Fig. 2).

$$Ho = pK_{BH^+}^{H_2O} - \log\frac{(BH^+)}{(B)}$$

$pK_{BH^+}^{H_2O}$ is the negative logarithm of the thermodynamic dissociation constant of BH^+ in water.

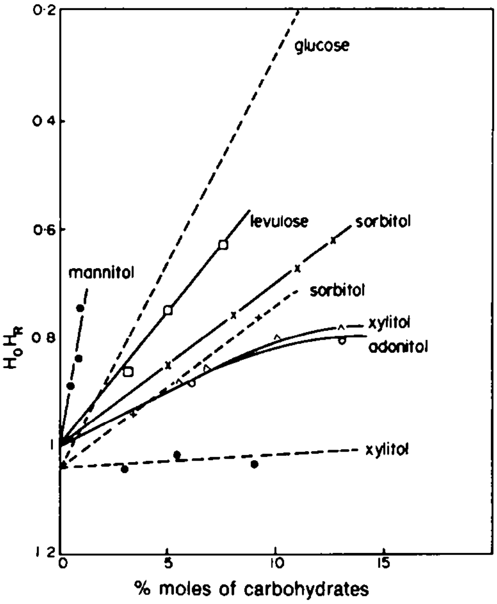


Fig. 2. Values of acidity functions Ho (——) and H_R (---) in aqueous solutions of carbohydrates. (HCl = 0·1 Ml^{-1}).

Measurement of the H_R function

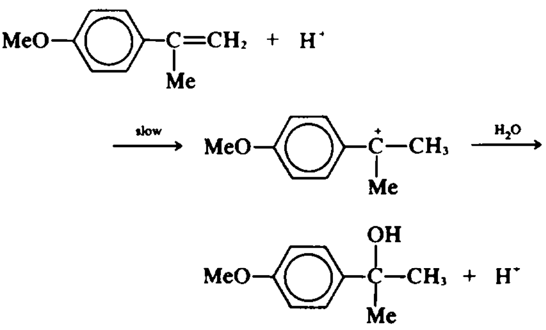
$$H_R = -\log\frac{a_{H^+}f_{ROH}}{a_{H_2O}f_{R^+}} = pK_{R^+} + \log\frac{(ROH)}{(R^+)}$$

We measured the function H_R (3,4) in several aqueous mixed solvents (HCl = 0·2 Ml^{-1}) and found the same sequences for H_R as with Ho (Fig. 2 and Table 1).

Table 1. H_R values at 25°C in some aquo-organic mixtures (HCl = 0·2 Ml^{-1})

% moles glycerol	0	9·57	15·6		24·9
H_R	0·72	0·68	0·56		0·29
% moles ethyleneglycol	0	5·3	12		19·6
H_R	0·72	0·82	0·90		0·96
% moles 1,2 propanediol	0	7·5	14		26·6
H_R	0·72	0·95	1·12		1·32
% moles 1,5 pentanediol	0	4·8	10		20
H_R	0·72	1·18	1·55		1·80
% moles 1,6 hexanediol	0	1	1·5	6	13
H_R	0·72	0·96	1·13	1·70	1·87

Studies of reaction rates. We studied *p*-methoxy α-methyl styrene hydration rates as a function of the proportions of the organic solvent with a constant acid concentration (Figs. 3 and 4). The mechanism of this reaction—the slow transfer of a proton to an olefin—has already been demonstrated[5,6]



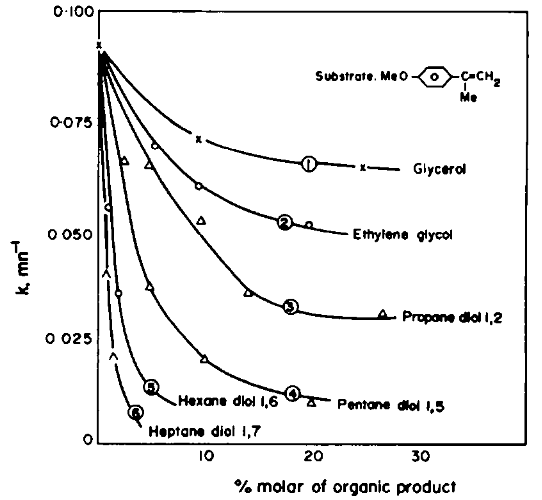


Fig. 3. Hydration of p methoxy α-methyl styrene in aquo organic mixtures. (HCl = 0·2 Ml^{-1}).

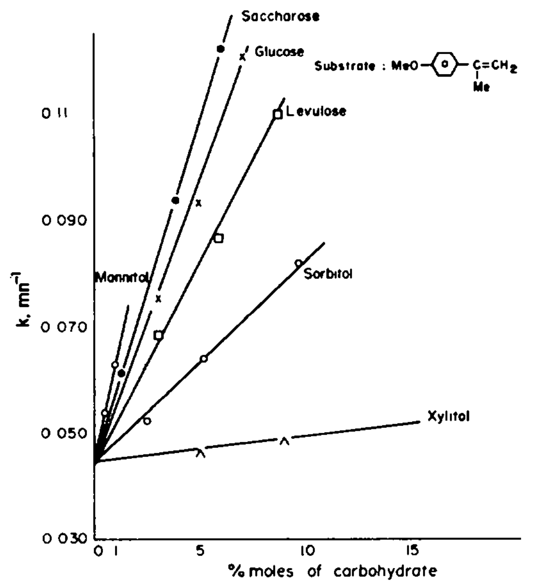


Fig. 4. Hydration of p methoxy α methyl styrene in aqueous solutions of carbohydrates. (HCl = 0·1 Ml^{-1}).

We checked that sucrose inversion was negligable throughout our studies of the reaction rates of aqueous solutions of sucrose.

Measurement of water activity. In Fig. 5, we reported the variations of the activity coefficient of water as a function of the percentage of organic compound.

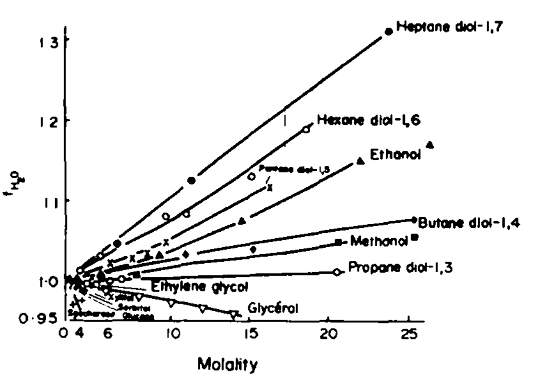


Fig. 5. Values of the activity coefficient of water versus molality of different organic products. (For MeOH and EtOH see Ref. 25.)

DISCUSSION

After compiling the experimental results, we consider that the acidity of the aqueous mixtures is modified by the relative proportions of the solvents. The arguments are those indicated in the preceeding paper.[1] Therefore the results obtained with Ho and H_R are quite comparable, whereas the indicators used for these measurements varied considerably. With regards to p-methoxy α-methylstyrene hydration, we found that this reaction is modified in the same way as the acidity functions Ho and H_R.

This work shows the importance of the carbon chain (hydrophobic part) and of the –OH groups (hydrophilic part) of the organic solvent on the acidity of these mixtures.

Likewise, from the data, we are able to infer the following conclusions:

(1) The basicity of the aqueous systems increases with an increase in the hydrocarbon chain length of the organic compound as illustrated in the following sequence: ethylene glycol < 1,3 propanediol < 1,4 butane diol < 1,5 pentane diol < 1,6 hexane diol < 1,7 heptane diol (shown in order of increasing basicity).

(2) The basicity of the aqueous mixtures decreases proportionally as H atoms are substituted on to the carbon chain by OH groups: thus with regards to basicity, one finds: H_2O - 1 - propanol > H_2O - 1,2 propane diol > H_2O-glycerol, and H_2O-1,6 hexane diol > H_2O-1,2,6 hexane triol.

Acidity increases as the hydrophilic character of the organic substituent.

(3) In all cases, the acidity of aqueous carbohydrate solutions was greater than the acidity of pure water (Fig. 2).

(4) In the different systems the order of the water activity coefficients is the same as the one found with Ho and H_R values and the kinetic measurements (Fig. 5).

We limited our studies to rich water mixtures; so it seems reasonable to assume that the proton is essentially solvated by water[7–14] in spite of certain arguments showing to the contrary[15]. Thus, all modifications of the activity coefficient of water would have direct consequences on the activity coefficient of the proton.

We interpreted our results with regards to the structure of water and the effects on this structure by the molecular structure of the organic solvents. For the structure of water, we used the model proposed by Frank and Wen[16–18]. This model is, at present, the one most generally accepted by the majority of opinions.

According to Frank and Wen, the remarkable properties of water are to be attributed to the existence of self-stabilizing three dimensional H–bonded flickering clusters with life times of the order of 10^{-11} sec. These entities are maximally H–bonded and voluminous. In equilibrium with the structured solvent, there is another form of water, not H–bonded and relatively dense. A dynamic order-disorder balance within liquid water is important to an explanation of the properties of this liquid.

Thus we have to consider at least two species: one in which the water molecules are linked by H–bonding, and one in which the water molecules are free.

The activity of water should depend, on the concentration of the free water molecules. Thus, a variation in the concentration of the monomeric species should produce a modification in the activity coefficient of the proton.

Using these hypotheses, we analysed successively the effects on the structure of water of (1) compounds with a hydrophilic character and (2) compounds with a hydrophobic character.

(1) *Aqueous solutions of carbohydrates.* All the results obtained showed an increase in order of the mixture when compared with water; the acidity of the mixtures increased with an increase in carbohydrate concentration (Figs 2 and 4).

The entropy of the aqueous glucose solutions is negative (at 25°, the variation of TΔS between water and a solution containing 15% glucose (by mole) had 3 cal/mole less than water).

The activity coefficient of water decreases with the concentration of glucose[19] and saccharose.[20]

Thus, these mixtures are more ordered than water and their structures are such that there is much less H–bonding. This fact explains the decrease in f_{H_2O}. The number of monomeric water molecules is less important and it follows that the proton is solvated to a lesser degree which explains the increase in acidity with the increase in carbohydrate concentration.

It is interesting to note that for compounds with an equal number of C atoms and OH groups ($n_{OH} = n_c$), the acidity of aqueous solutions of these compounds increases with the value of n in the following order (Fig. 6).

MeOH (n = 1) < ethylene glycol (n = 2) < glycerol (n = 3) < adonitol (n = 5) < mannitol (n = 6).

Thus, an increase in the value of n gives more possible sites for formation of H–bonds between the organic compound and water. On the other hand, we know that the formation of H–bonds results according to Frank and

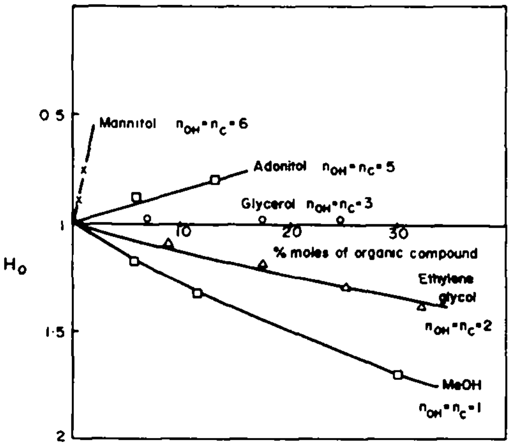
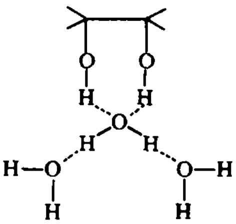


Fig. 6. Values of the acidity function Ho in different aquo organic mixtures at constant acid concentration (HCl = 0·1 Ml^{-1}).

Wen,[18] by an essentially cooperative process and further one would expect a greater number of agregates with a larger values of n.

Schematically:



The solvation of protons is reduced. Consequently, the number of the water molecules and the activity of the proton increases. Thus, the formation of various important agregates can explain the progressive evolution of the acid properties of different aquo-organic solutions.

(2) *Systems with hydrophobic character.* The relative experimental data of these systems were more difficult to interpret. First, the acidity decreases regularly with the increase in size of the hydrocarbon group of the organic compound (Fig. 1).

The water activity in those aquo-organic mixtures increases with the increase of the hydrophobic part in the organic compound (Fig. 5).

Furthermore, it seems reasonable to consider that the entropy of the water diol mixtures is negative by analogy to the results obtained with aqueous alcohol mixtures[17]. This seems *a priori* in contradiction to variations of Ho and f_{H_2O} which denote a greater freedom between water molecules.

One can consider that entropy is a mean measure of the interaction between the substituents of a mixture. At the same time, there is not a qualitative distinction between the different types of bonds in the system. (bonds between solute-solute, solute-solvent or solvent-solvent are not differentiated). This fact leads one to consider, for the aquo-organic systems, the possibility of structure of a different nature than those which exist in the aqueous solutions of carbohydrates.

We explain these results as the progressive destruction of three dimensional clusters in water by the hydrocarbon groups of the organic molecules. The thermodynamic equilibrium existing between the monomeric water molecules and the agregates is then shifted towards the monomers. The rupture of the agregates is a function of the increase of the hydrocarbon group of the organic compound. Thus, there is a greater solvation of the proton due to the liberation of non bonded water molecules (increase in f_{H_2O}).

According to Frank and Wen,[18] the unique properties of water are due to the existence of these 3- dimensional clusters. Consequently, their destruction gives the systems properties different than those of water. This is what we observed experimentally.

The system's increased order ($\Delta S < 0$) would no longer be due to H–bonding as in the case of the aqueous carbohydrate solutions but instead to hydrophobic forces. Hydrophobic bonding may be defined[21] as an interaction of molecules with each other which is stronger than the interaction of the separate molecules with water and which cannot be accounted for by covalent, electrostatic, H–bond or charge transfer forces. Thus the hydrocarbon groups of the molecules come together in aqueous solutions; the water molecules group around these agregates. In doing so, a new water structure is formed. These interactions do not imply H–bonding and the interactions themselves contribute to lessen H–bonds. This fact agrees with the variations in activity coefficients of water in the different systems (Fig. 5).

We accounted for the acidity of the aquo-organic systems by structural modifications of water because of addition of the organic solvent. We have shown that these structural modifications depended on the organic solvent and more particularly on the relative hydrophilic and hydrophobic character of the solvent.

EXPERIMENTAL

p-*Methoxy-α-methylstyrene.* *p*-Methoxyphenyl-2-hydroxy-2-propane was prepared by addition of MeMgBr on *p*-methoxyacetophenone followed by hydrolysis. The alcohol was *distilled in the presence of hydroquinone, giving p-methoxy-α*-methylstyrene ($Eb_2 = 90°C$). This was recrystallized from EtOH (mp = 32°C) and refrigerated.

Tri-p-*anisylmethanol.* This was prepared by oxidation of tri *p*-anisylmethane[22] with an equimolar amount of lead oxide in acetic acid (mp 82–82,5°).

Measurement of Ho.

$$Ho = pK_{BH^+} - \log \frac{(BH^+)}{(B)}$$

$$Ho = pK_{BH^+} - \log \frac{D_B - D}{D - D_{BH^+}}$$

D_B, D_{BH^+} and D represent respectively the optical densities of the indicator solutions under basic, acidic and measured conditions. The indicators used were *p*-nitraniline ($pK_{H_2O} = 0{\cdot}99$) and *m*-nitraniline ($pK_{H_2O} = 2{\cdot}50$).

Measurements of Ho were made with a thermostated D. B. Beckman UV Spectrophotometer at 25°.

Measure of H_R

$$H_R = pK_{R^+} + \log \frac{(ROH)}{(R^+)}$$

we used tri *p*-anisylmethanol ($pK = 0{\cdot}82$) as the indicator.

$$\frac{(ROH)}{(R^+)} = \frac{D_{R^+} - D}{D - D_{ROH}}$$

D_{R^+}, D_{ROH} et D represent respectively the optical densities of solutions of the indicator under acidic, basic and measured conditions.

Measurements of D_{R^+} and D were made with a maximum absorption of the indicator in the tested solutions.

Kinetic measurements. The hydration reaction of *p-methoxy-α*-methylstyrene in the aqueous acid homogeneous mixture was followed directly on the UV spectrum by the variation in the optical density of the olefin during transformation in the alcohol.

We considered the reaction as a first order reaction at least during two half-lives.

$$v = k_1 |\text{olefine}|_t = -d \frac{|\text{olefine}|_t}{dt}$$

$$\text{Log} \frac{|\text{olefine}|_t}{|\text{olefine}|_0} = \text{Log} \frac{D_t}{D_0} = k_1 t$$

The rate constant of hydration can be easily calculated by using the slope of the linear part of the graph $\log D_t = f(t)$. We used the Beckman UV Spectrophotometer at 25° for the kinetic measurements.

Determination of activity coefficients of water in different water alcohol solutions. We used the isopiestic method. Processes and apparatus used were as described by Scatchard.[23]† As reference solns, we employed either saccharose solns[24] or glycerol solutions.[23]

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†This apparatus has been constructed by M. G. Guiraud technician (C.N.R.S.).

Table 2. Isotonic concentrations at 25°C (moles/kg water)

Exp.	Saccharose	Glucose	Sorbitol	Xylitol	Glycerol	Ethylene glycol	1,3 proPanediol	1,4 butanediol	1,5 pentanediol	1,6 Hexatanediol	1,7 Heptanediol
1	2·82				3·45			3·87	4·13	4·42	6·49
2					3·57			4·22	4·70	5·65	11·19
3					4·43			5·29	6·11	9·66	23·78
4	3·66	4·76	4·65	4·91							
5	3·91								6·88	10·91	
6	3·92	4·91	5·02	5·14							
7	3·96				5·20	5·47	6·14	6·04	7·44		
8											
9	4·26				5·73	5·79	6·40	6·59	7·88		
10					5·82		6·59		8·42	15·12	
11					5·94		6·83	7·20	9·61	18·60	
12					8·32			11·67	17·20		
13					10·65			15·30			
14					15·90		20·50	25·47			

A correspondance between these last solns and the solns of saccharose was established by Scatchard.[23]

In Table 2 are indicated the concentrations of different isopiestic solutions and in Fig. 5 are found the rational activity coefficients of water f_{H_2O}, as a function of the molality of the alcohol.

Products. Ethylene glycol and 1,4-butane diol were distilled using a column packing with glass rings.

1,2-propane diol, 1,3-propane diol, glycerol, 1,5-pentane diol, 1,2,6-hexane triol and 1,6-hexane diol (Merck products).

1,7-heptane diol (Schuchardt product).

D(+) glucose, xylitol, adonitol, D(−) fructose D(−) sorbitol, D(−) mannitol (Merck products).

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