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Calculation of the Dispersion of Specific Refractive Index Increments

Values of the specific refractive index increment, $\nu \equiv dn/dc$, are needed for the determination of molecular weights by light scattering. In particular for the study of copolymers it is often important to mask one of the monomers, i.e., to make ν of that monomer (nearly) zero by choosing an appropriate solvent and wavelength. The finer adjustments of ν can be achieved by the selection of the wavelength. It would therefore be convenient if dispersions in ν could be calculated in a simple way. From the Lorenz–Lorentz equation one may derive[1] for $c \to 0$

$$\nu \equiv dn/dc = \frac{(n_1^2 + 2)^2}{6n_1\rho_2}\left(\frac{\rho_2 R_2}{M_2} - \frac{\rho_1 R_1}{M_1}\right) \tag{1}$$

Here n is the refractive index of the solution; c is the polymer concentration; n_1 is the refractive index of the solvent; ρ_2 and ρ_1 are the densities of polymer and solvent; M_2 and R_2 are the molecular weights and the molar refractions of the repeating units of the polymer; and M_1 and R_1 are those of the solvent. Although it is well-known that eq. (1) gives rather poor results for the absolute values of ν, it might be expected to give much better accuracy for the dispersion in ν. In Table I, calculated and experimental values of $\Delta \equiv \nu(436\text{ nm}) - \nu(546\text{ nm})$ are compared. Only ν's specified to four significant figures were used as tabulated by Huglin.[2] Values of R were calculated from Eisenlohr's bond refractions;[3] n_1 and ρ_1 were obtained from tabulations of Huglin[4] at 20°C, and ρ_2 from tabulations of Van Krevelen.[5] The molar refractions of the phenyl group were obtained from averaged values of the molar refractions of monosubstituted benzene derivatives minus the bond refractions of the substituents ($R(C_6H_5) = 25.20, 25.96, 26.44$, respectively, at 656.3, 486.1, 434 nm). The molar refractions of the monosubstituted benzene derivatives were calculated from densities and refractive indexes, using the Lorenz–Lorentz equation.

Apparently the accuracy of the calculated Δ is 0.0020 ml/g or better. The following additional comments can be made:

1. There is no correlation between the magnitude of Δ and of $\Delta(\text{calc}) - \Delta(\text{exp})$.
2. When neither polymer nor solvent contains benzene rings, Δ is several times smaller than when polymer or solvent contain benzene rings.
3. Δ is *negative* when only the solvent contains a benzene ring. The existence of negative values of Δ is not always recognized.[6]

TABLE I
Dispersion of Refractive Index Increments[2]

Polymer	Solvent	$\Delta_{calc.}$	$\Delta_{calc.} - \Delta_{exp.}$
Poly(ethyl acrylate)	butanone	0.0014	0.0000
Poly(propylene oxide)	isooctane	0.0007	0.0007
Poly(methyl methacrylate)	isoamyl acetate	0.0020	0.0000
Poly(*n*-butyl methacrylate)	acetone	0.0014	0.0001
Poly(propylene oxide)	benzene	−0.0100	−0.0018
Poly(propylene oxide)	chlorobenzene	−0.0100	−0.0020
Poly(methyl methacrylate)	benzene	−0.0056	0.0015
Poly(methyl methacrylate)	toluene	−0.0052	0.0021
Polystyrene	cyclohexane	0.0105	−0.0008
Polystyrene	butanone	0.0109	−0.0017
Poly(α-methylstyrene)	carbon tetrachloride	0.0086	−0.0014
Poly(α-methylstyrene)	cyclohexane	0.0098	−0.0022
Polystyrene	benzene	0.0026	−0.0006
Polystyrene	toluene	0.0029	−0.0005

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5. D. W. van Krevelen in *Properties of Polymers*, Elsevier, Amsterdam, 1972, Appendix 2.
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J. LAVEN
M. W. J. VAN DEN ESKER
A. VRIJ

Van't Hoff Laboratorium
voor Fysische en Colloidchemie
der Rijksuniversiteit
Padualaan 8
Utrecht, The Netherlands

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