

COMMENTS

Comment on “Effect of Pressure on Colloidal Behavior in Hydrothermal Water”

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We comment on the article entitled “Effect of Pressure on Colloidal Behavior in Hydrothermal Water” by Ghosh et al. appearing in a recent issue of *The Journal of Physical Chemistry B*.¹ The article reports experimental and theoretical study on the effect of pressure on the dispersion stability of colloids in water at high temperatures and high pressures. Unfortunately, it does not refer to closely related works, and the theoretical treatment and interpretation of the numerical analysis are erroneous.

First, the dispersion stability of colloids in water at high temperatures and high pressures was studied already both experimentally and theoretically, mainly in terms of the coagulation temperature where coagulation of colloids started.^{2–7} Ghosh et al. justify the publication of their work by stating in the Introduction that “To elucidate the mechanism of colloidal stability in high-temperature water, one must examine the effect of pressure, which is still unknown”.¹ However, this statement is incorrect. The effect of pressure on the coagulation temperature of colloids was already studied, and no significant pressure effect was reported.^{2,3} Experimental results in the article¹ merely confirm the previous results. The coagulation temperature they obtained for diamond nanoparticles (~200 °C, Figures 1 and 2) is in excellent agreement with the value reported previously,⁶ and no significant pressure effect is seen on either the coagulation temperature or the coagulation kinetics (Figure 3). Ghosh et al. do claim pressure effect on the coagulation kinetics of the polystyrene latex (Figure 4). However, thermal decomposition of polystyrene is significant in water at 300 °C,⁵ which certainly complicates the results.⁷

Second, most of the article is devoted to theoretical consideration on the pressure effect on the dispersion stability. However, if the article is compared side-by-side with the previous paper,⁶ it is apparent that the theoretical parts of two papers are essentially the same. The only difference is seen in section D, which deals with the surface potential, ψ_s , in water at high temperatures and high pressures. This section is added because “The temperature and the pressure dependencies of the properties of water are expected to modify the surface properties

of the particles”.¹ Previously, ψ_s was considered independent of temperature and pressure.⁶ When the issue is addressed properly, it would significantly advance our understanding of the colloidal behavior in water at extreme conditions.⁶ As it is assumed that ψ_s is proportional to the surface charge density, Q_s (eq 12),¹ such consideration has to deal with the temperature- and pressure-dependent change of Q_s . It is very regrettable that Ghosh et al. in judiciously assume Q_s is independent of temperature and pressure, and effectively invalidate the argument. Their calculation (Figure 8) shows that ψ_s takes the similar value at ambient temperatures and near the critical temperature of water ($T_c = 374$ °C). ψ_s also becomes highly pressure-dependent at around T_c . Accordingly, the net DLVO potential barrier shows the same trend (Figure 10), suggesting that colloids that coagulate at high temperatures should become stable at even higher temperatures near T_c . It also suggests the profound pressure effect near T_c . However, previous experiments showed the opposite.³

Third, based on the numerical analysis using DLVO theory, it was shown previously that a large decrease of ϵ of water was the primary cause for the coagulation of colloids at high temperatures.⁶ Ghosh et al. performed essentially the same numerical analysis but reached a different conclusion that “the pressure dependence of the stability of the particles in hydrothermal water results from the pressure dependence of pK_w ”.¹ Oddly enough, their theoretical consideration is concerned with the pressure effect on the coagulation temperature, on which no pressure effect was observed in either previous studies^{2,3} or this study.¹ Apart from the question of significance of their theoretical consideration, the results of the numerical analysis are not interpreted appropriately. The strong effect of the change of pK_w of water on κ^{-1} was also shown previously.⁶ However, its effect on V_R , and thus on the net DLVO potential, turned out to be minor,⁶ because V_R depends linearly on the dielectric constant whereas the dependence of V_R on pK_w is indirect (see eq 7 of the article). In contrast, no such thoughtful analysis is given in this article.¹ Instead, they simply compare Figure 5b to Figure 6, and state that “The pressure dependence of ϵ in the temperature range of 20–300 °C is practically negligible (Figure 5)... whereas the pressure dependence of pK_w is significantly strong in the temperature regime of 150–300 °C”.¹ Surprisingly, the visual comparison is the sole rationale behind their conclusion. Such comparison is simply not enough to compare the effect of ϵ and pK_w on the net DLVO potential,⁶ and their conclusion has to be met with much skepticism.

To conclude, the article by Ghosh et al. does not provide any new insights to what is known for colloidal behavior in water at high temperatures and high pressures.

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