ORIGINAL CONTRIBUTION

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Modified Booth equation for the calculation of zeta potential

Abstract An easy-to-use computer program based on the modified Booth equation (MBE) is developed to calculate the zeta potential of a spherical nonconducting particle from knowledge of the electrophoretic mobility, particle size, and the type and concentration of ions present in the solution. The program is applied to five sets of previously published literature data and the resulting zeta potentials are compared with the values given by the Henry equation to illustrate the extent of the relaxation effect in each case. In four cases, the output zeta potential data are compared with the corresponding values obtained from the rigorous numerical solution of O'Brien and White. Results indicate that the computer program developed here gives a reliable estimate of the zeta potential. The main advantage in using the MBE lies in its capability of calculating the zeta potential even for cases where the experimentally measured mobility exceeds the maximum theoretical mobility predicted by the O'Brien and White solution.

Key words: Modified Booth equation – zeta potential – electrophoretic mobility – relaxation effect – computer program – Henry equation – polystyrene latex particles – bitumen-in-water emulsions – ionic strength – Debye length – electrical double layer

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Introduction

In many practical situations the value of the zeta potential, ζ, obtained from electrophoresis experiments, is used to characterize the potential at the outer or diffuse part of the electrical double layer and hence is valuable in discussing electrical double layer interactions between the surfaces. Dukhin and Derjaguin [1] and Hunter [2] have presented a comprehensive discussion on the experimental and theoretical aspects of the zeta potential and its relevance in the general double-layer potential theory.

Calculation of zeta potential is one of the first steps used to acquire information on the extent to which colloidal particles are charged. The determination of the zeta potential is indirect and is done via the measurement of the electrophoretic mobility, u_E, which is defined as the ratio of the terminal velocity, v (in cm/s), to the applied electric field, E (in V/cm):

$$u_E = v/E \ . \tag{1}$$

Besides surface charge density, the electrophoretic mobility of a particle depends on a number of other factors such as pH, electrolyte concentration (ionic strength), dielectric permittivity of the medium, viscosity, temperature and particle size and geometry. For a spherical nonconducting particle, the variable κa, where κ^{-1} is the Debye length and a is the radius of the

particle, decides the functional relationship between the measured electrophoretic mobility and zeta potential. The Helmholtz–Smoluchowski equation and Hückel's equation relate the zeta potential to the electrophoretic mobility under two limiting cases, viz. for very large and very small values of κa, respectively, and both these equations may be combined [3] into a single equation in SI units as:

$$u_E = C\,(\varepsilon\zeta/\eta) \qquad (2)$$

where ε and η are the dielectric permittivity and viscosity of the medium and C is a constant, equal to 2/3 for $\kappa a < 0.1$ and equal to 1 for $\kappa a > 100$.

Although the Helmholtz–Smoluchowski and Hückel equations are useful limiting cases, most interesting and important problems involve κa's between these two limits. The above two limiting cases were examined by Henry [4] who showed that the basic difference between the two approaches was in the way in which the electric field in the neighborhood of the particle was taken into account. Hückel's derivation had ignored the deformation of the applied electric field around the particle whereas Smoluchowski's approach had assumed the field to be uniform and parallel to the surface of the particle [2]. Henry [4] developed the following relation between the mobility and zeta potential taking into account the superimposition of the applied field on the local field around the particle:

$$u_E = (2\varepsilon\zeta/3\eta)\,f_1(\kappa a)\ . \qquad (3)$$

In Eq. (3), $f_1(\kappa a)$ depends on the geometry of the particle and for $\kappa a < 1$:

$$f_1(\kappa a) = 1 + \frac{(\kappa a)^2}{16} - \frac{5(\kappa a)^3}{48} - \frac{(\kappa a)^4}{96} + \frac{(\kappa a)^5}{96}$$
$$- \left[\frac{(\kappa a)^4}{8} - \frac{(\kappa a)^6}{96}\right] e^{\kappa a} \int_\infty^{\kappa a}\left(\frac{e^{-t}}{t}\right)dt \qquad (4)$$

whereas for $\kappa a > 1$

$$f_1(\kappa a) = \frac{3}{2} - \frac{9}{2\kappa a} + \frac{75}{2(\kappa a)^2} - \frac{330}{(\kappa a)^3}\ . \qquad (5)$$

Eqs. (3)–(5) reduce to the Hückel equation and the Helmholtz–Smoluchowski equation for very small and very large values of κa, respectively.

The function $f_1(\kappa a)$ is known as the Henry correction factor and comparing Eqs. (2) and (3) it may be seen that $(2/3)f_1(\kappa a) = C$. The smooth transition of constant C between the two limits (Fig. 1) is given by the function $f_1(\kappa a)$. Two restrictions on the use of Henry's equation are that the potentials of the surfaces should be low (less than 25 mV), and the distortion of the electrical double layer
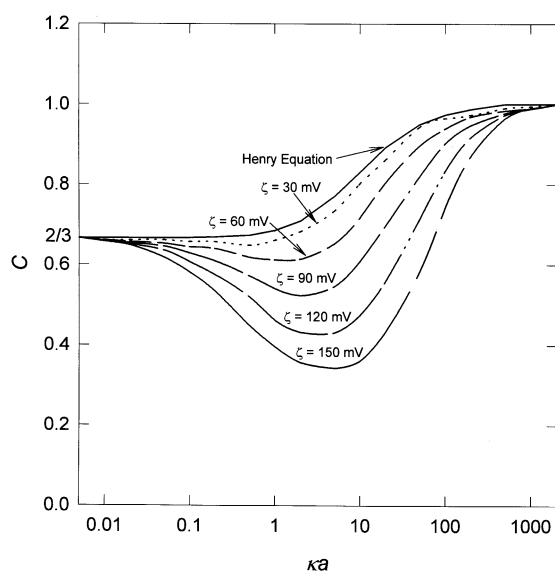

Fig. 1 The variation of constant C in Eq. (2) for various zeta potentials due to the correction from the relaxation effect (data from Ottewill and Shaw [12])

should be minimal during particle migration in electrophoresis. The distortion of the electrical double layer due to the applied field results in two effects which are described [2, 3] as follows. First, the ionic atmosphere and therefore the fluid surrounding the charged particle moves in a direction opposite to the particle's movement thereby retarding it (retardation effect). Second, because of particle motion an asymmetry in the ionic atmosphere surrounding the particle is created. Thus, the ions have to constantly rearrange themselves (relaxation effect) so that the center of positive charge attempts but fails to coincide with the center of negative charge. Both these effects originate from the electrical double layer. Retardation is accounted for in the above equations [Eqs. (2)–(5)] whereas the relaxation effects are not. In many colloid systems of interest the surface potentials are considerably higher than 25 mV, and at long Debye length the relaxation effect becomes significant.

Figure 1 describes how the relaxation effect influences constant C used in Eq. (2) which relates electrophoretic mobility and zeta potential. It is seen that the relaxation effect is minimal for lower potentials (less than 25 mV) and also at the limiting values of κa for which the Hückel equation and the Helmholtz–Smoluchowski equation are applicable (i.e., for $\kappa a \ll 1$ and $\kappa a \gg 1$, respectively). The relaxation effect has been treated by Dukhin and Derjaguin [1], Overbeek [5], Booth [6], Wiersema [7], Wiersema et al. [8] and O'Brien and White [9] among other researchers and their works have been described in detail

by Hunter [2]. In literature, it has been noted that the Wiersema procedure [7] or the procedure due to Dukhin and Derjaguin have been used [2, 10] to calculate the zeta potential from mobility data for cases where the relaxation effect is considered to be significant. The determination of zeta potentials by the Dukhin and Derjaguin procedure [10] involves the iterative solution of the following equation for ζ:

$$E = \frac{3\overline{\zeta}}{2} - 6\left\{\frac{\overline{\zeta}}{2} - \frac{\ln^2}{z}\left[1 - \exp(-z\overline{\zeta})\right]\right\}$$
$$\times \left\{2 + \frac{\kappa a}{M}\exp\left(\frac{-z\overline{\zeta}}{2}\right)\right\}^{-1} \qquad (6)$$

where

$$E \equiv \frac{3\eta e u_E}{2\varepsilon_r kT}, \quad \overline{\zeta} = \frac{e\zeta}{kT}, \quad M = \frac{2\varepsilon_r N_{Av} kT}{\eta \Lambda_\pm^\infty}.$$

In these expressions, ε_r is the dielectric constant, N_{Av} is the Avagadro number, k is the Boltzmann constant and $\Lambda_\pm^\infty$ is the specific conductance of the solution.

Hunter [2] mentions that the calculation of zeta potential from mobility data using the Wiersema [7] method is cumbersome and requires the preparation of a number of graphs in order to interpolate the values of the functions needed for the calculation. This situation was greatly improved with the rigorous treatment of the relaxation effect by O'Brien and White [9] and the development of the exact numerical solution and computer program called the MOBILITY program [11]. The program calculates the zeta potential of spherical particles from any given set of particle radius, ion valences, concentrations, and limiting ion conductivities [2]. Although this computation method is much simpler and rapid than the Wiersema method [7], for many systems [12–14] it was seen that the experimentally measured mobilities were far greater than the maximum mobility predicted from both methods, i.e. from the computed tables using the Wiersema treatment [7] or from the O'Brien and White solution [9]. Further, Chow and Takamura [13, 14] reported that the O'Brien and White computer solution overestimated the electrokinetic relaxation effect.

In this communication, a simple direct procedure based on the modified Booth equation (MBE), as described by Hunter [2], is presented in the form of computer program in the FORTRAN 77 language (http://colloid.che.tulane.edu). It must be noted that the MBE is applicable only for the symmetric case (i.e., $z_+ = z_-$). The program is used to calculate the zeta potential from published data on electrophoretic mobilities in five cases viz., four data sets for aqueous suspensions of polystyrene latex (the data of Chow and Takamura [14], Zhao and Brown

[15] and Zukoski and Saville [16]), and one data set for bitumen-in-water emulsions (data of Chow and Takamura [14]). The zeta potentials obtained from the MBE are compared with the values obtained from the Henry equation and with the corresponding values obtained from the computer solution of O'Brien and White as given in the above articles. Results show that the computer code based on the MBE gives a reliable estimate of the relaxation correction. This easy procedure for the calculation of zeta potentials is very useful for the case where the experimentally measured mobility exceeds the maximum mobility predicted by the O'Brien and White solution.

The modified Booth equation

The modified Booth equation is a straightforward procedure which also takes the relaxation effect into consideration in calculating zeta potential from electrophoretic mobility data and is described by Hunter [2]. For single symmetrical electrolytes at $25\,^\circ\mathrm{C}$, the equation is $\zeta = 25.7Z$, where ζ is expressed in mV and Z is given by

$$Z = \frac{E}{f_1} - \left[\frac{C_3\left(\frac{E}{f_1}\right)^3 + C_4\left(\frac{E}{f_1}\right)^4}{f_1 + 3C_3\left(\frac{E}{f_1}\right)^2 + 4C_4\left(\frac{E}{f_1}\right)^3}\right] \qquad (7)$$

and $E = 7520 u_E$ where u_E is expressed in $\mathrm{cm}^2/\mathrm{V\,s}$. The coefficients C_3 and C_4 are given by

$$C_3 = z^2 f_3^*(\kappa a) + 38.6z\left[\frac{1}{\Lambda_+^0} + \frac{1}{\Lambda_-^0}\right]Z_3^*(\kappa a), \qquad (8)$$

$$C_4 = 38.6z^2\left[\frac{1}{\Lambda_+^0} - \frac{1}{\Lambda_-^0}\right]Z_4^*(\kappa a). \qquad (9)$$

Calculations require the graphical determination of the Henry function, f_1, and the Booth relaxation correction functions, f_3^*, Z_3^* and Z_4^* for a given value of κa. It has probably been for this reason and because of the availability of alternative methods that the modified Booth equation has not been used extensively in literature. The relaxation correction functions together with the average limiting molar conductances $(\Lambda_\pm^0)$ of the co-ions and counter-ions at infinite dilution define the coefficients C_3 and C_4 as given in Eqs. (8) and (9). Original graphs of the functions f_1, f_3^*, Z_3^* and Z_4^* are available in Booth's paper [6], and also reproduced in the book by Hunter [2].

Table 1 Polynomial functions representing the Henry function, f_1, and the Booth relaxation correction functions, f_3^*, Z_3^* and Z_4^*

Function f_1

For $x \leqslant -1.00$

$f_1 = 1.000$

for $-1.00 < x \leqslant 0.55$

$f_1 = 1.0275157930 + 0.0857619670x + 0.1058385007x^2 + 0.0464011331x^3$

for $0.55 < x \leqslant 1.55$

$f_1 = 1.0622739775 - 0.0740929226x + 0.3832612499x^2 - 0.1256407214x^3$

for $1.55 < x \leqslant 3.00$

$f_1 = 0.7682190386 + 0.6988704751x - 0.2263212573x^2 + 0.0248691121x^3$

for $x > 3.00$

$f_1 = 1.500$

Function f_3^*

For $x \leqslant -1.80$

$f_3^* = 0.000$

for $-1.80 < x \leqslant 0.03$

$f_3^* = -0.0112083080 - 0.0191429549x - 0.0104365214x^2 - 0.0018170981x^3$

for $0.03 < x \leqslant 1.00$

$f_3^* = -0.0108002771 - 0.0291175642x + 0.0275123971x^2 - 0.0087070838x^3$

for $1.00 < x \leqslant 1.50$

$f_3^* = -0.0955590948 + 0.2116711423x - 0.2004411643x^2 + 0.0635055100x^3$

for $1.50 < x \leqslant 2.00$

$f_3^* = -0.2907559481 + 0.408629776x - 0.1991348646x^2 + 0.0330388653x^3$

for $2.00 < x \leqslant 3.50$

$f_3^* = -0.0568068165 + 0.0479486433x - 0.0139825680x^2 + 0.0014028004x^3$

for $x > 3.50$

$f_3^* = 0.000$

Function Z_3^*

For $x \leqslant -1.37$

$Z_3^* = 0.000$

for $-1.37 < x \leqslant 0.52$

$Z_3^* = -0.0060322035 - 0.0046707625x + 0.0009779153x^2 + 0.0008956332x^3$

for $0.52 < x \leqslant 1.52$

$Z_3^* = -0.0036002402 - 0.0127882770x + 0.0084012685x^2 - 0.0004954541x^3$

for $1.52 < x \leqslant 3.40$

$Z_3^* = -0.0296594772 - 0.0256531567x + 0.007420778x^2 + 0.0007183267x^3$

for $x > 3.40$

$Z_3^* = 0.000$

Function Z_4^*

For $x \leqslant -0.68$

$Z_4^* = 0.000$

for $-0.68 < x \leqslant 0.52$

$Z_4^* = 0.0012020613 + 0.0024949625x + 0.0005770172x^2 - 0.0007466722x^3$

for $0.52 < x \leqslant 1.50$

$Z_4^* = 0.0002280473 + 0.0056141588x - 0.0020766421x^2 - 0.0003154705x^3$

for $1.50 < x \leqslant 2.72$

$Z_4^* = -0.0001730427 + 0.0089680199x - 0.0062341106x^2 + 0.0010892474x^3$

for $x > 2.72$

$Z_4^* = 0.000$

In all the above equations $x = \log_{10}(\kappa a)$

The graph of each function [2] was subdivided into κa ranges and a polynomial function of order 3 was fitted by regression in each range of κa values. To do this, the graphs were scanned and digitized using a freely available Windows™ digitization software package WINDIG Ver. 2.0 on the Internet (http://life.bio.sunysb.edu/morph/windig.html). This software helps extract (x, y) data points from published graphs. The polynomial expressions for each function and the applicable $\log_{10}(\kappa a)$ ranges are given in Table 1. In these equations, $x = \log_{10}(\kappa a)$. The regression coefficient in each case was greater than 0.997.

The polynomials accurately reproduced the published [2, 6] graphs of the functions they represented as shown in Figs. 2 and 3. The polynomials along with the modified Booth equation [Eqs. (7)–(9)], forming the basis of the FORTRAN program code mentioned previously, calculate zeta potentials with input data values of: particle radii electrophoretic mobilities and concentrations of ions in solution.
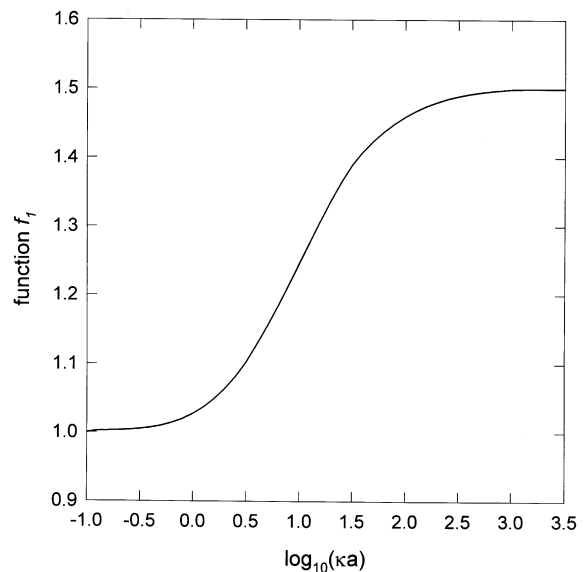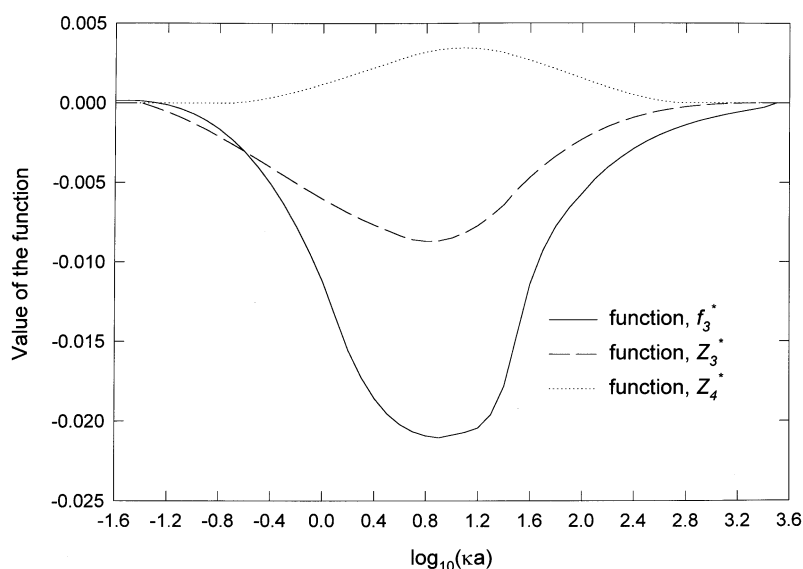
Fig. 2 Regenerated graph of the function $f_1(\kappa a)$

Fig. 3 Regenerated graphs of the functions $f_3^*(\kappa a)$, $Z_3^*(\kappa a)$, $Z_4^*(\kappa a)$

Table 2 Zeta potential calculations using the electrophoretic mobility data of Zhao and Brown [15]

pH	u_E	a	$[H^+]$	$[OH^-]$	$[Na^+]$	$[Cl^-]$	κ	κa	f_1	f_3^*	z_3^*	z_4^*	ζ_{MBE}	ζ_{Henry}
2.0	+0.26	77.8	1.000×10^{-2}	1.000×10^{-7}	0.00	1.00×10^{-2}	3.281×10^8	25.530	1.367	−0.0177	−0.0063	0.0031	+3.7	+3.7
3.0	−0.12	77.0	1.000×10^{-3}	1.000×10^{-7}	0.00	1.00×10^{-3}	1.038×10^8	7.989	1.215	−0.0211	−0.0087	0.0034	−1.9	−1.9
4.0	−0.72	78.5	1.001×10^{-4}	1.000×10^{-7}	0.00	1.00×10^{-4}	3.283×10^7	2.577	1.084	−0.0187	−0.0077	0.0023	−12.9	−12.8
5.0	−2.02	85.4	1.010×10^{-5}	1.000×10^{-7}	0.00	1.00×10^{-5}	1.043×10^7	0.891	1.023	−0.0103	−0.0058	0.0011	−39.5	−37.9
6.0	−2.21	85.4	1.100×10^{-6}	1.000×10^{-7}	0.00	1.00×10^{-6}	3.441×10^6	0.294	1.005	−0.0037	−0.0034	0.0002	−43.2	−42.2
7.0	−2.11	84.6	1.000×10^{-7}	1.000×10^{-7}	0.00	0.00	1.038×10^6	0.088	1.000	−0.0005	−0.0011	0.0000	−40.9	−40.5
8.0	−2.13	83.8	1.000×10^{-7}	1.100×10^{-6}	1.00×10^{-6}	0.00	3.441×10^6	0.288	1.005	−0.0036	−0.0034	0.0001	−41.6	−40.7
9.0	−2.14	82.3	1.000×10^{-7}	1.010×10^{-5}	1.00×10^{-5}	0.00	1.043×10^7	0.858	1.022	−0.0100	−0.0057	0.0010	−42.0	−40.2
10.0	−2.50	82.3	1.000×10^{-7}	1.001×10^{-4}	1.00×10^{-4}	0.00	3.283×10^7	2.702	1.088	−0.0189	−0.0078	0.0023	−48.1	−44.1
11.0	−2.55	74.4	1.000×10^{-7}	1.000×10^{-3}	1.00×10^{-3}	0.00	1.038×10^8	7.720	1.211	−0.0211	−0.0087	0.0034	−43.4	−40.4
12.0	−2.54	73.8	1.000×10^{-7}	1.000×10^{-2}	1.00×10^{-2}	0.00	3.281×10^8	24.120	1.361	−0.0182	−0.0065	0.0032	−37.3	−35.8

u_E	electrophoretic mobility $\times 10^{+4}$, cm^2/v s
a	hydrodynamic radius, nm
κ	Debye parameter, 1/m
f_1	Henry's correction function
f_3^*	Booth relaxation correction function
z_3^*	Booth realxation correction function
z_4^*	Booth realxation correction function
ζ_{MBE}	zeta potential from modified Booth equation, mV
ζ_{Henry}	zeta potential from Henry equation, mV

Results and discussion

To investigate the extent of the relaxation effect, the data of Zhao and Brown [15] are first analyzed. This system was chosen from literature because its κa values lie between 1 and 100, the range where the relaxation effects are known to be most significant. Zhao and Brown [15] report hydrodynamic radii and electrophoretic mobilities as a function of pH for a surfactant-free polystyrene latex in aqueous suspensions without added salt at 25 °C. Their data are shown in the first three columns in Table 2. In their paper the pH of the system was increased by the addition of NaOH, whereas it was not mentioned what was used to lower the pH. Assuming that the pH's were lowered by the addition of HCl, the relative concentrations of the univalent ions were calculated from the pH value and are also shown in Table 2. The variables in columns 2–6 in Table 2 form the input to the computer program. The output from the program gives values of κ, κa, the Booth relaxation correction functions and the zeta

potential (ζ_{MBE}), which are also tabulated in Table 2. To determine the extent of relaxation correction and to verify whether the results from the computer program are reliable, a comparison with the Henry zeta potential [Eq. (3)] is warranted. The ζ_{Henry} values are shown in the last column of Table 2. For this system the data from the O'Brien and White [9] computer solution is not available. Comparing the zeta potentials indicates that the values computed from the computer program match closely those given by the Henry equation for potentials below ∼ 25 mV and are therefore reliable. When the potentials are higher than 25 mV, ζ_{MBE} is higher than ζ_{Henry}, as expected from the relaxation correction. Since the potential is below 50 mV the relaxation correction is not significant.

Zukoski and Saville [16] have published data for κa between 1 and 100 and for much higher potentials, which were obtained from the rigorous O'Brien and White computer program (ζ_{OBW}). The first, second and last columns of Table 3 list the reported electrolyte concentrations electrophoretic mobility, and ζ_{OBW} for their two polystyrene latex systems, Latex A ($a = 83$ nm) and Latex B (235 nm). The output from the program along with ζ_{Henry} are shown in columns 3–9. Comparing ζ_{MBE} and ζ_{OBW} with ζ_{Henry} in Table 3, the relaxation correction is indeed significant. It should be noted that even ζ_{OBW}, considered the most rigorously obtained zeta potential, has been criticized [13, 14] for overestimating the relaxation correction at certain ranges of high potentials.

Table 3 Zeta potential calculations using the electrophoretic mobility data of Zukoski and Saville [16]

Salt Concn. (M)	u_E	κa	f_1	f_3^*	z_3^*	z_4^*	ζ_{MBE}	ζ_{Henry}	ζ_{OBW}
Latex A ($a = 83$ nm)									
HCl									
1.00×10^{-2}	− 3.92	27.25	1.374	− 0.0169	− 0.0061	0.0031	− 60.81	− 54.80	− 58.38
5.00×10^{-3}	− 3.90	19.27	1.333	− 0.0198	− 0.0072	0.0033	− 64.55	− 56.19	− 59.92
1.00×10^{-3}	− 3.55	8.62	1.225	− 0.0211	− 0.0086	0.0034	− 65.80	− 55.66	− 62.74
5.00×10^{-4}	− 3.12	6.09	1.179	− 0.0209	− 0.0087	0.0032	− 58.16	− 50.83	− 55.80
1.00×10^{-4}	− 3.00	2.73	1.089	− 0.0190	− 0.0078	0.0023	− 61.09	− 52.91	− 59.66
5.00×10^{-5}	− 3.00	1.93	1.062	− 0.0171	− 0.0073	0.0019	− 62.33	− 54.26	− 61.72
2.00×10^{-5}	− 3.24	1.22	1.036	− 0.0131	− 0.0064	0.0014	− 68.97	− 60.07	− 68.15
KCl									
1.00×10^{-2}	− 4.90	27.25	1.374	− 0.0169	− 0.0061	0.0031	− 81.92	− 68.49	− 78.69
1.00×10^{-3}	− 3.92	8.62	1.225	− 0.0211	− 0.0086	0.0034	− 76.86	− 61.46	− 76.12
1.00×10^{-4}	− 3.26	2.73	1.089	− 0.0190	− 0.0078	0.0023	− 69.49	− 57.50	− 68.92
Latex B ($a = 235$ nm)									
HCl									
5.00×10^{-3}	− 5.67	54.56	1.430	− 0.0086	− 0.0037	0.0023	− 85.59	− 76.15	− 82.81
1.00×10^{-3}	− 5.30	24.40	1.362	− 0.0181	− 0.0065	0.0032	− 100.10	− 74.74	− 87.44
5.00×10^{-4}	− 4.48	17.25	1.319	− 0.0202	− 0.0075	0.0034	− 81.91	− 65.23	− 74.32
1.00×10^{-4}	− 3.42	7.72	1.211	− 0.0211	− 0.0087	0.0034	− 63.58	− 54.24	− 58.63
5.00×10^{-5}	− 3.40	5.46	1.166	− 0.0208	− 0.0087	0.0031	− 67.00	− 56.01	− 64.29
KCl									
5.00×10^{-3}	− 6.70	54.56	1.430	− 0.0086	− 0.0037	0.0023	− 104.80	− 89.99	− 110.07
1.00×10^{-3}	− 5.48	24.40	1.362	− 0.0181	− 0.0065	0.0032	− 103.30	− 77.28	− 100.29
5.00×10^{-5}	− 4.20	5.46	1.166	− 0.0208	− 0.0087	0.0031	− 98.98	− 69.18	− 109.81

u_E	electrophoretic mobility $\times 10^{+4}$, cm²/v s
a	hydrodynamic radius, nm
κ	Debye parameter, 1/m
f_1	Henry's correction function
f_3^*	Booth relaxation correction function
z_3^*	Booth relaxation correction function
z_4^*	Booth relaxation correction function
ζ_{MBE}	zeta potential from modified Booth equation, mV
ζ_{Henry}	zeta potential from Henry equation, mV
ζ_{OBW}	zeta potential from the computer solutions of O'Brien and White by Zukoski and Saville [16]

The data of Chow and Takamura [14] for a heat-treated latex suspension and a bitumen-in-water emulsion system, are analyzed next with the modified Booth equation. NaCl, at a concentration of 10^{-4} M was present in all these measurements. Even though pH changes affect the values of κ, this was ignored in their calculations and a constant value of $\kappa = 3.284 \times 10^7$/m, based on 10^{-4} M NaCl concentration was used [14]. Table 4 lists their data [14], the output from our computer program (f_1, f_3^*, $Z_3^*, Z_4^*, \zeta_{MBE}$) as well as ζ_{Henry} and ζ_{OBW}. The ζ_{OBW} values shown in the table were interpolated from the graphs [14] of dimensionless mobility, U^*, vs. zeta potential for the corresponding κa values. For cases where the experimentally measured mobility exceeded the maximum mobility predicted by the O'Brien and White solution, the dimensionless zeta potential value at U_{max}^* was used. Therefore, there are only four data points in Table 4 (two at pH 4.0 for both systems, and two at pH's 8.0 and 8.8 for the bitumen emulsion system) where the MBE and the

computer solution of O'Brien and White [14] can actually be compared. It may be seen that the zeta potentials obtained from the MBE and the O'Brien and White solutions for both the systems are comparable. Besides providing a very easy tool for calculating zeta potential reliably, a major advantage in using the MBE program described in this communication lies in its ability to calculate the zeta potentials even in the cases where the experimentally measured mobility (U^*) exceeds the theoretical maximum (U_{max}^*) of O'Brien and White. This program has been used to calculate the zeta potential in recent studies on the coalescence of microscopic oil drops [17, 18] and the hetero-aggregation/selective-aggregation among oil drops and polystyrene latex particles [19].

Table 4 Zeta potential calculations using the electrophoretic mobility data of Chow and Takamura [14]

pH	u_E	f_1	f_3^*	z_3^*	z_4^*	ζ_{MBE}	ζ_{Henry}	ζ_{OBW}[a]
Heat treated latex ($a = 675$ nm, $\kappa a = 22.0$)								
4.0	− 5.09	1.350	− 0.0189	− 0.0068	0.0033	− 92.09	− 70.4	− 84.0
5.0	− 6.43	1.350	− 0.0189	− 0.0068	0.0033	− 156.60	− 90.9	− 127.0
5.5	− 7.10	1.350	− 0.0189	− 0.0068	0.0033	− 244.10	− 100.7	− 127.0
6.0	− 6.96	1.350	− 0.0189	− 0.0068	0.0033	− 218.50	− 98.9	− 127.0
7.0	− 6.83	1.350	− 0.0189	− 0.0068	0.0033	− 198.30	− 97.0	− 127.0
7.8	− 6.43	1.350	− 0.0189	− 0.0068	0.0033	− 156.60	− 91.3	− 127.0
9.0	− 6.70	1.350	− 0.0189	− 0.0068	0.0033	− 181.90	− 94.8	− 127.0
Bitumen-in-water emulsion ($a = 900$ nm, $\kappa a = 30.0$)								
4.0	− 4.95	1.412	− 0.0109	− 0.0045	0.0026	− 80.53	− 67.3	− 80.0
5.0	− 6.70	1.387	− 0.0151	− 0.0056	0.0029	− 134.80	− 92.6	− 130.0
5.8	− 7.10	1.384	− 0.0155	− 0.0057	0.0030	− 155.60	− 98.4	− 130.0
6.7	− 6.56	1.383	− 0.0158	− 0.0058	0.0030	− 128.90	− 91.1	− 130.0
7.0	− 6.16	1.383	− 0.0158	− 0.0058	0.0030	− 113.70	− 85.5	− 130.0
8.0	− 5.89	1.383	− 0.0157	− 0.0058	0.0030	− 105.00	− 81.8	− 125.0
8.8	− 5.76	1.386	− 0.0153	− 0.0057	0.0030	− 101.00	− 79.7	− 110.0

u_E	electrophoretic mobility $\times 10^{+4}$, cm^2/v s
a	hydrodynamic radius, nm
κ	Debye parameter, 1/m
f_1	Henry's correction function
f_3^*	Booth relaxation correction function
z_3^*	Booth realxation correction function
z_4^*	Booth realxation correction function
ζ_{MBE}	zeta potential from modified Booth equation, mV
ζ_{Henry}	zeta potential from Henry equation, mV
ζ_{OBW}	zeta potential from the computer solutions (graphs) of O'Brien and White given by Chow and Takamura [14]

$\kappa = 3.284 \times 10^7$/m in all cases

[a]In this column, the constant values of − 127.0 and − 130.0 mV for the two systems, respectively, are obtained from the U_{max}^* predicted by the O'Brien and White solution in [14]

References

1. Dukhin SS, Derjaguin BV (1974) In: Matijevic E (ed) Surface and Colloid Science. Vol 7, Wiley-Interscience, New York
2. Hunter RJ (1981) Zeta Potential in Colloid Science. Academic Press, New York
3. Hiemenz P, Rajagopalan R (1997) Principles of Colloid and Surface and Chemistry, 3rd ed. Marcel Dekker, New York
4. Henry DC (1931) Proc Roy Soc (London) Ser A 133:106
5. Overbeek JThG (1943) Kolloid-Beih 54:287
6. Booth F (1950) Proc Roy Soc (London) Ser A 203:514
7. Wiersema PH (1964) PhD thesis, University of Utrecht, Netherlands:98
8. Wiersema PH, Loeb AL, Overbeek JThG (1966) J Colloid Interface Sci 22:78
9. O'Brien RW, White L (1978) J Am Chem Soc Faraday II 74:1607
10. Hubbe MA (1987) Colloids Surfaces 25:325
11. Kihara H, Ryde N, Matijevic EJ (1992) Am Chem Soc Faraday Trans 88 16:2379
12. Ottewill RH, Shaw JN (1972) J Electroanal Chem 37:133
13. Chow RS, Takamura K (1988) J Colloid Interface Sci 125:213
14. Chow RS, Takamura K (1988) J Colloid Interface Sci 125:226
15. Zhao J, Brown W (1996) J Colloid Interface Sci 179:255
16. Zukoski CF, Saville DA (1985) J Colloid Interface Sci 107:322
17. Deshiikan RS, Papadopoulos KD (1995) J Colloid Interface Sci 171:303
18. Deshiikan RS, Papadopoulos KD (1995) J Colloid Interface Sci 171:313
17. Deshiikan RS, Papadopoulos KD (1997) Colloid Polym Sci 275:440