

Analysis of colloids

IX. Investigation of the electrical double layer of colloidal inorganic nanometer-particles by size-exclusion chromatography¹

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Abstract

In a liquid containing ions an electrical double layer is formed close to any charged solid surface. Thus a charged dispersed species wears a “coat” of ions. In size-exclusion chromatography (SEC) of charged colloidal particles the effective size including this electrical double layer has to be considered. For the investigation of the effective size crystalline colloids with rigid core are advantageous, as their core diameters can be determined by electron microscopy. According to the Gouy–Chapman model the thickness of the double layer is inverse proportional to the square root of the ionic strength of the liquid. Thus the particles investigated (CdS colloids) were chromatographed on the same SEC column with eluents with different ionic strength. It was found that the retention times increased with increasing concentration and valency of the electrolyte present in the eluent. It could be shown that adsorption or repulsion did not play a significant role for this retention time shift as long as the electrolyte content is not too high. The layer thickness and its ionic strength dependence, derived from the SEC experiments with CdS particles in the low nm range were found in good agreement with theory. The sum of diameter of the particle core and the Debye length $1/\kappa$ (as predicted from theory) agreed with effective particle size measured chromatographically.

Keywords: Colloids; Effective size; Inorganic particles; Electrical double layer; Cadmium sulfide

1. Introduction

Inorganic nanometer-particles play an important role in the construction of solar cells and they are of particular interest for the basic research in physicochemistry [4–8]. Size-exclusion chromatography (SEC) is a well established method for the determination of the molar mass of organic macro-

molecules, such as synthetic polymers or natural proteins. It was applied also for the size analysis of polymer latexes down to 28 nm in diameter [9–11]. However, SEC is suitable also for the investigation of colloidal inorganic particles in the low nm-size regime. Silica sols [12,13] as well as colloidal particles of semiconductors [2,3,14–16] and of gold [17] have been separated by size. The diameter range lies between 23 nm and 1.3 nm. Due to developed instrumentation the high speed of analysis enables studies of growth mechanisms even in the case of very unstable sols [15].

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¹ For part VIII see Ref. [1], for part VII see Ref. [2] and for part VI see Ref. [3].

By coupling of chromatography with optical spectroscopy by a diode array detector the size depending optical spectra (Q , or size quantization effect, nature of the peaks in the spectra of very small semiconductor particles, plasmon band in gold sols) can easily be investigated [14,17]. By scaling up the dimensions of the separation system monodisperse colloids can be obtained from polydisperse ones in a preparative way [18].

Recently the chromatographic conditions were inspected more in detail, especially the influence of the concentration of the constituents of the sample [1]. It turned out that the concentration of the electrolytes present in the sample plays a much more important role than that of the particles. With increasing electrolyte content the recovery dropped dramatically, while the effect on the elution time was obvious, but not very strong. It was concluded from these SEC experiments that the particles were separated from their initial medium and were very soon surrounded by the eluent with the given constant composition. Anyhow, all effects could be explained in terms of the changing electrical double layer of the particles, which is responsible for the stability of the latter. To the best of our knowledge chromatographic investigations of the double layer have been published only concerning organic polymers. The influence of the ionic strength on the chromatographic behaviour of polystyrene latex [9,10] and of anionic polyelectrolytes, such as sodium polystyrene sulphonates [19] or proteins [20] was described. Dubin and coworkers discussed the ionic strength dependence in SEC and SEC-ion-exchange chromatography (IEC) mixed mode chromatography [21–23]. Theoretical considerations about electrostatic double layer interactions for spherical colloids in cylindrical pores and their effects on the partitioning between bulk solution and pores were presented by Smith and Deen [24,25]. The effective size of the particles including the double layer and the thickness of the latter have not been considered. Similar problems with the double layer occur in capillary zone electrophoresis (CZE) [26,27].

2. Theoretical

At all interfaces between a charged solid-phase

and a liquid-phase containing electrolytes a so called electrical double layer is formed by the charges of the surface and that of the counterions in solution. Analogues to the Debye–Hückel model the Gouy–Chapman model describes the potential distribution theoretically by combining the Boltzmann distribution of energy and the Poisson equation, which gives the relation between potential and charge density [28]. For a flat surface the potential Ψ at distance x from the interface, where Ψ_0 is the potential at $x=0$ [29] is given by

$$\Psi = \Psi_0 e^{-\kappa x} \quad (1)$$

For a spherical surface (with radius a) the potential distribution is given as a function of the radial coordinate, r , by

$$\Psi = \Psi_a (a/r) e^{\kappa(a-r)} \quad (2)$$

In both equations, parameter κ is

$$\kappa = (8\pi n z^2 e^2 / \epsilon k T)^{0.5} \quad (3)$$

This parameter κ comprises the number of ions n , their valency z , elemental charge e , dielectricity constant ϵ , Boltzmann constant k and temperature T . Eq. (2) is applicable for the cases where the product $a\kappa$ is not much larger than unit [28].

Eqs. (2) and (3) enable us to calculate the electrical potential as a function of the distance from the surface and its dependence on the electrolyte valency and concentration. The potential Ψ drops to Ψ_0/e at distance $x=1/\kappa$, which is called the thickness of the diffuse double layer or Debye length. From Eq. (3) it can be seen that the Debye length, $1/\kappa$, is dependent on the ionic strength J (which is $J=0.5\sum_i z_i^2 m_i$, with m_i , the molarity of the ions)

$$1/\kappa \sim J^{-0.5} \quad (4)$$

It can easily be derived from Eq. (3) that for diluted electrolyte solutions the thickness of the double layer, $1/\kappa$, is in the range of 10^3 to 10^2 nm, for more concentrated ones about 1 to 10^{-1} nm.

It is clear that colloidal particles are also surrounded by such a double layer. Moreover this double layer enables the stability of the colloid by repulsion and therefore by avoiding the direct contact

of the particles, which would lead to coagulation and finally flocculation. It is well known in colloid chemistry that high electrolyte content destabilizes the colloids because of the decreasing double layer thickness. It was shown in chromatographic investigations of polyelectrolytes that this double layer is quite rigid [20]. Therefore in SEC one has to take this layer thickness into consideration. The double layer, in the chromatographic sense used in this paper, is half of the difference between the particle core diameter d_p and a hypothetical larger one (Eq. (5)), called effective diameter $d_{p,eff}$, which corresponds to the measured retention time being shorter than expected for the

$$d_{p,eff} = d_p + 2d_{dl} \quad (5)$$

core size. This decrease in retention time is caused by repulsion, charge repulsion between the particle plus surrounding ions and the packing.

The thickness d_{dl} which is relevant for the SEC does not necessarily equal the Debye length $1/\kappa$, because charge densities of the particle and the column packing are of importance. SEC, however, represents a unique tool to investigate this microscopic length, given that the core diameter d_p of the colloidal particles is known. For such an investigation, as presented in this paper, rigid solid particles are much better suited than organic polyelectrolytes, because in contrast to the former the coils of the latter shrink or swell, i.e., their size is also dependent on the environment.

3. Experimental

SEC was carried out with equipment consisting of an autosampler (AS-2000A, Merck–Hitachi, Darmstadt, Germany; 20 μ l sample volume), a high pressure pump (L 6000 Merck, Darmstadt, Germany), and a UV–Vis detector operating at 250 nm (Merck–Hitachi L4200), or a diode array detector (Waters 990, Milford, MA, USA). A set of two columns (125 mm \times 4 mm I.D.; Knauer, Berlin, Germany) was used in most cases, the first packed with Nucleosil 500 C₄ (7 μ m) and the second with Nucleosil 1000 C₄ (7 μ m) (both Macherey–Nagel, Düren, Germany). Under standard conditions the

mobile phase (flow-rate 0.5 ml/min) was an aqueous solution of 6 mM sodium polyphosphate (Riedel-de-Haen, Seelze, Germany; the molarity refers to the phosphate units) and 1 mM cadmium perchlorate (Ventron, Karlsruhe, Germany). In some experiments sodium chloride or magnesium sulphate, respectively (both Merck, analytical grade) was added to the standard eluent. The calibration of the standard system was described in Ref. [3]. Data collections were carried out either with a Chromstar system (Bruker, Bremen, Germany) or with a 990 Waters system (Waters).

Colloidal cadmium sulphide was prepared from 1 mM cadmium perchlorate (Johnson Matthey, Karlsruhe, Germany), 6 mM polyphosphate (Riedel-de-Haen) and hydrogen sulphide (resulting solution 1 mM, Messer Griesheim, Düsseldorf, Germany). Different particle sizes were obtained by using different pH values or by aging. The details were described in the previous papers [3].

For evaluation of the limiting retention time a calibration “hydrodynamic diameter-retention time” was established for polystyrene on Nucleosil 500 C₄ (7 μ m) plus Nucleosil 1000 C₄ (7 μ m) with dichloromethane as eluent. The hydrodynamic diameters were calculated by the Mark–Houwink equation with the coefficients $K=0.00716$ and $a=0.76$ [30].

The standard deviation of the retention time was found to be 0.17% [3]. Therefore retention time instead of volume could be used.

4. Results and discussion

4.1. Dependence of the chromatographic retention of colloidal CdS particles on the salt concentration

During the SEC process colloidal particles of a few nm in diameter are immediately separated from small ions because of the large difference in size. In practice the particles of samples with different electrolyte contents are immediately surrounded by the eluent with given composition. This offers the possibility to bring particles into defined electrolyte environments and to follow the change of its effective diameter $d_{p,eff}$ by changing the salt concentration of the eluent. This was carried out by injecting CdS sols of various particle sizes several

times into the same SEC column set but using eluents with different ionic strength.

The standard eluent for CdS analysis consisted of an aqueous solution of 1 mM cadmium perchlorate with 6 mM polyphosphate (molarity refers to the phosphate units) as stabilizer. Under these conditions the column set was calibrated with CdS sols, the size of which was measured by transmission electron microscopy (TEM) [3,15]. This series served as reference for the investigations where the eluent composition was varied.

Sodium chloride was added to the standard eluent at concentrations from 3 mM to 30 mM. As an example the resulting chromatograms of one CdS sample with an average particle size of 5.7 nm are shown in an overlay plot in Fig. 1. Increasing retention times were found with increasing salt content of the eluent, though the particle size d_p had not changed during the experiment. This was proved by final injection of samples in the standard eluent again, finding the original retention times. Moreover, if particles changed in size, they would grow, not shrink. Therefore, for a supposed pure or predominant SEC mechanism it follows that the retention is affected by the variation of the effective diameter $d_{p,eff}$ of the particles, caused by the reduction of the thickness of the electrical double layer with increase of ionic concentration of the eluent.

Another effect can also be seen from Fig. 1.: the

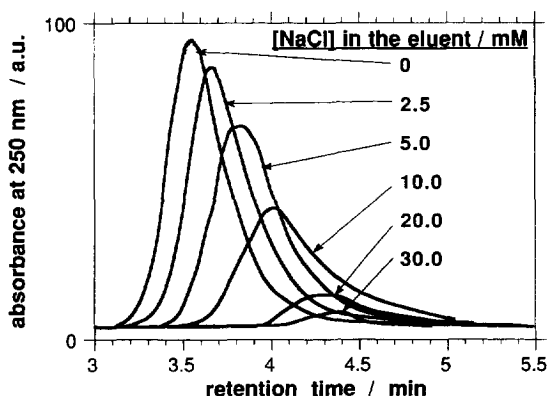


Fig. 1. Chromatograms of a CdS-sol (average size 5.7 nm) obtained on Nucleosil 500 C₄ plus Nucleosil 1000 C₄ with the standard eluent [1 mM Cd(ClO₄)₂–6 mM sodium polyphosphate] and various concentrations of NaCl added from 0 mM to 30 mM. Details in Sections 3 and 4.1.

peak area decreases with increasing ionic strength of the eluent. This is in accordance with previous experiments, when the salt concentration in the sample was varied [1]. It is likely that the double layer acts as a protection coat not only against coagulation, but also against adsorption at the surface of the column filling. When this protection layer shrinks, the probability of adsorption on the stationary phase increases resulting in a mass loss. Similar effects on recovery were observed in protein analysis [31]. This adsorption process seems to be irreversible to a great extent. The role of adsorption will be discussed in Section 4.3.

In another series magnesium sulphate, a divalent electrolyte was used as an additive to the standard eluent. In Fig. 2 the retention times for several CdS sols of different particle sizes are plotted versus the additional NaCl or MgSO₄ concentration, respectively. The retention times for NaCl addition increase with increasing concentration and almost reach a plateau. The retention times for eluents containing MgSO₄, on the other hand, increase much faster as compared with NaCl. This is in clear accordance with theory (Eq. (4)), which predicts an inverse proportionality between double layer thickness and valency of the electrolyte. It should be noted that the retention times of aqueous acetone, i.e., a non-ionic compound, were found to be independent of the electrolyte content of the eluent.

4.2. Comparison of the chromatographically measured double layer thickness with the Debye length

In the following the SEC results were compared in detail with the results derived from the Gouy–Chapman model. The SEC columns had been calibrated for CdS under standard conditions, i.e., the eluent being aqueous 1 mM Cd(ClO₄)₂–6 mM polyphosphate. The core diameters of the CdS particles were obtained from TEM. It is obvious that calibration is only valid under these standard conditions as long as the solid particles themselves are considered. In the typical plot $\log d_p = f(t)$ (t being the retention time) linearity was found between 20 nm and 2 nm (Fig. 3, full triangles). The curve fit revealed the calibration Eqs. (6) and (7), respectively, when converted into the exponential form [3].

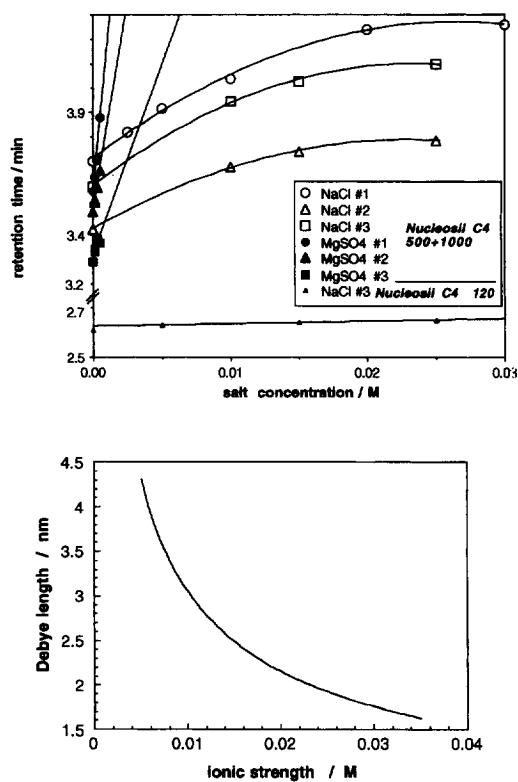


Fig. 2. (Upper part) Retention time as a function of salt concentration for SEC of CdS-sols of various particle size on Nucleosil 500 C₄ plus Nucleosil 1000 C₄. NaCl (open symbols) or MgSO₄ (filled symbols), respectively, was added to the standard eluent [1 mM Cd(ClO₄)₂–6 mM sodium polyphosphate]. For comparison the retention times of colloid 3 on Nucleosil 120 C₄ are given (small triangles). Details in Sections 4.1 and 4.2. (Lower part) Debye length $1/\kappa$ as a function of ionic strength for an 1:1-electrolyte.

$$\log d_p = -0.899t + 3.949 \quad (6)$$

$$d_p = 8890 \cdot 10^{-0.899t} \quad (7)$$

with particle diameter in nm and retention time in min.

This calibration curve can be used, however, neither for the determination of the effective particle diameter $d_{p,\text{eff}} = d_p + 2d_{\text{dl}}$, see Eq. (5) nor for that of the double layer thickness d_{dl} .

In the upper part of Fig. 2 the retention times are plotted over the salt concentration added to the standard eluent. The retention times increase with increasing salt concentration and come into satura-

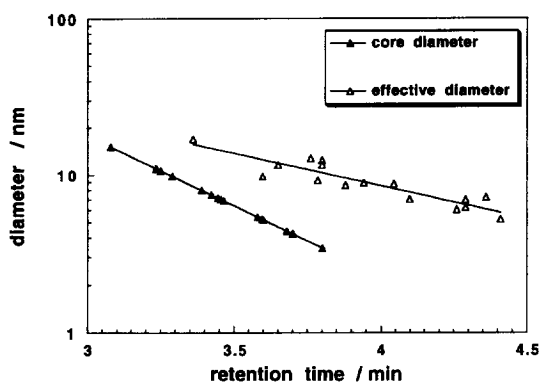


Fig. 3. Calibration for SEC of CdS-sols on Nucleosil 500 C₄ plus Nucleosil 1000 C₄. (▲) Standard calibration. Diameter of the particle core d_p , determined by TEM, as a function of retention time with standard eluent composition [1 mM Cd(ClO₄)₂–6 mM sodium polyphosphate]. (△) Effective diameters $d_{p,\text{eff}}$ as a function of the plateau retention time t_{max} in Fig. 2, upper part, obtained with NaCl added to the standard eluent in high concentration (typical ionic strength of the eluent $J=0.03$ M). $d_{p,\text{eff}}$ was calculated from the diameter of the particle d_p , determined from SEC under standard conditions (standard calibration based on TEM) plus 1.8 nm, the theoretical Debye length $1/\kappa$ for an ionic strength $J=0.03$ M. The data of the 16 CdS colloids used here are compiled in Table 1. These samples were different from those for standard calibration. Please note that both retention times were obtained under different conditions (with and without NaCl in the eluent). Details in Section 4.2.

tion for all investigated samples with sodium chloride addition. The principal similarity with the dependence of the Debye length $1/\kappa$ from the ionic strength (given in the lower part of Fig. 2) is obvious. Maximum retention times t_{max} were reached at NaCl concentrations between 0.02 and 0.025 M. For the calculation of the ionic strength J that of the standard eluent $J_0=0.008$ M has to be added, which is determined iteratively (see below). This value is not very critical, because in this area the Debye length $1/\kappa$ is not very sensitive towards variation in ionic strength (compare Fig. 2, lower part). For ionic strengths about 0.03 M the Debye length is still about 1.8 nm. Therefore in a first approximation the following assumption is made: when the retention time is in saturation i.e., when it does not increase with increasing ionic strength, the effective particle diameter $d_{p,\text{eff}}$ equals the core diameter d_p plus 1.8 nm for the double layer thickness.

From the results of sixteen colloidal CdS samples summarized in Table 1 a calibration for the effective

Table 1

Experimental results of sixteen colloidal CdS samples used for the calibration of effective diameters $d_{p,\text{eff}}$ in Fig. 3

Sample	t (min) (standard conditions)	d_p (nm)	t_{max} (min) (high J)	$d_{p,\text{eff}}$ (nm)
1	3.08	15.214	3.36	17.014
2	3.23	11.017	3.76	12.817
3	3.25	10.681	3.80	12.481
4	3.29	9.8323	3.65	11.632
5	3.29	9.8323	3.80	11.632
6	3.39	7.9946	3.60	9.7946
7	3.42	7.4670	3.79	9.2670
8	3.45	7.1200	3.94	8.9200
9	3.46	6.9742	4.04	8.7742
10	3.46	6.8455	3.88	8.6455
11	3.58	5.3960	4.36	7.1960
12	3.60	5.2203	4.10	7.0203
13	3.60	5.1773	4.29	6.9773
14	3.68	4.3875	4.29	6.1875
15	3.70	4.2096	4.26	6.0096
16	3.80	3.4158	4.41	5.2158

Retention times t are obtained under standard HPLC conditions and the resulting core diameters d_p are calculated by Eq. (7), which is based on TEM calibration. Retention times t_{max} refer to eluents with high ionic strength J , where the increase of $t(J)$ comes to saturation as shown in Fig. 2, upper part (typically at $J=0.03\text{ M}$). For these cases the corresponding effective particle diameters $d_{p,\text{eff}}$ are assumed to be the sum of d_p and the Debye length for $J=0.03\text{ M}$ $1/\kappa=1.8\text{ nm}$. The pH value of all eluents was about 5.8.

diameter $d_{p,\text{eff}}$ is constructed using the particle core diameters d_p (calculated from the standard calibration Eq. (7)) plus 1.8 nm ($1/\kappa$ for $J=0.03\text{ M}$) and the maximum retention time t_{max} corresponding to the plateau in Fig. 3. The curve fit resulted in Eq. (8)

$$\log d_{p,\text{eff}} = -0.528t + 2.934 \quad (8)$$

The linear regression coefficient has the moderate value of 0.91. Two reasons for the scattering of the measured effective particle diameters can be given. Firstly, in order to save time, during which a particle growth could take place, the number of eluent compositions was limited resulting in a rather coarse determination of the plateau retention time t_{max} . Secondly, some differences of surface charge among the samples cannot be excluded.

Eq. (8) was converted into the exponential form leading to Eq. (9). From that the effective diameters $d_{p,\text{eff}}$ of the colloidal CdS particles in the various electrolyte solutions were calculated.

$$d_{p,\text{eff}} = 859 \cdot 10^{-0.528t} \quad (9)$$

For the comparison of the results with the Gouy–

Chapman model (Eqs. (3) and (4), respectively) the overall ionic strength J and therefore also J_0 of the standard eluent are required. J can easily be calculated for $\text{Cd}(\text{ClO}_4)_2$, NaCl or MgSO_4 , respectively, but calculation is not straightforward for sodium polyphosphate (added at a concentration of 6 mM, referring to the phosphate units), because neither its exact valency nor the extent of chelating of polyphosphate to Cd^{2+} ions is known. Finally the ionic strength J_0 of the standard eluent was evaluated iteratively. For this purpose values of 0 mM, 3 mM, 5 mM, 8 mM, 12 mM, 20 mM and 30 mM for J_0 were added to the actual ionic strength of NaCl in the particular electrolyte solutions. In Fig. 4 the effective diameter $d_{p,\text{eff}}$ is plotted versus the reciprocal square root of the resulting ionic strengths for one CdS sol assuming various J_0 values. It can be seen that a linear fit is obtained for $J_0=8\text{ mM}$ as the assumed ionic strength of the standard eluent, the value which is taken further. It comes out that from this eluent mainly sodium ions and perchlorate ions contribute to the ionic strength. It can be followed that the cadmium ions are completely masked by the polyphosphate and the contribution of polyelectrolytes to the ionic strength is minute. This is in

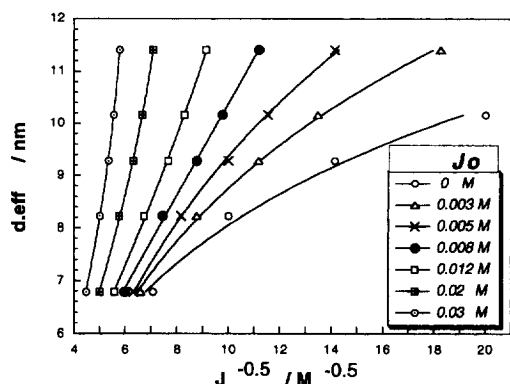


Fig. 4. Effective particle diameter $d_{p,\text{eff}}$ for a CdS-sol (average size 9.5 nm) chromatographically determined in the standard eluent [1 mM $\text{Cd}(\text{ClO}_4)_2$ –6 mM sodium polyphosphate] with and without NaCl addition as a function of the reciprocal square root of ionic strength J according to Eq. (9). Various J_0 values from 0 mM up to 30 mM were used. Details in Section 4.2.

accordance with findings from organic polyelectrolytes [32].

In Fig. 5 the effective diameters $d_{p,\text{eff}}$ of several CdS samples (calculated from Eq. (9)) were plotted over $J^{-0.5}$ (including $J_0=8$ mM). The linear fit is good in all cases for both, NaCl and MgSO_4 . The regression coefficients are mostly between 0.96 and 0.99. A deviation towards smaller sizes is found only for the highest ionic strength, the reason might be a

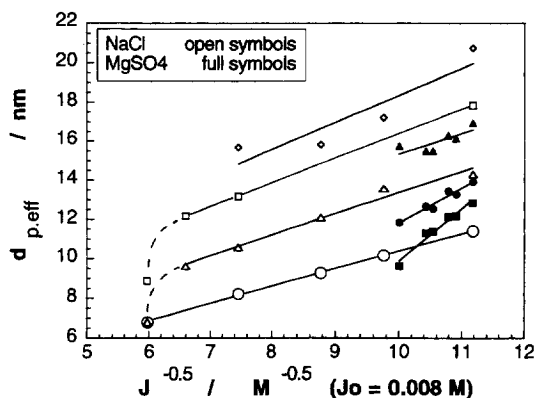


Fig. 5. Effective particle diameter $d_{p,\text{eff}}$ for CdS-sols of different particle size, chromatographically determined in the standard eluent [1 mM $\text{Cd}(\text{ClO}_4)_2$ –6 mM sodium polyphosphate] with and without NaCl- or MgSO_4 -addition as a function of the reciprocal square root of ionic strength J according to Eq. (9). For the ionic strength J_0 of the standard eluent a value of 8 mM was taken. Details in Section 4.2.

disturbing influence of adsorption. Potschka described the same deviation for surfactant-coated polystyrene latex beads [10]. Although among the electrolyte with the same valency the slopes vary slightly, that obtained from the divalent electrolyte MgSO_4 were significantly steeper in most cases.

This good agreement between theory and experimental results were nevertheless encouraging enough to compare the values d_{dl} obtained from experiment with the Debye length, $1/\kappa$. It should be mentioned that in principle this is allowed also for the CdS particles under investigation, because the band bending in semiconductor material takes place only in distances longer than the diameters of the particles used in the present work. Particle diameters d_p and effective particle diameters $d_{p,\text{eff}}$ were calculated with the measured retention time from Eqs. (7) and (9). The double layer thickness d_{dl} was determined from Eq. (5).

In Fig. 6 the experimental d_{dl} values for ionic strengths $J=8$ mM (standard conditions) as well as $J=10.5$ mM, 13 mM, 18 mM and 23 mM are given as a function of the particle core diameter d_p . It can be seen that d_{dl} is constant within the experimental error, there is no evidence for systematic dependence of d_{dl} from d_p . The theoretical values for the Debye lengths at the selected ionic strengths were calculated from Eq. (3) and marked on the y-axis. For $J=8$ mM, for example, d_{dl} ranges between 3.4 nm and 3.7 nm. This is in good agreement with the Debye length $1/\kappa=3.4$ nm for an ionic strength $J=8$ mM. Also

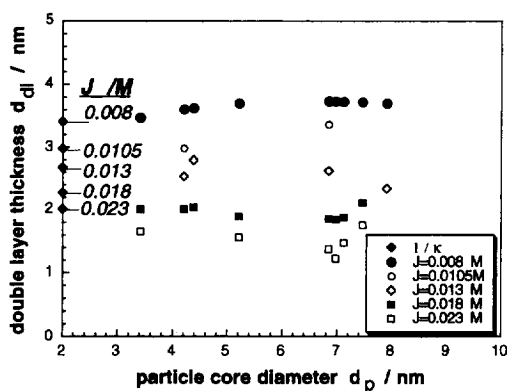


Fig. 6. Experimentally determined double layer thickness d_{dl} of CdS particles as a function of the particle size d_p for various ionic strengths. Details in Section 4.2.

for higher ionic strengths the agreement is not bad, though there is a trend to smaller values for d_{dl} .

The results allow the conclusion that the Debye length can approximately be used for the estimation of the effective size of colloidal particles in SEC.

4.3. The role of adsorption

From the recovery the presence of adsorption is evident. By reinjection experiments any preferential adsorption could be excluded. The role of adsorption is crucial for the interpretation of the SEC data in terms of double layer thickness. If adsorption of the particles at or repulsion from the stationary phase had an overcoming influence, one could argue, that the retention time shift was based only or mainly on these effects and only to a minor part on the change of the double layer. Therefore we made many efforts to investigate this point.

The experiments were repeated on a Nucleosil 120 C_4 column (5 μm , 250 \times 4 mm) instead of Nucleosil 500 C_4 and 1000 C_4 (7 μm , 120 \times 4 mm each), i.e., the same material as before but with a smaller pore size, where the colloidal particles were excluded. With other words, now only adsorption or repulsion should be relevant and no longer a SEC mechanism. Nucleosil 120 C_4 was available only as 5 μm material, however, the larger specific surface was a partial compensation for the inaccessible surface inside the pores. Indeed, no significant time shift with increasing salt content was observed supporting that adsorption was not responsible for this effect of ionic strength on elution time (Fig. 2).

The easiest way of calibration for the effective size would be the run of a series of organic polymers with various molar masses under the same conditions. The hydrodynamic volume and therefore the hydrodynamic diameters d_{hydrodyn} can be calculated quite well. Unfortunately water soluble polymers were completely retained on Nucleosil C_4 with aqueous mobile phase, neither pullulanes nor polyethyleneoxides eluted.

However, a calibration with polystyrene in dichloromethane was established, in order to get at least information about the time range in which SEC calibration is linear. The hydrodynamic diameters d_{hydrodyn} were calculated via the volume by the Mark–Houwink equation with the coefficients $K=0.00716$ and $a=0.76$ [30]. In Fig. 7 d_{hydrodyn} of

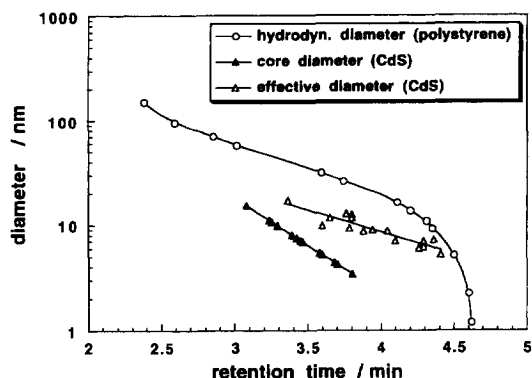


Fig. 7. Comparison of various calibrations on Nucleosil C_4 500 plus Nucleosil C_4 1000: hydrodynamic diameters of polystyrene of various molar mass in dichloromethane (calculated by the Mark–Houwink equation with the coefficients $K=0.00716$ and $a=0.76$ [31]) as well as core diameters d_p and effective diameters $d_{p,\text{eff}}$ of CdS in aqueous eluents as a function of retention time.

polystyrene is plotted together with the effective diameters and the core diameters of CdS under standard conditions as a function of retention time. It is obvious that the biggest part of the effective calibration for CdS falls in the linear time range and even the retention time values (4.4 min) for the smallest particles under investigation are still quite distant from the limiting retention time (4.62 min). The hydrodynamic diameters of polystyrene are bigger than the effective diameters of CdS for the same retention time. It is mentioned in the literature that viscosity radii can be somewhat smaller than electron microscopy radii [10]. Any further agreement between calibration of the neutral polystyrene in an apolar eluent and calibration of the charged CdS particles in an aqueous eluent could not be expected, since for the latter the effective pore size must be a different one.

Tailing can also be considered for estimation of adsorption. A closer inspection of the peaks at increasing ionic strengths shows that tailing increases linearly, but within a single peak it begins quite low in the peak foot and the upper part of the peak is almost symmetric. Above 50% peak height there is practically no increase of asymmetry with ionic strength and stronger tailing factors in the peak foot were found only at high salt contents of the eluents (above 20 mM NaCl). This is the reason, why for the highest salt contents the values for the double layer

deviate from the theoretical ones. The calibrations are based on both, the TEM measurements of the particle cores and the measured retention times. If there are smaller disturbing effects the calibrations are compensated for in the particular eluents.

Finally, in the SEC of organic polymers a fulfilled Gouy–Chapman correlation has always been attributed to the change of the double layer thickness [9,10]. This correlation was also found for the inorganic particles. It is difficult to believe that any effect of adsorption would also be proportional to the reciprocal square root of the ionic strength. Moreover, just the deviation from this relation observed with many CdS samples for the highest ionic strength (Fig. 5), where adsorption becomes more important, supports the hypothesis that at lower ionic strengths adsorption does not play an important role. The same situation is found for latexes [10].

For all these reasons we think, as long as not very high ionic strengths are considered the SEC results reflect the effective size of colloidal particles, which is the sum of core size and double layer thickness.

5. Conclusion

In SEC of colloidal particles the retention time increases with electrolyte concentration and even stronger with electrolyte valency. These findings are in qualitative agreement with the Gouy–Chapman model of the electrical double layer.

A SEC calibration for the effective particle size including the double layer is established from the comparison of retention time with Debye length, both as a function of electrolyte concentration.

This allows the quantitative evaluation of the double layer thickness by chromatography resulting in a good agreement with the theoretical data. Also the linear relation between effective particle size and reciprocal square root of ionic strength is fulfilled.

A disturbing effect of adsorption could be ruled out for low and medium ionic strengths.

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