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Potentiometric determination of ionization constant of N-arylhydroxamic acid in non-aqueous solvent; a comparative study with spectroscopic method

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The structure, acid-base equilibria and overall stability of hydroxamic acids are known to have an important bearing on their general usefulness and of their applications. In this study, a series of N-arylhydroxamic acids such as N-(o-methyl)phenylbenzohydroxamic acid [I], N-phenylbenzohydroxamic acid [II], N-(o-chloro)phenylbenzohydroxamic acid [III], N-(o-bromo)phenylbenzohydroxamic acid [IV] and N-(o-methoxy)phenylbenzohydroxamic acid [V] were synthesized and the ionization constant of these acids was determined using three different methods namely as Jannik Bjerrum method, H. M. Irving and H. S. Rossotti method and Theo P. A. Kruck and Bibudhendra Sarkar method. The value obtained by these methods was compared with the values obtained from spectroscopic method.

In the Jannik Bjerrum method a single potentiometric titration was used to calculate the average number of ionizable hydrogen ions ($\tilde{n}_H$ value) at different pH intervals. If the data are taken from a single potentiometric titration (weak acid alone) then especially at low pH, the amounts of NaOH and OH^- present in the solution are negligible and the amount of mineral acid present in the solution is very much greater than the amount of H_jA present and the calculated values of $\tilde{n}_H$ will be very sensitive to small errors in pH meter readings. Therefore two different novel methods such as Irving and Rossotti method and Kruck and Sarkar method were used to calculate the $\tilde{n}_H$ values. In all three methods, the pH at which the value of $\tilde{n}_H = 0.5$ was equated to the guess value of ionization constant and was refined by iterative least square method to obtain the correct pK_a value.

A good agreement with all four methods was observed. Comparatively, Theo P. A. Kruck and Bibudhendra Sarkar method is a good and efficient method to minimize the errors in pH meter readings at lower and higher pH values. When this method is based on a series of titrations, the experimental and personal errors are minimized. The pK_a values obtained are given in table 1.

Table 1. Comparison of pK_a values obtained by different methods

Compound	Bjerrum method	Irving and Rossotti method	Kruck and Sarkar method	Spectroscopic method
[I]	9.903	9.912	9.904	9.924
[II]	9.797	9.806	9.806	9.800
[III]	9.640	9.641	9.639	9.671
[IV]	9.734	9.735	9.724	9.701
[V]	9.970	9.968	9.965	9.975