CONTRAST VARIATION WITH TEMPERATURE IN LIGHT SCATTERING FOR SILICA PARTICLES IN DILUTED SOLUTIONS

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The contrast variation technique by varying the temperature is applied to a light scattering study of a colloidal dispersion of spherical silica particles in cyclohexane. It is found that a refractive index variation occurs in the particle and the refractive index at the periphery is higher than at the center of the particle. The inhomogeneity parameter E has a value of 26 nm^2.

1. Introduction

Contrast variation is a fully developed technique in small-angle X-ray scattering and small-angle neutron scattering. This method, for example, is used to analyse the complex structure of biological macromolecules in situ [1], to determine the structure of adsorbed phases on particles in liquid dispersion [2] and to determine various components inside micro-emulsion particles This technique was introduced to light scattering [3] to characterize colloidal particles.

The intensity of light scattering of colloidal particles surrounded by a continuous medium is determined by the difference in refractive index between the particle and the medium. By an appropriate choice of solvent the particle scattering can be minimized. At this (so-called) matching point, the (mean) index of refraction of particles and solvent is the same Around the matching point the light scattering properties become sensitive to local variations of refractive index inside the particle The systematic observation of the scattered intensity as a function of refractive index constitutes the contrast variation technique. This method affords one to determine particle properties like the average refractive index, refractive index increment with temperature, the radius of gyration and a parameter which is a measure of the variation in refractive index inside the particles.

In a previous study of contrast variation in light scattering [3] the refractive index of the medium was varied by using mixtures of solvents with different composition However, a disadvantage of using mixtures of solvents is the possibility of preferential adsorption on the particles of one solvent with respect to the other This preferential adsorption may vary with varying composition of the solvents.

In this paper we exploit a new method of contrast variation in light scattering where the complication of preferential adsorption is avoided. This is accomplished by changing contrast between particle and the medium by varying the temperature. In cases that the refractive index variation with temperature for colloidal particles differs from that of solvent, it is possible to change the contrast between the particle and the medium

In this communication we report the experimental results of contrast variation experiments with temperature for low concentrations of lyophilic silica spheres dispersed in cyclohexane.

2. Theory

For a monodisperse, diluted system, the normalized excess scattering of a dispersion over that of the solvent medium is given by Rayleigh–Gans–Debije (RGD) theory,

$$R(K) = MK^*c\,P(K)(1 + \cos^2\theta)[(\bar{n}_p - n_0)/\rho]^2 , \quad (1)$$

with

$$K^* = 2\pi^2 n^2 \lambda_0^{-4} . \quad (2)$$

$R(K)$ is the Rayleigh ratio, M is the molar mass of the particles, c is the particle concentration, ρ is the mass density of the particle, $P(K)$ is the intra-particle interference factor depending on wave vector

$$K = (4\pi n/\lambda_0)\sin(\theta/2) , \quad (3)$$

θ is the scattering angle, λ_0 is the wavelength of the light in vacuo. Further $\bar{n}_p$ is the average refractive index of particle, n and n_0 are the refractive indices of dispersion and solvent. For a very diluted solution n is nearly equal to n_0.

Considering first the limit $K \to 0$ (forward scattering) $P(K) = 1$ and eq (1) becomes

$$R(K=0) = 2MK^*c[(\bar{n}_p - n_0)/\rho]^2 \quad (4)$$

The average refractive index of the particle and the medium can be expressed as

$$\bar{n}_p = n_p^0 + (d n_p/dT)\,T , \quad (5)$$

$$n_0 = n_0^0 + (d n_0/dT)\,T . \quad (6)$$

where n_p^0 and n_0^0 are the refractive indices of particle and solvent at $T = 0°C$. $d n_p/dT$ and $d n_0/dT$ are the increments in refractive index with respect to temperature. With eqs (4), (5) and (6) this yields,

$$n_0^{-1}[R(K=0)/2c]_{c\to0}^{1/2}$$

$$= K'[(n_p^0 - n_0^0) + T(d\bar{n}_p/dT - d n_0/dT)] . \quad (7)$$

where $K' = (2\pi^2 \lambda_0^{-4} \rho^{-2} M)^{1/2}$.

From eq. (7) it is seen that a linear dependence must be found by plotting $n_0^{-1}[R(K=0)/2c]_{c\to0}^{1/2}$ versus T. The intercept and slope give $\bar{n}_p - n_0^0$ and $d\bar{n}_p/dT - d n_0/dT$.

In the case that the light scattering of spherically symmetrical monodisperse particles is considered for $K \neq 0$ the intra-particle interference factor is given by,

$$P^{1/2}(K) = \frac{\int_0^R 4\pi r^2[n_p(r) - n_0][\sin(Kr)/Kr]\,dr}{\int_0^R 4\pi r^2\,dr} , \quad (8)$$

where $n_p(r)$ is the refractive index of the particle at a

distance r from the centre of the particle.

For small K formula (8) can be Taylor-expanded as follows:

$$P(K) = 1 - \tfrac{1}{3}K^2 R_g^2 , \quad (9)$$

or in the Guinier approximation:

$$P(K) = \exp(-\tfrac{1}{3}K^2 R_g^2) , \quad (10)$$

with

$$R_g^2 = \int_0^R 4\pi r^4 [n_p(r) - n_0]\,dr\bigg/ \int_0^R 4\pi r^2 [n_p(r) - n_0]\,dr \quad (11)$$

From eq (10) it can be seen that in the Guinier approximation a $\ln[R(K)]$ versus K^2 plot will give a straight line with a slope which is equal to $\tfrac{1}{3}R_g^2$. For particles with a uniform, homogeneous refractive index, R_g is the same as the geometrical radius of gyration of a sphere, R_{g0}^2, and so the particle radius can be calculated. For a non-homogeneous particle R_g is not the geometrical radius of gyration but an optical radius of gyration. The relation between the geometrical radius of gyration and the optical radius of gyration can be found as follows. we write

$$n_p(r) = \bar{n}_p + \Delta n_p(r) . \quad (12)$$

where $\Delta n_p(r)$ is the deviation of the mean value defined by the relation

$$\int_0^R 4\pi r^2 \Delta n_p(r) = 0 . \quad (13)$$

Using eqs (11), (12) and (13) one obtains after some rearrangement

$$R_g^2 = R_{g0}^2 + E/(\bar{n}_p - n_0) , \quad (14)$$

$$R_{g0}^2 = \int_0^R 4\pi r^4\,dr\bigg/ \int_0^R 4\pi r^2\,dr = \tfrac{3}{5}R^2 \quad (15)$$

and

$$E = \int_0^R 4\pi r^4 \Delta n_p(r)\,dr\bigg/ \int_0^R 4\pi r^2\,dr \quad (16)$$

R_g and R_{g0} are the optical and geometric radius of gyration of the particle and E is a measure of the inhomogeneity in refractive index within the particle:

I is positive when the refractive index at the periphery is larger than at the core of the particle.

From eq (14) it is seen that R_g^2 of a non-homogeneous particle depends on the contrast between the scattering particle and the surrounding medium. The value of R_{g0}^2 can be found when R_g^2 is plotted as a function of $(\bar{n}_p - n_0)^{-1}$ and extrapolated to $(\bar{n}_p - n_0)^{-1} = 0$ (infinite contrast). The slope of the plot gives the sign and magnitude of E.

The above analysis is restricted to particles with a spherically symmetric distribution of material around the particle centre. The general case is treated in ref. [3] It turns out that the interpretation of E for non-symmetrical particle is somewhat more complicated and that an extra term arises in the formula (14) which is proportional to $\frac{1}{3}(\bar{n}_p - n_0)^{-2}\mu^2$ where μ is the *optical* dipole moment of the particle. However, we did not find such a term in our experiments so μ is apparently too small to detect and we may use eq. (14)

3. Preparation and characterization

Lyophylic silica particles were prepared as described in the literature [4]. The particles consist of a silica core coated with stearyl aliphatic chains (18 carbon atoms). Experiments were performed with very dilute dispersions ($c = 5.6$ mg/ml). The results are given in table 1. The diffusion coefficient obtained from the dynamic light scattering was K independent, indicating that the particles are monodisperse Particle size and the size distribution were calculated from electronmicroscope photographs. The silica particles were dispersed in cyclohexane. The solutions were made dust free by filtering through millipore filters of 0.45 μm The molar mass of the particle was determined using the Svedberg equation $M_{SD} = S_0 RT[D_0 \times (1 - \bar{v}\rho_0)]^{-1}$ where S_0 and D_0 are the sedimentation and diffusion coefficients at infinite dilution, ρ_0 is the density of cyclohexane and $\bar{v}$ is the partial specific volume of silica obtained from the density measurements The results are given in table 1.

Table 1
Summary of characterization experiments on diluted silica dispersions in cyclohexane

Dynamic light scattering	
diffusion coefficient	$D_0 = (3.3 \pm 0.1) \times 10^{-12}$ m^2/s
hydrodynamic radius	$R_h = 71 \pm 2$ nm
quality factor [5]	$Q = 0.01$
density	$\rho = 1.77$ g/cm^3
Electron microscopy	
radius	60 ± 6 nm
standard deviation	9.2%
sedimentation coefficient	$S_0 = (9.8 \pm 0.1) \times 10^{-10}$ s
molar mass from sedimentation and diffusion coefficient	$M_{S_0}D_0 = 1.3 \times 10^9$ g mol^{-1}
refractive index of cyclohexane at 25°C	$n_0^{25} = 1.4461$ ($\lambda = 546$ nm)
	$n_0^{25} = 1.4560$ ($\lambda = 436$ nm)
refractive index increment with temperature for cyclohexane	$dn/dT = 5.6 \times 10^{-4}$ deg^{-1}
match temperature	$T = 0.8$°C ($\lambda = 546$ nm)
	$T = 2.2$°C ($\lambda = 436$ nm)
Time-averaged light scattering	
contrast variation (temperature)	$R_{cv} = 68 \pm 3$ nm
mean index of refraction of the particles at 25°C	$\bar{n}_p = 1 4384 \pm 0.001$ ($\lambda = 546$ nm)
	$\bar{n}_p = 1.4465 \pm 0.001$ ($\lambda = 436$ nm)
change in refractive index with temperature of the particles	$dn_p/dT = -1.2 \times 10^{-5}$ deg^{-1} ($\lambda = 546$ nm)
	$dn_p/dT = -4.7 \times 10^{-5}$ deg^{-1} ($\lambda = 436$ nm)

4. Experiment

Dynamic light scattering and sedimentation velocity experiments were carried out as described elsewhere [5]. Transmission electron microscope photographs were made with a Philips EM 301 apparatus. Carrier grids covered with carbon coated parlodion films were dipped in a dilute dispersion and the electron micrographs were taken of the particles on the film

The densities were measured with the digital density measuring device DMA-201 from Anton Paar, KL, Austria Time-averaged light scattering experiments have been performed at wavelengths $\lambda_0 = 436$ nm. $\lambda_0 = 546$ nm with an apparatus described elsewhere [4]. The temperature was kept constant to $\pm0.1°C$ As scattering standard pure benzene was used. ($R_{g0} = 15 8 \times 10^{-6}$ cm^{-1} at $\lambda_0 = 546$ nm and $R_{g0} = 45 6 \times 10^{-6}$ cm^{-1} at $\lambda_0 = 436$ nm). The angular range studied was $15° < \theta < 150°$

Measurements of the time-averaged light scattering intensity were performed at different temperatures Gunier plots obtained by plotting the logarithm of intensity versus the square of the wave vector gave straight lines for all temperatures varying from 10 to 36°C Straight line plots obtained at high contrast indicates the silica particles are rather monodisperse From the intercepts and slopes the values of $R(K=0)$ and optical radius of gyration R_g was obtained By varying the temperature one changes the refractive index of both particle and solvent Fig 1 shows plots of $n_0^{-1} [R(K=0) 2c^{-1}]^{1/2}$ versus temperature It is seen that a good linearity is observed for the two
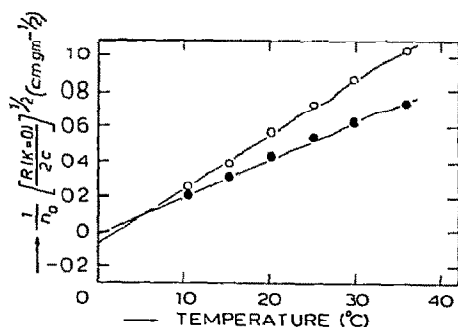

Fig. 1. The square root of the $K \to 0$ extrapolated scattered intensity is plotted versus temperature. O, $\lambda_0 = 436$ nm, ●, $\lambda_0 = 546$ nm
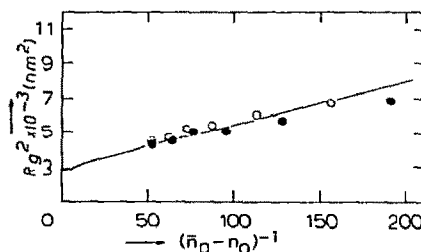

Fig. 2. The square of the optical radius of gyration as a function of the reciprocal of the contrast. O, $\lambda_0 = 436$ nm, ●, $\lambda_0 = 546$ nm.

wavelengths $\lambda = 436$ and $\lambda = 546$ nm, as predicted by eq (6). The obtained refractive index n_p^0 and dn/dT for the silica particles after temperature correction (n_p^{25}) are shown in table 1 Use was made of the literature values of n_0 and dn/dT for cyclohexane at different temperatures.

In fig. 2 the square of the optical radii of gyration (R_g) is plotted against ($\bar{n}_p - n_0)^{-1}$ for wavelengths $\lambda = 436$ and $\lambda = 546$ nm. As expected from eq (13) a straight line was obtained. The intercept gives the radius of gyration R_{g0} and the radius of the silica particle was calculated using $R^2 = \frac{5}{3}R_{g0}^2$ The slope of the line gives L The results are given in table 1

5. Discussion

The refractive index of silica measured by contrast variation using temperature is in the same order as measured by contrast variation using mixtures of solvents [3] The radius of the particle obtained from contrast variation (68 ± 3 nm) agrees well with that measured (71 ± 2 nm) from dynamic light scattering The electron microscopy radius is low compared to light scattering radius and this is probably due to the shrinking of silica particles when exposed to electron bombardment [4] The obtained value of L (26 nm^2) shows that within the particle there are variations in refractive index.

The positive sign of L indicates that the refractive index of the periphery of the particle is larger than that of the core. An attempt was made to calculate the refractive index of the core and the chains from the obtained value of L and the average refractive index using eq (16). It was assumed that the particle

was made up of a homogeneous core of 66 nm radius and an alkane layer of 2 nm. We obtained for $E = 26$ nm^{-2} a refractive index of silica $n_{silica} = 1.4384$ and $n_{alkane} = 1.60$ for $\lambda = 546$ nm. This refractive index for stearyl chain (1.60) seems very high. Therefore the silica core must be inhomogeneous. The inhomogeneity cannot be accounted by the above simple model. We performed another model calculation assuming two homogeneous concentric layers. Taking the radius of the particle 71 nm and $E = 26$ nm^{-2}, we obtained refractive indices of 1.4010 for the inner layer of radius 43 nm and 1.4600 for the outer layer. It seems to indicate that the inner part of the particle being loose and the outer region relatively compact. A more detailed approach should take into consideration the polydispersity of silica particles.

We can conclude that the contrast variation using temperature is a very useful method for the determination of the average refractive index of particle, the change of refractive index with temperature and the inhomogeneity parameter of the particle.

Acknowledgement

References

[1] H.B. Stuhrmann and A. Miles, J. Appl. Cryst. 11 (1978) 325.
[2] C. Taupin, I.P. Cotton and R. Ober, J. Appl. Cryst. 11 (1978) 613.
[3] A.K. van Helden and A. Vrij, J. Colloid Interface Sci. 76 (1980) 418.
[4] A.K. van Helden, J.W. Jansen and A. Vrij, J. Colloid Interface Sci. 81 (1981) 354.
[5] M.M. Kops-Werkhoven and H.M. Fijnaut, J. Chem. Phys. 74 (1981) 1618.