EVALUATION OF COLOUR CHANGES OF SCREENED ACID-BASE INDICATORS

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Based on computer-assisted calculations, six screened indicators were prepared and used for visual titration end point indication. Three of them were evaluated in terms of objective colour characteristics. Their colour changes were characterized in the CIE-*xy* (1931) international colorimetric system, by the Helmholtz coordinates, complementary Q_x, Q_y coordinates, perceptibility and course of the $\Delta J/\Delta pH = f(pH)$ function. In addition, new indices were introduced, viz. partial quality indices I_E, I_p and I_m, related with the colour difference between the two indicator species (I_E), their colour purity (I_p) and the experimenter's ability to remember the colour in the titration end point (I_m). Summed up, the three indices constitute the total quality index of the chemical indicator I_t. These indices were employed for comparing the single and the corresponding screened indicators.

The use of modified indicators is convenient for improving the precision of titrimetric determinations with visual indication. As compared to single indicators, modified indicators exhibit more expressive colour changes, their limiting forms being complementarily coloured and the middle of the colour transition being grey.

The trial and error approach to screened indicator mixing has been recently replaced by calculations based on the complementary tristimulus system[1,2], using computers for the rather complex mathematical treatment[3,4].

In the present work, a computer program described elsewhere[4] is employed for the preparation of six screened indicators, three of which are objectively evaluated by conventional as well as newly suggested numerical characteristics. All of the indicators then are applied to the visual indication of acid-base titrations.

THEORETICAL

Objective colour measurement is performed in terms of the CIE (1931) system[5,6] based on the *X*, *Y*, *Z* (in general, *R*) tristimulus components determined by the transmittance, spectral composition of illuminant and tristimulus components.

The CIE-xy (1931) colorimetric triangle is used for an illustrative graphic representation, where relative chromaticity coordinates x, y (in general, r) are assigned to each colour:

$$r = R/(X + Y + Z) . \qquad (1)$$

The colour then can be described in terms of the coordinates x, y and the relative transmission factor Y.

Colours are also conveniently described in terms of the natural (Helmholtz) coordinates[6], dominant λ_d and complementary λ_c wavelengths (for purple colours) and coordinate p_e or colorimetric p_c purity.

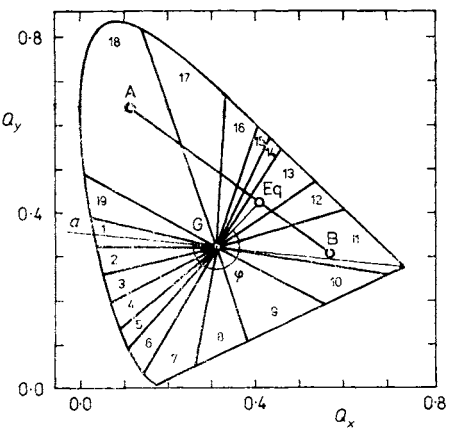
Reilley and coworkers[1] devised a so-called complementary tristimulus system where the tristimuli chromaticity components X_c, Y_c, Z_c (in general, R_c), in contrast to X, Y, Z, are determined by absorbance. Analogously as the coordinates x, y, the coordinates Q_x, Q_y (in general, Q_r) of the complementary tristimulues chromaticity triangle Q_xQ_y are used for a graphic representation.

For describing the colour change of indicators, Reilley and coworkers[1] employ the weighted sum of three indices. The first is the chromaticity index I_{Ch}, associated with the colour difference between the two forms of the indicator. It is expressed by the colour line segment in the Q_xQ_y complementary triangle, whose incongruity is solved by means of MacAdams ellipses.

The second factor is the memory step index I_M, corresponding to the experimenter's ability to remember the colour in the titration end point. It is expressed by means of hue circle sectors in the complementary triangle (Fig. 1). The authors[1] attributed ten memory steps to each colour field. The change in the number of memory steps df with respect to the angle difference dφ, the so-called angular density function

FIG. 1

Colour sections in the Q_xQ_y complementary triangle: 1 red, 2 reddish orange, 3 orange, 4 yellowish orange, 5 yellow, 6 greenish yellow, 7 yellow-green, 8 yellowish green, 9 green, 10 bluish green, 11 blue-green, 12 greenish blue, 13 blue, 14 purplish blue, 15 bluish purple, 16 purple, 17 reddish purple, 18 red-purple, 19 purplish red; a baseline, G achromatic grey point, A, B points showing the colour of the limiting indicator forms, Eq point corresponding to the indicator colour in the titration end point, φ angle determined for the evaluation of I_M



$(df/d\varphi)$, is determined by the change in the indicator hue in the end point range. For evaluation of the memory step index, Reilley and coworkers[1] derived the relation

$$d\varphi/d\delta = [E_A E_B(V_{x,B}V_{y,A} - V_{x,A}V_{y,B})]/\{[E_A V_{x,A}(1 - \delta) + E_B V_{x,B}\delta]^2 + [E_A V_{y,A}(1 - \delta) + E_B V_{y,B}\delta]^2\}, \quad (2)$$

where δ is the distribution coefficient, E_A and E_B are the total absorptivities of the two indicator forms A, B related to the complementary system, and V_x and V_y (in general $V_r = Q_r - G_r$) are the differences between the coordinates Q_r of the colour point in the chromaticity diagram and the coordinates G_r of the achromatic grey point G. The memory step index I_M for the equivalence point Eq is given by the product[1]

$$I_M = (d\varphi/d\delta)_{Eq}\,(df/d\varphi)_{Eq}\,. \quad (3)$$

The third index is the greyness index I_g, related with greyness g and expressing the greyness content of the colour in the limiting indicator forms[1],

$$g = (G_y/Q_{y,S})\,(Q_{r,S} - Q_r)/(Q_r - G_r)\,, \quad (4)$$

where $Q_{r,S}$ (i.e. $Q_{x,S}$ and $Q_{y,S}$) are the coordinates of the point lying at the circumferential line of the chromaticity diagram. The total numerical characteristics of the indicator then is expressed by the weighted sum of these indices[1].

This approach to the evaluation is highly dependent on the set of indicators and so is not quite objective, which detracts from its suitability for expressing the overall quality. Therefore, we devised a system of other three indices for the evaluation of colour changes of chemical indicators.

The first quantity related to the colour change quality is the colour difference ΔE_c (in the complementary system) of the two indicator forms, replacing the chromaticity index[1]. The ΔE_c quantity was derived using the CIELAB system[7,8] where the X, Y and Z values were replaced by the complementary values X_c, Y_c and Z_c, moreover related to a unit concentration and unit absorbing pathlength. In this manner, independence of ΔE_c of the product of the two parameters (concentration c and absorbing pathlength d) was achieved:

$$\Delta E_c = [(\Delta L_c)^2 + (\Delta a_c)^2 + (\Delta b_c)^2]^{1/2}\,, \quad (5)$$

where

$$L_c = 116(Y'_c/Y_0)^{1/3} - 16 \quad (6)$$

$$a_c = 500[(X'_c/X_0)^{1/3} - (Y'_c/Y_0)^{1/3}] \quad (7)$$

$$b_c = 200[(Y'_c/Y_0)^{1/3} - (Z'_c/Z_0)^{1/3}] \quad (8)$$

and X'_c, Y'_c and Z'_c (in general, R'_c) are

$$R'_c = R_c/(cd)\,, \quad (9)$$

and X_0, Y_0 and Z_0 are the tristimuli components of conventional white light C (ref.[6]).

This modification was carried out with a view to replacing the MacAdams ellipses by the CIELAB system, which is a more recent version of solution of non-uniformity of the xy tristimulus chromaticity triangle, recommended by the CIE commission. The introduction of the complementary quantities in the relations for the calculation of the colour difference is feasible for indicator solutions at concentrations allowing characterization by the complementary coordinates.

In ref.[1], the second index used is I_M. This index, however, does not give satisfactory results for screened indicators – its values are too low. Eq. (2) was derived using the vector product of vectors describing the indicators in the complementary coordinates. For two linearly dependent vectors, by which screened indicators are practically described, this product is a zero vector and thus $I_M = 0$. This result does not correspond with reality for screened indicators.

This problem was solved by putting $(d\varphi/d\delta) = 109{\cdot}271$ for all indicators whose complementary points corresponding to pH_{Eq} (pH of the titration end point) have coordinates within the limits of $0{\cdot}3001 \leqq Q_x \leqq 0{\cdot}3201$ and $0{\cdot}3063 \leqq Q_y \leqq 0{\cdot}3263$ at the conventional white light C.

The above value of 109·271 was obtained by a treatment as follows. For indicators represented in the complementary coordinates by a straight line segment passing through the achromatic grey point and having the centre of transition in this point, the colour change gives rise to a change in angle φ by a value of π. Thus if an acidity change of $\Delta pH = 0{\cdot}05$ gives rise to an observable change in the indicator colour, the corresponding change in the distribution coefficient of the two coloured forms in the range of $\delta = 0{\cdot}5$ is $\Delta\delta = 0{\cdot}028751$ (for isolated protolytic equilibria). This leads to $(d\varphi/d\delta)_{Eq} = \Delta\varphi/\Delta\delta = 3{\cdot}141593/0{\cdot}028751 = 109{\cdot}271$. For screened indicators then I_M attains high values. Based on division of the complementary triangle where the colour sections pass through the grey point (Fig. 1), the $df/d\varphi$ values were determined. In program[4], one hundred steps were assigned to each section.

The third factor affecting the quality of the colour change is the grey content of the colour of the limiting indicator forms; indicators whose two forms have pure colours, with low grey contents, are more convenient for use. In ref.[1], greyness is expressed by factor g; other parameters, however, are also feasible. We elected the coordinate purity p applied to the complementary system,

$$p = (Q_r - G_r)/(Q_{r,S} - G_r)\,. \quad (10)$$

This expression is calculated for the two indicator forms A, B, and the grey content is characterized by the sum of the coordinate purities (in the complementary system) of the two forms,

$$p_t = p_A + p_B , \tag{11}$$

which increases with increasing colour quality of the indicator, i.e. with decreasing grey content.

In the form (*11*), this relation suits well for two-colour indicators. For one-colour indicators, p_A of the colourless form A is near or equal to zero, and $p_t = p_B$. This results in underestimation of one-colour indicators. If the colourless form is present solely at a particular pH, we can say that no dye, hence also no grey dye, is present. Then, the highest value, i.e. unity, is to be assigned to p_A. For a one-colour indicator, we have thus

$$p_E = 1 + p_B . \tag{12}$$

The above three factors jointly contribute to the overall indicator quality; the partial quality indices are functions of these parameters and their graphic representation is a sigmoid curve. The functional dependences were treated making use of the general function[9]

$$y = (y_1 + y_2)/2 + [(y_1 - y_2)/2] \operatorname{tgh} \{[(y_1 - y_2)/2] (ax + b)\} , \tag{13}$$

where a and b are constants and y_1 and y_2 are coordinates of the asymptotes. The constants a and b can be determined from the relations

$$x_{in} = \{1/[a(y_1 - y_2)]\} \ln [(y_1 - y_0)/(y_0 - y_2)] \tag{14}$$

$$ax_{in} + b = 0 , \tag{15}$$

where x_{in} is the x-coordinate of the inflection point of the curve and y_0 is the value of function (*13*) at $x = 0$.

For the partial indices to lie between zero and unity, we choose $y_1 = 1$ and $y_2 = 0$; then,

$$y = 0{\cdot}5 + 0{\cdot}5 \operatorname{tgh} [0{\cdot}5(ax + b)] \tag{16}$$

$$x_{in} = (1/a) \ln [(1 - y_0)/y_0] . \tag{17}$$

By the choice of x_{in} and y_0, the course of function (*16*) can be affected to obtain a suitable dependence for the calculation of the partial indices. The following dependences were thus obtained.

The index of quality with respect to the colour difference is given by the expression

$$I_E = 0{\cdot}5 + 0{\cdot}5 \text{ tgh } [0{\cdot}5(9{\cdot}060 \,.\, 10^{-4}\Delta E_c - 2{\cdot}944)] \qquad (18)$$

choosing $x_{in} = 3\,250$ and $y_0 = 0{\cdot}05$.

The partial index of quality with respect to memory (which is different from the index I_M in ref.[1]) is defined as

$$I_m = 0{\cdot}5 + 0{\cdot}5 \text{ tgh } [0{\cdot}5(0{\cdot}9190 I_M - 4{\cdot}595)] \qquad (19)$$

with $x_{in} = 5{\cdot}0$ and $y_0 = 0{\cdot}01$.

The partial index of quality with respect to the colour purity (grey content) of the two forms I_p is evaluated as

$$I_p = 0{\cdot}5 + 0{\cdot}5 \text{ tgh } [0{\cdot}5(2{\cdot}944 p_t - 2{\cdot}944)] \qquad (20)$$

at the chosen $x_{in} = 1{\cdot}0$ and $y_0 = 0{\cdot}05$.

The x_{in} values are estimates of the ΔE_c, I_M and p_t parameters for an indicator with an average-quality colour change. The choice of y_0 then ensures a suitable slope of the curve (Fig. 2) within the regions of values of the pertinent parameters, which can be obtained for substances applicable as indicators.

The course of the functions is shown in Fig. 2. The curves defined by Eqs (*18*–*20*) fit the required course but depart from it in the side regions. Thus, for the function $I_E = f(\Delta E_c)$, a zero value is assumed at $\Delta E_c = 0$, actually, however, it will take a value of 0·05. At high ΔE_c values (higher than 12 000), I_E is practically unity, which is the limiting value; for real indicator values with $\Delta E_c > 1\,000$, Eq. (*18*) is quite

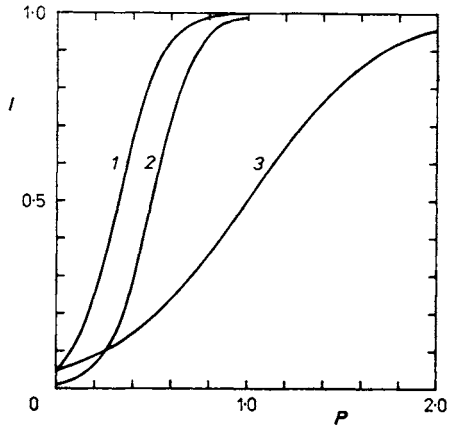


FIG. 2

Plots of functions (*18*)–(*20*), $I = f(P)$. *1* $I_E = f(\Delta E_c \,.\, 10^{-4})$, *2* $I_m = f(I_M \,.\, 10^{-1})$, *3* $I_p = f(p_t)$

satisfactory. For the function $I_m = f(I_M)$ we obtain $I_m = 0{\cdot}01$ at $I_M = 0$. This residual value is convenient to use because also for one-colour indicators the colour in the titration end point can be remembered and discerned (colour change takes place in a single hue). The I_m function limits to unity at $I_M > 13{\cdot}5$. It is clear from Eq. (*20*) that for the limiting values of $p_t = 0$ and 2, I_p is 0·05 and 0·95, respectively. For actual p_t values, however, this dependence gives sufficiently adequate parameters.

The indices will change according to the parameters ΔE_c, I_M and p_t, which will be mirrored by the colour quality of the indicator. Fig. 2 demonstrates that low parameter values do not contribute significantly to the quality; this only improves at higher parameters. However, if the parameters are so high that their additional increase is of no significance in the colour change monitoring during the titration, the growth of the partial indices slows down. In view of this, the use of the weighted sum of the indices according to Reilley and coworkers[1] does not seem quite precise and satisfactory.

The partial quality indices suggested enable the total quality index to be calculated as

$$I_t = I_E + I_p + I_m . \qquad (21)$$

From this relation it is clear that increase in any of the indices contributes to the improvement of the indicator quality. If, for a screened indicator, one or two indices (I_E, I_p) decrease, this effect must be outweighed by an increase in the third index (I_m). If this is not the case, the total quality index I_t will be lower than for the single indicator and screening is of no use.

In addition to giving the I_t value, the partial indices enable comparison of the individual parameters of different indicators and thereby, assessment of the quality of any indicator (disregarding concentration), single or modified.

EXPERIMENTAL

Stock solutions of the single indicators and inert dyes in a concentration of 1 mmol l^{-1} (for chlorophenol red, 0·5 mmol l^{-1}) were prepared by dissolving the approproate quantities of the chemicals in water. For facilitating the dissolution, 93% (m/m) ethanol was added in a minimal necessary amount. Indicators used were methyl orange (henceforth MO), methyl red (MR), chlorophenol red (CPR), bromophenol red (BPR), bromocresol purple (BCP) and phenolphthalein (PP) (all Lachema, Brno). Inert dyes were methylene blue (MB) (Carlo Erba, Italy), patent blue V (PB) (Astrid, Prague) and picric acid (PA) (ammonium picrate supplied by P.P.H. Polskie Odczyniki Chemiczne, Gliwice, Poland, was converted to the acid and this was purified by recrystallization from benzene[10]).

Purity of the substances was checked by thin layer chromatography on Silufol plates (Kavalier, Votice) using 1-butanol–concentrated ammonia–water 4 : 1 : 5, propanol–concentrated ammonia 2 : 1 and 1-butanol–glacial acetic acid–water 4 : 1 : 5 systems.

Absorption–pH curves for all substances including scerened indicators were obtained titrimetrically using an ABU 12b automatic burette (Radiometer, Copenhagen) for unbuffered

systems. Titrant (0·1M-HCl or 0·1M-NaOH) was added directly to the sample cell (100 ml, $d = 3$ cm) through the lid of the cell compartment (adapted according to Karlíček[11] at the workshop of the Faculty of Pharmacy in Hradec Králové) of a Pye Unicam SP 1800 spectrophotometer (Philips Analytical, Cambridge). Electrodes for continuous pH monitoring with a PHM 26 pH-meter (Radiometer, Copenhagen) or Präcitronic MV 870 (Dresden), viz. a Beckman 40498 glass electrode and a Radiometer K 401 saturated calomel electrode, were also introduced into the cell compartment through the lid. Nitrogen of lamp grade was used for cell contents purging. Absorption curves in the visible spectral region were recorded after discontinuing the nitrogen purging and allowing pH to establish. Ionic strength of the working solution was adjusted at 0·1 with 1M-$NaClO_4$ or 1M-KCl. Absorbances were read from the absorption curves in 10 nm steps over the 380—770 nm region and processed on a minicomputer (56 kB operation memory).

RESULTS AND DISCUSSION

The principal requirement placed on an inert screening dye (or a mixture of two dyes) is that its colour be complementary to that of the single indicator in the point of equivalence. If several dyes are available, then a dye possessing a higher value of the coordinate purity p defined in the complementary system is given preference.

Screened indicators were prepared using the program[4] with entered data of sets of indicators and dyes. Suitable single indicators were sought for the pH range where the point of equivalence should be indicated, and appropriate dyes were assigned to them. The indicator–dye combinations obtained were compared by means of a numerical characteristics, viz. the so-called selection index I_s. A part of this index is the total quality index of the single indicator I_t and the so-called dye index I_d. The latter is defined as

$$I_d^2 = 0{\cdot}5 + 0{\cdot}5 \operatorname{tgh} [0{\cdot}5(2{\cdot}726p - 2{\cdot}944)] \qquad (22)$$

for a two-colour indicator, and

$$I_d^1 = 0{\cdot}5 + 0{\cdot}5 \operatorname{tgh} [0{\cdot}5(4{\cdot}461p - 2{\cdot}944)] \qquad (23)$$

for a one-colour indicator; it is related with the coordinate purity p of the dye in the complementary system and mirrors the effect of the dye on the screened indicator concerned. For the most suitable combination (with the highest I_s value), the composition and the principal characteristics of the screened indicator were calculated.

Six screened indicators were prepared by mixing the calculated volumes of the stock solutions of the single indicators and inert dyes, as given in Table I. Their colour transitions cover the most widely used pH region. Although less accurate than weighing-in, volume mixing is rapid and causes virtually no error during visual titrations. The accuracy of the objective characteristics of the screened indicators, however, may be somewhat poorer.

Three of the screened indicators prepared were evaluated by means of objective colour measurements.

The colour change of methyl red screened with the inert dyes, viz. MR–MB–PA, is shown in Figs 3 and 4. The transition of the simple indicator is also presented in the Q_x, $_y$ coordinates for a comparison. It is clear that the screening gives rise to an appreciable displacement of the line segment towards the grey point. The characteristics of the simple indicators were taken from ref.[4].

TABLE I

Calculated ratios of stock solution volumes for the preparation of screened indicators; c_{CPR} = = 0·5 mmol l^{-1}, for other substances c = 1 mmol l^{-1}

Indicator	Stock solution volume ratio
MR–MB–PA	1 : 0·654 : 3·258
BPR–MB–PA	1 : 0·086 : 1·058
PP–PB–PA	1 : 0·081 : 1·875
MO–MB	1 : 0·608
CPR–MB–PA	1 : 0·049 : 0·855
BCP–PA–MB	1 : 2·543 : 0·063

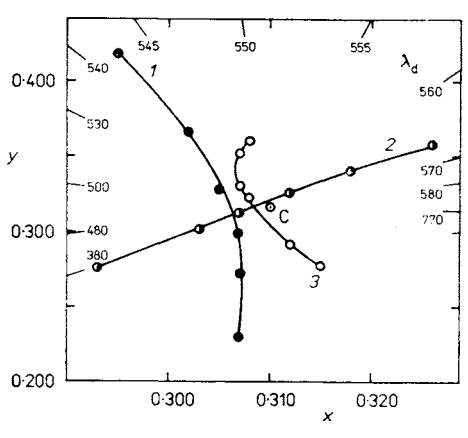


FIG. 3

Colour transitions of indicators represented in the section of the CIE-*xy* (1931) triangle. Indicator: *1* MR–MB–PA, *2* BPR–MB–PA, *3* PP–PB–PA. C is the point of conventional white light C, λ_d is the dominant wavelength

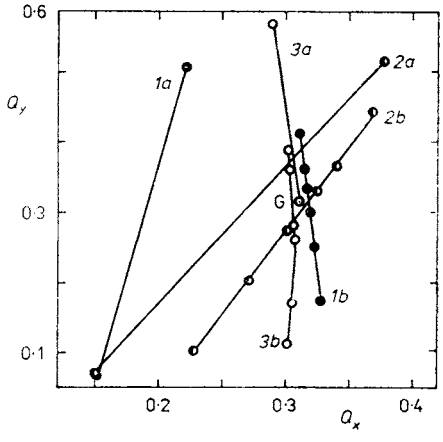


FIG. 4

Colour transitions of indicators represented in complementary coordinates. Indicator: *1a* MR, *1b* MR–MB–PA, *2a* BPR, *2b* BPR–MB–PA, *3a* PP, *3b* PP–PB–PA; G is the achromatic grey point

The colour of this screened indicator changes from red-purple ($\lambda_c = -552{\cdot}95$ nm) to grey to yellow-green ($\lambda_d = 542{\cdot}51$ nm). This change will be most marked at pH 5·0 to 5·8, where the perceptibility[12] attains the lowest values while the $\Delta J/\Delta\text{pH} = f(\text{pH})$ dependence[13] reaches high values (Figs 5, 6). In addition to other characteristics, Table II also contains the coordinate purity values. The purity of the two limiting forms is sufficient for visual indication. The change in the relative transmission factor Y is also sufficiently high and steep.

Save the complementary coordinates, all the quantities used for the description of the colour transition are dependent on the concentrations of the coloured substances and can be controlled by concentration variations. However, concentration increase, which brings about improvement in the colour characteristics, is limited by the solubility of the substances, dichromatism, formation of associates, etc. This dependence poses problems when comparing different indicators because they are present in different concentrations in their working solutions. A comparatively simple modification can be made concerning the $\Delta J/\Delta\text{pH} = f(\text{pH})$ function, namely, relating its value in the maximum, $(\Delta J/\Delta\text{pH})_{max}$, to a unit product of concentration and absorbing pathlength. For screened methyl red, the value of $\Delta J/\Delta\text{pH} = 3{\cdot}28 \,.\, 10^3$ is thus obtained (total concentration of components in the working solution is $2{\cdot}46 \,.\, 10^{-5}$ mol l^{-1}).

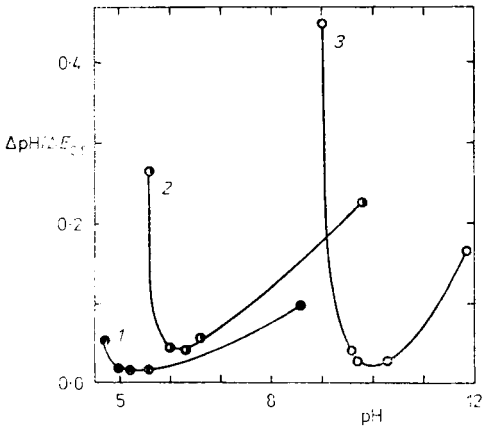


FIG. 5

Dependence of perceptibility[12] of the colour change of indicators $\Delta\text{pH}/\Delta E_{CIE} = f(\text{pH})$. Indicator: *1* MR–MB–PA, *2* BPR–MB–PA, *3* PP–PB–PA

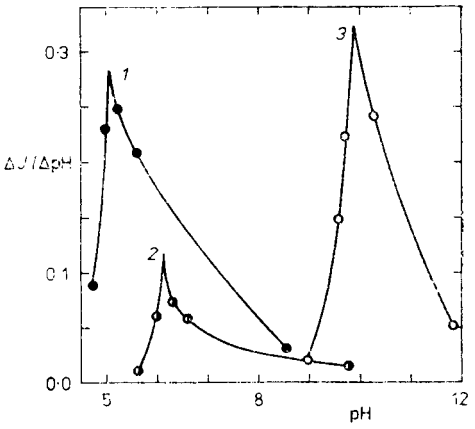


FIG. 6

Indicator colour change expressed in terms of the $\Delta J/\Delta\text{pH} = f(\text{pH})$ dependence. Indicator: *1* MR–MB–PA, *2* BPR–MB–PA, *3* PP–PB–PA

Using the Q_xJ and Q_yJ coordinates according to Reilley and Smith[14], the value of $pH_{Eq} = 5{\cdot}11$ is obtained. The difference from the value of 5·00 found by program[4] can be explained in terms of participation of an additional protolytic equilibrium of methyl red in the acid region ($pK \approx 2{\cdot}30$, ref.[14]).

Comparison with the predicted values[4] can be made by using parameters given in Table III. The results are given in Table IV. A very good agreement was achieved for ΔE_c, and thus also I_E, values. The I_M parameter differs from the predicted value, but the values are so high that I_m is equal to unity in either case. The highest difference is in the I_p values. This difference practically determines the deviation of the I_t values. The above differences can be explained by the effect of the protolytic equilibrium of methyl red at about pH 2·30 and errors arising during the preparation of the screened indicator (mixing volumes of the stock solutions) and during the

TABLE II
Colour transitions of screened indicators

pH	x	y	Y	ΔE_{CIE}	Q_x	Q_y	J	λ_d or λ_c nm	p_e
					MR–MB–PA				
3·48	0·307	0·229	25·49	—	0·308	0·411	1·142	−552·95	0·346
4·73	0·307	0·273	32·01	23·057	0·314	0·362	1·031	−554·64	0·169
4·99	0·307	0·299	36·74	13·326	0·316	0·333	0·971	−559·07	0·064
5·24	0·305	0·328	42·87	15·171	0·319	0·300	0·909	521·32	0·032
5·60	0·302	0·366	52·71	20·667	0·323	0·251	0·834	541·43	0·116
8·56	0·295	0·419	70·12	29·866	0·328	0·175	0·741	542·51	0·243
					BPR–MB–PA				
3·22	0·326	0·358	93·60	—	0·227	0·104	0·205	565·57	0·155
5·63	0·318	0·341	86·42	9·123	0·271	0·203	0·229	563·79	0·088
6·00	0·312	0·326	80·57	8·176	0·301	0·275	0·251	559·68	0·031
6·31	0·307	0·313	75·66	7·223	0·324	0·331	0·274	476·39	0·016
6·62	0·303	0·302	72·12	5·436	0·339	0·367	0·292	445·97	0·044
9·79	0·293	0·276	64·01	13·932	0·368	0·443	0·340	−566·72	0·130
					PP–PB–PA				
6·64	0·308	0·360	92·20	—	0·301	0·111	0·250	548·59	0·113
8·99	0·307	0·352	85·85	5·229	0·305	0·170	0·294	546·34	0·089
9·58	0·307	0·330	73·50	13·831	0·307	0·261	0·382	536·91	0·030
9·71	0·308	0·323	69·91	4·642	0·305	0·283	0·411	535·03	0·014
10·29	0·312	0·291	55·77	20·646	0·302	0·361	0·551	−547·03	0·106
11·85	0·315	0·277	49·89	9·330	0·301	0·388	0·631	−543·97	0·168

evaluation of the measurement (particularly the subjective error of absorbance reading from the curves).

It follows from a comparison of the indices for methyl red and screened methyl red (Table III) that the I_t value is higher for the latter than for the former. Actually, the I_E and I_p values decrease on passing from the single to the screened indicator, but this is outweighted by the increase in the I_m value so that the net effect on I_t is positive. Table III demonstrates that this also applies to the other two screened indicators.

For the BPR–MB–PA indicator, a shift towards the grey point as compared to the simple indicator is again apparent (Figs 3, 4). In the x, y coordinates the colour change of the screened indicator is characterized by a straight line segment from yellow-green (λ_d = 565·57 nm) to grey to blue-purple (λ_c = −566·72 nm). Although lower than for screened methyl red, the coordinate purity values of the limiting forms are sufficient for visual monitoring of the colour transition; they can be increased by using the screened bromophenol red in a higher concentration. A higher and steeper change in the relative transmission factor in dependence on pH can be attained likewise.

TABLE III

Characteristics of single and screened indicators calculated from spectrophotometric data

Indicator	$\Delta E_c \cdot 10^{-3}$	I_E	I_M	I_m	p_A	p_B	I_p	I_t
MR	7·270	0·975	1·895	0·055	0·367	0·906	0·691	1·720
MR–MB–PA	2·920	0·426	62·43	1·000	0·252	0·603	0·395	1·821
BPR	5·502	0·885	3·139	0·153	0·905	0·714	0·861	1·899
BPR–MB–PA	3·213	0·492	83·99	1·000	0·700	0·496	0·640	2·132
PP	3·213	0·492	0·000	0·010	1·000	0·634	0·866	1·368
PP–PB–PA	2·543	0·345	82·46	1·000	0·810	0·170	0·486	1·831

TABLE IV

Characteristics of screened indicators calculated from entered parameters of dyes and single indicators

Indicator	$\Delta E_c \cdot 10^{-3}$	I_E	I_M	I_m	p_A	p_B	I_p	I_t
MR–MB–PA	2·891	0·419	78·02	1·000	0·236	0·576	0·365	1·785
BPR–MB–PA	3·618	0·583	70·52	1·000	0·692	0·524	0·654	2·237
PP–PB–PA	2·133	0·267	78·09	1·000	0·666	0·177	0·387	1·653

The colour change of this screened indicator is clearest at pH 5·9 to 6·6 (Figs 5, 6). The $(\Delta J/\Delta pH)_{max}$ value related to the unit *cd* product is $3{\cdot}20 \cdot 10^3$ ($c = 1{\cdot}07 \cdot 10^{-5}$ mol l^{-1}).

Using the Q_xJ, Q_yJ coordinates[14], the value of $pH_{Eq} = 6{\cdot}24$ was obtained, which agrees well with the value of 6·20 found according to ref.[4].

The calculated and observed characteristics (Tables IV and III, respectively) differ particularly in the ΔE_c, and thereby I_E, values. This difference in I_E is the principal cause of the difference between the predicted[4] and observed total quality index of the screened indicator.

The difference in ΔE_c can be explained as follows. The straight line segment representing the colour transition of screened bromophenol red in the complementary triangle has a position such that because of the incongruity of the triangle, small errors in the position of the colour points of the limiting indicator forms induce rather high deviations in the ΔE_c values. The results can be improved by performing the colour measurements with a higher accuracy, particularly by eliminating the subjective data reading.

By modification of the transition of phenolphthalein, the one-colour indicator was transformed into a two-colour indicator, PP–PB–PA, exhibiting a grey point. The line segment representing the colour change of the screened indicator in the Q_x, $-Q_y$ coordinates exhibits a slight bend (Fig. 4). This is due to a 10 nm shift of the absorption maximum of patent blue V (from 630 to 640 nm) occurring at a pH change in the range of the colour transition of the indicator. This, as will be shown later, affects other parameters as well.

The colour change of screened phenolphthalein represented in the x, y,coordinates (Fig. 3) is from yellow-green ($\lambda_d = 548{\cdot}59$ nm) to grey to red-purple ($\lambda_c = -543{\cdot}97$ nm). The coordinate purity of the limiting indicator forms is rather low but sufficient for visual titration monitoring (with a possibility of increasing the total concentration of the screened indicator). The change in the relative transmission factor Y in dependence on pH is high and steep enough.

The colour change of screened phenolphthalein is most expressive at pH 9·7 to 10·4 (Figs 5, 6). The $(\Delta J/\Delta pH)_{max}$ value related to the unit *cd* product is $3{\cdot}14 \cdot 10^3$ ($c = 2{\cdot}96 \cdot 10^{-5}$ mol l^{-1}).

The value of $pH_{Eq} = 9{\cdot}81$ was derived from the Q_xJ–Q_yJ dependence[14] for screened phenolphthalein. The difference from the value[4] of 9·55 can be explained by the shift of the absorption maximum of patent blue V in the region of the colour transition of the screened indicator.

This is also the cause of the difference between the predicted[4] and observed I_E and I_p values of screened phenolphthalein (Tables III, IV). The actual values are higher than the predicted ones, and so is the I_t value. Thus the shift of the absorption maximum of patent blue V contributes positively to the quality of the colour transition of the screened indicator. This quality increase is so high that the actual I_t

value is higher for screened phenolphthalein than for screened methyl red (Table III) whereas the reverse is true of the calculated (predicted) values (Table IV).

Indicators can also be compared in terms of the $(\Delta J/\Delta pH)_{max}$ value related to the unit *cd* product. Although the data are approximate, it is clear that the differences between them are rather small ($3{\cdot}28 \cdot 10^3$, $3{\cdot}20 \cdot 10^3$ and $3{\cdot}14 \cdot 10^3$). This suggests that for the three screened indicators the expressiveness of the colour change in the grey point range will be roughly the same. This is also indicated by the identical values of $I_m = 1$. The differences in the total quality of this colour change is given by the differences in the two remaining partial indices, I_E and I_p, hence, by the different properties of the colour transitions characterized by them.

TABLE V

Results of titrations using single and screened indicators

Indicator		Average result of determination				
single	screened	single indicator		screened indicator		F
		mg ml^{-1}	s	mg ml^{-1}	s	
		H_3PO_4 titrated with NaOH				
MO	MO–MB	9·929	0·032	9·919	0·024	1·800
		4·981	0·063	4·947	0·025	6·621
		$Na_2B_4O_7.10\ H_2O$ titrated with HCl				
MR	MR–MB–PA	3·740	0·014	3·744	0·008	2·750
		1·863	0·024	1·869	0·009	6·845
		HCl titrated with NaOH				
CPR	CPR–MB–PA	0·3582	0·0023	0·3586	0·0016	2·143
		0·0360	0·0005	0·0358	0·0002	7·121
BPR	BPR–MB–PA	0·3597	0·0021	0·3593	0·0017	1·500
		0·0359	0·0004	0·0358	0·0002	3·767
BCP	BCP–PA–MB	0·3597	0·0016	0·3605	0·0016	1·000
		0·0361	0·0005	0·0362	0·0002	6·625
		H_3BO_3 titrated with NaOH				
PP	PP–PB–PA	0·6223	0·0029	0·6230	0·0027	1·143
		0·3131	0·0037	0·3118	0·0016	5·339

All the six screened indicators prepared were used for visual titrations. Five replicate determinations were performed using either the screened or simple indicators. The precision of determination was compared in terms of the Snedecor test[15]. Comparison of the critical F_α value ($F_\alpha = 6{\cdot}388$ for $n_A = n_B = 5$ and $\alpha = 0{\cdot}05$) with the calculated F values (Table V) shows that titrations using screened indicators are statistically significantly more precise for analytes present in lower concentrations. Thus, the application of screened indicators is reasonable during the optimization of titrimetric determinations of dilute solutions where the transition of single indicators is too dragging to enable the titration end point to be determined precisely enough and the improved colour quality of the indicator transition for screened indicators plays a major role.

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