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ABSTRACT

Session 6: Paper 2

ACID-BASE INDICATORS FOR FUNCTIONAL APPLICATIONS

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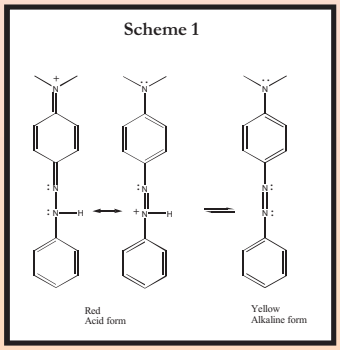
Introduction

Colour change has been a fascination of individuals for a long time. The two major types of dyes which are traditionally used for colour change are leuco dyes or acid-base indicators. Leuco dyes are of limited use because three components are required to effect the colour change transition. Generally, a color former (the leuco dye), a developer (such as a phenolic compound) and a reversible matrix, such as a long chain alcohol, are combined. An often noted drawback with leuco dye systems is their water insolubility, thus, leuco dyes can only be used in solvent based systems. Very few leuco dyes are commercially available. The synthetic methods of leuco dyes are complex, multi-steps and do not generate high yields.

Acid-base indicators are also commonly known as pH indicators. The major benefits of acid-base indicators over leuco dyes include: a) Acid-base indicator is a one component system compared to three components required for a colour change in leuco dye system; b) Acid-base indicators are generally soluble in organic solvent. They can be dissolved in water by making sodium or potassium salts. Thus, Acid-base indicators can be used in aqueous as well as solvent based systems; c) Acid-base indicators are commercially available or can be synthesized in excellent yield and purity.



Acid-base indicators are substances which change colour with pH. They are usually weak acids or bases, which when dissolved in water dissociate slightly and form ions. The literature reveals few books covering acid-base indicators nearly half a century ago, which are mostly out of prints. The most recent book on acid-base indicators highlights CAS numbers, CA index name, other names, Merck Index number, chemical structure, classification, molecular formula, molecular weight, pH range, colour change, pKa, physical form, melting point, boiling point, synthetic methods, major applications and safety/toxicity data. Baeyer's work on phenolphthalein was a major breakthrough in acid-base indicator chemistry in the early days. The use of acid-base indicators has exploded in the recent years, particularly in the field of electronics and biomedicine. The present review aims at providing systematic and up-to-date compiled data on acid-base indicators along with their chemical classes, chemical structures, colour change mechanisms, pH ranges, colour change at pH intervals, recent advances and functional applications.

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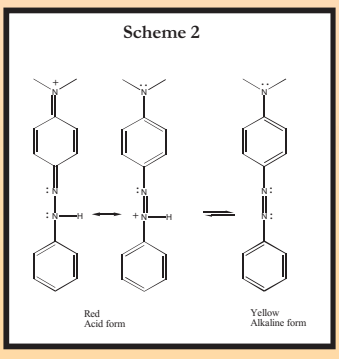
Classification

The acid-base indicators are commonly grouped into following classes: Azo, Benzein, Nitro, Phthalein, Sulfonphthalein, Triphenylmethane, Fluorescent and Miscellaneous

1) Azo acid-base indicators

The azo acid-base indicators are azo dyes which have phenolic hydroxy, carboxylic acid or sulfonic acid group. The yellow-red colour transition can generally be observed. Colour-change mechanism is given in Scheme 1. These indicators can be dissolved into water by making sodium salts of carboxylic acid or sulfonic acid as subsituents. Functional applications of azo acid-base indicators: Alizarin Yellow R, Ethyl Red and α-Naphthyl Red are selected from the group whose applications are given below:



Alizarin Yellow R: Display device, photoresist, nanoparticles, sensors, photoconductive materials, photography, electrorheological materials, copying materials, optical engineering applications, cosmetics, diapers, food storage, measurement of acidity in juice, determination of albumin, agent for plaque, method for counting leukocytes, antifungal agent

Ethyl Red: Optical materials, photoresists, flexible electronic circuitry, method for counting leukocytes, enzyme binding assays, DNA chips

α-*Naphthyl Red:* Display device, semiconductor, sensors, photosensitive materials, recording materials, imaging materials, inks, lubricants, hair dyes, food storage, dental materials

2) Benzein acid-base indicators

The benzeins contain neither carboxylic nor sulofonic acid group; they are therefore insoluble in water. Benzeins are dark coloured solid having quinonoid structure. The general structure of benzeins is given in scheme 2. The yellow-red colour transition can also be observed. Functional applications of benzein acid-base indicators are:

o-Cresolbenzein, and α-Naphtholbenzein are selected from the group whose applications are given below:

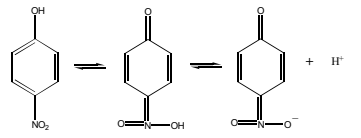
o-Cresolbenzein: Cosmetics

α-*Naphtholbenzein:* Semiconducting polymers, concrete, correction fluid, food storage, determining bacterial growth in packed food, personal hygiene products, detecting viable cells, detecting enzymes, detecting ammonia odours in patients having bacterial infection

3) Nitro acid-base indicators

The nitro indicators are generally colourless in acid form and intense yellow coloured in alkaline form. Colour-change mechanism is given in Scheme 3. These indicators form sodium salt with alkali which is water soluble & yellow colored. Functional applications of nitro acid-base indicators are:

Scheme 3



Ethyl bis-(2,4-dinitrophenyl)acetate and trinitrobenzoic Acid are selected from the group whose applications are given below:

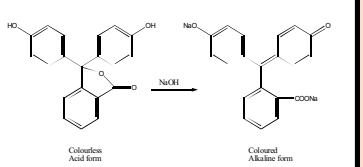
Ethyl bis-(2,4-dinitrophenyl)acetate: Imaging materials, microcapsule toner, electrophotographic toner, decoder system, inks, paints, adhesives

Trinitrobenzoic Acid: Explosive, liquefied gas fuels, energetic materials, anti-wear agent, photography, photoconductor, recording materials, inks, adhesives

4) Phthalein acid-base indicators

The phthalein acid-base indicators are rather insoluble in water but very soluble in alcohol. Most of them are colourless in acid form (lactone form) and deeply coloured (red, pink, purple, violet, & blue) in alkaline form. Colour-change mechanism is given in Scheme 4. These indicators form disodium salt with alkali which is water soluble & intensely colored. Functional applications of phthalein acid-base indicators are:

Scheme 4



o-Cresolphthalein and ?-Naphtholphthalein are selected from the group whose applications are given below:

O-Cresolphthalein: Sensors, display device, photoresists, recording materials, imaging materials, authentication system for secure documents, decoder system, lithium cells, inks, markers, toners, correction fluid, paints, adhesives, food storage, diapers, lotions, urine analysis test strips, drugs, blood analysis.

α–*Naphtholphthalein:* Sensors, sol-gel materials, thermochromic matetials, recording materials, imaging materials, authentication system for secure documents, inks, markers, toners, paints, adhesives, rubber, lubricants, food storage, fruits or vegetable packaging, detecting viable cells, drugs, oral hygiene products, dental materials

5) Sulfonephthalein acid-base indicators

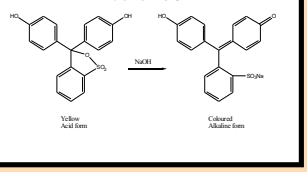
The sulfonephthalein indicators are closely related to phthaleins but the carboxylic acid group in phthaleins is merely replaced by sulfonic acid group. Most of them are yellow coloured in acid form and deeply coloured (red, purple, & blue) in alkaline form. Colour-change mechanism is given in Scheme 5. These indicators form sodium salt with alkali which is water soluble & intensely colored. Table 5 summarizes sulfonephthalein indicators with pH range and color change. Functional applications of sulfonephthalein acid-base indicators are:

Bromochlorophenol Blue and Bromophenol Red are selected from the group whose applications are given below:

Bromochlorophenol Blue: Display device, pH sensors, inks, photoreceptors, lithographic plates, photographic materials, lubricants, food shelf life, in protein assays, vaginal infection test, detecting proteins

Bromophenol Red: Sensors, sol-gel matrix, recording materials, thermochromic materials, inks, paints, lubricants, soaps, cosmetics, identifying fresh & stale rice, determining acidity in wine, food storage, determination of bacterial growth, anti-amyloid agents, evaluating dental caries activity, determination of Streptococci in human saliva, diagnosis of enterohemorrhagic Escherichia coli, treatment of acute leukemia

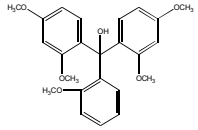
Scheme 5



6) Triphenylmethane acid-base indicators

The triphenylmethane acid-base indicators contain three phenyl groups attached to methane. These dyes behave like very weak polyacidic bases. The most important members of this group include crystal violet, malachite green, hexamethoxy red, heptamethoxy red, pentamethoxy red, methyl green, ethyl green, methyl violet and ethyl violet. The chemical structures of pentamethoxy red and crystal violet are given in Scheme 6A and Scheme 6B, respectively. Functional applications of triphenylmethane acid-base indicators: are:

Scheme 6A

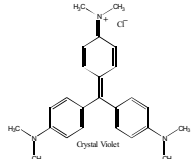


Heptamethoxy Red and Pentamethoxy Red are selected from the group whose applications are given below:

Heptamethoxy Red: UV-sensitive recording materials, inks

Pentamethoxy Red: image producing materials, recording materials, resist composition, xerographic copier materials, inks, cosmetics, dental adhesives

Scheme 6B



7) Fluorescent acid-base indicators:

The class of fluorescent acid-base indicators is extremely large. A separate paper can be presented on just fluorescent acid-base indicators.

8) Miscellaneous acid-base indicators

The miscellaneous acid-base indicators include anthraquinone, quinoline, indigoid, chalcone, phenazine, phenoxazine, flavonoid etc.