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A nonlinear isotherm model for sorption of anionic dyes on cellulose fibers: A case study

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ABSTRACT

The sorption data of an anionic dye on cellulose fiber are often correlated with a log-linear model to determine the internal accessible volume of the fiber to the anionic dye (V, L/kg) and as such the standard affinity of the anionic dye to the fiber ($-\Delta\mu^\circ$, J/mol), but without taking into account the influence of ionized carboxyl groups due to cellulose oxidation ($[COO^-]_f$, mol/kg). In this study, a nonlinear isotherm model was derived by incorporating $[COO^-]_f$, V and $-\Delta\mu^\circ$ as three model parameters. A set of classical sorption data of C. I. Direct Blue 1 on bleached cotton was correlated with the nonlinear isotherm model. The nonlinear curve fitting analysis showed that the nonlinear isotherm model was in excellent agreement with the sorption data and robust to determine the values of $[COO^-]_f$, V and $-\Delta\mu^\circ$ for describing the sorption behaviors of anionic dyes on cellulose fibers.

1. Introduction

The anion (D^{z-}) of an anionic dye (Na_zD) is substantive toward cellulose and tends to be adsorbed onto the fiber from an aqueous solution to which sodium chloride (NaCl) is often added to promote the sorption process (Shore, 1995). An equilibrium is reached when the chemical potential of the dye on the fiber (μ_f) is the same as that in the solution (μ_s). The sorption behavior of the anionic dyes on the fiber is generally described using a sorption isotherm and reported as the difference in the standard chemical potential of the dye in the aqueous solution and on the cellulose fiber ($-\Delta\mu^\circ$) as given in Eq. (1). $-\Delta\mu^\circ$ is also called the standard affinity of the direct dye to the cellulose fiber and regarded as the driving force in the kinetics of the sorption process.

$$-\Delta\mu^\circ = RT \ln\left(\frac{[D^{z-}]_f[Na^+]_f^z}{V^{z+1}[D^{z-}]_s[Na^+]_s^z}\right) \quad (1)$$

In Eq. (1), $[D^{z-}]_s$ is the concentration of dye anions in the solution (mol/L) which is commonly measured in the residual solution by spectrophotometry, $[D^{z-}]_f$ is the concentration of dye anions in the fiber (mol/kg) which can be determined either by the depletion of dye in the solution or by the extraction of dye from the fiber, $[Na^+]_s$ is the concentration of sodium ions in the solution (mol/L) which is approximately equivalent to the sum of all counter ions in the solution using electrical neutrality as given in Eq. (2), and $[Na^+]_f$ is the concentration of sodium ions in the fiber (mol/kg) which is derived from the electrical neutrality in the fiber (Eq. (3)) and Donnan membrane equilibrium (Eq. (4)) and is given in Eq. (5), V is the internal accessible volume of the fiber to the dye (L/kg), and z is the ionic charge of the direct dye.

$$[Na^+]_s = z[D^{z-}]_s + [Cl^-]_s \quad (2)$$

$$[Na^+]_f = z[D^{z-}]_f + [Cl^-]_f \quad (3)$$

$$\frac{[Na^+]_f[Cl^-]_f}{V^2} = [Na^+]_s[Cl^-]_s \quad (4)$$

$$[Na^+]_f = \frac{1}{2}[z[D^{z-}]_f + (z^2[D^{z-}]_f^2 + 4V^2[Na^+]_s[Cl^-]_s)^{1/2}] \quad (5)$$

$-\Delta\mu^\circ$ can be calculated by replacing $[Na^+]_f$ using Eq. (5). The parameter V in Eqs. (1) and (5), however, cannot be measured experimentally. As indicated in Eq. (1), the magnitude of V is comparable to those of other parameters, and it may have a great influence on the calculated value of $-\Delta\mu^\circ$. Additionally, the parameter V represents the internal pore or void space of the fiber that is accessible to the dye, and can be used to compare sorption behaviors of the same anionic dye on cellulose with different structures (Carrillo, Lis, & Valldeperas, 2002; Ibbett, Phillips, & Kaenthong, 2006; Ibbett, Phillips, & Kaenthong, 2007). Hence, it is of great importance to

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reach an accurate and reliable value of V. A conventional approach is to rearrange Eq. (1) to give a log-linear unitary relationship between $\ln([D^{z-}]_f[Na^+]_f^z)$ and $\ln([D^{z-}]_s[Na^+]_s^z)$ as given in Eq. (6). By inputting an arbitrary value of V, $\ln([D^{z-}]_f[Na^+]_f^z)$ is plotted against $\ln([D^{z-}]_s[Na^+]_s^z)$ to give a straight line. Adjusting the input value of V until the straight line is reached with a unitary slope corresponding to which the value of V is selected as the internal accessible volume of the fiber to the anionic dye. And also, it is required that the value of $-\Delta\mu^\circ$ calculated from the selected value of V should be constant for all sorption data.

$$\ln([D^{z-}]_f[Na^+]_f^z) = \ln([D^{z-}]_s[Na^+]_s^z) + (z+1)\ln(V) + \frac{-\Delta\mu^\circ}{RT} \quad (6)$$

The models and theoretical treatments demonstrated in Eqs. (1)–(6) were developed during the first part of the 20th century based on the pioneering work on the physical chemistry of cellulose fiber dyeing with direct dyes (Hanson, Neale, & Stringfellow, 1935; Marshall & Peters, 1947; Peters & Vickerstaff, 1948), which later constructed the best knowledge foundation of classical dyeing textbooks (Shore, 1995; Sumner, 1989; Vickerstaff, 1954). They are often referred to in research literature to interpret the equilibrium sorption data of anionic dyes on cellulose (Carrillo et al., 2002; Ibbett et al., 2006, 2007; Porter, 1993, 2002). However, the linear curve fitting is routinely carried out by assigning an arbitrary value to V by the trial-and-error method, which involves not only tedious graphical techniques but also is insensitive to the change in the value assigned to the parameter V.

Reworking Eqs. (1) and (5) results in a nonlinear isotherm model by which $[D^{z-}]_s$ is expressed as a function of $[D^{z-}]_f$, as given in Eq. (7), in which V and $-\Delta\mu^\circ$ are two unknown model parameters (Xu & Shamey, 2012a,b). The nonlinear sorption isotherm model can be fitted to the equilibrium sorption data by nonlinear curve fitting (Bates & Watts, 1988), from which V and $-\Delta\mu^\circ$ could be determined. Compared to the log-linear model, the nonlinear isotherm model is equivalent but more sensitive in determining the values of V and $-\Delta\mu^\circ$, and also avoids the complexity of the trial-and-error method.

$$[D^{z-}]_s = \frac{[D^{z-}]_f[z[D^{z-}]_f + (z^2[D^{z-}]_f^2 + 4V^2[Na^+]_s[Cl^-]_s)^{1/2}]^z}{2^z[Na^+]_s^z V^{z+1}\exp\left(\frac{-\Delta\mu^\circ}{RT}\right)} \quad (7)$$

It should be noted, however, that both the log-linear model (Eq. (6)) and the nonlinear isotherm model (Eq. (7)) are only valid for describing sorption behaviors of anionic dyes on the ideal carboxyl-free cellulose fibers due to the absence of a model parameter representing the ionized carboxyl groups ($[COO^-]_f$, mol/kg). As a matter of fact, carboxyl group is commonly contained in natural and regenerated cellulose fibers due to cellulose oxidation, of which only a fraction is in the ionized form (McGregor, 1972; McGregor & Ezuddin, 1974). The ionized carboxyl groups could produce negative charge on fiber which may significantly influence the sorption of anionic dyes on cellulose fibers (Daruwalla, Kangle, & Nabar, 1961). It is possible to estimate the value of $[COO^-]_f$ by the dissociation or association equilibrium of carboxyl groups in cellulose fibers under sorption conditions, for which the total carboxyl groups can be determined by titration methods (Fras et al., 2004). It is thus suggested in considerable research that $[COO^-]_f$ should be taken into account by modifying the electrical neutrality in the cellulose fiber to Eq. (8) (Bae, Motomura, & Morita, 1997; Daruwalla et al., 1961; McGregor, 1972; McGregor & Ezuddin, 1974; Neale & Stringfellow, 1940; Standing & Warwicker, 1949; Sumner, 1986). However, $[COO^-]_f$ is preferably neglected to retain simple models in for application (Carrillo et al., 2002; Holmes, 1958; Marshall & Peters, 1947; Muller, 1963; Peters & Vickerstaff, 1948; Porter, 2002; Porter & Perkins, 1970; Standing, 1954; Willis, Warwicker, Standing, & Urquhart, 1945; Xu & Shamey, 2012a,b).

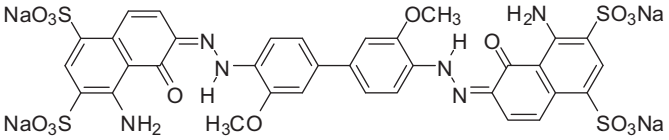

Fig. 1. The structure of C.I. Direct Blue 1.

$$[Na^+]_f = z[D^{z-}]_f + [Cl^-]_f + [COO^-]_f \quad (8)$$

In this study, we proposed to incorporate the model parameter $[COO^-]_f$ into the nonlinear isotherm model for describing the sorption behavior of anionic dyes on cellulose fibers. The derived nonlinear isotherm model was validated with a set of classical sorption data of C. I. Direct Blue 1 on the bleached cotton (Hanson et al., 1935). The model parameters $[COO^-]_f$, V and $-\Delta\mu^\circ$ were determined by the nonlinear curve fitting technique.

2. Experimental data

A set of previously published sorption data was used in this paper for validating the nonlinear isotherm model (Hanson et al., 1935). As shown in Table 1, these sorption data were experimentally obtained from 6 samples for sorption of C. I. Direct Blue 1 ($z = 4$, as shown in Fig. 1) on the bleached cotton at 90 °C in the presence of 0.0856 mol/L NaCl. This set of sorption data is classically referred to in main dyeing textbooks for its important role in developing the dyeing theories of cellulose fibers with anionic dyes (Shore, 1995; Sumner, 1989; Vickerstaff, 1954). Additionally, the value of $[COO^-]_f$ of the bleached cotton was unknown due to the fact that it was not possible for the investigators to make quantitative allowance for cellulose oxidation. The interested parameters such as $[COO^-]_f$, V and $-\Delta\mu^\circ$ for sorption of C. I. Direct Blue 1 on the bleached cotton will be determined by the nonlinear curve fitting technique.

Table 1
Equilibrium sorption data of C.I. Direct Blue on the bleached cotton at 90 °C in the presence of 0.0856 mol/L NaCl (Hanson et al., 1935).

Sample no.	$[D^{z-}]_s \times 10^4$ (mol/L)	$[D^{z-}]_f \times 10^3$ (mol/kg)	$[Na^+]_s \times 10^4$ (mol/L)	%*RD* of $[Na^+]_s$ [a]	%*RD* of $[Na^+]_s$ [c]
1	0.0958	2.58	0.0856	0.57	0.32
2	0.2520	3.79	0.0857	0.49	0.24
3	0.5040	4.95	0.0858	0.38	0.13
4	1.0100	6.19	0.0860	0.14	0.11
5	2.0200	7.60	0.0864	0.33	0.58
6[b]	4.0400	8.84	0.0872	1.26	–

[a] $\overline{[Na^+]_s} = 0.0861$ mol/L.
[b] Excluded from the nonlinear curve fitting because of its *RD* greater than 1%.
[c] $\overline{[Na^+]_s} = 0.0859$ mol/L.

3. Results and discussion

3.1. Model derivation

$[Cl^-]_f$ in the Donnan membrane equilibrium equation (Eq. (4)) was substituted to the electrical neutrality in the fiber (Eq. (8)) to give Eq. (9).

$$[Na^+]_f = z[D^{z-}]_f + \frac{[Na^+]_s[Cl^-]_s V^2}{[Na^+]_f} + [COO^-]_f \quad (9)$$

Eq. (9) was rewritten in a quadratic equation with one unknown variable ($[Na^+]_f$) as given in Eq. (10).

$$[Na^+]_f^2 - (z[D^{z-}]_f + [COO^-]_f)[Na^+]_f - [Na^+]_s[Cl^-]_s V^2 = 0 \quad (10)$$

$[Na^+]_f$ was obtained by solving the quadratic equation as expressed in Eq. (11).

$$[Na^+]_f = \frac{1}{2}\{(z[D^{z-}]_f + [COO^-]_f) + [(z[D^{z-}]_f + [COO^-]_f)^2 + 4V^2[Na^+]_s[Cl^-]_s]^{1/2}\} \quad (11)$$

$[Na^+]_f$ in Eq. (1) was replaced using Eq. (11), and the equation was rearranged to give Eq. (12) by which $[D^{z-}]_s$ was expressed as a function of $[D^{z-}]_f$.

$$[D^{z-}]_s = \frac{[D^{z-}]_f\{(z[D^{z-}]_f + [COO^-]_f) + [(z[D^{z-}]_f + [COO^-]_f)^2 + 4V^2[Na^+]_s[Cl^-]_s]^{1/2}\}^z}{2^z[Na^+]_s^z V^{z+1}\exp(-\Delta\mu^\circ/RT)} \quad (12)$$

Eq. (12) can be regarded as a nonlinear isotherm model. Assuming that all the model parameters are constant, the model parameters $[COO^-]_f$, V and $-\Delta\mu^\circ$ can be determined by nonlinear curve fitting. As a matter of fact, the model parameter $[Na^+]_s$ is a variable dependent on $[D^{z-}]_s$ as given in Eq. (2). A constant value of the model parameter $[Na^+]_s$ can be closely approximated using an average value of $[Na^+]_s$ of all sorption isotherm data ($\overline{[Na^+]_s}$) with respect to which the relative deviation (RD) of $[Na^+]_s$ of each sorption isotherm data is controlled to less than 1.0% using Eq. (13) by adding an adequate amount of NaCl (Xu & Shamey, 2012a).

$$\%RD = \frac{\left|[Na^+]_s - \overline{[Na^+]_s}\right|}{\overline{[Na^+]_s}} \times 100\% \quad (13)$$

It should be noted that, when $[COO^-]_f = 0$, Eq. (12) is equivalent to the nonlinear sorption isotherm model shown as Eq. (7) as well as the log-linear model shown as Eq. (6) plus Eq. (5) which is only valid for describing the sorption behavior of anionic dyes on the ideal carboxyl-free cellulose; but when $[COO^-]_f > 0$, Eq. (12) is equivalent to the log-linear model shown as Eq. (6) plus Eq. (11) which can be used for describing the sorption behavior of anionic dyes on the cellulose containing carboxyl groups due to oxidation.

3.2. Model validation

As shown in Table 1, the RD of $[Na^+]_s$ for the sixth sample was greater than 1%, indicating that this sample might bring a significant error in the results and thus was excluded from the nonlinear curve fitting. $\overline{[Na^+]_s}$ was recalculated to be 0.0859 mol/L with respect which the RDs of $[Na^+]_s$ for all the remaining samples were reduced to less than 1%, and was considered to be statistically constant at a 99% confidence level. Substituting $z = 4$, $[Na^+]_s = 0.0859$ mmol/L, $R = 8.314$ J/(K·mol) and $T = 363$ K to Eq. (12) resulted in Eq. (14).

$$[D^{4-}]_s = \frac{1152[D^{4-}]_f\{(4[D^{4-}]_f + [COO^-]_f) + [(4[D^{4-}]_f + [COO^-]_f)^2 + 0.03V^2]^{1/2}\}^4}{V^5\exp(-\Delta\mu^\circ/3018)} \quad (14)$$

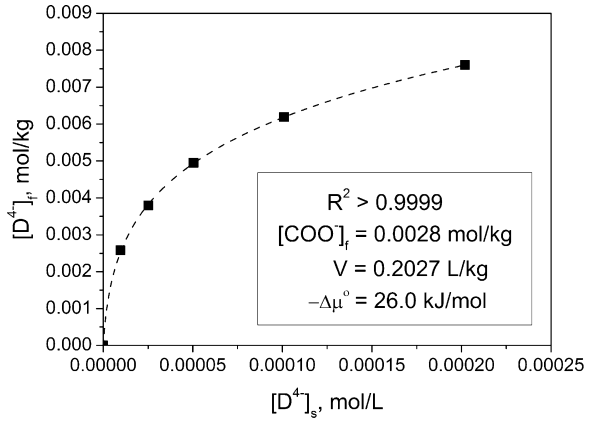

Fig. 2. Best-fit curve of the nonlinear isotherm model to the sorption data for sorption of C.I. Direct Blue 1 on the bleached cotton at 90 °C in the presence of 0.0856 mol/L NaCl.

The equilibrium sorption data was correlated with Eq. (14) by nonlinear curve fitting. The best-fit curve resulting from the nonlinear curve fitting is shown in Fig. 2. The coefficient of determination (R^2) greater than 0.9999 indicates that the equilibrium sorption data were in excellent agreement with the nonlinear isotherm model. The model parameters $[COO^-]_f$, V and $-\Delta\mu^\circ$ were found to be 0.0028 mol/kg, 0.2027 L/kg and 26.0 J/mol, respectively.

The robustness of the nonlinear isotherm model for estimating the values of $[COO^-]_f$, V and $-\Delta\mu^\circ$ was verified by correlating the sorption data with the log-linear model, for which $[Na^+]_f$ was calculated using Eq. (11) by substituting $[COO^-]_f = 0.0028$ mol/kg and $V = 0.2027$ L/kg. The results of linear curve fitting are shown in Fig. 3. Three common features were highlighted for the linear curve fitting: (1) the straight line resulting from the linear curve fitting had a slope of 0.9813 closely approximating the unitary slope, (2) the values of $-\Delta\mu^\circ$ calculated by Eq. (1) were constant for each sorption sample as shown in Fig. 4, and (3) the mean value of $-\Delta\mu^\circ$ was the same as the one determined by the nonlinear isotherm model. This indicates that the nonlinear isotherm model was perfectly equivalent to the log-linear model for correlating the equilibrium sorption data.

It seemed, however, that the log-linear model was impotent for correlating the sorption data when the model parameter $[COO^-]_f$ was unknown. For example, the linear curve fitting had to be

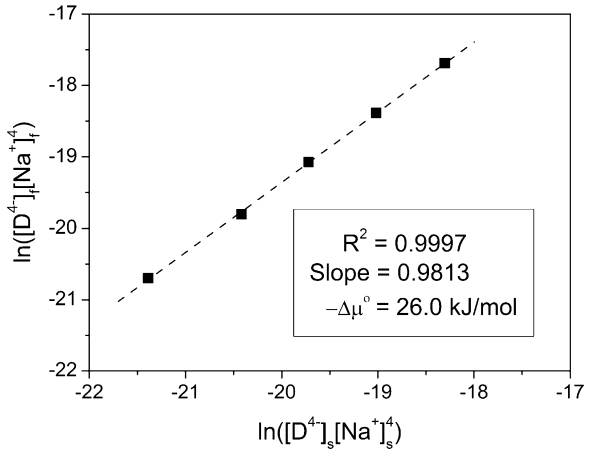

Fig. 3. Fit curve of the log-linear model to the sorption data for sorption of C.I. Direct Blue 1 on the bleached cotton at 90 °C in the presence of 0.0856 mol/L NaCl using $[COO^-]_f = 0.0028$ mol/kg and $V = 0.2027$ L/kg determined by the nonlinear curve fitting.

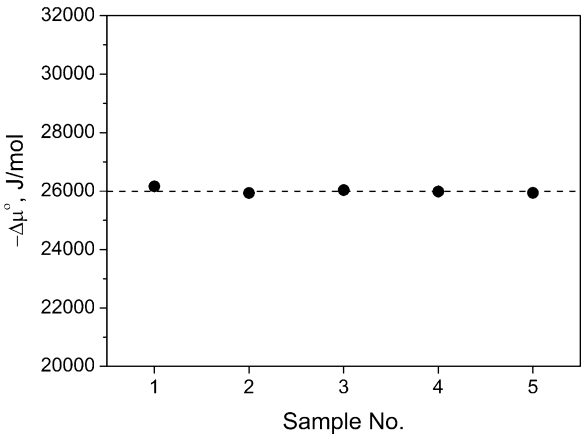

Fig. 4. Standard affinity calculated by Eq. (1) for sorption of C.I. Direct Blue 1 on the bleached cotton at 90 °C in the presence of 0.0856 mol/L NaCl using $[COO^-]_f$ = 0.0028 mol/kg and V = 0.2027 L/kg (*Note*: the dash line represents the average value of $-\Delta\mu^\circ$ from all data points).

performed by adjusting the value of V at a pre-set value of $[COO^-]_f$ until a straight line was reached with a slope of 1. Fig. 5 shows the best-fit curves of the log-linear model to the sorption data for which the model parameter $[COO^-]_f$ was assigned a value of 0, 5, 10 and 15 mmol/kg to simulate a various concentration of ionized carboxyl groups in cellulose due to oxidation. The results of the linear curve fittings were summarized in Table 2. As shown in the figure and table, no matter what value was assigned to $[COO^-]_f$, the linear curve fitting always resulted in a straight line with a coefficient of determination greater than 0.999. Additionally, an increase in the value of $[COO^-]_f$ resulted in a decrease in the estimated value of V

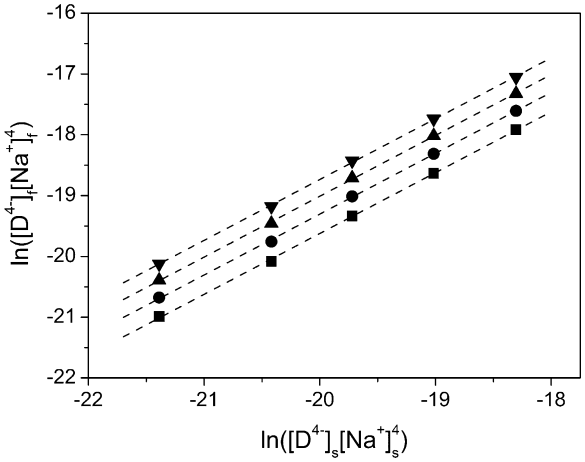

Fig. 5. Best fit curves of the log-linear model to the equilibrium sorption data of C.I. Direct Blue 1 on the bleached cotton at 90 °C in the presence of 0.0856 mol/L NaCl by pre-setting a value of $[COO^-]_f$ at 0 mmol/L (—■----), 5 mmol/L (—●—), 10 mmol/L (—▲—), and 15 mmol/L (—▼—).

Table 2
Results of curve fittings of the log-linear model to the equilibrium sorption data of C.I. Direct Blue on the bleached cotton at 90 °C in the presence of 0.0856 mol/L NaCl.

$[COO^-]_f$ (mmol/kg)[a]	V (L/kg)	$-\Delta\mu^\circ$ (kJ/mol)	R^2 [b]
0	0.2039	25.1 ± 0.1	>0.999
5	0.1850	27.6 ± 0.1	>0.999
10	0.1587	30.8 ± 0.0	>0.999
15	0.1206	35.7 ± 0.1	>0.999

[a] The pre-set value of $[COO^-]_f$ for linear curve fittings.
[b] Curve fitting was performed by adjusting the value of V at the pre-set value of $[COO^-]_f$ to reach a straight line with a slope of 1.

Table 3
Values of $[COO^-]_f$, V and $-\Delta\mu^\circ$ determined by the nonlinear model in comparison with those determined by the log-linear model as reported in Peters and Vickerstaff (1948).

Model parameter	Nonlinear model	Log-linear model
$[COO^-]_f$ (mmol/kg)	0.0028	0
V (L/kg)	0.2027	0.22
$-\Delta\mu^\circ$ (kJ/mol)	26.0	24.2

as well as an increase in the estimated value of $-\Delta\mu^\circ$. This indicates that using an inaccurate value of $[COO^-]_f$ in the log-linear model would underestimate or overestimate V and, consequently, overestimate or underestimate $-\Delta\mu^\circ$. This actually made problematic for the log-linear model to determine an accurate value of $[COO^-]_f$ and as such V and $-\Delta\mu^\circ$. The importance of $[COO^-]_f$ for determination of V and $-\Delta\mu^\circ$ can be demonstrated in Table 3. It can be seen that the values of V and $-\Delta\mu^\circ$ reported in the literature without consideration of $[COO^-]_f$ in the log-linear model were found to be respectively higher and lower than those determined by the nonlinear model from which $[COO^-]_f$ was determined to be 0.0028 mmol/kg.

It should be noted that the value of $[COO^-]_f$ determined by the nonlinear isotherm model was the concentration of ionized carboxyl groups which was only a fraction of the total concentration of carboxyl groups in cellulose due to oxidation. It was thought that only the ionized carboxyl groups interacted had influence on the sorption equilibrium (Daruwalla et al., 1961; McGregor, 1972; McGregor & Ezuddin, 1974). However, $[COO^-]_f$ in the log-linear model must be theoretically predicted by the dissociation or association equilibrium of carboxyl groups in cellulose under sorption conditions, for which the total carboxyl groups in cellulose must be determined by titration methods (Fras et al., 2004). It would be possible to extend the nonlinear isotherm model by including the dissociation or association equilibrium of carboxyl groups in cellulose. However, there was no need for such a further modification of the nonlinear isotherm model, but only at the expense of greater complexity.

4. Conclusions

A nonlinear isotherm model was derived for describing the sorption behaviors of anionic dyes on cellulose fibers. $[COO^-]_f$, V and $-\Delta\mu^\circ$ were three important parameters in the nonlinear sorption isotherm model, respectively representing the concentration of ionized carboxyl groups in cellulose, the internal accessible volume of cellulose to the anionic dye and the standard affinity of the anionic dye to cellulose. Nonlinear curve fitting of a set of classical sorption data demonstrated that the nonlinear isotherm model was robust to determine the values of $[COO^-]_f$ (0.0028 mol/kg), V (0.2027 L/kg) and $-\Delta\mu^\circ$ (26.0 J/mol). Using the values of $[COO^-]_f$ and V determined by the nonlinear sorption isotherm model, the sorption data was transformed to fit the log-linear model. The linear curve fitting indicated that the nonlinear isotherm model was perfectly equivalent to the log-linear model for correlating the sorption data. Unlike the log-linear model which required a known value of $[COO^-]_f$, the nonlinear sorption model was capable of determining the value of $[COO^-]_f$ as well as the values of V and $-\Delta\mu^\circ$ by nonlinear curve fitting. Hence, the nonlinear isotherm model provided a reliable approach to correlating sorption data of anionic dyes on cellulose fibers.

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