# THE BASIC STRENGTH OF FURAN

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The best possible $pK_a$ value of furan was found spectrophotometrically using Hammett $H_0$ indicator method. The value came out to be —0.11. The problem of polymerization of furan in high concentration of acid solution has been overcome by extrapolation method.

Furan, pyrrole, indole, thiophene form a distinct class of aromatic heterocyclic compounds. In these aromatics there is an excess sharing of electrons on the four carbon atoms as against a deficiency in six-membered heterocyclics such as pyridine. According to Albert[1] the five-membered heterocyclic compounds are classed as π-excessive and the six-membered as π-deficient. Coulson and Longuet-Higgins[2] have determined theoretically that the carbon atoms in the π-excessive heterocyclics are negatively charged and the hetero atom acquires a slight positive charge. That is why these compounds have very low basicity as against the six-membered heterocyclics.

Recently Naqvi and Zaidi[3] have determined the basicity of 2-methylindole and found its value to be —1.9 by modification of Hammetts $H_0$ indicator method. Furan is a member of the same family of compounds and presents the same difficulty as 2-methylindole. The ready resinification of these compounds in acid media makes it difficult to determine the $pK_a$ value. Naqvi and Fernando[4] overcame this problem of resinification by studying the kinetics of resinification of pyrrole and obtained extrapolated values of the absorption in acid solution at zero time.

The $pK_a$ value of π-excessive aromatics apart from providing a reliable data, will also help to understand the chemistry of these compounds, acid–base behaviour, electrophilic substitution pattern etc.

## Experimental and Results

(i) Freshly distilled furan (Light & Co. Ltd), sulphuric acid (E. Merk Co.) having a purity of 98.98%, and cyclohexane and methanol (B.D.H. analytical grade) were used.

(ii) Hilgers UV and visible spectrophotometer model H-108 was used for spectrophotometric studies.

(iii) UV spectrum of furan, $10^{-4}$M, in cyclohexane was taken and found that the maximum lies at $223 \pm 1$ nm and the change of concentration did not alter the position. The absorption spectra of different concentration in water at $212 \pm 1$ nm were taken. The absorbancies are shown in Fig. 1. The furan solutions in $H_2SO_4$ were run in UV and
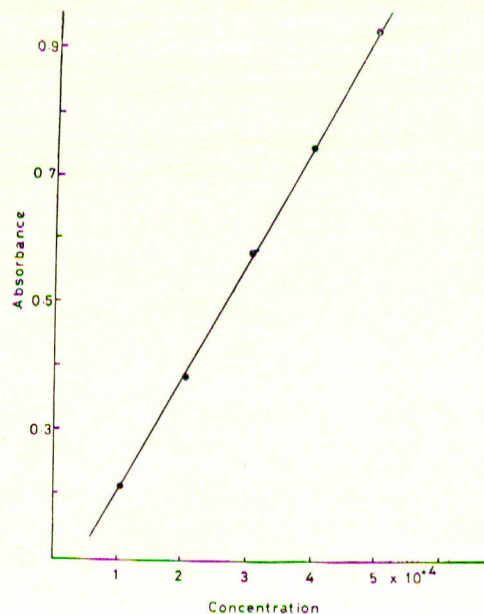


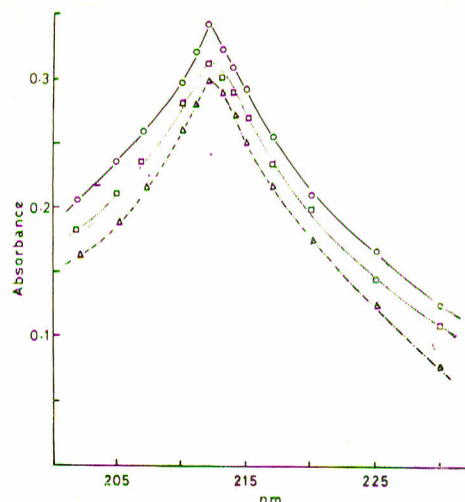Fig. 1.—The absorption of different concentration of furan in water at 212 nm, confirming the Beer's Law.



Fig. 2.—The absorption of furan in different concentration of acid viz. 0.3, 0.4, 0.5 molar $H_2SO_4$. The maxima at 212 nm.

the absorbancies were noted at different wavelengths (Fig. 2).

*Spectrophotometric Determination of* $pK_a$ *of Furan.*—
From $5 \times 10^{-2}$M solution of furan 5 ml were taken
and added to a series of volumetric flask of 500 ml
each, containing 455 ml of standard sulphuric acid
ranging from 0.11 to 3.3 molar-acid. A stop-
watch was started at the half delivery of furan in a
flask containing the acid solution. The solution
was at once shaken and the absorbancies were
noted at 221 nm with respect to time. The absorp
tion curves were obtained for each, values were
extrapolated to zero time (Table 1).

From the absorbancies between high and low
acid concentration, molar absorptivity of the un-

protonated furan in solutions that were between
0.10–0.40M in sulphuric acid, was determined
(Fig. 2). It was noted that furan is almost present
in the protonated form at acid concentrations of
1.5M but when the concentration of the acid was
more than 1M, polymerization started and made it
difficult to determine the molar absorptivity of the
protonated form. The $pK_a$ of furan was deter-
mined by Hammett's $H_0$ indicator[5] method.

$$H_0 = pK_a + \log (a - a_{BH^+})/(a_B - a)$$

Where $a$, $a_B$, $a_{HB+}$ are the molar absorbancies

TABLE 1(a).—VARIATION OF THE ABSORBANCE OF AN ACID SOLUTION OF FURAN ($5 \times 10^{-4}$M) WITH TIME.

| Time (min) | 3.3M | 2.75M | 2.2M | 1.65M | 1.32M | 1.1M | 0.99M |
|---|---|---|---|---|---|---|---|
| 0 | 0.718[a]* | 0.716[a] | 0.713[a] | 0.703[a] | 0.695[a] | 0.680[a] | 0.660[b] |
| 2 | 0.656 | 0.684 | 0.688 | 0.678 | 0.681 | 0.676 | 0.652 |
| 4 | 0.638 | 0.647 | 0.658 | 0.762 | 0.677 | 0.672 | 0.649 |
| 5 | 0.632 | 0.642 | 0.646 | 0.670 | 0.674 | 0.669 | 0.648 |
| 7 | 0.621 | 0.638 | 0.632 | 0.667 | 0.671 | 0.667 | 0.644 |
| 9 | 0.612 | 0.624 | 0.624 | 0.664 | 0.668 | 0.662 | 0.640 |
| 10 | 0.608 | 0.614 | 0.619 | 0.663 | 0.667 | 0.659 | 0.638 |
| 15 | 0.601 | 0.605 | 0.614 | 0.659 | 0.664 | 0.653 | 0.632 |
| 20 | 0.596 | 0.596 | 0.606 | 0.657 | 0.662 | 0.650 | 0.630 |
| 25 | 0.591 | 0.590 | 0.594 | 0.652 | 0.659 | 0.647 | 0.628 |
| 30 | 0.585 | 0.586 | — | 0.649 | 0.654 | — | — |
| 40 | 0.579 | 0.585 | 0.591 | 0.647 | — | 0.645 | 0.625 |
| 50 | — | — | — | — | — | — | — |
| 60 | — | 0.583 | — | 0.645 | — | — | 0.623 |
| 70 | — | — | 0.590 | — | 0.652 | — | — |
| 80 | — | — | — | — | — | 0.644 | 0.622 |

*a*, Absorbance values extraploted to zero time; $a^* = BH^+$; *b*, B

TABLE 1(b).—VARIATION OF THE ABSORBANCE OF AN ACID SOLUTION OF FURAN ($5 \times 10^{-4}$M) WITH TIME.

| Time (min) | Molarity of Acid | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0.825M | 0.77M | 0.66M | 0.55M | 0.275M | 0.22M | 0.11M |
| 0 | 0.637[a]* | 0.590[a] | 0.562[a] | 0.482[a] | 0.474[a] | 0.472[a] | 0.470[b] |
| 2 | 0.635 | 0.581 | 0.520 | 0.476 | 0.465 | 0.461 | 0.456 |
| 4 | 0.630 | 0.577 | 0.518 | 0.473 | 0.461 | 0.458 | 0.453 |
| 5 | 0.628 | 0.574 | 0.514 | 0.469 | 0.459 | 0.454 | 0.448 |
| 7 | 0.625 | 0.572 | 0.512 | 0.467 | 0.456 | 0.451 | 0.446 |
| 9 | 0.623 | 0.572 | 0.510 | 0.464 | 0.453 | 0.448 | 0.442 |
| 10 | 0.619 | 0.568 | 0.506 | 0.461 | 0.451 | 0.447 | 0.441 |
| 15 | 0.616 | 0.564 | 0.501 | 0.459 | 0.449 | 0.445 | 0.438 |
| 20 | 0.613 | 0.562 | 0.496 | 0.457 | 0.445 | — | 0.435 |
| 25 | 0.607 | 0.560 | — | — | — | 0.443 | 0.431 |
| 30 | 0.605 | 0.558 | — | 0.454 | 0.443 | — | 0.429 |
| 40 | — | — | 0.498 | 0.450 | — | 0.440 | 0.426 |
| 50 | — | 0.887 | — | — | 0.438 | — | 0.424 |
| 60 | 0.603 | — | 0.497 | — | — | 0.438 | — |
| 70 | 0.601 | 0.554 | 0.496 | 0.449 | 0.436 | — | 0.423 |
| 80 | — | — | — | 0.448 | — | — | — |

*a*, Absorbance values extraploted to zero time; $a^*$ BH$^+$ *b*, H
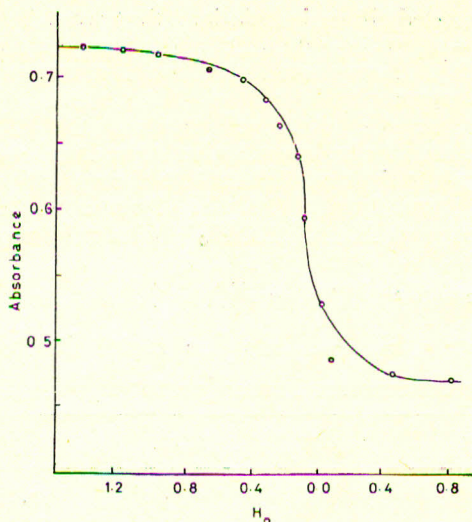
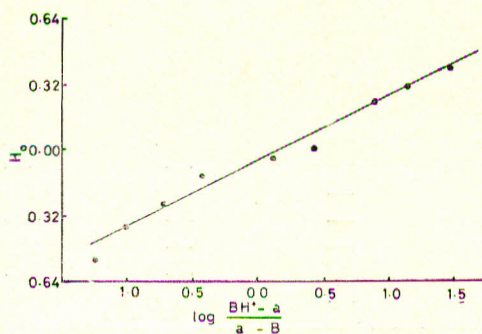Fig. 3.—The variation of absorbance of an acid solution of furan.



Fig. 4.—Curve $H_0$ versus $\log \frac{(BH^+ - a)}{(a - B)}$.



Fig. 5.—Plot of $\Delta a / \Delta H_0$ versus $H_0$.

of the two forms, the base and protonated base respectively (Fig. 3).

The value of $H_0$ acidity function at various molarities was determined experimentally and the value of the p$K_a$ was calculated (Fig. 4). To avoid any possible error, p$K_a$ was further determined by plotting $\Delta a / \Delta H_0$ (Fig 5). The value where it shows the maxima is the p$K_a$ of furan. The p$K_a$ by first method was found to be 0.11 and 0.09 by the second. Therefore, the value of $0.10 \pm 0.05$ was adopted.

## Discussion

The shift of maxima towards shorter wavelength with increasing dielectric and polarity is observed in pyrrole where the maximum is shifted from 210 nm to 205 nm in hexane and water, respectively. A similar shift is noted in the furan. The maxima in hexane is 223 nm and 212 nm in water. A consideration of the resonance structure of furan may be helpful in understanding these shifts.

*Resonance Structures.*—Charge separated structures[6] will be established in polar solvents. The charges are somewhat localised and energy is raised resulting in the blue shift.
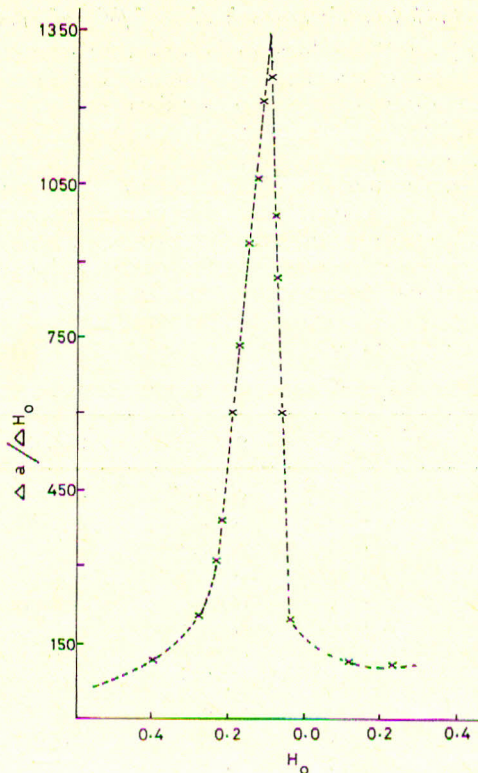
Pyrrole and furan have almost similar spectral behaviour. The aromatic character[7] of these π-excessive compounds is due to the six delocalised electrons, two of these are provided from these hetero atom leaving the hetero atom positively charged. It is evident that oxygen, which is more negative than nitrogen, will be reluctant to assume this positive charge and hence the charge-separated forms will contribute to a lesser extent than in the case of pyrrole. Thus furan will be slightly more basic than pyrrole as is evident from this work.

## References

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