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Abstract

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Kinetics of Hydrolysis of δ-Valerolactam and the Alkalinity Function of Aqueous Solutions of LiOH, NaOH, CsOH

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For the correct interpretation of the mechanism of reactions in alkaline media, the establishment of an alkalinity function, analogous to Hammett' s acidity function for acidic media, is of great importance. As is known, the acidity function is measured by the indicator method. In the present work, the alkalinity function of aqueous solutions of hydrazine ([1]) and diethylamine ([2]) was measured by the indicator method. Schwartzenbach ([3]) attempted by an analogous method to determine the alkalinity function of aqueous solutions of KOH and NaOH. However, his data cannot be used for quantitative characterization, since in the measurements the indicator and the solution under investigation were in different phases; moreover, it was not proved how the indicators he used ionize in alkaline media. We also undertook an attempt to determine the alkalinity function by the indicator method. A series of nitrobenzenes and nitroanilines was investigated. These compounds were characterized by extremely low solubility in alkali and, in addition, during the measurements there was a shift of the absorption maximum with the alkali concentration, which did not allow these compounds to be used as indicators.

In view of the impossibility of determining the alkalinity function by the indicator method, we decided to use a kinetic method for this purpose. In studying the alkaline hydrolysis of a series of lactams, aliphatic amides, and the decomposition of diacetone alcohol, it was established that for aqueous KOH solutions the mean ionic activity is the alkalinity of the medium and that the ratio of activity coefficients f_B/f_{BOH^-} does not depend on the nature of the reagent.

Table 1

Alkali, wt. %	T-ra, °C	K_{eff}, min^{-1}	Alkali, wt. %	T-ra, °C	K_{eff}, min^{-1}
LiOH	**LiOH**	**LiOH**	**LiOH**	**LiOH**	**LiOH**
0.68	25	$1.96 \cdot 10^{-3}$	6.39	25	$2.76 \cdot 10^{-2}$
0.68	40	$6.80 \cdot 10^{-3}$	10.40	25	$5.40 \cdot 10^{-2}$
0.68	50	$1.34 \cdot 10^{-2}$	10.40	40	$1.70 \cdot 10^{-1}$
2.60	25	$8.00 \cdot 10^{-3}$	10.40	50	$3.50 \cdot 10^{-1}$
2.68	25	$9.20 \cdot 10^{-3}$	10.40	60	$5.90 \cdot 10^{-1}$
NaOH	**NaOH**	**NaOH**	**NaOH**	**NaOH**	**NaOH**
1.46	25	$2.82 \cdot 10^{-3}$	20.47	15	$5.01 \cdot 10^{-2}$

Alkali, wt. %	T-ra, °C	K_{eff}, min^{-1}	Alkali, wt. %	T-ra, °C	K_{eff}, min^{-1}
5.06	25	$9.70 \cdot 10^{-3}$	20.47	25	$1.24 \cdot 10^{-1}$
5.06	40	$3.29 \cdot 10^{-2}$	20.47	40	$3.98 \cdot 10^{-1}$
5.06	50	$6.60 \cdot 10^{-2}$	20.47	50	$7.50 \cdot 10^{-1}$
5.06	60	$1.34 \cdot 10^{-1}$	26.97	25	$3.21 \cdot 10^{-1}$
9.21	25	$2.23 \cdot 10^{-2}$	30.65	25	$4.58 \cdot 10^{-1}$
CsOH	**CsOH**	**CsOH**	**CsOH**	**CsOH**	**CsOH**
4.62	40	$6.60 \cdot 10^{-3}$	16.51	40	$1.38 \cdot 10^{-2}$
4.62	50	$1.15 \cdot 10^{-2}$	16.51	50	$2.85 \cdot 10^{-2}$
4.62	60	$2.23 \cdot 10^{-2}$	16.51	25	$1.15 \cdot 10^{-2}$
4.62	70	$3.82 \cdot 10^{-2}$	16.51	40	$3.12 \cdot 10^{-2}$
8.08	25	$5.12 \cdot 10^{-3}$	16.51	50	$6.22 \cdot 10^{-2}$

In the present work, using the example of alkaline hydrolysis of δ-valerolactam, the alkalinity functions of aqueous solutions of LiOH, NaOH, and CsOH were determined by the kinetic method. The concentration interval for CsOH ranged from 4.62 to 16.51%, for NaOH from 1.46 to 26.97%, and for LiOH from 0.68 to 10.40%. Table 1 gives the values of the effective rate constants K_{eff} for various temperatures and alkali concentrations.

Experimental data on the alkaline hydrolysis of δ-valerolactam in KOH are described with satisfactory accuracy by the equation

$$\lg \frac{K_{\text{eff}}}{A_{\text{H}_2\text{O}}} + B_0 = \lg \frac{K_{\text{true}}}{K_p},$$

where K_{true} and K_p are, respectively, the true rate constant and the thermodynamic equilibrium constant of the process of addition of OH^- to the lactam, $A_{\text{H}_2\text{O}}$ is the thermodynamic activity of water, and

$$B_0 = -\lg A_{\text{OH}^-} \frac{f_{\text{B}}}{f_{\text{BOH}^-}}$$

is the alkalinity function.

Table 2

Alkali, wt. %	$\lg K_{\text{eff}}$	$\lg a_{\text{H}_2\text{O}}$	$-B_0$
LiOH	LiOH	LiOH	LiOH
0.68	−2.69		−0.61
2.60	−2.10	−0.01	0.12
2.68	−2.04	−0.01	0.06
4.00	−1.78	−0.02	0.21

Alkali, wt. %	$\lg K_{\text{eff}}$	$\lg a_{H_2O}$	$-B_0$
6.39	−1.56	−0.05	0.46
10.40	−1.27	−0.10	0.80
NaOH	NaOH	NaOH	NaOH
1.46	−2.55		−0.58
5.06	−1.98	−0.01	0.02
9.21	−1.65	−0.02	0.34
20.47	−0.90	−0.13	1.20
26.97	−0.48	−0.23	1.72
30.65	−0.34	−0.35	1.98
CsOH	CsOH	CsOH	CsOH
4.62	−2.66		−0.70
8.48	−2.29		−0.33
16.51	−1.94	−0.02	0.02

In determining the alkalinity function of aqueous solutions of LiOH, NaOH, and CsOH we assumed that the thermodynamic and kinetic parameters of the hydrolysis process of δ-valerolactam do not change on passing from one alkali solution to another, i.e., the value

$$\lg \frac{K_{\text{true}}}{K_p} = -1.96$$

must hold in LiOH, NaOH, and CsOH. This assumption is supported by the fact that, for a whole series of acid-catalytic processes investigated in various acidic media, the ratio

$$\frac{K_{\text{true}}}{K_p}$$

remains constant[(4)]. In addition, the effective activation energy of the hydrolysis process of δ-valerolactam in various alkalies is practically unchanged and is 14.0 ± 0.5 kcal $\cdot$ mol^{-1}. Thus, knowing

$$\frac{K_{\text{true}}}{K_p}$$

and determining K_{eff} and A_{H_2O} for LiOH, NaOH, and CsOH, one can readily calculate the values of B_0 for the corresponding alkalies. Table 2 gives the values of B_0 obtained in this way.

The alkalinity function of aqueous solutions of LiOH, NaOH, KOH, and CsOH can also be obtained by calculation, based on the following assumptions. In studies of the IR spectra of aqueous alkali solutions it was shown that the

hydroxyl ion strongly binds from two to three water molecules, whereas the cations are practically not hydrated[(5)].* The fact that the values of B_0 for different alkalies change in the same way with the molality of the solutions also confirms that B_0 does not depend on the nature of the cation and is determined mainly by the thermodynamic properties of the hydroxyl ion.

Fig. 1. Variation of experimental (1) and calculated (2) values of B_0 with the molality of LiOH, NaOH, KOH, and CsOH solutions.

Let us consider the process of addition of the hydroxyl ion to some substance B:

$$\mathrm{B} + \mathrm{OH}^-(\mathrm{H_2O})_n \overset{K_n}{\rightleftarrows} \mathrm{BOH}^- + n(\mathrm{H_2O}).$$

* In the present case, hydration manifested in the IR spectra is meant.

The thermodynamic equilibrium constant of this process is equal to

$$K_\mathrm{p} = \frac{A_\mathrm{B} \cdot A_{\mathrm{OH}^-(\mathrm{H_2O})_n}}{A_{\mathrm{BOH}^-} A^n_{\mathrm{H_2O}}}. \tag{1}$$

By definition, the alkalinity function is equal to

$$B_0 = -\lg K_\mathrm{p} + \lg \frac{C_\mathrm{B}}{C_{\mathrm{BOH}^-}}. \tag{2}$$

From equations (1) and (2) we obtain

$$-B_0 = \lg m_{\mathrm{OH}^-(\mathrm{H_2O})_n} - n \lg a_{\mathrm{H_2O}} + \lg \frac{f_\mathrm{B} f_{\mathrm{OH}^-(\mathrm{H_2O})_n}}{f_{\mathrm{BOH}^-}}. \tag{3}$$

It may be assumed that

$$\lg \frac{f_\mathrm{B} \cdot f_{\mathrm{OH}^-(\mathrm{H_2O})_n}}{f_{\mathrm{BOH}^-}} = \mathrm{const}.$$

Then

$$-B_0 = \lg m_{\mathrm{OH}^-(\mathrm{H_2O})_n} - n \lg A_{\mathrm{H_2O}} + \mathrm{const}. \tag{4}$$

The values of the hydration numbers "n" were taken from work (5), the values of $A_{\mathrm{H_2O}}$ in KOH and NaOH solutions from works (6, 7), and $A_{\mathrm{H_2O}}$ in LiOH was measured by us from the vapor pressure over LiOH solutions. The values of B_0 calculated from this equation for aqueous solutions of LiOH, NaOH, KOH,

and CsOH are in satisfactory agreement with the corresponding experimental values (Fig. 1).

Fig. 2. Change in $\lg K_{\text{eff}}$ for the decomposition process of diacetone alcohol relative to the values of B_0 for solutions of LiOH (3), NaOH (2), KOH (1)

In order to verify that the alkalinity function of aqueous alkali solutions is just as universal as Hammett' s acidity function, we attempted to apply it to other base-catalyzed reactions. Unfortunately, there is only one work in which the decomposition of diacetone alcohol in alkaline media was studied (7). As can be seen from Fig. 2, in the coordinates $\lg K_{\text{eff}}$—B_0 for KOH, NaOH, and LiOH solutions, a linear dependence is obtained.

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