UNIVERSAL ACIDITY SCALE

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A new acidity scale is proposed for aqueous as well as nonaqueous solutions, based on the determination of individual activity coefficients of hydrogen ions from the rate constant of a specifically acid-catalysed reaction. The proposed acidity function is together with the medium effect for the hydrogen ion tabulated for mixed solvents 1,4-dioxane–water, methanol–water, ethanol––water, and propanol–water.

The problem of finding a universal acidity scale leads to determining the individual activity coefficient of hydrogen ions. This must be done for principal reasons in a nonthermodynamic way[1,2]. The present work is based on a new assumption that the ratio of the activity coefficients of a large acetal molecule and its protonated form is constant in a given medium[3,4].   It is a common postulate that an acidity scale should be an objective measure of the acidity of solutions in any solvent and at any ionic strength. We therefore accept the convention[3] which attributes the individual activity coefficient, γ_H, (corresponding to the transfer of hydrogen ions from a solution of zero ionic strength into the given solution) to the effect of the ionic strength, and the medium effect, $_m\gamma_H$, (corresponding to the transfer of H^+ ions from an aqueous medium into the given one) to the solvent. Equations for their calculation from the decreasing rate of the specifically acid-catalysed hydrolysis of certain aromatic acetals were derived in our preceding work[3] in the form

$$_m\gamma_H = \left(k'_m/k'_{H_2O} \right) \gamma_H^{H_2O} \gamma_H^m a_{H_2O} , \qquad (1)$$

$$\gamma_H = k'/k'^0 , \qquad (2)$$

where $\gamma_H^{H_2O}$ and γ_H^m denote individual activity coefficients of H^+ ions in an aqueous and in the studied medium, respectively, k'_{H_2O} and k'_m corresponding rate constants of the hydrolytic reaction, k' hydrolytic rate constant referred to a unit concentration of H^+ ions, and k'^0 its value extrapolated to zero ionic strength. With respect to the accepted convention, the equation for the new, universal acidity scale (pU)

can be written in the form

$$pU = -\log a_H = -\log \left(\gamma_{H\ m}\gamma_H c_H \right). \tag{3}$$

Here γ_H and $_m\gamma_H$ can be expressed from Eqs (1) and (2) (γ_H^m and $\gamma_H^{H_2O}$ is obtained from

TABLE I

Dependence of the Acidity Function pU on Volume Concentration of 1,4-Dioxane in Water at Selected Concentrations of HCl or HClO$_4$ (25°C)

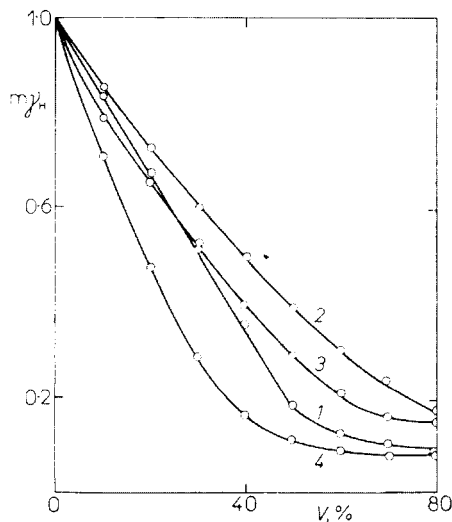| c_H	10^{-4}	10^{-3}	$5 . 10^{-3}$	10^{-2}
pH	4	3	2·301	2
V %		pU		
10	4·078	3·081	2·411	2·135
20	4·176	3·183	2·515	2·241
30	4·289	3·301	2·638	2·362
40	4·468	3·483	2·833	2·564
50	4·812	3·836	3·201	2·943
60	4·996	4·020	3·426	3·200
70	5·071	4·137	3·577	3·400
80	5·044	4·143	3·678	—

FIG. 1

Dependence of pU on Concentration of HClO$_4$ or HCl, c_H, for *1* 10, *2* 30, *3* 50, and *4* 70 Vol.% of 1,4-Dioxane at 25°C

TABLE II

Dependence of the Acidity Function pU on Volume Concentration of Ethanol in Water at Selected Concentrations of HCl (25°C)

c_H	$5 . 10^{-4}$	10^{-3}	$5 . 10^{-3}$	10^{-2}
pH	3·301	3	2·301	2

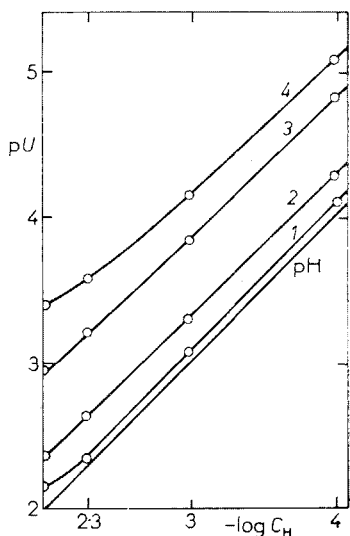| V %		pU		
10	3·406	3·106	2·456	2·184
20	3·490	3·194	2·519	2·248
30	3·586	3·298	2·622	2·354
40	3·710	3·425	2·753	2·476
50	3·855	3·572	2·914	2·652
60	3·998	3·710	3·091	2·824
70	4·128	3·839	3·222	2·932
80	4·161	3·893	3·225	2·996

FIG. 2

Dependence of pU on Concentration of HCl or HClO$_4$, c_H, for 50 Vol.%

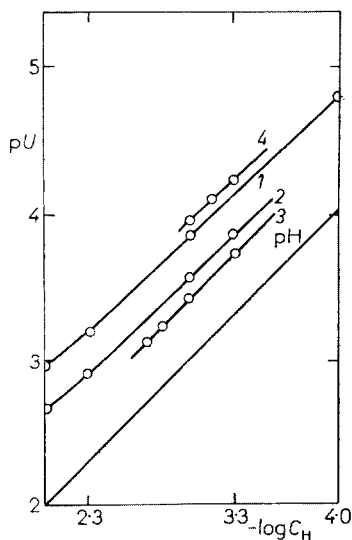*1* 1,4-Dioxane *2* Methanol, *3* Ethanol, and *4* n-Propanol at 25°C.

FIG. 3

Dependence of the Medium Effect for H$^+$ Ions, $_m\gamma_H$, on Volume Concentration of *1* 1,4-Dioxane, *2* Methanol, *3* Ethanol, *4* n-Propanol at 25°C.

Eq. (2) written for the aqueous and then for the given medium); after rearrangement we obtain finally

$$pU = \log\left(k'^0_{H_2O} a_{H_2O}\right) - \log k_m \,. \tag{4}$$

TABLE III

Dependence of the Acidity Function pU on Volume Concentration of Methanol in Water at Selected Concentrations of HCl (25°C)

c_H	$5 \cdot 10^{-4}$	$8 \cdot 10^{-4}$	10^{-3}	$1 \cdot 5 \cdot 10^{-3}$	$2 \cdot 10^{-3}$
pH	3·301	3·097	3·000	2·824	2·699
V %			pU		
10	3·375	3·170	3·074	2·900	2·778
20	3·443	3·240	3·144	2·971	2·849
30	3·518	3·317	3·221	3·049	2·927
40	3·611	3·409	3·315	3·144	3·023
50	3·712	3·511	3·418	3·245	3·124
60	3·828	3·629	3·538	3·366	3·246
70	3·932	3·735	3·638	3·470	3·353
80	4·083	3·879	3·812	3·654	3·685

TABLE IV

Dependence of the Acidity Function pU on Volume Concentration of n-Propanol in Water at Selected Concentrations of HCl or $HClO_4$ (25°C)

c_H	$5 \cdot 10^{-4}$	$7 \cdot 10^{-4}$	10^{-3}
pH	3·301	3·155	3·000
V %		pU	
10	3·451	3·310	3·151
20	3·629	3·482	3·331
30	3·850	3·710	3·562
40	4·101	3·958	3·810
50	4·260	4·112	3·969
60	4·377	4·231	4·090
70	4·422	4·277	4·131
80	4·423	4·278	4·140

TABLE V

Medium Effect of H^+ Ions $(_m\gamma'_H)$ at Different Volume Concentrations of Water in Binary Solvent Mixtures

25°C; *I* 1,4-dioxane, *II* methanol, *III* ethanol, *IV* n-propanol.

V % H_2O	*I*	*II*	*III*	*IV*
90	0·841	0·851	0·797	0·709
80	0·672	0·725	0·651	0·473
70	0·517	0·611	0·525	0·280
60	0·356	0·495	0·395	0·160
50	0·183	0·391	0·284	0·111
40	0·118	0·301	0·207	0·085
30	0·101	0·234	0·156	0·077
20	0·089	0·171	0·147	0·079

This equation, which is the definition of the new, universal acidity scale, shows that the acidity of any solution is obtained from a single experimental value of the rate constant k_m. The rate constant of the studied hydrolysis under standard conditions (*i.e.*, at infinite dilution), $k'^0_{H_2O}$, is characteristic for the given acetal and temperature, hence it has to be determined only once. The activity of water can be either found in the literature or replaced by the molar fraction.

RESULTS AND DISCUSSION

The rate constants were evaluated graphically from the time course of the concentration of the hydrolysis product, an aldehyde[3], obtained polarographically. The hydrolytic rate constants of 2-phenyl-1,3-dioxolane were measured in 1,4-dioxane–water[3,4], methanol–water[5], ethanol–water[6], and n-propanol–water[7] mixtures. In the case of 1,4-dioxane, also two other, similar acetals were employed[3,4]. Introducing these rate constants into Eq. (4) gives the acidity functions for these mixed solvents (Tables I – IV). In the case of 1,4-dioxane the rate constants for the three acetals were much different, nevertheless they led to the same values of pU, an evidence for the practical value of the proposed scale. The dependences of pU on the ionic strength in different media are shown in Figs 1 and 2.

To calculate the value of pU for other concentrations of H^+ ions, we proceed as follows. By comparing the individual activity coefficients and medium effects[3,4] it is seen that in the media under study the activity of diluted solutions is decisively influenced by the solvent used. If we consider only this influence, we can write Eq. (3)

in the form

$$pU \approx -\log\left({}_m\gamma_H c_H\right).\tag{5}$$

The error due to neglecting the individual activity coefficients is, *e.g.*, 0.7% for 10^{-3}M-HCl and 4.5% for 10^{-2}M-HCl in a 50% dioxane–water mixture. On the other hand, the pU value of 10^{-2}M-HCl changes by 32% when replacing pure water by 50% dioxane.

If the medium effect is known, the objective acidity can be assessed by using Eq. (5). The medium effects measured kinetically and calculated from Eq. (1) are given in Table V. It is seen from Fig. 3 that the dependence of the medium effect of the H^+ ions (and hence the acidity) does not change very much if the same part of one of the nonaqueous solvents used is added to a chosen amount of water. It seems therefore that the hydroxonium ion sets free a proton much easier than a protonated molecule of a nonaqueous solvent, *i.e.*, the acidity is due mainly to the hydroxonium ion. The decrease in the acidity of a solution in which the water is replaced gradually by another solvent can be attributed to the decrease in the concentration of hydroxonium ions. Fig. 3 shows also the dependence of the medium effect on the molecular mass of the alcohols used. The activity of H^+ ions solvated with a given solvent decreases with increasing molecular mass of the solvent.

The reliability of the individual activity coefficients depends on to what extent the nonthermodynamic assumption involved is justified[3]. With the proposed universal acidity scale, the rate of the specifically acid-catalysed reaction is in any case directly proportional to the activity of hydrogen ions, hence to the acidity. The fact that the state of the solution is in most cases best described by data obtained by chemical methods is a further support of the proposed scale.

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