# The Application of Specific Interaction Theory for Describing the Behaviour of Free and Immobilized Acid–Base Indicators

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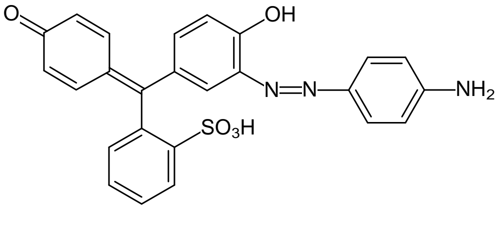
The application of specific interaction theory for describing the behaviour of organic indicators in free and immobilized states leads to the possibility of using a localized charge-distribution model.

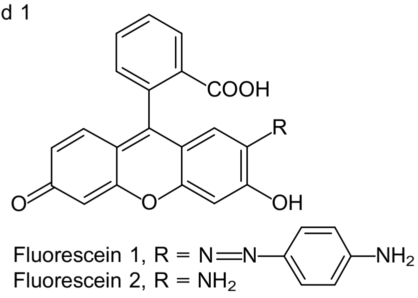
Acid–base indicators immobilized on a polymer matrix have been used as the sensitive element in the design of optical pH-sensors. The more preferable and reliable immobilization method is the covalent method, since it combines sensor stability and sensitivity control by changing the quantity of immobilized indicator.[1]

The purpose of this work was to compare the behaviour of immobilized and free indicators used in optical sensors and to examine their protolytic properties taking into account the thermodynamics of the electrolyte solutions.

We have investigated acid–base indicators synthesized by a previously known method,[2] and added aminophenylazo groups (modification 1) or amino groups (modification 2) to the molecules of Phenol Red and Fluorescein. The above groups were necessary in order to link the molecules with a hydrolysed cellulose triacethyl matrix by acylating modified indicators with amino groups with the help of cyanuric chloride.



Phenol Red 1



Fluorescein 1, R = N═N—C₆H₄—NH₂
Fluorescein 2, R = NH₂

The method of spectrophotometric titration has been used to determine stoichiometric mixed ionization constants for two compared indicator groups. With reference to the earlier work,[3] we called the p$K_a$ value indicator constant, because it defines different processes in which the most important part is protonation.

Different ionic medium concentrations (Table 1) significantly changed the indicator constant value by changing the coefficients of activity, according to the Debye–Huckel theory.

We obtained more detailed information about the behaviour of free and immobilized indicators by investigating the dependence of the indicator constant of ionic medium concentration in accordance with the specific interaction theory (SIT).[4] This theory states that the coefficient of specific interaction does not depend on the ionic medium concentration if the ionic strength is less than 0.2. That is why in evaluating the activity coefficients of multicharged organic ions, such as Phenol Red 1, Fluorescein 1 and Fluorescein 2, their charge can be considered to be distributed over the whole particle, like small inorganic ions, or over separate ionised groups of polyfunctional organic ion, *i.e.* global charge model. The alternative variant is a model of ions with isolated charges.

The choice of model depends on the charge distribution over the indicator molecule. This is evident from the main equation of this theory,[4]

$$\mathrm{p}K_\mathrm{a} = \mathrm{p}K_{\mathrm{a}\,\mu\to 0} + Z[(0.5\mu^{\frac{1}{2}})/(1+1.5\mu^{\frac{1}{2}})] + S\mu$$

in which $Z$ is the sum of the squares of the reagent charges calculated in different cases and $S$ is the sum of the squares of specific interaction coefficients.

The analysis of these two compared alternatives for Phenol Red 1, Fluorescein 1 and Fluorescein 2 is given in Table 1 which shows that the $Z$ value obtained by plotting p$K_a$ *vs.* $[(0.5\mu^{1/2})/(1+1.5\mu^{1/2})]$ is a straight line with slope much closer to those values calculated according to the isolated charge model, whereas in the case of Fluorescein 2 this is not so.

The $Z$ value for Phenol Red is 2.5 for solution and immobilized indicator (see Table 1, $Z = 2$ for the protonated form and the charges are omitted for simplicity). Similar $Z$ values for solution and immobilized indicator are connected with their structures and electronic density distribution in the indicator molecule, which makes it easier during immobilization to form an isotopic ionic atmosphere around the immobilized indicator molecule, *i.e.* their behaviour in both cases compared is similar.

The $Z$ values for Fluorescein 1 and Fluorescein 2 are 1.5 and 0.8 for solution and 0.5 and 3.4 for immobilized indicator. The lower $Z$ value for immobilized Fluorescein 1 and the higher $Z$ value for immobilized Fluorescein 2 might be caused by difficulties in forming an isotropic ionic atmosphere around the molecules of this indicator and the electrostatic field of the surface matrix.

This can be confirmed by the value of the surface potential of the membrane with the immobilized indicator, but the complicated character of protolytic and other equilibria, as well as Gibbs's energy division into inner and electrostatic parts,[5] does not allow us to use this idea strictly and correctly.

According to SIT we evaluated specific interaction coefficients.[4] The second part of Table 1 shows small $S$ values for free and immobilized indicators (Phenol Red 1, Fluorescein 1 and Fluorescein 2), which confirms the correct use of SIT to determine the thermodynamic properties of the indicator both in solution and in the matrix and to underline the importance of the specific interaction of protonated indicators.

Therefore, the use of SIT for describing the behaviour of organic ionic indicators in free and immobilized states leads to a possible use of a model of localized charge distribution in both cases. This corresponds to the information obtained for other indicators in solution,[4] but is quite new for understanding the role of immobilized acid–base indicators in optical sensors.

**Table 1** The influence of ionic medium on the protonation indicators and evaluation of specific interaction theory.
(*a*)

| Concentration of ionic medium | $pK_a$ | | | | | |
|---|---|---|---|---|---|---|
| | Phenol Red 1 | | Fluorescein 1 | | Fluorescein 2 | |
| | Free | Immobil. | Free | Immobil. | Free | Immobil. |
| 0.1 | 7.56±0.07 | 7.02±0.11 | 6.22±0.08 | 7.57±0.1 | 6.33±0.06 | 8.14±0.11 |
| | 7.55±0.09 | 6.98±0.1 | 6.25±0.06 | 7.52±0.11 | 6.31±0.07 | 8.17±0.1 |
| | 7.58±0.06 | 7.10±0.12 | 6.28±0.07 | 7.58±0.1 | 6.35±0.04 | 8.11±0.09 |
| 0.02 | 7.71±0.05 | 7.17±0.1 | 6.32±0.05 | 7.60±0.07 | 6.39±0.08 | 8.39±0.1 |
| | 7.69±0.07 | 7.21±0.09 | 6.31±0.08 | 7.55±0.1 | 6.37±0.07 | 8.35±0.12 |
| | 7.72±0.08 | 7.12±0.11 | 6.37±0.06 | 7.60±0.08 | 6.40±0.05 | 8.37±0.1 |
| 0.002 | 7.78±0.07 | 7.24±0.07 | 6.35±0.05 | 7.61±0.09 | 6.40±0.06 | 8.43±0.09 |
| | 7.79±0.06 | 7.29±0.06 | 6.36±0.07 | 7.58±0.12 | 6.39±0.08 | 8.40±0.1 |
| | 7.81±0.09 | 7.26±0.09 | 6.37±0.04 | 7.60±0.1 | 6.40±0.07 | 8.41±0.1 |
| $\mu \to 0$ | 7.83±0.09 | 7.30±0.08 | 6.39±0.08 | 7.62±0.1 | 6.42±0.07 | 8.48±0.1 |

(*b*) Theory.

| Protonation equilibrium | Sum of the squares of charges ($-Z$) | |
|---|---|---|
| | Global charge model | Isolated charge model |
| $R^{2-} + H^+ \leftrightarrow HR^-$ | 4 | 2 |

(*c*) Theory checking.

| Indicator | Sum of the squares of charges ($-Z$) | | Sum of the squares of specific interaction ($S$) | | Thermodynamic constants ($pK_T$) | |
|---|---|---|---|---|---|---|
| | Free | Immobil. | Free | Immobil. | Free | Immobil. |
| Phenol Red 1 | 2.5±0.4 | 2.5±0.9 | −0.04 | −0.01 | 7.86±0.07 | 7.32±0.07 |
| Fluorescein 1 | 1.5±0.6 | 0.5±0.6 | 0.05 | 0.01 | 6.40±0.07 | 7.62±0.09 |
| Fluorescein 2 | 0.8±0.4 | 3.4±0.9 | −0.02 | −0.2 | 6.43±0.06 | 8.52±0.05 |

## References

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