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Abstract

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IONIZATION OF TRIPHENYLCARBINOL IN A SULFURIC ACID MEDIUM CONTAINING ISOPROPYL ALCOHOL

MEASUREMENT OF THE DEN0 ACIDITY FUNCTION

(Presented by Academician N. N. Semenov, 7 VIII 1959)

In connection with the growing interest in the kinetics and mechanism of acid-catalyzed reactions in nonaqueous and mixed solvents, a need has arisen for measurements of the values of acidity functions in these systems. Of especially great interest were measurements in alcohol-water media. The first quantitative studies (^{1}) devoted to this question showed that the dependence of the acidity function H_0 on the composition of the medium is very complex and does not lend itself to a simple interpretation from the standpoint of changes in the basicity of the medium, as had been possible in other, simplest cases (^{2}).

As Bartlett and Tsvetkova showed, the molar decrease of the acidity function H_0 in the systems H_2SO_4—H_2O (^{3,4}) and H_3PO_4—H_2O (^{4}) upon addition of isopropyl alcohol greatly exceeds the decrease caused by addition of water. An even more complex dependence of the acidity function on the composition of the medium was to be expected in the case of ionization of an indicator of the triphenylcarbinol type (^{5}), with elimination of a water molecule:

$$\mathrm{Ph_3COH} + \mathrm{H^+} \overset{K_{\mathrm{ArOH}}}{\rightleftarrows} \mathrm{Ph_3C^+} + \mathrm{H_2O}, \qquad K_{\mathrm{ArOH}} = \frac{a_{\mathrm{H^+}} a_{\mathrm{Ph_3COH}}}{a_{\mathrm{H_2O}} a_{\mathrm{Ph_3C^+}}}. \qquad (1)$$

Data on the value of the acidity function C_0 for mixed solvents are absent from the literature. Values of the J_0 function were obtained by Gold and Hawes (^{5}) for the system H_2SO_4—H_2O—CH_3COOH.

In the present work the dependence of the Den0 acidity function C_0 of sulfuric acid (43—60% H_2SO_4) on the concentration of added isopropyl alcohol (from 0.2 to 1.5 mole/liter) was measured at temperatures of 40, 54, and 60°. Triphenylcarbinol, which ionizes in acid according to equation (1) (^{5}), served as the indicator in the measurements. The acidity function of solutions containing various concentrations of alcohol was calculated from the equation

$$C_{0i} = \mathrm{p}K_{\mathrm{ArOH}} + \lg I_i, \tag{2}$$

where K_{ArOH} is the equilibrium constant of the reaction in the system $\mathrm{H_2SO_4}$—$\mathrm{H_2O}$, and

$$I_i = \frac{[\mathrm{Ph_3COH}]_i}{[\mathrm{Ph_3C^+}]_i}$$

is the indicator ratio at the i-th concentration of alcohol; the concentrations of the species are indicated in square brackets. The indicator ratio I_i was determined spectrophotometrically at $\lambda_{\mathrm{max}}432\ \mathrm{m}\mu$, in the region where only the ionized form absorbs, and, according to the Lambert–Beer law, the measured optical density $D = \varepsilon l[\mathrm{Ph_3C^+}]$. The concentration $[\mathrm{Ph_3COH}]$ was found from the material-balance equation. Measurements were carried out on a recording double-beam spectrophotometer of the SF-2M type in cuvettes 5 cm long, placed in a thermostated cuvette holder. Direct measurement of the equilibrium optical density D_i for the system $\mathrm{H_2SO_4}$—$\mathrm{H_2O}$—i-$\mathrm{C_3H_7OH}$ is made difficult by the fact that, when isopropyl alcohol is added to a solution of triphenylcarbinol in sulfuric acid, a pseudo-first-order reaction occurs, causing–

···decrease in optical density with time. Therefore the density D_i was found by extrapolating straight lines in the coordinates $\lg D$—t to the initial moment of time ($t = 0$) (see Fig. 1).

In calculating I_i for a system containing alcohol, it is necessary to take into account the change in the specific gravity of sulfuric acid upon addition of alcohol to it.

Fig. 1. Plot for calculating the initial optical density at $t = 40°$; 50.96% H_2SO_4 and $C_{\mathrm{sp}} = 0.5$ mol/l

Fig. 2. Plot for determining the pK of triphenylcarbinol at $t = 40°$

Fig. 3. Dependence of the acidity function C_0 on the concentration of added alcohol at $t = 40°$; 50.46% H_2SO_4

For this purpose we used the formula proposed in the work of V. I. Tsvetkova (4):

$$d_i = d_0(1 - 0.054\,C_{\mathrm{sp}}),$$

where d_0 is the specific gravity of the initial sulfuric acid; d_i is the specific gravity of the acid containing isopropyl alcohol; C_{sp} is the concentration of alcohol in gram-moles per 1000 g of the initial sulfuric acid. For calculations of C_0 by equation (2) we used values obtained in the H_2SO_4—H_2O system not containing u-C_3H_7OH, assuming that in the concentration interval of isopropyl alcohol studied (from 0.2 to 1.5 mol/l) the value pK_{ArOH} practically does not change. The values of pK_{ArOH} at elevated temperatures, which are absent from the literature, were measured by us in a special series of experiments at 30, 40, 50, and 60°. The values of pK_{ArOH} were found graphically from the dependence of $\lg I$ on C_0 at $\lg I = 0$, according to equation (2). Table 1 gives the dependence of $\lg I$ on C_0 and the values of pK_{ArOH} for 30, 40, 50, and 60°. Fig. 2 presents

Table 1

Dependence of the indicator ratio on the concentration of H_2SO_4

$t =$ 30°			$t =$ 40°			$t =$ 50°			$t =$ 60°		
H_2SO_4, %	C_0	$\lg I$	H_2SO_4, %	C_0	$\lg I$	H_2SO_4, %	C_0	$\lg I$	H_2SO_4, %	C_0	$\lg I$
43.22	−5.37	+1.416	44.35	−5.55	+0.524	46.78	−5.96	+0.482	43.19	−5.24	+0.776
45.05	−5.65	+0.78	44.90	−5.64	+0.845	47.80	−6.13	+0.086	43.29	−5.27	−0.627
46.95	−6.00	+0.495	47.28	−6.05	+0.356	48.72	−6.29	−0.104	45.10	−5.67	+0.491
48.22	−6.21	+0.182	48.66	−6.29	−0.04	50.43	−6.59	−0.414	47.33	−6.04	+0.160
49.17	−6.38	+0.083	49.90	−6.51	−0.213	52.01	−6.89	−0.746	49.42	−6.40	−0.20
50.66	−6.65	−0.286	50.48	−6.62	−0.396	53.47	−7.17	−1.062	51.44	−6.77	−0.60
52.06	−6.92	−0.782	51.46	−6.81	−0.599	54.50	−7.38	−1.242	52.14	−6.90	−0.744
53.89	−7.31	−1.194	53.42	−7.19	−0.942	55.60	−7.61	−1.638	53.28	−7.11	−0.895
55.62	−7.67	−1.95	55.70	−7.67	−1.773				54.19	−7.27	−0.985
56.72	−7.95								55.02	−7.47	−1.477
57.59	−8.16								56.10	−7.70	−1.645
	$pK =$ −6.38			$pK =$ −6.31			$pK =$ −6.21		57.34	−7.97	
										$pK =$ −6.17	

Table 2

Temperature dependence of the acidity function of the medium C_0 on the concentration of added alcohol

C_{sp}, mol/l	C_0	C_{sp}, mol/l	C_0	C_{sp}, mol/l	C_0	C_{sp}, mol/l	C_0
$t = 40°$ $C_{\mathrm{H_2SO_4}} =$ 48.18%		$t = 40°$ $C_{\mathrm{H_2SO_4}} =$ 50.46%		$t = 40°$ $C_{\mathrm{H_2SO_4}} =$ 51.46%		$t = 40°$ $C_{\mathrm{H_2SO_4}} =$ 53.42%	
0	−6.21	0	−6.62	0	−6.81	0	−7.19
0.16	−6.01	0.13	−6.69	0.07	−6.83	0.10	−7.16
0.32	−6.01	0.16	−6.69	0.096	−6.84	0.14	−7.18
0.43	−5.84	0.21	−6.60	0.19	−6.79	0.144	−7.19
0.59	−5.81	0.22	−6.62	0.195	−6.81	0.19	−7.09
0.69	−5.79	0.48	−6.49	0.21	−6.69	0.45	−7.02
0.71	−5.61	0.53	−6.46	0.250	−6.77	0.47	−6.96

C_{sp}, mol/l	C_0	C_{sp}, mol/l	C_0	C_{sp}, mol/l	C_0	C_{sp}, mol/l	C_0
$C_{H_2SO_4}$ = 49.30%		0.60	−6.40	0.28	−6.77	0.48	−7.02
0	−6.41	0.65	−6.35	0.31	−6.71	0.83	−6.87
0.31	−6.01	0.715	−6.31	0.44	−6.73	$C_{H_2SO_4}$ = 58.60%	
0.33	−6.10	0.84	−6.26	0.75	−6.38	0	−8.39
0.36	−6.13	0.97	−6.16	0.76	−6.45	0.19	−8.09
0.46	−6.14	1.99	−5.93	1.38	−6.09	0.80	−7.94
0.68	−6.01						
$t = 54°$		$t = 54°$		$t = 60°$		$t = 60°$	
$C_{H_2SO_4}$ = 46.76%		$C_{H_2SO_4}$ = 51.57%		$C_{H_2SO_4}$ = 44.24%		$C_{H_2SO_4}$ = 49.37%	
0	−5.94	0	−6.79	0	−5.46	0	−6.40
0.30	−5.78	0.305	−6.45	0.25	−5.24	0.23	−6.25
0.40	−5.66	0.49	−6.44	0.36	−5.34	0.35	−6.19
0.51	−5.66	0.60	−6.31	0.37	−5.27	0.37	−6.195
0.66	−5.50	$C_{H_2SO_4}$ = 52.34%		0.40	−5.28	0.44	−6.12
$C_{H_2SO_4}$ = 49.55%		0	−6.95	0.48	−5.26	0.46	−6.14
0	−6.42	0.39	−6.78	0.49	−5.25	0.47	−6.13
0.29	−6.21	0.53	−6.39	$C_{H_2SO_4}$ = 46.55%		0.48	−6.13
0.46	−6.13	0.49	−6.66	0	−5.91	$C_{H_2SO_4}$ = 51.26%	
0.46	−6.15	0.55	−6.51	0.18	−5.78	0	−6.74
0.60	−5.99	0.70	−6.57	0.29	−5.81	0.28	−6.62
0.63	−6.00	$C_{H_2SO_4}$ = 54.14%		0.40	−5.73	5.38	−6.50
$C_{H_2SO_4}$ = 50.70%		0	−7.30	0.53	−5.63	0.51	−6.55
0	−6.65	0.29	−7.18	0.54	−5.66		
0.31	−6.42	0.51	−7.16	$C_{H_2SO_4}$ = 46.88%			
0.52	−6.35	0.68	−7.24	0	−5.97		
0.64	−6.31			0.49	−5.78		
0.77	−6.23			0.51	−5.76		
				0.53	−5.76		

the graph of such a dependence for 40°. The tangent of the angle of inclination of the straight line is close to unity.

The values of the acidity function C_0 needed to find pK_{ArOH} at temperatures of 30, 40, 50, and 60° are absent from the literature. To calculate them we used

Fig. 4

Figure 1: Fig. 4

the well-known formula (3)

$$C_0 = H_0 + \lg a_{H_2O} + \lg \frac{f_{ArC^+}}{f_{ArOH_2{}^+}}, \tag{3}$$

where a_{H_2O} is the thermodynamic activity of water, and $f_{ArC^+}/f_{ArOH_2{}^+}$ is the ratio of the activity coefficients of the carbonium ion and of the protonated carbinol. In calculations by formula (3), the values of H_0 at different temperatures were taken from work (^{6}). The values of a_{H_2O} for the system H_2SO_4—H_2O were calculated from tabular data (^{9}) from the vapor pressures of water over sulfuric acid (p) and water (p_S). The last term in equation (3) was taken as temperature-independent. Its value for different concentrations of H_2SO_4 at 25° was taken from Deno' s work (^{7}).

Fig. 4. Dependence of the parameter n on the acidity function C_0 of the initial acid at $t = 40°$

From the data of Table 1, the values of the heat and entropy of protonation of triphenylcarbinol in the H_2SO_4—H_2O system were calculated; these

respectively equal to $\Delta H = 3280 \pm 100$ kcal/mole and $\Delta S = -18.4 \pm 0.10$ cal/mole • deg, whence

$$2.3RpK_{ArOH} = -\frac{3280}{T} - 18.4.$$

Table 2 presents the values of the acidity function C_0 of sulfuric acid of various concentrations with additions of isopropyl alcohol, calculated from equation (2).

Despite the fact that the accuracy of the data obtained does not exceed 20%, and near 60% H_2SO_4, where the values of C_{Ph_3COH} are very small, the error sometimes reaches 100%, the following regularities can clearly be established.

The acidity function C_0, like H_0, decreases with increasing concentration of alcohol in the system according to a linear law (Fig. 3)

$$\Delta C_0 = C_{0i} - C_0 = nC_{\text{sp}}. \tag{4}$$

Table 3

Dependence of the parameter n on the acidity C_0 of the initial acid

$t = 40°$		$t = 54°$		$t = 60°$	
C_0	n	C_0	n	C_0	n
−6.21	0.755	−5.94	0.565	−5.46	0.496
−6.41	0.700	−6.42	0.455	−5.91	0.380
−6.62	0.626	−6.65	0.334	−5.97	0.320
−6.81	0.610	−6.79	0.310	−6.40	0.53
−7.19	0.456	−6.95	0.285	−6.74	0.21
−8.39	0.247				

This dependence has a more abrupt character than the dependence for H_0. The values of n decrease with increasing concentration of the initial acid and with temperature; moreover, as is seen from Fig. 4, within one temperature the relation

$$n = a(C_0 + A), \tag{5}$$

is satisfied, where C_0 refers to the initial H_2SO_4.

For example, at 40°, $a = 0.304$, $A = 8.69$; at 54°, $a = 0.281$, $A = 7.93$, and at 60°, $a = 0.228$, $A = 7.60$. The dependence of n on C_0 for three temperatures is presented in Table 3 and for $t = 40°$ in Fig. 4.

The change in the character of the dependence between C_{0i} and C_{sp} in the investigated range of temperatures and concentrations of H_2SO_4 is in accord with the hypothesis that the effect of added alcohol on the acidity of the acid-water system is reduced mainly to the destruction of hydrogen bonds in the structure of water and thereby to an increase in the basicity of its molecules ([1,8,10]). If this is so, then an increase in temperature, as well as an increase in acid concentration, should lead to a decrease in the degree of association of water molecules and thus contribute to a reduction of the influence of alcohol on the change in the structure of the solvent, and hence on its basicity. This consequence of the hypothesis is confirmed by the data obtained: a decrease in n with increasing concentration of H_2SO_4 and a decrease in the parameters a and A with temperature. The difference in the behavior of C_0 and H_0 ([3,4]) upon addition of alcohol to the acid is associated with the influence of alcohol on the thermodynamic activity of unionized water; the alcohol added to the H_2SO_4-H_2O system binds part of the acid, thereby liberating water and increasing a_{H_2O}. An increase in a_{H_2O} leads to a decrease in C_0.

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Note: Figure translations are in progress. See original paper for figures.