A SIMPLE METHOD OF PLOTTING THEORETICAL CURVES
OF NET IONOPHORETIC MOBILITY AS A FUNCTION OF pH

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CONSDEN, GORDON AND MARTIN[1] derived a formula relating the net ionophoretic mobility of an organic electrolyte to the pH of the buffer solution present in the paper strip. They also gave formulas for the pH value at which the difference in net mobilities of two electrolytes is maximal, and worked out a chart by means of which this pH value can be found. It must be pointed out, however, that in certain cases the position of the maximum does not correspond to the optimum separation conditions and larger net mobility differences are obtained when both electrolytes are completely ionized. Such a case is illustrated in Fig. 1. Moreover, when the mixture
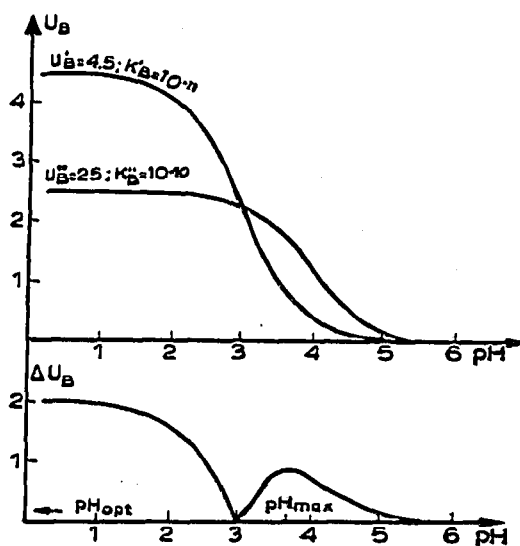

Fig. 1.

to be separated is composed of three or more components, a different pH_{opt} is obtained for each pair of components. Therefore, it would be more convenient to know the graphical dependence of the net mobilities of the components in the whole pH range; plotting of such a dependence is a much simpler task than it appears to be at first sight, if some mathematical properties of the function $U = f(pH)$ are taken into account.

The formulas for net mobility given by CONSDEN *et al.*[1] can be represented as follows:

$$U_A = \frac{u_A}{1 + \dfrac{[H^\cdot]}{K_A}} \text{ (acid)} \qquad U_B = \frac{u_B}{1 + \dfrac{[OH']}{K_B}} \text{ (base)} \tag{1}$$

where u is the ionic mobility and U is the observed, net mobility (at a given pH). The indices A, B denote acid and base, respectively.

$U = \mathrm{f(pH)}$ curves are S-shaped ;the height of a curve is equal to u, the ionic mobility; the inflexion point of a curve is its center of axial symmetry, and lies at half-height of the curve ($\frac{u}{2}$), and at a pH equal to the pK_A of the acid (or $pK_A = 14 - pK_B$ of a base). It can easily be shown that the position of a curve depends solely upon the ionization constant, and the shape solely upon the ionic mobility u.

Denoting anionic net mobility as positive, and cationic net mobility as negative, the relationship between net mobility and pH can be represented as shown in Fig. 2.
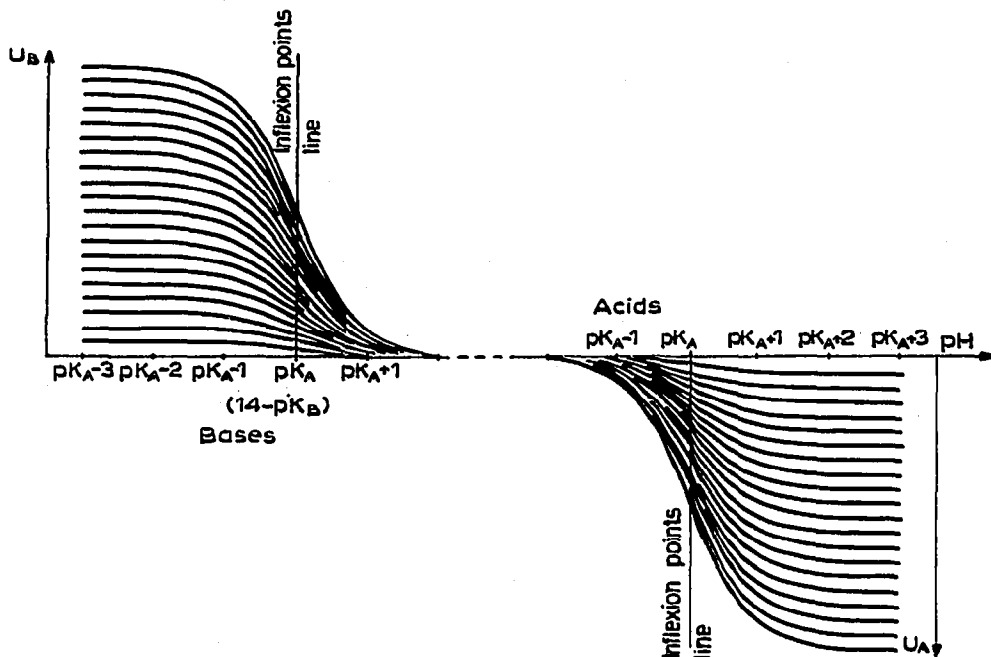

Fig. 2.

The diagram can be used to plot the theoretical curve $U = \mathrm{f(pH)}$ in the whole pH range for a substance of any ionization constant and ionic mobility u. First, on a sheet of tracing paper a system of coordinates is drawn with the pH axis in the same scale as in Fig. 2, and the net mobility (U) axis in such a scale that the ionic mobility u of the substance does not exceed the highest curve of Fig. 2. The sheet of tracing paper is then laid upon Fig. 2 (right hand side if the substance is an acid, left hand side if the substance is a base) and then shifted horizontally, with the pH axes overlapping, until the line of inflexion points of Fig. 2 coincides with the pH value on the tracing paper equal to the pK_A of the substance. The correct position of the

TABLE 1

NET IONOPHORETIC MOBILITY U

pH / pK_A	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100
$pK_A \pm 3$	5.00	10.0	15.0	20.0	25.0	30.0	35.0	40.0	45.0	50.0	55.0	60.0	65.0	70.0	75.0	80.0	85.0	90.0	95.0	100.0
$pK_A \pm 2.5$	5.0	10.0	14.9	19.9	24.9	29.9	34.9	39.9	44.9	49.8	54.8	59.8	64.7	69.7	74.7	79.6	84.6	89.6	94.6	99.6
$pK_A \pm 2$	5.0	9.9	14.8	19.8	24.8	29.7	34.6	39.6	44.5	49.5	54.4	59.4	64.3	69.2	74.2	79.2	84.1	89.0	94.0	99.0
$pK_A \pm 1.5$	4.9	9.7	14.5	19.4	24.2	29.1	33.9	38.8	43.6	48.5	53.3	58.2	63.0	67.8	72.7	77.5	82.4	87.2	92.1	97.0
$pK_A \pm 1$	4.5	9.1	13.6	18.2	22.8	27.3	31.8	36.4	40.8	45.5	50.0	54.5	59.1	63.7	68.2	72.8	77.3	81.8	86.4	90.9
$pK_A \pm 0.5$	3.8	7.6	11.4	15.2	19.0	22.8	26.6	30.4	34.2	38.0	41.8	45.6	49.3	53.3	57.0	60.8	64.7	68.5	72.2	76.0
pK_A	2.5	5.0	7.5	10.0	12.5	15.0	17.5	20.0	22.5	25.0	27.5	30.0	32.5	35.0	37.5	40.0	42.5	45.0	47.5	50.0
$pK_A \mp 0.5$	1.2	2.4	3.6	4.8	6.0	7.2	8.4	9.6	10.8	12.0	13.2	14.4	15.7	16.7	18.0	19.2	20.4	21.6	22.8	24.0
$pK_A \mp 1$	0.5	0.9	1.4	1.8	2.3	2.7	3.2	3.6	4.1	4.6	5.0	5.5	5.9	6.4	6.8	7.3	7.7	8.2	8.6	9.1
$pK_A \mp 1.5$	0.15	0.31	0.46	0.61	0.77	0.92	1.07	1.23	1.38	1.53	1.69	1.84	2.00	2.15	2.39	2.46	2.61	2.76	2.92	3.07
$pK_A \mp 2$	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	0.55	0.60	0.64	0.70	0.74	0.79	0.84	0.89	0.94	0.99
$pK_A \mp 2.5$	0.01	0.03	0.05	0.06	0.08	0.09	0.11	0.13	0.14	0.15	0.17	0.19	0.21	0.22	0.23	0.25	0.27	0.28	0.30	0.32
$pK_A \mp 3$	0.00	0.01	0.02	0.02	0.03	0.03	0.04	0.04	0.05	0.05	0.06	0.06	0.07	0.07	0.08	0.08	0.09	0.09	0.10	0.10

* The upper sign refers to acids, the lower sign to bases.

plot having thus been found, the curve of which the height is equal to the u of the substance is copied. If experimental points have been plotted on the tracing paper and one of the theoretical curves of Fig. 2 is made to fit these points, then the line of inflexion points of Fig. 2 will indicate a pH value on the experimental plot on the tracing paper, that is equal to the pK_A of the substance (cf. SILLÉN[4]).

For plotting theoretical curves in any scale, Table I may also be used.

The method is similar to that of plotting theoretical $R_F = f(pH)$ curves in buffered paper chromatography[2] and $K = f(pH)$ curves[3] (K = partition ratio).

Example

Three bases have the following ionic mobilities and ionization constants:

(1) $\qquad\qquad u'_B = 5 \qquad K'_B = 10^{-10}$

(2) $\qquad\qquad u''_B = 4.5 \qquad K''_B = 10^{-11}$

(3) $\qquad\qquad u'''_B = 2.5 \qquad K'''_B = 10^{-8}$

The plotted theoretical curves are given in Fig. 3. It can be seen that the resolution of all three components is obtained when pH = 3.5. At this pH substance 1 is the fastest and substance 2 the slowest.
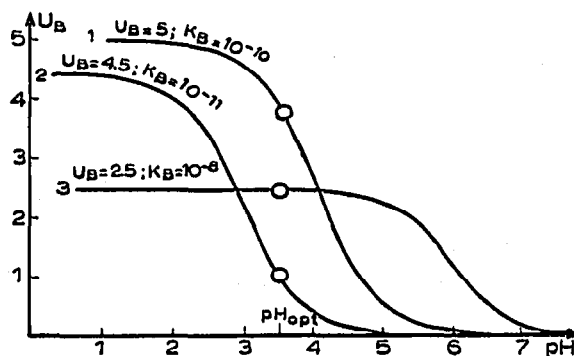

Fig. 3.

Of course, in formula (1) adsorption and other phenomena have not been taken into account, so that deflections from the theoretical curves are to be expected in practice.

SUMMARY

A graphical method for the estimation of separation efficiency as a function of pH in paper ionophoresis of organic acids and bases is described.

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