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Abstract

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On the Problem of Reducing Basicities to a Single Standard State.

Investigation of the Basicity of Acetone

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In considering a number of problems of the kinetics, mechanism, and equilibrium of heterolytic reactions in solutions, it is necessary to know the degree of protonation of a base in a solvent to which a strong acid has been added. This quantity can be calculated if the concentration basicity constant $K^s_{a\mathrm{B}}$ of the base B under the given conditions is known:

$$K^s_{a\mathrm{B}} = \frac{[\mathrm{B}]}{[\mathrm{BH}^+]} a_{\mathrm{H}^+} \tag{1}$$

and the value of the proton activity a_{H^+}. Since there are no free protons in solution, a_{H^+} does not have such a direct physical meaning as, for example, a_{Cl^-}. In passing from one solvent to another, a_{H^+} in the general case cannot be equated to the activity of the solvated proton, since the discussion concerns particles of different composition and structure, depending on the solvent. Therefore a precise definition must be given to the quantity a_{H^+}, which can be done in the following way ([1,2]):

$$a_{\mathrm{H}^+} = K^0_{a\mathrm{S}} \frac{[\mathrm{SH}^+]}{[\mathrm{S}]} \frac{\gamma_{0\,\mathrm{SH}^+}}{\gamma_{0\,\mathrm{S}}} = K^0_{a\mathrm{B}} \frac{[\mathrm{BH}^+]}{[\mathrm{B}]} \frac{\gamma_{0\,\mathrm{BH}^+}}{\gamma_{0\,\mathrm{B}}} = \dots, \tag{2}$$

where [S], [B], $[\mathrm{SH}^+]$, $[\mathrm{BH}^+]$ are the concentrations of the bases S, B and of their conjugate acids SH^+ and BH^+; γ_0 are unified zero activity coefficients ([3]); $K^0_{a\mathrm{S}}$ and $K^0_{a\mathrm{B}}$ are the thermodynamic basicity constants of the bases S and B, respectively. In the standard solvent, taken to be water, $\gamma_{0\,\mathrm{H_3O^+}} = \gamma_{0\,\mathrm{H_2O}} = \gamma_{0\,\mathrm{B}} = \gamma_{0\,\mathrm{BH}^+} = 1$, $a_{\mathrm{H}^+} = [\mathrm{H_3O^+}]$, and, consequently, $K^0_{a\mathrm{H_2O}} = [\mathrm{H_2O}]$ and $K^0_{a\mathrm{B}} = K^0_{a\mathrm{B}}$.

To calculate the value of $K^0_{a\mathrm{B}}$ in some arbitrary solvent S, it is necessary to know the quantities: $K^0_{a\mathrm{S}}$, $K^0_{a\mathrm{B}}$, $K^s_{a\mathrm{S}}$, $\gamma_{0\mathrm{S}}$, $\gamma_{0\mathrm{B}}$, $\gamma_{0\mathrm{SH}^+}$, and $\gamma_{0\mathrm{BH}^+}$, since

$$K^s_{a\mathrm{B}} = \frac{K^0_{a\mathrm{B}}}{K^0_{a\mathrm{S}}} K^s_{a\mathrm{S}} \frac{\gamma_{0\mathrm{S}}\gamma_{0\mathrm{BH}^+}}{\gamma_{0\mathrm{SH}^+}\gamma_{0\mathrm{B}}}. \tag{3}$$

Usually only the numerical values of $K^0_{a\mathrm{B}}$ and $K^s_{a\mathrm{S}}$ are known. In the case of media in which the concept of the acidity function H_0 can be used, the calculation is considerably simplified because ratios of the type $\gamma_{0\mathrm{B}}/\gamma_{0\mathrm{BH}^+}$ are equal for all bases (^{4}). However, in most organic solvents this condition is not fulfilled, and such a method of calculation cannot be used.

In the present work, acetone was chosen as the nonstandard solvent and *p*-nitroaniline as the base B.

The values of $K^0_{a_\mathrm{B}}$ for *n*-nitroaniline at various temperatures are given in work (5). The quantity $K^s_{a_\mathrm{B}}$ was determined by one of us jointly with V. H. Maymber (6) and is equal to

$$\mathrm{p}K^s_{a_\mathrm{B}} = \frac{7150}{4.575T} - \frac{17.78}{4.575}. \tag{4}$$

The basicity of acetone in aqueous solutions for the purpose of determining $K^0_{a_S}$ was studied by us by several methods. Measurement of the ultraviolet absorption spectra of acetone made it possible to determine only the order of magnitude of $K^0_{a_S}$ ($-\mathrm{p}K^0_{a_S} = 0.2 \div 1.2$), since the molar extinction coefficient of the protonated form of acetone did not remain constant with increasing concentration of HCl or H_2SO_4 (7). A study of the kinetics of bromination of acetone gave values of $K^0_{a_S}$ of the same order (7, 8). Taking into account the magnitude of possible experimental errors and the approximations made, a more precise value of $K^0_{a_S}$ could not be calculated from the kinetic data.

In this connection we developed a new procedure for determining the basicity of electroneutral bases B in H_2O–HCl and H_2O–H_2SO_4 media, based on the different electrical conductivities of the ions H_3O^+ and BH^+. The experimental work was carried out with an apparatus for measuring the electrical conductivities of electrolytes designed by V. A. Reben, which made it possible to measure the resistance of electrolytes under the conditions of our experiments with a sensitivity of $\pm 5 \cdot 10^{-3}\%$ at a frequency of 10^3 Hz.

The experimental part of the work was reduced to measuring the resistances of well-thermostated ($\pm 0.003^\circ$) aqueous solutions of HCl or H_2SO_4 before and after the addition to them of small amounts (1-2%) of the base B under investigation. The effect of base B on the electrical conductivity of the acid solution was characterized by the quantity

$$y = \frac{1}{[\mathrm{B}]_0}\left(\frac{k}{R_0 + \Delta R} - \frac{k}{R_x}\right) = \frac{1}{[\mathrm{B}]_0}(\chi_1 - \chi_2), \tag{5}$$

where k is the cell constant (in cm^{-1}); $[\mathrm{B}]_0$ is the concentration of the added base (in mol/l); R_0 and R_x are the resistances of the electrolyte before and after addition of base B; ΔR is the change in the resistance of the electrolyte due to dilution of the solution (in ohms). In calculating the value of ΔR, we proceeded from the change in the resistance of the electrolyte upon addition, instead of base B, of the corresponding volume of pure water. In order to reduce the volume of added acetone to the equivalent volume of water, the contraction of the solution was also taken into account. The quantity $k/(R_0 + \Delta R) = \chi_1$ is the expected value of the specific electrical conductivity of the solution if dilution with base B is equivalent to dilution with an equivalent volume of water. The experimentally measured values of the specific electrical conductivity of the solution $k/R_x = \chi_2$ do not coincide with the expected quantity χ_1; in this case the difference $\chi_1 - \chi_2$ is proportional to the concentration of the added base B. Assuming that the difference between χ_1 and χ_2 is caused by protonation of base B, we have:

$$1000(\chi_1 - \chi_2) = [\mathrm{BH}^+](\lambda_{\mathrm{H_3O^+}} - \lambda_{\mathrm{BH^+}}), \tag{6}$$

where $\lambda_{\mathrm{H_3O^+}}$ and $\lambda_{\mathrm{BH^+}}$ are the equivalent conductivities of $\mathrm{H_3O^+}$ and $\mathrm{BH^+}$, respectively. The difference between χ_1 and χ_2 is caused by the difference in the equivalent conductivities of the ions $\mathrm{H_3O^+}$ and $\mathrm{BH^+}$. In this case $\lambda_{\mathrm{H_3O^+}} > \lambda_{\mathrm{BH^+}}$, as should be expected. Substituting (6) into (5), we obtain

$$y = \frac{[\mathrm{BH}^+]}{[\mathrm{B}]_0}(\lambda_{\mathrm{H_3O^+}} - \lambda_{\mathrm{BH^+}}) \cdot 10^{-3}, \tag{7}$$

where $[\mathrm{B}]_0 = [\mathrm{B}] + [\mathrm{BH}^+]$. Equation (7) makes it possible to determine the value of $[\mathrm{B}]/[\mathrm{BH}^+]$ as a function of the acidity of the medium, if $\lambda_{\mathrm{H_3O^+}} - \lambda_{\mathrm{BH^+}}$ remains practically constant within the concentration limits considered.

HCl and $\mathrm{H_2SO_4}$. Then the quantity $\lambda_{\mathrm{H_3O^+}} - \lambda_{\mathrm{BH^+}}$ can be determined if $[\mathrm{BH}^+] \gg [\mathrm{B}]$ and $[\mathrm{BH}^+] \simeq [\mathrm{B}]_0$, which is observed at medium acidities $H_0 < pK_{a_B} - 1$. The value $(\lambda_{\mathrm{H_3O^+}} - \lambda_{\mathrm{BH^+}}) \cdot 10^{-3}$ was taken to be equal to the maximum value of y, since in some cases, upon a further increase in the concentration of HCl or $\mathrm{H_2SO_4}$ after the maximum value of y has been reached, y begins to decrease.

In order to test the method described, values of $pK^0_{a_B}$ were determined for n- and o-nitroanilines. The values obtained agree well with the values given in (5) (see Table 1 and Fig. 1), which confirms the applicability of the method for determining the basicity constants of electrically neutral bases. In this connection, the procedure was used to determine the basicity constant of acetone. The values of pK^0_{as} obtained at different temperatures are given in Table 1 and are described by the relation:

$$pK^0_{as} = \frac{2624}{4.575T} - \frac{11.89}{4.575}. \tag{8}$$

Fig. 1. Dependence of y on the acidity of the medium. 1 —n-nitroaniline at 40° in the H_2O—HCl system; 2 —o-nitroaniline at 60° in the H_2O—H_2SO_4 system; 3 —acetone at 25° in the H_2O—HCl system

The obtained values of pK^0_{as} (8) were substituted into the equation describing the kinetics of acetone bromination (8). Taking into account the influence of activity coefficients, i.e., taking $f_{\mathrm{SH}^+} f_{\mathrm{Cl}^-}/f_{\neq} = f_{\mathrm{BH}^+} f_{\mathrm{Cl}^-}/f_{\mathrm{B}}$, the values k_1 were calculated. The quantities $f_{\mathrm{BH}^+} f_{\mathrm{Cl}^-}/f_{\mathrm{B}}$ were taken from (1). The largest deviations of the calculated values k_1 from the experimental ones are observed in the region $-H_0 = 0.5 \div 2.0$, but they are not more than 30% of $k_{1,\mathrm{exp}}$ at 35° and not more than 50% at 15°. As a result of applying activity coefficients to refine the calculation, new values of $k_{\mathrm{H_2O}}$ and k_{Cl^-} were obtained, differing from those given in (8): $k_{\mathrm{H_2O}} = 6.96 \cdot 10^{10} e^{-22340/RT}$ and $k_{\mathrm{Cl}^-} = 8.20 \cdot 10^6 e^{-15190/RT}$.

Table 1

Basicity constants of n- and o-nitroanilines and acetone

Base and medium	Temp., °C	$pK^0_{a_B}$, by electrical conductivity method	$pK^0_{a_B}$, spectrophotometrically (5)
n-Nitroaniline in the H_2O—HCl system	40	+0.90	+0.91
o-Nitroaniline in the H_2O—H_2SO_4 system	60	−0.49	−0.43
Acetone in the H_2O—HCl system	5	−0.55	
Acetone in the H_2O—HCl system	15	−0.60	
Acetone in the H_2O—HCl system	25	−0.66	
Acetone in the H_2O—HCl system	40	−0.81	

It should be noted that the proton-transfer reaction from H_3O^+ to acetone is not exothermic, as we reported earlier in (8), but endothermic: $-\Delta H_0 = 2.6$ kcal/mol.

We also determined values of γ_0 for n-nitroaniline, on the basis of the corresponding solubilities and distribution coefficients. It was

a "chain" of solutions of p-nitroaniline in the solvents acetone—glycerin—CCl_4—water was used, according to the scheme: pure acetone—(1)—saturated solution of glycerin in acetone—(2)—saturated solution of acetone in glycerin—(3)—pure glycerin—(4)—saturated solution of CCl_4 in glycerin—(5)—saturated solution of glycerin in CCl_4—(6)—p-nitroaniline (solid phase)—(7)—water. Transitions 2, 5, 6, and 7 were investigated experimentally; the remaining ones were calculated on the basis of the assumption that the solution is ideal. The obtained values of $\gamma_{0\mathrm{B}}$ are given in Table 2.

Table 2

Values of $\gamma_{0\mathrm{B}}$, $\gamma_{0\mathrm{S}}$ and $\gamma_{0\mathrm{SH}^+}/\gamma_{0\mathrm{BH}^+}$

Temp., °C	$\gamma_{0\mathrm{B}} \cdot 10^3$	$\gamma_{0\mathrm{S}}$	$\gamma_{0\mathrm{SH}^+}/\gamma_{0\mathrm{BH}^+}$
15.0	0.93	0.70	5700
25.0	1.11	0.67	3550
35.0	1.86	0.64	1500
45.0	3.04	0.61	600

In addition, the values of $\gamma_{0\mathrm{S}}$ were calculated according to equation (9), from the equilibrium between liquid and vapor in the acetone—water system; the corresponding data were taken from (9-12):

$$\gamma_{0\mathrm{S}} = \frac{p_{\mathrm{S}0}}{[\mathrm{S}]^s} \lim_{[\mathrm{S}]\to 0} \frac{[\mathrm{S}]}{p_\mathrm{S}}, \tag{9}$$

where $p_{\mathrm{S}0}$ is the vapor pressure of acetone over pure acetone, $[\mathrm{S}]^s$ is the concentration of pure acetone (in mol/l); [S] is the concentration of acetone in its aqueous solution (in mol/l), and p_S is the vapor pressure of acetone over its aqueous solution. The obtained values of $\gamma_{0\mathrm{S}}$ are given in Table 2.

Using equations (3), (4), and (8), and taking for $\gamma_{0\mathrm{B}}$ and $\gamma_{0\mathrm{S}}$ the values given in Table 2, we calculated the values of $\gamma_{0\mathrm{SH}^+}/\gamma_{0\mathrm{BH}^+}$ (see Table 2). In doing so, the values of $K^0_{a_\mathrm{B}}$ were taken from (5).

Thus, the change in the value of the dissociation constant of the acid p-NO_2—C_6H_4—NH_3^+ upon transition from an aqueous solution to a solution in acetone is associated with a change in all the activity coefficients entering formula (3); at the same time, no mutual compensation occurs in the change of $\gamma_{0\mathrm{S}}$ and $\gamma_{0\mathrm{B}}$, as well as $\gamma_{0\mathrm{SH}^+}$ and $\gamma_{0\mathrm{BH}^+}$. In this connection, for solving the problem of calculating $K^s_{a_\mathrm{B}}$, knowledge of the quantities $K^0_{a_\mathrm{B}}$, $K^0_{a_\mathrm{S}}$, $K^s_{a_\mathrm{S}}$, $\gamma_{0\mathrm{B}}$ and $\gamma_{0\mathrm{S}}$ is insufficient; an experimental determination or calculation of the ratio $\gamma_{0\mathrm{SH}^+}/\gamma_{0\mathrm{BH}^+}$ is also necessary.

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