International Journal of Pharmaceutics, 80 (1992) R21–R24

IJP 10043

Rapid Communication

Alternative statistical method to determine pH-zero point of charge

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(Received 5 November 1991)
(Accepted 10 December 1991)

Key words: pH-zero point of charge; Raw material; Ionic strength effect; pH-shift characteristics

Summary

The empirical function for calculating the zero point of charge (ZPC) from a previous paper (Wongpoowarak, W. and Worakul, N., *Int. J. Pharm.*, 75 (1991) R9–R11 is discussed. The nature of the pH shift of a raw material due to the ionic strength is suggested to be invariant with respect to both pH and ionic strength. The characteristics of the pH shift can thus be used for raw material characterization. With this method, the titrant concentration can be unknown.

The zero point of charge (ZPC) could be used in raw material quality characterization or as a control parameter in the manufacturing process. For example, at pH near the ZPC, the rate of filtration of iron oxides was found to be maximum due to flocculation which did not block the pores of the filter paper (Ankomah, 1991). Moreover, the pH-zero point of charge relationship for aluminum hydroxide has a significant effect on the viscosity (Feldkamp et al., 1981; Morefield et al., 1986), adsorption properties (Shah et al., 1982; Sepelyak et al., 1984; Morefield et al., 1985), rate of filtration (Feldkamp et al., 1982) and removal of sodium (Scholtz et al., 1985). The conventional titration method determines a ZPC graphically from the point of intersection of acid or base quantity added vs pH profile at various ionic strengths (Feldkamp et al., 1981). Paradoxically, adding more experimental data leads to a less reliable ZPC reading because more intersection points exist. Recently, we proposed a mathematical model for calculating ZPC from the titrant volume-pH profile at various ionic strengths (Wongpoowarak and Worakul, 1991) by fitting pH data to an empirical model, i.e.

$$\mathrm{pH} = P_1 + P_2 \cdot V + P_3 \cdot V^2 + P_4 \cdot V^3 + P_5 \cdot V^4 + P_6 \cdot \sqrt{\mu} + P_7 \cdot V \cdot \sqrt{\mu} \qquad (1)$$

where V is the volume of acid or base as titrant and μ denotes the ionic strength or is directly proportioned to ionic strength. The ZPC could thus be calculated at titrant volume equal to $-(P_6/P_7)$ at which no effect from ionic strength is concerned. Even in its simplest form, this method entails the limitation in routine aspects

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for some laboratories that appropriate software is unavailable. An alternative method with similar accuracy is proposed here from the fact that, beyond the ZPC, the direction of the pH shift due to the ionic strength effect will be reversed.

From the same previous concept (Wongpoowarak and Worakul, 1991), the pH shift at any particular titrant volume is assumed to be proportional to $\sqrt{\mu}$ according to the Debye-Hückel concept. Henceforth, μ denotes the ionic strength value only:

$$\text{pH shift} = h(V) \cdot \sqrt{\mu} \tag{2}$$

where pH shift is a function of both V and μ. By definition, pH shift is the difference between pH (at any μ) and the pH at $\mu = 0$.

This formula should hold true for low ionic strengths ($\mu < 0.01$). $\sqrt{\mu}$ can be replaced by $\sqrt{\mu}/(1 + \sqrt{\mu})$ which is a modification of the Debye-Hückel concept (James, 1986) to deal with the case of higher ionic strength ($\mu < 0.25$) which is within the practical range. The equation will thus be slightly changed on merely replacing $\sqrt{\mu}$ by $\sqrt{\mu}/(1 + \sqrt{\mu})$. As a shorter notation, we will use $S(\mu)$ for the term $\sqrt{\mu}/(1 + \sqrt{\mu})$ throughout this paper.

At any fixed V, $h(V)$ can be regarded as a constant which is independent of μ. This indicates the invariant nature of $h(V)$. The $h(V)$ can be regarded as the 'pH-shift characteristics' because it does not depend on μ. If all pH data at fixed V are used to calculate $h(V)$, the complete profile of such invariant pH-shift characteristics will be obtained. If indeed feasible, it could be useful in raw material characterization.

From the concept of the least square of the residuals, we can prove that at each specified titrant volume (V) and n sets of titration profiles (including at $\mu = 0$), the value of $h(V)$ is

$$h(V) = \frac{\sum_{i=1}^{n} (\text{pH shift}_i \cdot S_i(\mu))}{\sum_{i=1}^{n} [S_i(\mu)]^2} \tag{3}$$

TABLE 1

Effect of KOH on pH at different ionic strength (μ)

Volume of KOH (V)	μ	0	0.0500	0.1000	$h(V)$
	$\sqrt{\mu}/(1+\sqrt{\mu})$	0	0.1827	0.2403	
0		5.92	6.94	7.14	5.2626
1		6.75	7.33	7.44	2.9826
2		7.39	7.79	7.74	1.7251
3		7.86	7.98	8.03	0.6889
4		8.25	8.29	8.31	0.2384
4.2		8.31	8.34	8.36	0.1920
4.4		8.36	8.39	8.4	0.1656
4.6		8.45	8.42	8.41	−0.1656
4.8		8.55	8.5	8.48	−0.2848
5		8.64	8.59	8.57	−0.2848
6		8.99	8.91	8.82	−0.6087
7		9.34	9.14	9.08	−1.0867

$$= \frac{\sum_{i=1}^{n} \left((\text{pH}_i - \text{pH}_{\mu=0}) \cdot S_i(\mu)\right)}{\sum_{i=1}^{n} [S_i(\mu)]^2} \tag{4}$$

To treat the data, the titrant volume-pH profile at various ionic strengths must first be determined. The only condition for Eqn 4 is that at any corresponding titrant volume, the pH at $\mu = 0$ must also be known, preferably with repeat runs.

For the purpose of illustration, titration of aluminum hydroxide (batch no. 87-335-30, Giulini Chemie) with potassium hydroxide was performed, using a Hanna instrument pH meter. Ionic strength was adjusted using potassium chloride. The results are listed in Table 1.

Plotting $h(V)$ from Eqn 4 on the y-axis vs the corresponding pH (standard pH), the ZPC can be read directly from the x-axis intercept. Being singly linear in nature, the reliability of this method should increase when more data are obtained. The only question concerns what the standard pH should be on the x axis. No single pH-titrant volume profile, should be regarded as accurate enough to rely upon because random noise in pH measurement always exists for all experimental readings. If the standard pH value is the average of all pH values at that same titrant volume (regardless of ionic strength) (Fig. 1), is

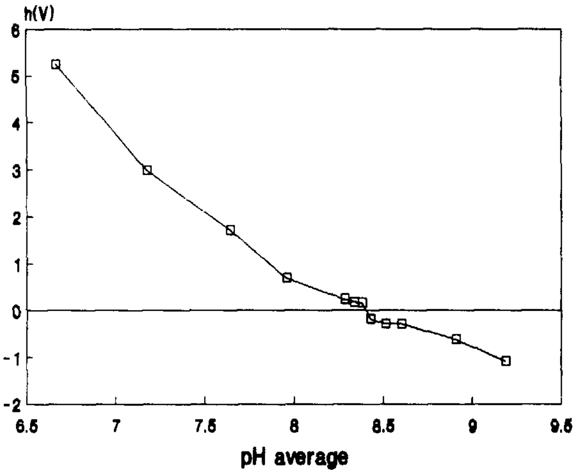

Fig. 1. Plot of pH-shift characteristics vs average value of all pH measured.

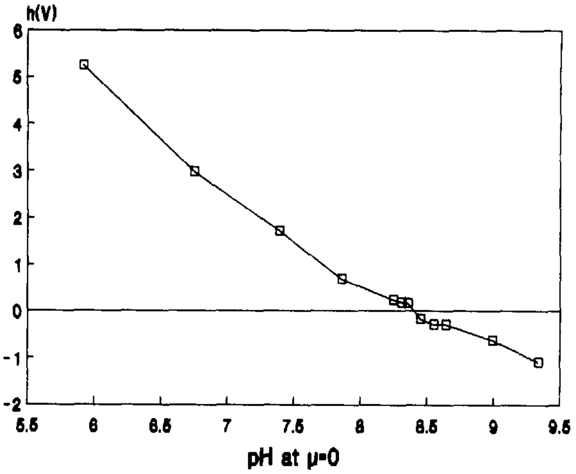

Fig. 2. Plot of pH-shift characteristics vs pH measured at $\mu = 0$.

the line obtained meaningless in nature? The answer is yes, except at the ZPC where, *by definition*, all measured pH values are equal to the ZPC itself. Furthermore, even at pH different from ZPC, the ZPC can still be interpolated for the x-axis intercept. Moreover, the average line of the pH will be more reliable because the experimental error should be cancelled by the process of averaging. This is useful when only the ZPC is the value to be found.

On the other hand, if the standard pH is the pH at $\mu = 0$, the plot of the pH-shift characteristics, or $h(\mu)$, vs standard pH can be used, as the invariant line profile represents the raw material characterization curve (Fig. 2). The weak point is that the value of pH at $\mu = 0$ will be used repetitively, so repeat runs at $\mu = 0$ should thus be performed in order to increase the accuracy in the calculation process.

The task of titration can be reduced by performing titration with only either a monovalent acid or monovalent base. Before titration, or at zero volume of titrant, increasing ionic strength also shifts pH upward or downward exclusively. For a downward shift, the titrant should be acidic because the ZPC lies in a more acidic region. The opposite is also true for an upward shift of pH due to the ionic strength effect. The experiment should thus be focussed only at pH near the suspected ZPC.

This method can still be modified by using the standard deviation value of all pH at fixed titrant volume multiplied by the sign of the pH shift as the y-axis: the ZPC reading on the x-axis scale is still the same. Graphical plotting in this manner yields ZPC as 8.41, equal to that determined using other forms of graphical plotting. To improve the reliability of the pH profile at $\mu = 0$, repeat runs at $\mu = 0$ should be performed.

By plotting the pH-shift characteristics or $h(V)$ vs titrant volume (V) (Fig. 3), the assumption for the derivation of Eqn 1 could also be validated.

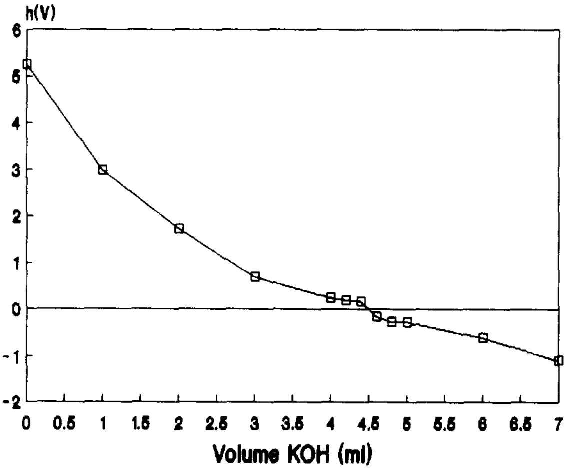

Fig. 3. Plot of pH-shift characteristics vs titrant volume.

In this case, a certain degree of deviation from linearity is observed, suggesting that Eqn 1 should be more acceptable if the weighted least-squares method is used or data which are far from the suspected ZPC point are ignored. Where necessary, modification of Eqn 1 by changing $h(V)$ may be more appropriate.

In comparison with the previously suggested method (Wongpoowarak and Worakul, 1991). These methods do not demonstrate the reliability of the ZPC achieved in statistical terms. In such cases, fitting with an empirical model is more useful because the regression function can be used to predict the range of any parameter involved in a specified confidence interval.

In conclusion, this method can be used without prior knowledge of titrant concentration (if the same titrant solution is used throughout the experiment). Furthermore, titration with both acid and base to cover the whole range of possible pH is unnecessary except where the overall pH shift characteristics are to be established.

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