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Ion-specific repulsive interactions in colloidal silica dispersions evidenced through osmotic compression measurements and implication in frontal ultrafiltration experiments

J.L. Trompette *, M.J. Clifton, P. Bacchin

Laboratoire de Génie Chimique UMR5503, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex, France

Abstract

Comparative osmotic compression experiments were performed on colloidal silica dispersions in the presence of various chloride salts at the same 0.01 M concentration with different counterions and highlighted the influence of ionic specificity on the resistance to water removal. These results were complemented with frontal ultrafiltration measurements that demonstrate modulation of the permeate flux according to the salt used.

Keywords: Ionic specificity; Colloidal silica dispersions; Osmotic compression; Frontal ultrafiltration

1. Introduction

In the past decade much experimental and theoretical work has been devoted to the study of jamming transitions experienced by colloidal systems [1–6]. These transitions were studied both at the fundamental level, to identify their unifying features, and at the applied level, owing to their impact on the rheological properties of industrial fluids or on the behavior of biological systems. Starting from an initial dispersion (solid particle, polymer latex, globular protein), the jamming transition refers to the change from liquidlike to solidlike behavior characterized by a sudden arrest of the internal dynamics and the resultant appearance of elastic properties. Two limiting cases have been well described depending on the magnitude of the interaction energy and the particle content in the system [4,6]. In the case of particles with strong attractive interactions, colloidal gels are formed at very low volume fractions by interconnection of fractal clusters generated through diffusion-limited cluster

aggregation (DLCA). Their elasticity is related to the ratio of the spring constant of the network to its characteristic correlation length. On the other hand, particles with repulsive interactions form colloidal glasses, but only at quite high volume fractions, when the particles become trapped within cages defined by their surrounding neighbors. Here the elasticity is of entropic origin and it is related to the ratio of thermal energy to a characteristic volume corresponding to the structural length of the system.

As is well documented in the literature, the interaction energy between particles may be controlled in many ways for a given colloidal system (polymer depletion, salt addition, etc.) [7]. Traditionally the total interaction energy is often estimated within the framework of the DLVO model, considered as the cornerstone theory in the stability of colloids. In spite of its numerous recognized limitations [8,9], this model has been found to define two important parameters in the general behavior of aqueous colloidal systems consisting of charged particles: the range of the electrostatic double-layer repulsion, called the Debye length ($1/\kappa$), and the concept of the critical coagulation concentration (CCC). The Debye length can be modulated by varying the ionic strength of the medium. In the case of water at 298 K, the relationship be-

* Corresponding author.

E-mail address: jeanluc.trompette@ensiacet.fr (J.L. Trompette).

tween $1/\kappa$ (in nm) and the ionic strength I is given by [7]

$$1/\kappa \approx \frac{0.3}{\sqrt{I}}, \quad (1)$$

where $I = \frac{1}{2} \sum_i c_i z_i^2$ (c_i and z_i being respectively the molar concentration and the charge number of the ions). As salt concentration increases, interactions become more attractive as the electrostatic repulsion decreases in magnitude with respect to the attractive van der Waals forces.

The CCC refers to the salt concentration for which the aggregation of particles is no longer inhibited by electrostatic repulsion. As confirmed by experimental measurements on various systems [10,11], this electrolyte concentration was found to correspond to the transition between a reaction-limited cluster aggregation regime (RLCA) when $c < \text{CCC}$ and a DLCA regime when $c > \text{CCC}$, for which the aggregation kinetics remains unchanged by salt addition. For salt concentrations well below the CCC, the suspensions remain in a nonaggregated (stable) state. So knowing the CCC of a specific system was found to be important in anticipating the type of aggregation regime and the related structure of the aggregates. Particle clusters generated in an RLCA regime were found to present a fractal dimension of 2.2, whereas those presenting a more open structure with a fractality of 1.75 were characteristic of a DLCA regime [11,12].

Because of the ubiquitous Hofmeister effect, the study of ionic specificity on the stability behavior of colloidal systems has attracted increasing attention [13–18]. Indeed, the energy of interaction between colloids can be modulated by the chaotropic (structure-breaker) or kosmotropic (structure-maker) nature of the ions, thus contradicting the predictions of the DLVO model [8,19]. As emphasized by many authors [8,9], solvent–ion, solvent–surface, and ion–surface interactions are neglected in this continuum model, even though these interactions are expected to play a crucial role at high electrolyte concentrations and/or small separation distances. Considerable experimental evidence of ion specificity in many systems has been reported in the literature and various theoretical approaches have aimed at a deeper understanding of the origin of such behavior [19–21]. Although some experimental findings, such as the observed influence of ionic specificity on bubble coalescence, still remain unclear and open to debate [22,23], the development of direct surface-force measurement techniques with the surface-force apparatus (SFA) and the atomic-force microscope (AFM) have demonstrated the involvement of short-range forces. These additional non-DLVO forces were found to be attractive or repulsive depending on the nature of the surfaces, the solvent, and the experimental conditions [8,24]. Among these short-range forces, the attractive van der Waals-like ion–ion correlation force (resulting from correlated fluctuations of dense ion clouds) and the repulsive hydration force (originating from the ability of certain ions to structure the water molecules in their vicinity) have been expected to play an important role when the ionic entities become confined between the approaching surfaces [25–27].

A previous study [28] demonstrated the influence of ionic specificity (the chaotropic NH_4^+ counterion and the kosmotropic Na^+ ion) on the experimental CCC value and the gelation kinetics of a model colloidal silica dispersion (Ludox HS-40). Further complementary results at relatively high salt concentration have shown how the comparative strength and microstructure of the resulting gels depended on the electrolyte present [29]. This discrepancy was assumed to originate in the ion-dependent magnitude of the attractive ion–ion correlation force (greater with the chaotropic ammonium ion) and the repulsive hydration force (greater with the kosmotropic sodium ion).

The present study is aimed at detecting any manifestation of ion specificity (with lithium, sodium, and ammonium ions) in the behavior of the same colloidal system within a stable repulsive regime, i.e., at a low electrolyte concentration (0.01 M) well below the CCC. Traditional osmotic stress measurements were performed to force the particles to crowd together, thus generating colloidal glasses through a jamming transition, in the presence of the different salts. The results were complemented by frontal ultrafiltration experiments of dilute colloidal silica dispersions: this situation is similar to osmotic compression because of the accumulation of particles at the membrane surface during the filtration process.

2. Materials and methods

2.1. Materials

A Ludox HS-40 dispersion (Dupont, Belgium) with a 40% w/w solid content (silica density 2.2 g/ml) was used. The average particle radius and the specific surface area are respectively 12 nm and 220 m²/g, as indicated by the manufacturer. The pH and the density of the stock dispersion (0.234 volume fraction) are respectively 9.8 and 1.29 g/ml. The zeta potential of a dilute sample, measured with a Zetasizer 5000 apparatus (Malvern Instruments), was found to be −30 mV at pH 9.8. Lithium chloride, sodium chloride, and ammonium chloride salts were purchased from Fluka (France) and were used as received. Distilled and deionized water was taken as a solvent.

2.2. Osmotic stress technique

This technique has been used for many years [30,31]. It is based on equilibration of the chemical potentials of all species that are able to cross a membrane (or a dialysis bag) separating the studied dispersion and a reservoir containing a stressing hydrophilic polymer (unable to cross the membrane). At equilibrium, the chemical potential of water on either side of the membrane is equal and therefore the osmotic pressure of the sample equals that of the polymer in the reservoir. Increasing the amount of polymer in the reservoir allows the dispersion to be concentrated to a set value of

the osmotic pressure [32]. The stressing polymer chosen was a commercial Dextran (Fluka, France). This neutral polymer, having an average molar mass of 10^5 g/mol, is insensitive to ionic strength and the relationship between the osmotic pressure (Π in Pa) and the concentration (in % w/w) has already been established [33]:

$$\Pi = 286c + 87c^2 + 5c^3. \quad (2)$$

To avoid exchange of the stressing polymer and of the Ludox particles across the membrane, dialysis bags (Spectra/Por) having a molar mass cutoff of 6000–8000 were used. Before the experiments, the bags were immersed for 1 day in a 0.01 M aqueous salt solution. Then 4 ml of the stock Ludox dispersion was placed in closed bags and equilibrated with 200 ml of an aqueous solution at 0.01 M of each salt with varying polymer content in the reservoir. The samples were swirled gently for 1 month at 25 °C and were exposed for 4 min daily to UV radiation in order to prevent any bacterial contamination. When equilibrium was reached, the particle volume fraction in each equilibrated bag was determined with a drying mass balance (Mettler-Toledo, Switzerland) at 120 °C and calculated from the relationship

$$\phi = \frac{\rho_w}{\rho_w - \rho_s + \rho_s m_t / m_s} \quad (3)$$

in which the density of water and silica are respectively $\rho_w = 1.0$ and $\rho_s = 2.2$ g/ml; m_t and m_s are respectively the total mass before drying and the residual mass of silica after drying. The residual mass of salt in the dry residue was checked and found negligible.

For each sample, the equilibrated concentration of Dextran in the reservoir was determined by refractometry with the aid of a calibration curve. Then the corresponding osmotic pressure was calculated using Eq.(2).

2.3. Frontal ultrafiltration experiments

All these experiments were performed with regenerated cellulose membranes (Millipore, USA) with a molar mass cutoff of 30 kDa. Filtration measurements were undertaken using a 50-ml filtration cell (Amicon Corporation, Model 8050). The cell was not stirred and the temperature was kept constant at 25 °C. The effective membrane area was 11.3 cm². The hydraulic resistance of the membranes used was determined by filtering the aqueous electrolyte solutions and was found to be $R_m = 1.66 \times 10^{12}$ m⁻¹.

Dilute colloidal silica dispersions with a particle volume fraction of 0.01 were prepared with aqueous electrolyte solutions at 0.01 M concentration of each salt studied. The dilute samples were stored at rest for 1 day before undergoing ultrafiltration.

The system was pressurized with dry air at constant operating pressures in the range 20–100 kPa. The cumulative mass of permeate collected was recorded at intervals of 1 min by an electronic balance connected to a microcomputer: the permeate collected was covered with a layer of

vegetable oil to prevent evaporation. The experiments were stopped when the flow through the membrane had ceased (20 ml dilute dispersion).

3. Results and discussion

3.1. Comparative osmotic stress measurements

The osmotic stress method is a simple and convenient way of concentrating aqueous colloidal dispersions at constant temperature. This method has been found to offer a suitable way of directly evaluating the interactions between the particles of a dispersion under varying experimental conditions [32]. When particles experiencing repulsive electrostatic interactions, as in a medium of a low ionic strength, are forced to crowd together, the related osmotic pressure represents the resistance that the concentrated suspension opposes to a decrease in the available volume for the particles. This can also be seen as a resistance to the removal of water molecules.

A preliminary study was performed to investigate the kinetic aspect of the osmotic compression process. The time-dependent variation of the volume fraction was determined for many samples equilibrated with a Dextran solution at 11% w/w in the presence of each salt at 0.01 M. All the samples were prepared at the same time and the volume fraction was checked at regular intervals. The results are reported in Fig. 1.

In the case of the ammonium salt, the volume fraction reaches its equilibrium value after only 1 week, whereas with sodium and lithium salts it takes about 2 and 3 weeks, respectively. Moreover, the volume fraction at equilibrium is found to decrease as the cation becomes more cosmotropic (lithium being more cosmotropic than sodium); the equilibrated sample with ammonium was a relatively hard solid, whereas it remained fluid with the lithium counterion. This

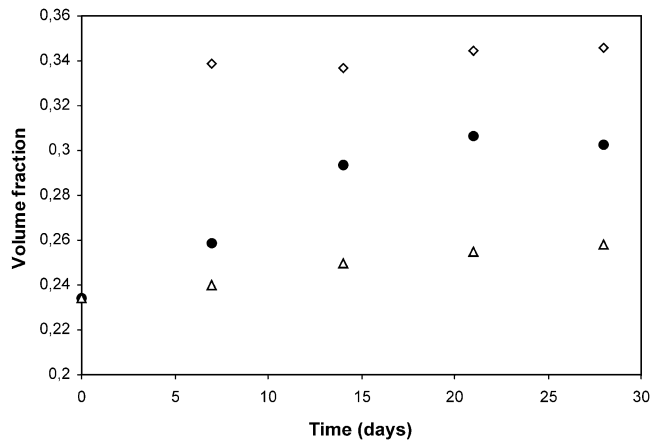


Fig. 1. Variation of the volume fraction as a function of time for samples equilibrated with a 11% w/w Dextran solution in the presence of NH₄Cl (◇), NaCl (●), and LiCl (△) at 0.01 M.

kinetic result suggests that the resistance to water removal is much more pronounced in the presence of cosmotropic ions.

The osmotic compression experiments in the presence of the three salts (duration 1 month) gave values of the osmotic pressure whose comparative variation as a function of the volume fraction is shown in Fig. 2. Qualitative reversibility tests were carried out on the equilibrated samples by immersing them in an excess of water to see whether they could be dispersed.

At first sight the curves present the same qualitative behavior. Up to low volume fraction, say $\phi < 0.2$, the curves are not very distinct. In this region the ion clouds surrounding the particles do not overlap. So the colloidal dispersion can be considered as a gas of repelling hard spheres having an effective radius equal to the sum of the particle radius and the Debye length, say here 15 nm (since $1/\kappa = 3$ nm). All the samples remained fluid. Above $\phi = 0.25$ the ion clouds begin to overlap and the curves start to diverge: the osmotic pressure is higher in the presence of the cosmotropic ions and it is highest with the lithium ion. As the volume fraction further increases, the osmotic pressure rises steeply for each salt, thus indicating the progressive overlap of ion clouds and an increasing resistance to the removal of the aqueous solution between the approaching particles. Up to a volume fraction of about 0.3 all the equilibrated dispersions in the dialysis bags were transparent soft colloidal materials that could be fully dispersed in water. The related effective volume fraction may be estimated from the relation

$$\phi_{\text{eff}} = \phi \left(\frac{R + 1/\kappa}{R} \right)^3, \quad (4)$$

where R is the particle radius, say 12 nm. The calculated value $\phi_{\text{eff}} = 0.58$ corresponds in fact to the volume fraction at which colloidal glasses form [2,6]. This reflects the crowding of the particles into a glassy structure where the motion of the individual particles becomes very difficult. Beyond $\phi = 0.3$ the osmotic pressures are still found to increase with volume fraction; however, the corresponding samples were hard solids that could be fractured but could no longer be dispersed in water, suggesting the presence of relatively strong attractive interaction between the particles.

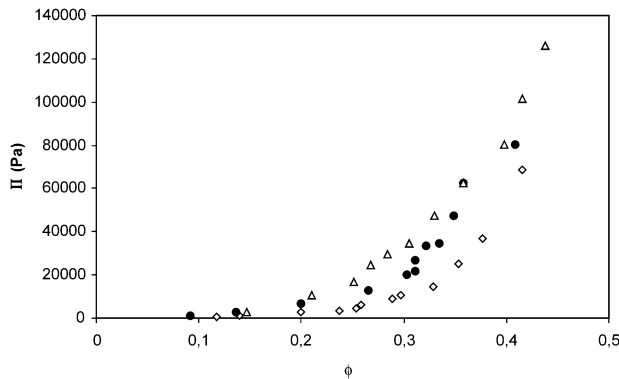


Fig. 2. Variation of the osmotic pressure as a function of the volume fraction in the presence of NH_4Cl (\diamond), NaCl (\bullet), and LiCl (\triangle) at 0.01 M.

These observations are in accordance with recent studies that were aimed at understanding the amorphous glassy states in dense colloidal suspensions [34]. Experiments, theory, and simulations have shown the existence of two qualitatively different glassy states where a small change in the interparticle potential can lead to a transition between one dominated by repulsion (with structural arrest due to caging) and the other by attraction (with structural arrest due to bonding), implying dramatic changes in material properties [35]. In parallel, various experimental and theoretical studies were devoted to provide evidence for an unexpected attractive interaction between similarly charged colloidal particles in concentrated suspensions and/or for particles confined between charged walls [36,37]. Nevertheless, the underlying physical reason for this attraction, probably of electrostatic origin, is still far from being well understood. Moreover, it has been argued [18,19] that, at high enough ionic concentrations, dispersion forces (depending on the relative polarizability of the ions) may play a dominant role and that in some situations they can lead to an attractive double layer pressure between the surfaces. In the present case, where multibody interactions are expected to occur, it may be assumed that upon intensive compression (when the separation distance becomes very short) an additional van der Waals-like attraction could originate from ionic correlation forces between the thin and very close counterion clouds surrounding the particles [14,29].

Assuming that the concentrated particles adopt a similar spatial configuration whatever the counterion present during the compression process, the higher resistance (osmotic pressure) at the same volume fraction in the presence of the most cosmotropic ions indicates a stronger interparticle repulsive energy. At the same 0.3 volume fraction the osmotic pressure is about four times greater with lithium (40 kPa) than that in the presence of the chaotropic ammonium ion. In order to interpret the origin of such results, the zeta potentials of diluted Ludox samples in the presence of each electrolyte at 0.01 M concentration were measured. With LiCl and NaCl salts the obtained value, -28 mV at pH 9.8, is similar to that for dilute sample in pure water. In the presence of NH_4Cl the measured value was found to be -22 mV so indicating the increased screening of the electrostatic repulsion between the particles. The invoked reason may be ascribed to the concept of “like adsorbs like,” where, at pH 9.8, say, far away from the isoelectric point of silica (pH 2), low-iep materials have a low degree of hydration (the number density of neutral silanol sites is low) and so preferentially adsorb poorly hydrated ions such as the ammonium counterions [8, 26,28]. These measurements indicate that there exists an ion-specific repulsive electrostatic contribution that may affect the higher hindrance to close encounter of the particles especially in the case of cosmotropic ions.

Although the zeta potential was similar for LiCl and NaCl , the previous comparative kinetic study and osmotic pressure measurements suggest there is a substantial difference between lithium and sodium ions. In fact, these results

can also be interpreted as reflecting the concomitant effect of the cosmotropic nature of the confined (well hydrated) ions, which generate repulsive hydration forces much stronger than those for the chaotropic ammonium counterions. The dehydration of cosmotropic ions, especially lithium, is expected to be energetically much more unfavorable [8] and this contribution is enhanced as the particles become increasingly concentrated.

All these qualitative observations of the samples are in accordance with previous schematic phase diagrams of aqueous colloidal silica dispersions [32]. Although osmotic pressure measurements have already been performed on similar colloidal silica samples [38], these results do indicate the significant influence of ionic specificity in such compression experiments and indicate that even at low electrolyte concentration, electrostatic and hydration forces may have an important effect (sometimes underestimated). Although the repulsive hydration force has been modeled either as a double-exponential function or as a simple exponential law [8,24,27,39,40], no clear dependence of these empirical expressions on the nature of the ion has yet been formulated. The present experimental results indicate that an ion-specific osmotic term related to hydration forces should have to be taken into account in the theoretical analysis of the various contributions to the overall osmotic pressure.

3.2. Frontal ultrafiltration experiments

For various operating conditions (nature and concentration of the feed suspension, frontal or cross-flow filtration process, build-up or not of a filtration cake, type of membrane fouling), numerous filtration models have been proposed in the literature to interpret the observed decline in permeate flux with time [41–43]. Frontal ultrafiltration of colloidal dispersions (where flow takes place normal to the membrane surface) is a dynamic process where the filtration rate, at constant applied pressure, continuously diminishes due to increasing resistance from particles concentrated in the polarization layer near the membrane surface. In this process, the filtered solvent transports the colloidal particles toward the membrane by convection, while diffusive back-transport arises as particles accumulate, creating a concentration gradient at the membrane surface. In the ultrafiltration of electrostatically stabilized colloidal systems, the effective osmotic pressure between the concentrated particles in the polarization layer plays a fundamental and significant role in the permeation process [41,43,44]. The permeate flux J obtained during the frontal ultrafiltration of such colloidal suspensions is given by

$$J \equiv \frac{1}{A_m} \frac{dV}{dt} = \frac{\Delta P - \Delta \Pi_m}{\eta_s R_m}, \quad (5)$$

where A_m is the membrane area, dV/dt is the rate of increase of the permeate volume with time, ΔP is the applied pressure, $\Delta \Pi_m$ is the osmotic pressure difference across the membrane, η_s is the dynamic viscosity of the solvent, and

R_m is the hydraulic resistance of the membrane. The permeate flux should be zero when the applied pressure is equal to the interparticle osmotic pressure.

Frontal ultrafiltration measurements of colloidal silica samples were used by Bowen et al. [45,46] to evaluate the osmotic pressure, through Eq. (5), and compare the results with the theoretical values calculated from the DLVO model. However, the model was found to overpredict the filtration rate even when hydration forces were considered [46].

As time proceeds, the accumulated particles near the membrane experience between them an increasing osmotic pressure that partially counteracts the applied pressure. This indicates that permeate flux is intimately related to the particle–particle interactions and suggests that ion-specific repulsive forces can be manifest at the relatively short separation distances between particles during the filtration process. As indicated in the experimental section, filtration experiments were recorded until no more permeate volume was collected: this is shown by a plateau in the plots of cumulative volume. The beginning of the plateau corresponds with the point in time where the liquid/air interface reaches the layer of accumulated particles. The effect of the applied pressure on the variation in cumulative volume for dilute Ludox dispersions (0.01 initial volume fraction) in the presence of ammonium and lithium chloride at 0.01 M is presented in Figs. 3a–3c. The results for sodium lie between those for ammonium and lithium.

As expected, the collected volume is higher and the time at which the cumulative amount levels off is shorter as the applied pressure is increased. The curves are completely superimposed for filtration performed at 100 kPa (Fig. 3a). However, when the applied pressure is lowered (Figs. 3b and 3c), the cumulative volume curves become increasingly distinct and the lower of the two is for the cosmotropic lithium ion. The difference in volume between the two curves, when the ammonium curve levels off at 20 kPa, corresponds to about 2 ml, i.e., ~10% of the original volume.

For acquisition times well beyond the plateau the filtrate residue on the membrane for the samples corresponding to the lowest applied pressure (20 kPa) was observed to be fluid, whereas a pasty residue was obtained at higher pressures. However when the experiments performed at higher pressures were repeated and stopped around the plateau, the filtrate residue was fluidlike, thus confirming the absence of any observable deposit on the membrane during the filtration process. The presence of the pasty residue in these dead-end filtration experiments is ascribed as a consequence of an air-drying process when the applied pressure is sufficiently high.

Although the exact correspondence between the equilibrium osmotic pressure obtained through compression experiments and the effective osmotic pressure experienced by the concentrated particles during the dynamic filtration process may be questioned (the role of the membrane surface is often neglected), the qualitative difference should remain. When the applied pressure is much higher than the repulsive osmotic contribution between the particles there is no

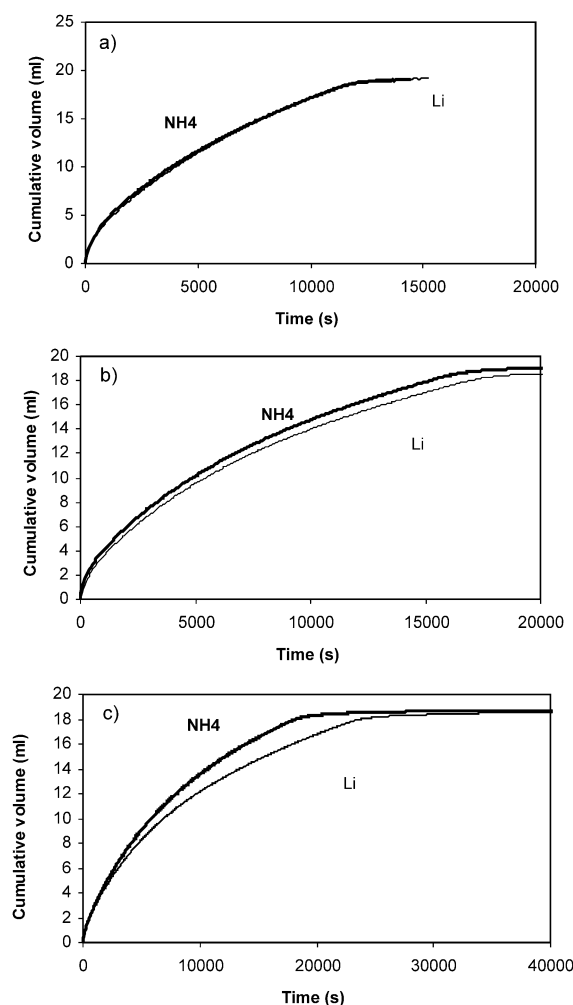


Fig. 3. Variation of the cumulative volume as a function of time for various applied pressures in the presence of NH₄Cl (thick curve) and LiCl (light curve) at 0.01 M: $\Delta P = 100$ (a), 40 (b), and 20 (c) kPa.

difference in permeate flux whatever the electrolyte used. When the applied pressure is lower, the compensation created by the interparticle osmotic pressure—the difference $\Delta P - \Delta \Pi_m$ in Eq. (5)—becomes more significant and it is expected to depend on the nature of the counterion, as seen in Fig. 2. This is effectively observed since the volume collected is lower with the cosmotropic lithium ion and the discrepancy is amplified at low values of applied pressure.

These results indicate that during the concentration process of the particles near the membrane, the ion-specific resistance to water removal becomes significant at short separation distances. This clearly demonstrates how the permeation properties of colloidal dispersions are affected by the repulsive interactions between particles.

4. Conclusion

This experimental study has shown, for the first time to our knowledge, the pronounced effect of ionic specificity on

the osmotic compression behavior of colloidal dispersions at low electrolyte concentration. The results obtained in frontal ultrafiltration exhibit the subtle role played by the nature of the electrolyte in the permeation process through the varying magnitude of the repulsive electrostatic and hydration forces involved.

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