Colloid Polym Sci (2009) 287:659–670
DOI 10.1007/s00396-009-2024-1

ORIGINAL CONTRIBUTION

The effects of multivalent electrolytes on the gravity-induced flocculation of colloidal particles in binary suspensions

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Received: 22 January 2009 / Revised: 18 February 2009 / Accepted: 12 March 2009 / Published online: 1 April 2009

Abstract The effects of multivalent electrolytes on gravity-induced heteroflocculation behavior of binary suspensions under different gravity forces are investigated based on the turbidity measurement method. The heteroflocculation behavior of the binary suspensions described by the stability ratio is well analyzed by using the stability diagram and the DLVO theory. It is found that the stability ratios of the binary suspensions decrease with the increase of either the electrolyte concentration and valence or the gravity forces and with the decrease of the size ratio of the latexes components of the binary suspension. Because the theoretical stability ratios obtained by the trajectory analysis method are always higher than the corresponding heteroflocculation experimental values obtained by turbidity measurements, we successfully apply the "regressed" surface potentials determined from the flocculation experiments of monodispersed suspension to predict the stability ratios of the corresponded binary suspension.

Keywords Flocculation · Stability · Electrolyte · Gravity · Colloid

Introduction

Experimental efforts to investigate the gravity-induced heteroflocculation behavior in polydispersed colloidal suspension have been continuing for the last 30 years. For example, Matthews and Rhodes [1] investigated this problem for particle size ranged from 0.5 to 2.0 μm but could not obtain quantitative results since both hydrodynamic retardations and interparticle forces were neglected. Melik [2] took the hydrodynamic interactions and interparticle forces of DLVO theory [3] into consideration and conducted gravity-induced flocculation experiment to measure the stability ratios (i.e., in terms of calculating the capture efficiencies) of a binary suspension composed of polystyrene latexes with diameters of 0.166 and 0.255 μm under different electrolyte concentrations. Melik applied the stoppd-flow turbidity technique [4] and the Rayleigh–Gans–Debye theory of light scattering [5, 6] and found that the stability ratios obtained experimentally are always lower than the theoretical values calculated by the trajectory analysis method [7–10], especially when the electrostatic repulsion forces existed between particles. The higher measured zeta potentials of colloidal samples used in his experiments were considered as the major reason caused this disparity. Later on, Uricanu et al. [11] published the experimental results on the stability measurements for a binary suspension with large disparity in size containing poly(vinyl acetate) (PVAc) latexes of 0.24 μm diameter and Ludox silica sols of 0.024 μm diameter, their stability experiments proved that the adsorption of small silica particles onto the larger PVAc latexes can be viewed as a composite heteroparticle even when both particles were negatively charged. Hanus et al. [12] and Shenoy et al. [13] also did a series of heteroaggregation experiments on different sized acrylic latexes. By assuming that the fractal dimension of the aggregates of the binary suspension remains the same as that of the monodispersed system, they successfully analyzed the formations of particle–cluster and cluster–cluster aggregations in the later stages of their heteroaggregation experiments. All of the above experiments were conducted under normal gravity.

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Recently, Chang and Wang [14] carried out a series of gravity-induced flocculation experiments to investigate the effects of various monovalent electrolyte concentrations, pH values, particle size ratios, and enhanced gravity forces on the heteroflocculation behavior of equal numbers in a binary suspension. They found that the latex dispersions become unstable with increase either in ionic strength, or in the gravity forces, and decrease in pH value. Also, the stability ratio decreased when the size ratio of two different latexes was reduced (i.e., the size difference between two latexes was increased). Those experimental results were successfully analyzed by using the stability diagrams [8–10] constructed in that paper.

In the present paper, the effects of adding different concentrations of mono-, di- and trivalent electrolytes on the stability ratios under normal gravity and enhanced gravitational field were studied based on the same experimental and stability diagram methods adopted from our previous paper [14]. Based on turbidity measurements combined with light-scattering calculation method proposed by Lichtenbelt et al. [5, 6], a series of gravity-induced flocculation experiments for artificial latexes of various sizes with equal numbers in a binary dispersion were conducted. The experimental results will be investigated by using the stability diagrams and the total interaction energy curve of the DLVO theory. Since the theoretical stability ratios are always higher than experimental values, the "regressed" surface potential of colloidal samples is considered more meaningful and will be determined based on the stability ratios obtained from the flocculation experiments of monodispersed suspension; i.e., the regressed surface potentials of colloidal samples will be determined by using the regression analysis method according to the Eqs. 11 and 12 below. Then, the accuracy of applying those "regressed" surface potentials to predict the stability ratios of the corresponding binary suspension will be tested at the final part of the present paper.

Stability ratio

The stability ratio is generally used to describe the flocculation rates of colloidal suspension system. For the monodispersed colloidal suspension, the stability ratio can be evaluated from the following equation [15]:

$$W_{ii} = \frac{k_2^0}{k_2} \tag{1}$$

where k_2^0 is the Smoluchowski rate constant for rapid flocculation (i.e., diffusion controlled), k_2 is the slow flocculation rate constant when the electrostatic repulsive energy barrier of DLVO theory is included. Therefore, when there is a repulsive energy barrier, only a fraction, $1/W_{ii}$, of the encounters between colloidal particles lead to permanent contact. Usually, the higher the stability ratio, the more stable the colloidal suspension becomes and the smaller the flocculation rate resulted. In Eq. 1, the value of k_2 can be determined from the initial slope of the temporal turbidity variation curve of colloidal dispersion for each sample as mentioned in the turbidity measurement (see chapter 8 of [15]).

However, for a binary suspension containing two different sized particles, the stability ratio shall be expressed as [11]:

$$\frac{1}{W_{\text{mix}}} = \frac{X_1^2}{W_{11}} + \frac{X_2^2}{W_{22}} + \frac{2X_1X_2}{W_{12}} S(a_1, a_2) \tag{2}$$

where the subscripts 1 and 2 represent particles 1 and 2, X_j is the ratio of the particle number concentration of the jth-type particle (N_j) to the total number concentration of particles (N_{tot}) in the suspension, and $S(a_1, a_2)$ is the size correction factor for spherical particles differing in radius and is defined by

$$S(a_1, a_2) = \frac{(a_1 + a_2)^2}{4a_1a_2} \tag{3}$$

For a binary suspension, $X_1 + X_2 = 1$. When $X_1 \cong X_2 \cong 0.5$, as mentioned in the Melik's thesis (see Chapter 5 of [2]), the effect of gravity-induced flocculation will attain its maximum contribution relative to that of creaming flocculation. Therefore, in the present paper, we will conduct a series of binary heteroflocculation experiments with equal initial particle concentration as shown below.

In Eq. 2, W_{ij} can be expressed by [2]

$$W_{ij} = \frac{2k_{\text{B}}T}{3\mu_f k_{ij}} \frac{(1+\lambda)^2}{\lambda} \text{ with } \lambda = \frac{a_i}{a_j} \left(\text{i.e. } a_i \le a_j\right) \tag{4}$$

where k_{B} is the Boltzmann constant, T is the absolute temperature, μ_f is the viscosity of the dispersion, k_{ij} is the rate of doublet formation, and λ is the size ratio of particles a_i and a_j. In Eq. 4, k_{ij} can either be k_{11}, k_{22}, or k_{12}. The values of k_{11} and k_{22} can be determined from the initial slope of the temporal turbidity variation of monodispersed suspension as mentioned in Eq. 1, while k_{ij} must be determined based on the turbidity measurements combined with the light-scattering calculation method proposed by Lichtenbelt et al. [4] and the Rayleigh–Gans–Debye theory of light scattering [5, 6].

DLVO theory

According to the DLVO theory [3], the total interaction energy V_{int} is the sum of the van der Waals attractive and the electric double-layer repulsive energies:

$$V_{\text{int}} = V_{\text{A}} + V_{\text{R}} \tag{5}$$

In the present paper, the retarded van der Waals equation established by Ho and Higachi [16] and Gregory [17] is adopted,

$$V_{\mathrm{A}} = -\frac{A_{132} a_1 a_2}{3(a_1 + a_2)(R - 2)} Z(P_0) \tag{6}$$

where A_{132} = Hamaker constant

$Z(P_0)$ = correction factor to the retarded van der Waals attraction

$Z(P_0) = \frac{1}{1+1.7692P_0}$ for P_0 for > 1.0

$= \frac{2.45}{5P_0} - \frac{2.17}{15P_0^2} + \frac{0.59}{35P_0^3}$ for $P_0 > 1.0$

with $P_0 = \frac{2\pi(R-2)}{\upsilon}$, $\upsilon = \frac{2\lambda_L}{(a_1+a_2)}$ (degree of retardation), $R = \frac{2h}{(a_1+a_2)}$ and $\lambda_L = 10^{-5}$ cm (characteristic London wavelength of atoms), where h is the surface-to-surface distance between two interacting latexes. In Eq. 6, the Hamaker constant A_{ijk} for the two interacting particles (i and k) in the dispersion (j) can be calculated by [15]

$$A_{ijk} = \left(A_{ii}^{1/2} - A_{jj}^{1/2}\right)\left(A_{kk}^{1/2} - A_{jj}^{1/2}\right) \tag{7}$$

where the values of $A_{ii}=1.68\times10^{-19}$J for the polystyrene latex, $A_{ii}=1.0\times10^{-19}$ the styrene divinylbenzene latex, and $A_{ii}=0.4\times10^{-19}$J for water molecules are adopted in the present study [18] (i.e., those values of the Hamaker constants are referred to the nonconducting materials at 300 K). Hence, in the water solution, the Hamaker constants A_{ijk} of monodispersed polystyrene and styrene divinylbenzene latexes are 4.4×10^{-20} and 1.35×10^{-20}J, respectively. The Hamaker constant of the binary mixture of polystyrene and styrene divinylbenzene latexes is 2.4×10^{-20}J.

For the electrostatic repulsion energy between two different sized spherical particles, the equation obtained by Hogg, Healy, and Fuerstenau [19] is adopted (i.e., constant and low surface potentials are assumed),

$$V_{\mathrm{R}} = \frac{\varepsilon a_1 a_2 \psi_0^2}{(a_1 + a_2)} \ln\{1 + \exp[-\kappa(R - 2)]\} \tag{8}$$

where ε = dielectric constant of suspending medium

$$\psi_0 = \frac{1}{2}\left[\frac{\psi_1^2 + \psi_2^2}{2}\right] \text{(averaged surface potential)}$$

$$\kappa = \left[\frac{4\pi e^2 \sum C_i Z_i^2}{\varepsilon k_{\mathrm{B}} T}\right]^{1/2} \times \frac{(a_i + a_2)}{2}$$

(dimensionless reciprocal of Debye-Huckel double layer thickness)

e charge of electron, 1.6×10^{-19}C
C_i concentration of ion i
Z_i valence of ion i

The basic principle of the DLVO theory is that the total interaction energy between two interacting colloidal particles is the sum of the van der Waals attractive energy and the electrostatic repulsive energy. Its configuration profile can be characterized by the height of the primary maximum and the depth of the secondary minimum. The rate of colloidal flocculation was found to be exponentially proportional to the height of the primary maximum when the diffusive motion of particles over this energy barrier is the rate-determining step [20]. Usually, the height of the primary maximum of the interaction energy profile is dependent on the values of the particle size, the Hamaker constant, the ionic strength of the dispersion, and the surface potentials of the two interacting surfaces. If the ionic strength of the dispersion remains unchanged, the height of the primary maximum and also the magnitude of the electrostatic repulsion energy can be increased by either decreasing the particle size or increasing the surface potentials of the two interacting surfaces. With the increased height of the primary maximum, the stability of colloidal dispersion can be increased consequently. Therefore, the higher the primary maximum barrier, the higher the stability ratio of colloidal dispersion is.

Materials and methods

Artificial latexes

Polystyrene latexes of averaged sizes of 1.16 and 3.04 μm and density of $\rho = 1.06\mathrm{g/cm}^3$, and styrene divinylbenzene latex of averaged size 6.2 μm and density of 1.089 g/cm^3 were purchased from Sigma Chemical Inc., USA. These colloidal latexes are proved to be spherical, smooth, and monodispersed. The stock solution of each latex sample were prepared by diluting the concentrated dispersion with deionized water to the volume fraction ranged from 10^{-5} to 10^{-4} prior to each set of flocculation experiments. In order to minimize the effect of creaming, the initial number concentration of each latex dispersion was set equal and was confirmed by the Coulter counter measurements (Multi-Sizer II with a 30-μm aperture tube, i.e., $N_{01}\cong N_{02}\cong 10^6$particles/cm^3) in the binary flocculation experiments described below.

Zeta potential measurement

The electrophoretic measurements of zeta potentials of latexes were conducted at 20°C using a zeta meter purchased from Malvern Instruments Ltd. (Zetasizer 3000, Malvern, UK). Two different types of effects on the colloidal zeta potentials were investigated: (a) the effect of adding NaCl (monovalence), $MgCl_2$ (divalence), and $AlCl_3$

(trivalence) electrolytes and (b) the effect of changing their concentrations. All chemicals used in the experiments were of analytic grade.

Turbidity measurement

The turbidity of the suspension was measured at ambient temperature in a 15-mL standard bottle using nephelometer (Model 2100 P, Hach Co., Loveland, CO, USA). For each sample bottle, the turbidity was measured after 30 min of settling time. From the initial slope of the temporal turbidity variation curve, the stability ratio of the suspension for each experimental run can be determined. In the present study, the effects of adding different concentrations of mono- and multivalent electrolytes and the gravitational forces on the gravity-induced flocculation rates of both monodispersed and binary suspension with various size ratios will be investigated.

Experiments of different enhanced gravitational forces (i.e., G-force) were carried out on a Sanyo Micro-Centrifuge (Harrier 18/80) with maximum rotation speed of 6,000 rpm.

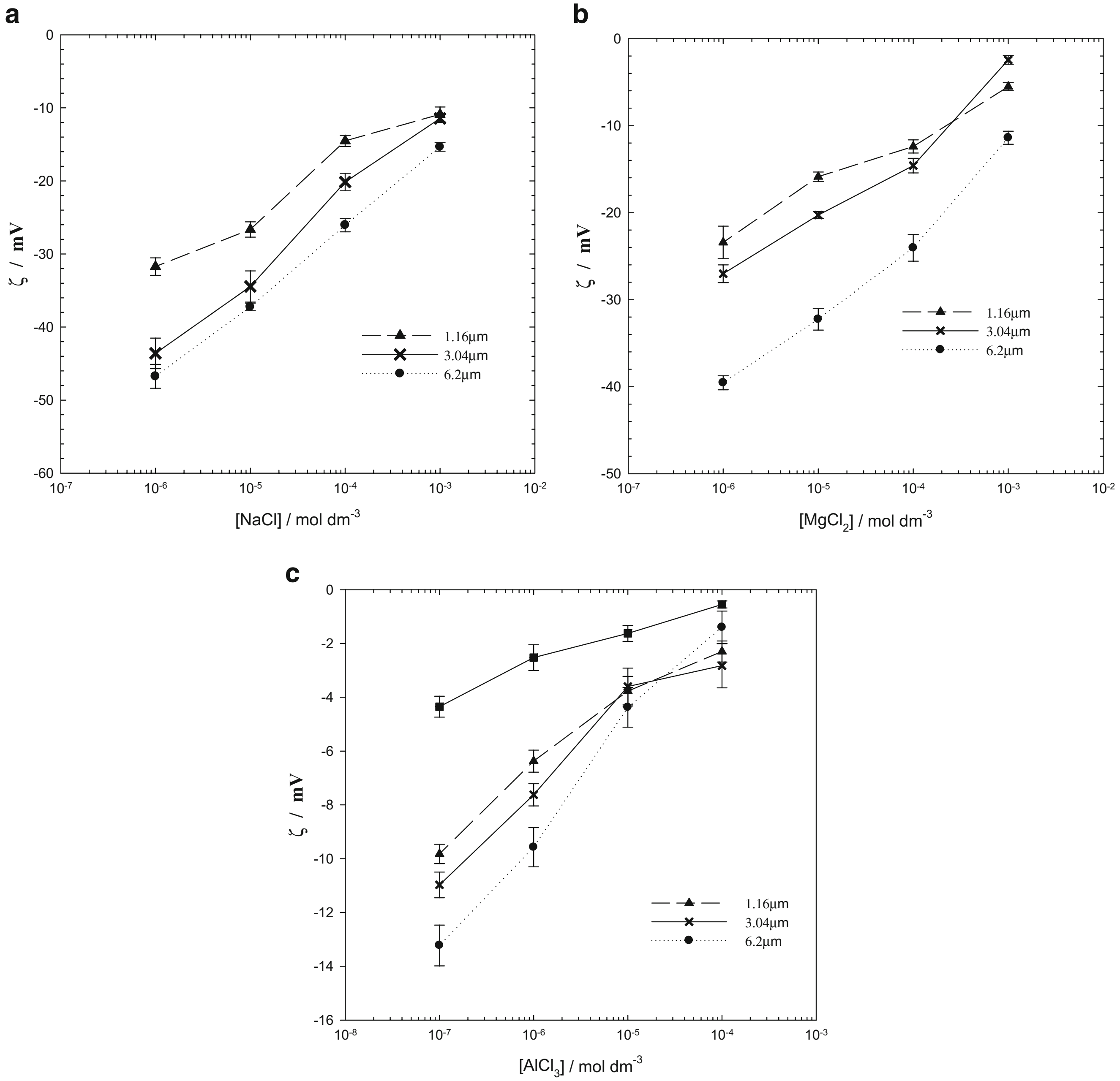

Fig. 1 The results of measured zeta potentials of three different-sized latexes at different concentrations of multivalent electrolytes added in the present heteroflocculation experiments. **a** NaCl, **b** $MgCl_2$, **c** $AlCl_3$

Results and discussion

The results of zeta potential measurements for the four latexes samples of different size ratios and different NaCl, $MgCl_2$, and $AlCl_3$ concentrations are shown in Fig. 1, respectively. It is found that because of the effect of double-layer compression, the zeta potentials of all four latexes become less negative with the increase in electrolyte concentrations. When the electrolyte concentration is kept at a constant value, the magnitude (negatively) of the zeta potentials for those four different sized latexes is 6.2>3.14 >1.16 μm, and the zeta potentials of all the four latexes reach the highest (negatively) when NaCl is added and the lowest when $AlCl_3$ is added. We use the binary mixture of 6.2 μm styrene Divinylbenzene latex and 3.04 μm polystyrene latex as an illustrative example to explain the general results of heteroflocculation experiments obtained. Figure 2a, b shows the values of stability ratio W_{ii} and

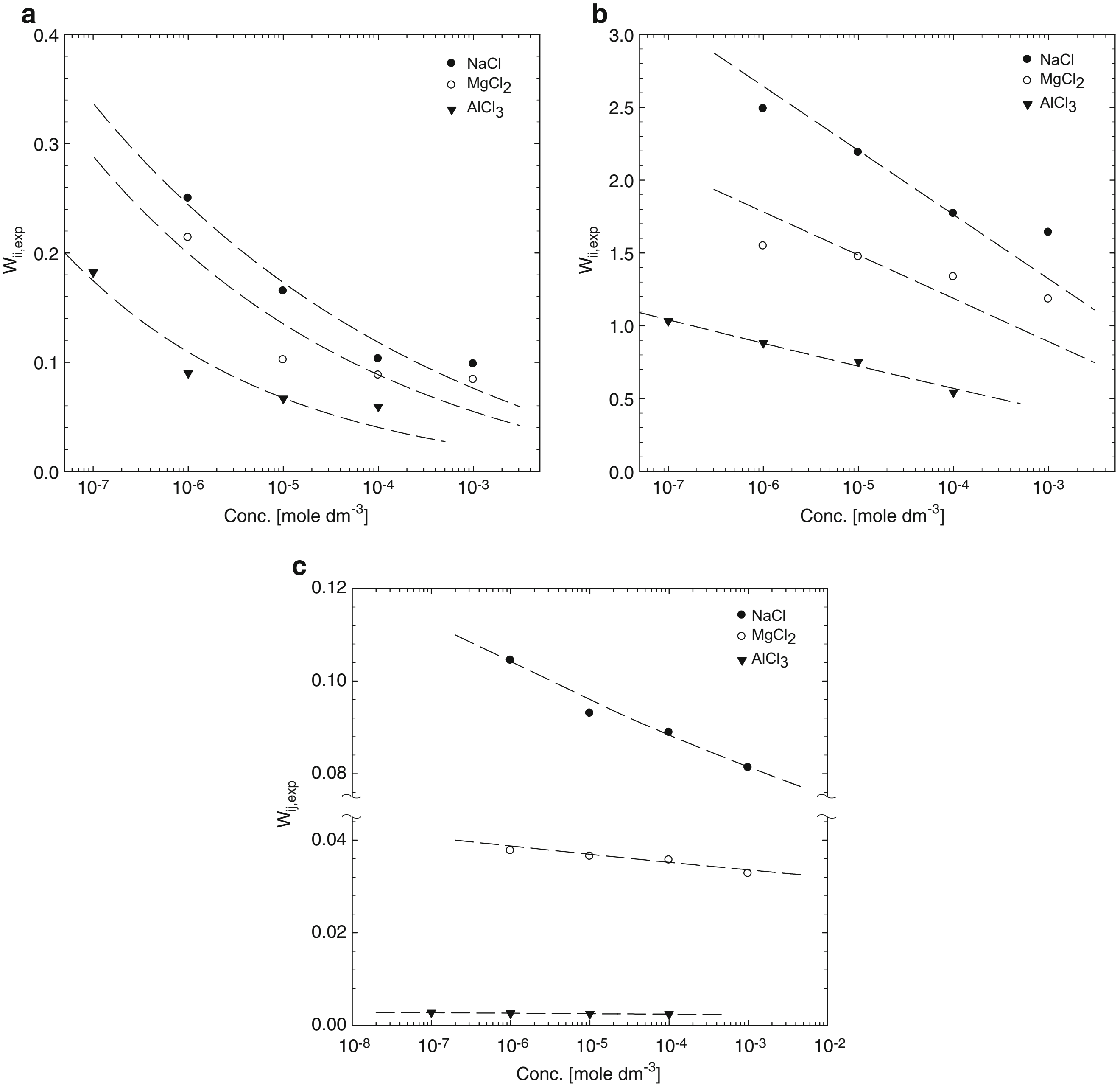

Fig. 2 Experimental values of the stability ratios W_{ii} and W_{ij} for 6.2- and 3.04-μm latexes at different concentrations of *NaCl*, *MgCl2*, and *AlCl3* when G-force=1.0*g*. **a** W_{ii} for 6.2-μm latexes, **b** W_{ii} for 3.04-μm latexes, **c** W_{ij} for the binary suspension composed of equal numbered 6.2- and 3.04-μm latexes

Fig. 2c shows the values of W_{ij} obtained experimentally at different concentrations of multivalent electrolytes when G-force=1.0 G. The 6.2-μm monodispersed latexes are shown in Fig. 2a; it can be found that: (1) because of the compression of the double layer thickness and the decrease in the electrostatic repulsion force, the stability ratio of the suspension will decrease with the increase of electrolyte concentration. (2) At a given electrolyte concentration, because of the decreased zeta potentials (see Fig. 1a), the stability ratio of the suspension decreases with the increase of electrolyte valence. Same results are observed for the 3.04-μm latex suspension shown in Fig. 2b. Note that because of the smaller size, the stability ratios of 3.04-μm latexes are always higher than that of 6.2 μm. Since we find that the gravity force dominates the flocculation behavior of large latexes when their sizes are greater than 5 μm, so those 6.2-μm latexes always own small stability ratio even they have high negative surface potentials. For the heteroflocculation experiments of these two latexes, the obtained stability ratio W_{ij} is shown in Fig. 2c when G-force=1.0*g* (i.e., N_G=165.6, see Eq. 10 below). We can find that the values of W_{ij} are lower than the values of W_{ii} at the corresponded electrolyte concentration. Substituting values of W_{ii} and W_{ij} into Eq. 2, we can get the

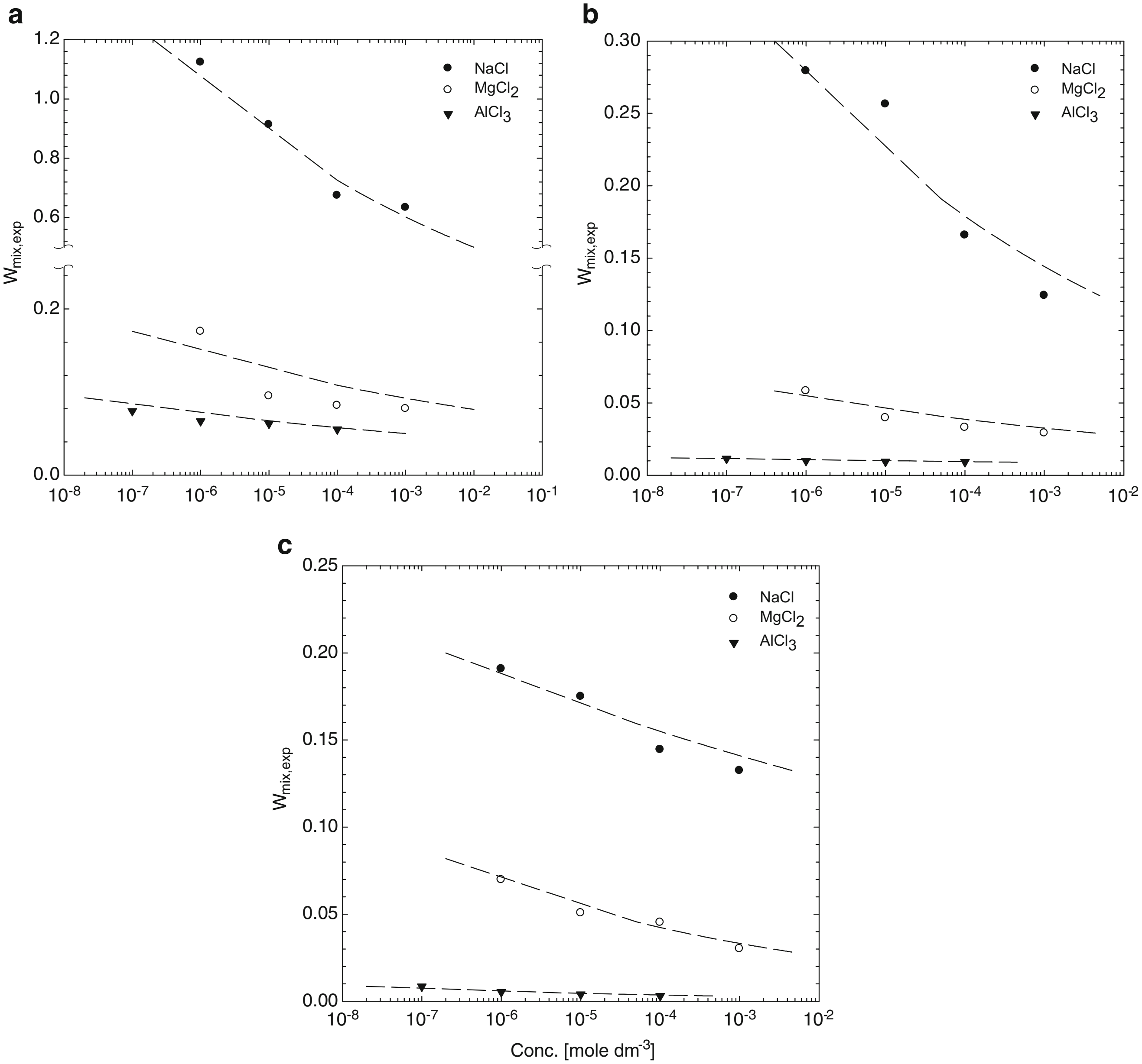

Fig. 3 Experimental values of the stability ratios W_{mix} at different concentrations of NaCl, $MgCl_2$, and $AlCl_3$ for the binary suspension composed of equal numbered 6.2- and 3.04-μm latexes. **a** when G-force=1.0*g*, **b** when G-force=1.5*g*, and **c** when G-force=2.0*g*

corresponded values of W_{mix}. As shown in Fig. 3a, the variation tendency of W_{mix} is the same as the curves in Fig. 2. When comparing Figs. 2 and 3a, we can find that the values of W_{ij} dominate the magnitudes of W_{mix}. Same results are observed in Fig. 3b, c when G-force is equal to $1.5g$ (i.e., N_G=248.4) and $2.0g$ (i.e., N_G=331.2), respectively. In Fig. 3, it can be found that the stability ratio of the binary suspension decreases with the increase of the gravity forces because the gravity forces can overcome the primary maximum energy barrier existed between two latex particles. In order to investigate the results obtained in Fig. 3 in details, the stability diagram mentioned above will be adopted for explanation as follows.

Based on the experimental data of Fig. 3, the example of the stability diagram for the binary suspension composed of 3.04- and 6.2-μm latexes (i.e., size ratio λ=0.490) for different concentrations of NaCl is shown in Fig. 4. In Fig. 4, the dimensionless groups of N_R and N_G are expressed by

$$N_R = \frac{\varepsilon \psi_0^2 (a_1 + a_2)}{A_{132}} \text{ with } \psi_0 = \left(\frac{\psi_1^2 + \psi_2^2}{2} \right)^{1/2} \tag{9}$$

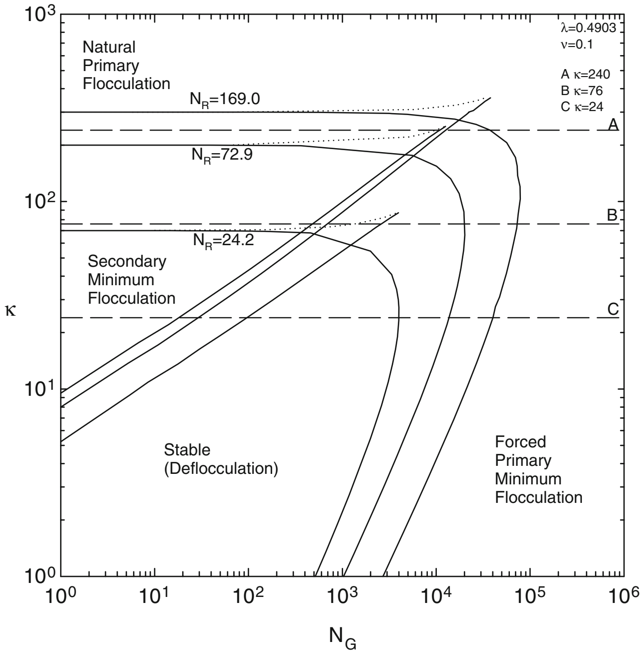

Fig. 4 Effect of the surface potentials (i.e., N_R) on the κ versus N_G stability diagrams for the binary suspension composed of equal numbered 6.2- and 3.04-μm latexes (i.e., λ=0.490) at different concentrations of NaCl. In this figure, the *solid lines* of N_R=169.0, 72.9, and 24.2 represent four different flocculation regimes when the concentration of NaCl is equal to 10^{-5}M (κ=24 represented by the *dashed lines curve C*), 10^{-4}M (κ=76 represented by the *dashed lines curve B*), and 10^{-3}M (κ=240 represented by the *dashed lines curve A*), respectively

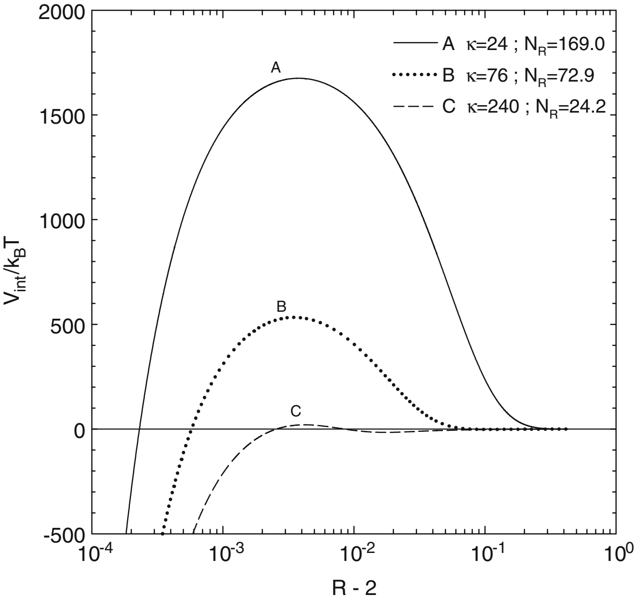

Fig. 5 Effect of the surface potentials (i.e., *NR*) and ionic strengths (i.e. κ) on the total interaction energy curves of the DLVO theory for the binary suspension composed of equal numbered 6.2- and 3.04-μm latexes (i.e., λ=0.490) at different concentrations of NaCl

= the dimensionless electrostatic repulsion number
= the gravitational force/(diffusion force × attractive force)

$$N_G = \frac{(u_{02}-u_{01})(a_1+a_2)}{2D_0 N_A} = \frac{\pi g\left(\rho_p-\rho_f\right)a_2^4}{6A_{132}}(1+\lambda)^2\left(1-\lambda^2\right) \tag{10}$$

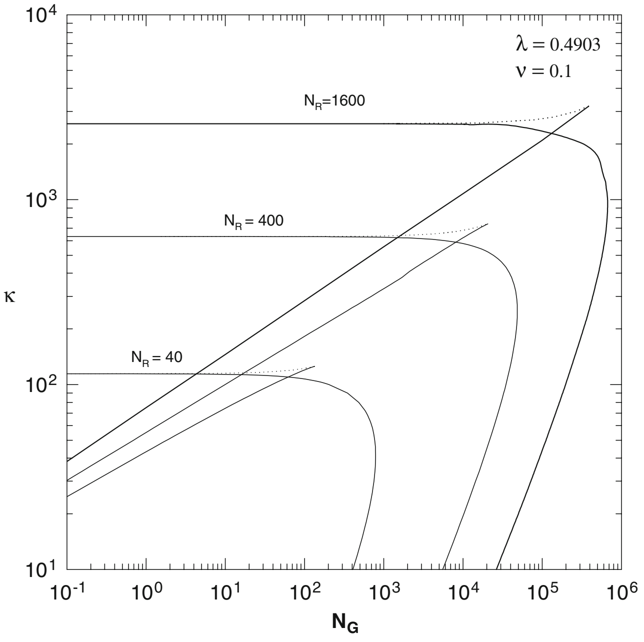

Fig. 6 Effect of the values of N_R on the κ versus N_G stability diagram

where

$$D_0 = \frac{k_B T}{6\pi\eta\mu_f}\left[\frac{1}{a_1}+\frac{1}{a_2}\right]$$

$$\eta = \frac{(2/3)+\left(\mu_p/\mu_f\right)}{1+\left(\mu_p/\mu_f\right)}\text{(viscosity ratio)}, \begin{bmatrix} n=1 & \text{for grid sphere} \\ n=2/3 & \text{for gas bubble} \end{bmatrix}$$

$$N_A = \frac{A_{132}a_1a_2}{k_BT(a_1+a_2)^2} = \frac{A_{132}}{k_BT}\frac{\lambda}{(1+\lambda)^2}$$

= the dimensionless van der Waals attractive number.

In Eq. 10, $(u_{02}–u_{01})$ is the relative velocity between two approaching particles a_1 and a_2, and g is the gravitational acceleration. The detailed method of constructing this stability diagram and the physical meanings of those four distinct regions of flocculation delineated: (a) flocculation at the primary minimum of the total interaction energy curve of DLVO theory; (b) flocculation at the secondary minimum of the total interaction energy curve of DLVO theory; (c) an extremely narrow region of simultaneously flocculation at both the primary minimum and the second-

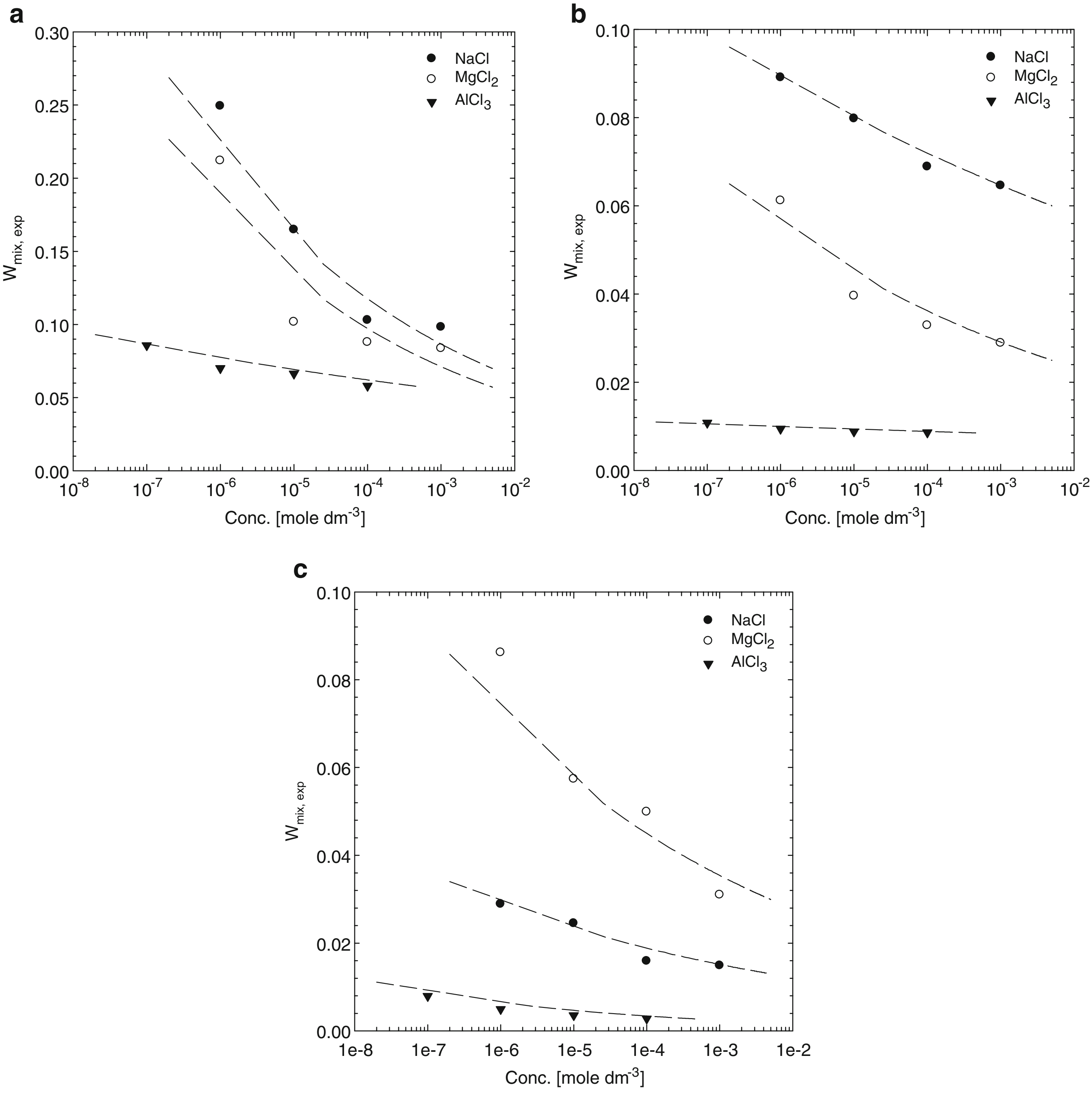

Fig. 7 Experimental values of the stability ratios W_{mix} at different concentrations of NaCl, $MgCl_2$ and $AlCl_3$ for the binary suspension composed of equal numbered 6.2- and 1.16-μm latexes. **a** when G-force=1.0g, **b** when G-force=1.5g, **c** when G-force=2.0g

ary minimum of the total interaction energy curve of DLVO theory, and (d) a region of deflocculation where colloidal suspension remains stable can be found from author's previous paper [14].

Hence, the effect of adding NaCl is shown in Fig. 4, the zeta potential data obtained for latexes of 3.04 and 6.2 μm (see Fig. 1a, b), we can obtain N_R=169.0, 72.9, and 24.2, when the concentration of NaCl is equal to 10^{-5}M (κ=24), 10^{-4}M (κ=76) and 10^{-3}M (κ=240), respectively. As shown by curve A in Fig. 4 where κ=240 and that these two different sized latexes will always flocculate at the position of secondary minimum in the total interaction energy curve (see curve C shown in Fig. 5) when G-force= 1.0g (N_G=165.6). But, when the G-force is increased to 1.5g (N_G=248.4) and 2.0g (N_G=331.2), since the increased G-force still cannot overcome the height of the primary

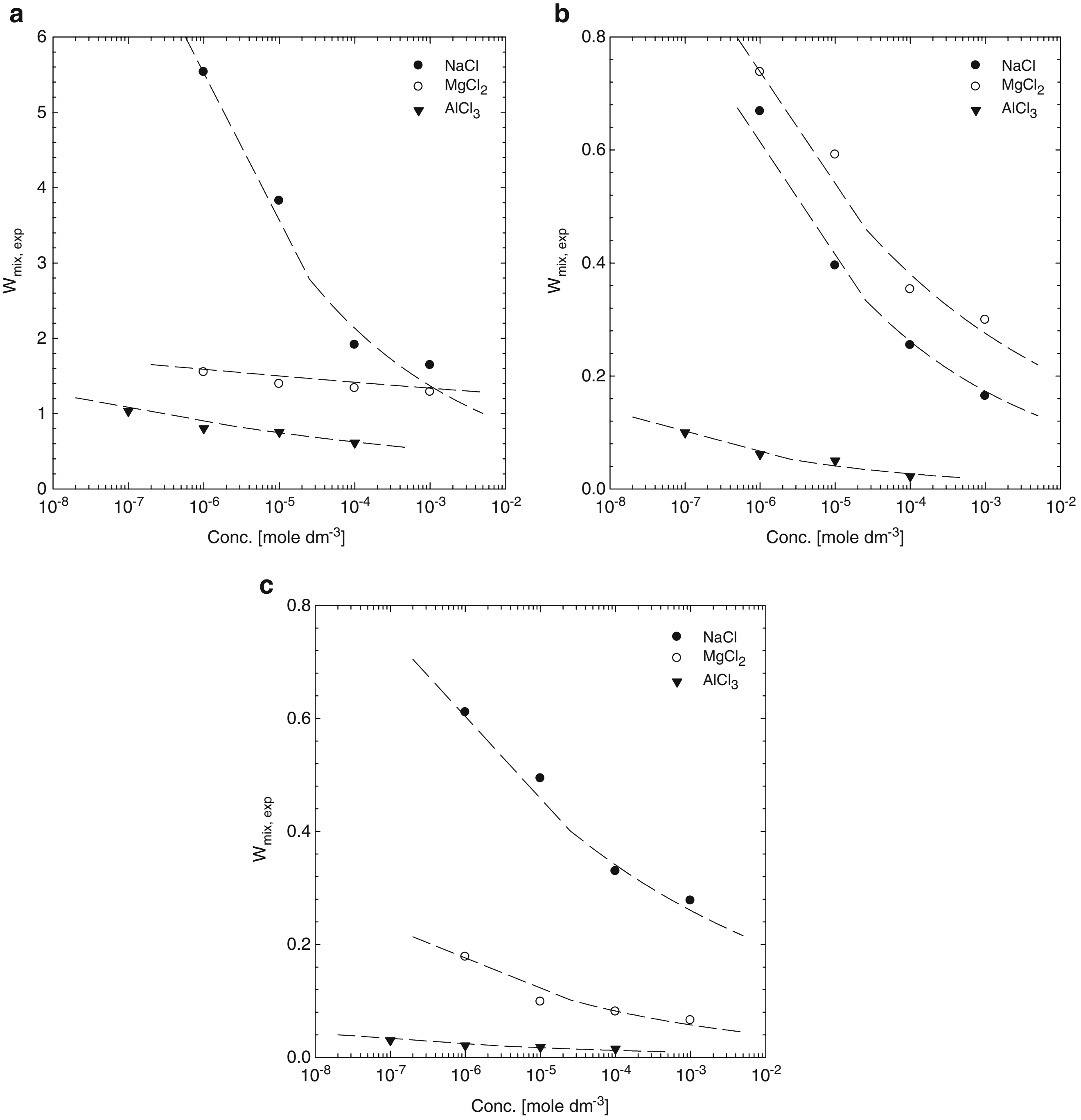

Fig. 8 Experimental values of the stability ratios W_{mix} at different concentrations of NaCl, $MgCl_2$, and $AlCl_3$ for the binary suspension composed of equal numbered 3.04- and 1.16-μm latexes. **a** when G-force=1.0g, **b** when G-force=1.5g, **c** when G-force=2.0g

maximum, we can find that the two latexes will at the deflocculation situation and, therefore, exhibit high stability. Also, when the concentration of NaCl is decreased from 10^{-3}M (κ=240) to 10^{-5}M (κ=24) when N_R=169.0, these two latexes will always be at the deflocculation condition under the gravity forces mentioned above (i.e., see curve C in Fig. 4). The existence of the highest primary maximum energy barrier in the total interaction energy curve will deflocculate these two latexes (see curve A in Fig. 5), unless $N_G>10^5$ where two latexes will be forced to flocculate at the position of the primary minimum. Therefore, the stability ratios of the binary suspension composed of 3.04- and 6.2-μm latexes will be increased when the G-force is increased to 1.5g (N_G=248.4) and 2.0g (N_G=331.2) in the present experiments. Same results are observed in the stability diagrams when $MgCl_2$ and $AlCl_3$ are served as the adding electrolytes, respectively. However, all of these results are opposite to the above experimental conclusion obtained in Fig. 3 that the stability ratio of the binary suspension decreases with the increase of the gravity forces. Since the zone area of the secondary minimum flocculation and deflocculation shown in Fig. 5 will decrease with the decrease of N_R (i.e., when the surface potentials of two interacting latexes become smaller, see example illustrated in Fig. 6), we will try to get the "regressed" surface potentials of latexes from the experimental values of W_{mix} by the regression method shown below (i.e., see Eqs. 11 and 12). With lower surface potentials and therefore lower values of N_R, the latexes will easily flocculate at the primary minimum position existed in the total interaction energy curve and consequently their stability ratios will decrease with the increase of the gravity forces.

The results of the heteroflocculation experiments of 6.2- and 1.16-μm latexes (λ=0.187) and of 3.04- and 1.16-μm (λ=0.382) under different enhanced gravity forces are shown in Figs. 7 and 8, respectively. Same as above, the values of W_{mix} decrease with the increase of the valence value of the electrolyte added or the increase of the ionic strength. The stability ratios of these two binary mixtures also decrease with the increase of the gravity forces. As shown in Figs. 4, 7, and 8, it can be found that the mixture of 6.2- and 1.16-μm latexes has the lowest W_{mix} value at the same electrolyte concentration, ionic strength, and gravity forces; the smaller the λ value, the lower the W_{mix} value. When comparing with different NaCl, $MgCl_2$, and $AlCl_3$ concentrations at constant G-force, it can be found that NaCl always has the greatest effect on decreasing the W_{mix} values when its concentration increases from dilute to concentrate. On the other hand, $AlCl_3$ has the smallest effect on decreasing W_{mix} when its concentration increases, since the double-layer thickness around the colloidal samples is already compressed when the concentration of $AlCl_3$ is as low as 10^{-6}M. Also, the effect of increasing the electrolyte valence on decreasing the W_{mix} values is larger at low electrolyte concentration than that at high electrolyte concentration when G-force=1.0g. But, this decreasing tendency becomes less pronounced when the G-force is increased to 2.0g.

As pointed out in the Melik's thesis [2], where $MgSO_4$ was the electrolytes in his heteroflocculation experiments that the theoretical values of W_{mix} are always higher than the corresponded experimental W_{mix} values shown in Figs. 3, 7, and 8 (i.e., the theoretical W_{mix} values can be determined by using the trajectory analysis method as illustrated in author's previous papers [9, 10]). The disparity between experimental and theoretical values of W_{mix} might be caused by the heterogenities of the colloidal surface charges and potentials [21], the retardation factor affecting the magnitude of the Hamaker constant [22], and the surface roughness of the colloidal samples [23]. Among which, the higher-measured zeta potentials of colloidal samples were considered as the major reason to cause this disparity between experimental and theoretical works. As proposed by Melik [2], we first use Eq. 11 derived by Reerink and Overbeek [24] to calculate the "regressed" surface potentials for the three different sized latexes by using the regression analysis method first (see Eq. 12 below). Then, by applying those "regressed" surface potentials of colloidal samples, the theoretical W_{mix} values of the corresponded binary suspensions can be deter-

Table 1 The "regressed" surface potentials of three different-sized latexes obtained by using Eqs. 11 and 12 at different concentrations of multivalent electrolytes added in the present heteroflocculation experiments

a			
NaCl	6.2 μm	3.04 μm	1.16 μm
$10^{-3}M$	−8.1 mV	−6.5 mV	−4.7 mV
$10^{-4}M$	−11.5 mV	−10.6 mV	−5.9 mV
10^{-5}M	−15.7 mV	−12.4 mV	−7.0 mV
10^{-6}M	−17.3 mV	−14.2 mV	−8.3 mV
b			
$MgCl_2$	6.2 μm	3.04 μm	1.16 μm
$10^{-3}M$	−6.9 mV	−5.8 mV	−4.3 mV
$10^{-4}M$	−9.2 mV	−7.9 mV	−5.7 mV
10^{-5}M	−13.5 mV	−11.5 mV	−6.9 mV
10^{-6}M	−15.5 mV	−13.2 mV	−8.0 mV
c			
$AlCl_3$	6.2 μm	3.04 μm	1.16 μm
$10^{-3}M$	−1.5 mV	−1.4 mV	−0.7 mV
$10^{-4}M$	−4.1 mV	−1.7 mV	−1.0 mV
10^{-5}M	−4.6 mV	−3.2 mV	−1.3 mV
10^{-6}M	−6.1 mV	−4.1 mV	−3.3 mV

a NaCl, *b* $MgCl_2$, *c* $AlCl_3$

mined by assumed that $\psi_i^2 = \psi_1^2 + \psi_2^2/2$ as shown in Eq. 11.

$$1nW_{\text{mix}} = A1nC_i + B \tag{11}$$

where $A = -\frac{1.475\varepsilon k_B T}{e^2}\frac{a_i\gamma^2}{z_i^2}$ and

$$\gamma = \frac{\exp[z_i e\psi_i/2kT] - 1}{\exp[z_i e\psi_i/2kT] + 1}$$

and

$$\sum_{j=1}^{n}\left[\frac{(1nW_{ii})_{theory} - (1nW_{ii})_{\exp}}{(1nW_{ii})_{\exp}}\right]^2 \tag{12}$$

The results are shown in Table 1 which summarizes the “regressed” surface potentials of colloidal samples at different electrolyte concentrations in the monodispersed suspensions. In this table, we can find that the “regressed” surface potentials are much lower than those “measured” surface potentials as shown in Fig. 1a–c, especially when NaCl serves as the added electrolyte. With those lower surface potentials, the corresponded N_R values of Fig. 5 will become small and the latexes of the present experiments can easily flocculate at the primary minimum position of the total interaction energy curve; therefore, the stability ratio of the binary suspension will decrease with the increase of the gravity forces as expected in the present experiments. The theoretical values of W_{mix} determined by using the “regressed” surface potentials are shown by the dashed lines in Figs. 2, 3, 7, and 8. It is evident that the theoretical W_{mix} values of the binary suspensions obtained by using the “regressed” surface potentials can fit well with the experimental values of W_{mix}.

Conclusion

Under different gravity forces, the effect of adding different concentrations of mono- and multivalent electrolytes (NaCl, $MgCl_2$ and $AlCl_3$) on the stability behavior of binary mixtures of equal numbers of different sized particles (1.16, 3.04, and 6.2 μm) is studied in the present paper. With the aid of the stability diagram and the DLVO theory, we have successfully analyzed the heteroflocculation behavior of those binary suspensions composed of different sized particles. Based on the experimental results obtained by the turbidity measurements, there are five conclusions can be drawn: (1) At a constant G-force, the stability ratio of the binary suspension decreases with the increase of the added electrolyte concentration because of the compression of the double layer thickness; therefore, the decrease in the electrostatic repulsion force. (2) At constant electrolyte concentration and G-force, the stability ratio of the binary suspension decreases with the increase of electrolyte valence because of the decreased zeta potentials. (3) At a given electrolyte concentration, the stability ratio of the binary suspension decreases with the increase in gravity forces since the gravity forces can overcome the primary maximum energy barrier existed in the DLVO theory. (4) The mixture of 6.2- and 1.16-μm latexes has the smallest size ratio in the present experiments, also exhibits the lowest stability ratio at constant electrolyte concentration and G-force; i.e. the stability ratio decreases with the decrease of the size ratio. (5) Since the theoretical stability ratios obtained from the trajectory analysis method are higher than those corresponded heteroflocculation experimental values obtained by the turbidity measurements, based on those stability ratios obtained from the flocculation experiments of monodispersed suspension and the method of the regression analysis, we have successfully applied the “regressed” surface potentials of colloidal samples to predict the experimental stability ratios of the corresponded binary suspensions obtained.

Acknowledgement The financial support received from the National Science Council of the Republic of China, research grant no. NSC 96-2221-E-029-014-MY3, is greatly appreciated.

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