SOME STUDIES ON DIFFUSION IN MACROMOLECULAR SOLUTIONS

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ABSTRACT

The construction and performance of a Pulsed Field Gradient system for use with a commercial, high-resolution, Fourier-Transform NMR spectrometer is described. The self-diffusion coefficient of benzene as measured by the calibrated system is in agreement with the current literature value, within the overall experimental error of the system (±2%). The use of an external lock in conjunction with signal averaging facilitates the measurement of self-diffusion coefficients for solution components in small concentrations. During signal accumulations, the system exhibits freedom from the spin-echo phase and envelope instabilities mentioned as sources of error even in recent publications dealing with the Pulsed Field Gradient technique (e.g. von Meerwall et al., 1979). The ability of the system to investigate dilute solutions is demonstrated by measurements made on 0.5% (w/v) solutions of polystyrene in carbon tetrachloride. Homogeneity coils included in the NMR probe have allowed the self-diffusion coefficients of some single components in multi-component systems to be investigated, and results for the binary system butanol-benzene are presented.

Polymer self-diffusion coefficients have been obtained for 110,000 molecular weight random-coil polystyrene in the solvents carbon tetrachloride, deuterated-chloroform and deuterated-toluene. The Pulsed Field Gradient NMR method was used for the measurements, and the polystyrene concentrations ranged from 0.5% (w/v) to 25% (w/v). For each solvent a concentration regime is found in which the de Gennes' polymer self-diffusion scaling law is obeyed; and the upper concentration limit at which this scaling law breaks down is defined. The self-diffusion coefficient of polystyrene in the solvent deutero-benzene has also been determined, and is shown to agree with Forced Rayleigh Scattering self-diffusion results for similar molecular weight polystyrenes in normal benzene. In contrast, values of the self-diffusion coefficient obtained for polystyrene random-coils by calculation from sedimentation data are shown to differ significantly from those directly determined. The mutual diffusion coefficients of the polystyrene solutions have been obtained from Quasi-Elastic Laser Light-Scattering experiments. These mutual diffusion coefficients do not approach the directly measured self-diffusion coefficients even at concentrations where the random-coils are on average well separated. It is proposed that migrating polymers must suffer transient entanglement effects over the experimental time scales

employed in the diffusion measurements.

Quasi-Elastic Laser Light-Scattering has also been used to measure the diffusion coefficient of polystyrene latex spheres in 0.01M and 0.001M sodium chloride. Experiments were conducted over the latex sphere concentration range 0.004% (w/v) to 4.46% (w/v), and several measurements were also made for low concentrations of latex spheres in triply distilled water. The diffusion coefficient was found to be ionic strength dependent over the entire concentration range studied. Solutions of polystyrene spheres at moderate concentrations exhibit the phenomenon of multiple scattering. The available literature on multiple scattering is reviewed and criteria adopted for the reliable interpretation of data collected during experiments on these solutions. The diffusion coefficients so obtained show substantial agreement with the mutual-diffusion coefficient results of Anderson et al., obtained by a capillary penetration technique. The conclusion reached in this section of the work is that Quasi-Elastic Laser Light-Scattering is able to provide a measure of the mutual diffusion coefficient in the presence of interactions between charged macromolecules. This conclusion is seen to be in accord with earlier laser light-scattering studies on solutions of the protein Bovine Serum Albumin, provided that a reassessment of available mutual diffusion data on these systems is undertaken.

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D_S	-	macromolecular self-diffusion coefficient.
D_{Solv}	-	solvent self-diffusion coefficient.
D_M	-	macromolecular solution mutual-diffusion coefficient.
$\overline{r^2}$	-	mean-squared displacement.
J	-	the flow of solute molecules, per unit time, across a unit area perpendicular to that flow.
c	-	macromolecular concentration.
D_0	-	infinite dilution macromolecular diffusion coefficient.
k_B	-	Boltzmann constant (1.38×10^{-23} joule.deg^{-1}).
T	-	absolute temperature, or correlator sample time.
f_0	-	frictional coefficient per macromolecule at infinite solute dilution.
R	-	non-hydrated hard sphere radius.
π	-	the constant 3.14159.
η_0	-	the solvent viscosity.
M_w, M_n	-	the weight and number average molecular weights.
R_H	-	the hydrodynamic sphere radius.
D_S^+	-	indirectly determined self-diffusion coefficient.
$\bar{v}$	-	solute partial specific volume.
s	-	sedimentation coefficient.
ρ	-	solution density.
θ	-	the scattering angle (except in Chapter 3 where θ is the magnetisation rotation angle).
$\underset{\sim}{q}$	-	the scattering vector.
$\underset{\sim}{k}_i, \underset{\sim}{k}_s$	-	initial and scattered wave vectors.
q	-	magnitude of the scattering vector.
λ_0	-	vacuum wavelength of the incident laser radiation.
$\hbar$	-	Planck's constant (6.6256×10^{-34} joule.deg^{-1}) divided by 2π.
$E_S(0)$	-	magnitude of the total scattered electric field at the photodetector at time t′.
$E_S(t)$	-	E_S at the later time t′+t.
I(0)	-	the scattered intensity, defined similarly to $E_S(0)$.
I(t)	-	the scattered intensity, defined similarly to $E_S(t)$.
*	-	indicates that the complex conjugate has been taken (Chapter 2 only).

$g^{(2)}(t)$ - the normalised intensity autocorrelation function (second order electric field autocorrelation function).

$g^{(1)}(t)$ - the normalised first order electric field autocorrelation function.

ω_0 - incident electric field angular frequency.

$I(t,T)$ - the average intensity during the short time interval T which is centred on the time $t'+t$.

$n(t,T)$ - number of photodetections during T.

$C_p(t,T)$ - the un-normalised, full photocount autocorrelation function.

$\eta_k(T)$ - the clipped count.

k - clipping level.

$C_k(t), C_k(mT)$ - single-clipped, un-normalised photocount autocorrelation function.

$g_k^{(2)}(t,T)$ - normalised, single-clipped photocount autocorrelation function.

Γ - the decay rate of a photocount autocorrelation function.

$\bar{\Gamma}$ - average decay rate of a photocount autocorrelation function.

$G(\Gamma)$ - normalised distribution of the decay rates.

$\mu_r/\bar{\Gamma}^r$ - rth normalised moment of $G(\Gamma)$.

D_{ML} - the quantity extracted by a cumulants analysis of QELS data obtained from concentrated, non-random-coil, macromolecular solutions.

Q' - the variance of the decay rate distribution.

$G_k^{(2)}(\infty)$ - the calculated baseline: the value of the normalised, single-clipped autocorrelation function at infinite time.

A_{coh} - the detector coherence area.

Ω - the solid angle subtended by the source, at the detector (Chapter 2 only; otherwise an Ohm symbol).

I - nuclear spin quantum number (Chapter 3 only; otherwise symbolises current).

B_0 - magnitude of the steady magnetic field.

γ - nuclear gyromagnetic ratio.

$\underset{\sim}{i},\underset{\sim}{j},\underset{\sim}{k}$ - laboratory frame unit vectors

$\underset{\sim}{i}',\underset{\sim}{j}',\underset{\sim}{k}'$ - rotating frame unit vectors.

μ - magnitude of the nuclear magnetic moment (Chapter 3 only; otherwise the multiplier "micro" i.e. $x10^{-6}$).

M	-	the magnitude of the macroscopic magnetisation.
ω_L	-	Larmor frequency.
B_1	-	the magnitude of a magnetic field applied along the x´-axis.
t_p	-	the time for which $\underset{\sim}{B}_1$ is applied.
τ	-	the 90^o-180^o rf pulse spacing.
G	-	the magnitude of the magnetic field gradient.
$A(0)$	-	the magnitude of the spin-echo at $t=2\tau$ in the absence of an applied magnetic field gradient.
$A(G)$	-	the magnitude of the spin-echo when the field gradient is applied.
T	-	the time for which a nucleus remains at a position z.
ζ	-	the rms jump displacement of a nucleus.
Δ	-	the magnetic field gradient pulse separation.
δ	-	the magnetic field gradient pulse width.
d	-	the separation between the 90^o rf pulse and the first gradient pulse.
$P(\phi_D)$	-	the probability of obtaining a phase difference ϕ_D.
Q_T	-	quality factor of the transmitter circuit.
L_1, L_2, L_3	-	inductances in the NMR probe circuitry.
R_{in}, R_1, R_2, R_3	-	resistances in the NMR probe circuitry.
C_1, C_2, C_3	-	capacitances in the NMR probe circuitry.
D_1-D_4	-	diodes in the NMR probe circuitry.
$2l$	-	separation of the magnet pole-pieces.
Q_A, Q_B	-	sets of Darlington connected transistors.
R_S	-	the Kepco sensing resistor.
R_{CC}	-	Kepco current control potentiometer.
g_0	-	residual field gradients due to inhomogeneities in the steady field $\underset{\sim}{B}_0$.
g_e	-	the eddy current induced gradient.
$\Delta\nu$	-	the off-resonant frequency.
Aco	-	the ratio of the correlator off-to-on times.
S_M	-	the slope of a ln(NIAF-1) vs. time plot; or the initial slope of such a plot if the plot is multi-exponential.
R_F	-	the radius of random-coils in the very dilute regime.
ℓ	-	the Kuhn statistical segment length.
M	-	the polymer molecular weight.
m	-	molecular weight of ℓ.
ν	-	Flory number (except in Chapter 3 where $\Delta\nu$ denotes the off-resonant frequency).

c^* - the polymer concentration such that the average distance between two neighbouring coil centres is equal to $2R_F$.

ξ - the average distance between polymer entanglements in the gel regime.

T_r - the chain disentanglement time.

S_L - the long time decay rate.

D_L - the quantity with the dimensions of a diffusion coefficient, calculated from the long-time part of a ln(NIAF-1) vs. time plot.

R_S - the calculated mean latex sphere separation.

σ - latex sphere surface charge density.

ε - permittivity of the latex sphere.

a - latex sphere radius.

B_M - latex sphere bulk modulus.

ε_0 - the permittivity of free space.

k - defined through the equation

$$D_M = D_0(1 + k.c + \text{---})$$

E(r) - the pair potential energy for two charged particles separated by a centre-to-centre distance r.

ψ_0 - the surface potential of a charged sphere.

R - the normalised intersphere separation (Chapter 7 only).

κ^{-1} - the Debye-Hückel shielding length.

e - electronic charge (1.602×10^{-19}C).

f,Ξ - parameters used to evaluate equation 7.6.

$(\frac{\partial \pi}{\partial c})_{p,T}$ - isothermal osmotic compressibility.

Φ - volume fraction.

β - the rise-time of a ramped magnetic field gradient pulse.