Magnetic Birefringence of a Series of Nematogenic Compounds

Klaus Fuhrmann and Andreas Martin

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55021 Mainz, FRG

Georg Maret[†]

Hochfeld-Magnetlabor des Max-Planck-Instituts für Festkörperforschung 166X, F-38042 Grenoble, France

Ulrich Tiesler and Matthias Ballauff*

Polymer-Institut, Universität Karlsruhe, Kaiserstrasse 12, 76128 Karlsruhe, FRG

Received: November 15, 1993[⊛]

Cotton–Mouton constants $_mC$ of nematogenic oligomers of the oxybenzoate series have been determined in solution. The experimental values of $_mC$ were compared with the Cotton–Mouton constant calculated from group additivity schemes: For the tensor of the diamagnetic susceptibility, the scheme of Flygare (*Chem. Rev.* **1974,** *74*, 653) was used, and for the polarizability tensor group, contributions deduced previously from depolarized Rayleigh scattering (DRS; *J. Phys. Chem.* **1990,** *94*, 3215) were employed. Good agreement of measured and calculated $_mC$ values is found. The influence of the local field correction used for the evaluation of both the DRS and the Cotton–Mouton constant is discussed.

Introduction

Nematogens, i.e., substances that occur as nematic liquid crystals under suitable conditions,[1,2] have in general an elongated, rodlike shape. Concomitantly, the molecular tensors of the polarizability α and of the diamagnetic susceptibility κ are also characterized by a pronounced anisotropy which can be used to determine the molecular order present in the liquid crystalline phase. Thus by very accurate measurements[3] of the magnetic susceptibility by a SQUID-magnetometer,[4] the nematic order parameter[1,2] can be deduced if the anisotropy of the molecular susceptibility tensor κ is known with sufficient accuracy. An important prerequisite of such an analysis is the precise knowledge of the conformation of the nematogenic molecules. Also, the incremental scheme for the calculation of the tensor of the magnetic susceptibility devised by Flygare[5] had to be used. An assessment of the accuracy of the underlying assumptions and data analysis based on independent measurements is therefore highly desirable.

In this paper we present a study of the diamagnetic tensor by precise determination of the Cotton–Mouton constants (CM) of dilute solutions of compounds 1–9 in Chart 1 and a comparison with calculated values.

Compounds 8 and 9 (for definition of compounds, see Table 1), which form stable nematic phases, have already been investigated previously by SQUID-magnetometry.[3] By use of an extrapolation procedure, the anisotropy of the tensor of molecular susceptibility was obtained[3] and compared to values deduced from Flygare's increments.[5] The optical anisotropy of all materials has been studied carefully in solution by depolarized light scattering[6,7] (DRS). The latter data were used to derive a consistent set of increments of the tensor α of the optical polarizability within the frame of the group additivity scheme.[6,7] Given the increments[5–7] for the evaluation of κ and α, the absolute value of $_mC$ may be predicted for all compounds 1–9 under consideration here and compared to the experimental data. This comparison therefore provides an independent test of both incremental schemes applied previously for different sets of data.[3,6,7]

CHART 1

methyl benzoate   phenyl acetate
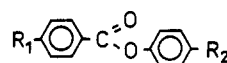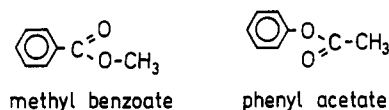
Compounds 3–6, R_1, R_2: H, OCH_3
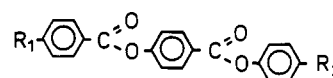
Compounds 7–9, R_1, R_2: H, OCH_3

It has to be noted that the increments used for the calculation of the α-tensor were derived in refs 6 and 7 with the assumption of a quadratic Lorentz correction for the local electrical field. Keyes and Ladanyi[8–10] however, have advanced theoretical arguments for using the fourth power of the Lorentz factor in order to correct for the local field in DRS. Data of $\Delta\alpha$ deriving from the latter treatment of data have been used by Madden and co-workers[11,12] and by Burnham and Gierke[13] for a determination of the orientational correlation factor from a combination of DRS and CM data.

A similar problem arises when the evaluation of the Cotton–Mouton data is discussed: The usual treatment[11–13] of the CM data rests on the expression of the Born–Langevin theory containing the quadratic Lorentz factor (see eq 2 below). On the other hand, Hüttner and co-workers[14] as well as Schröer[15] have given theoretical and experimental arguments that the CM constants should be evaluated from an expression using the linear Lorentz factor.

In this publication we will combine the DRS data deriving from refs 6 and 7 together with the CM constants evaluated according to Born–Langevin theory. Within certain limits, the data given herein can be compared to the other expressions employing different powers of the Lorentz factor. Since the nematogens 3–9 may be viewed as model oligomers of stiff-chain
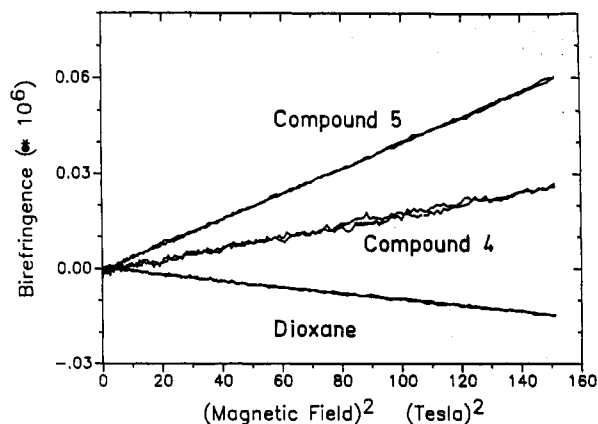
Figure 1. Plot of the observed birefringence versus the square of the magnetic field strength (cf. eq 1). For the definition of compounds, see Chart 1 and Table 1.

polymers, as e.g. the poly(4-oxybenzoate), this analysis bears important implications for studies of rodlike polymers[16-18] in solution.

Experimental Section

Materials. Phenyl acetate and methyl benzoate were synthesized by standard methods[19] and purified carefully by repeated distillation in vacuo. 1,4-Dioxane (Merck-Schuchardt, zur Synthese) was purified by distillation. Compounds 3-9 were synthesized according to the route given previously.[20] Details of the synthesis will be given elsewhere.

Measurements and Evaluation of Data. The magnetic birefringence has been determined using the experimental setup described previously.[18] As a light source, an argon ion laser operating at 488 nm was used. The magnetic field was generated by a Bitter magnet (B_{max} = 13.5 T). A full sweep cycle of the magnetic field was performed in 90 s.

All measurements of compounds 1-9 were done at 25 °C in dioxane. This particular solvent had been used already for the studies of the optical anisotropies[7] and exhibits a rather small CM constant ($_mC$ = -0.799 × 10^{-27} A^{-2} m^5 mol^{-1}). Dilute solutions of a given compound have been placed in cells of 3-cm path lengths, and the birefringence Δn was measured during a sweep of the magnetic field.

As demonstrated in Figure 1, the birefringence Δn is found to be strictly proportional to the square of the strength of the magnetic field B^2. Therefore, the result of each measurement consisting of all Δn data obtained during a sweep of the magnetic field could be well described by the bulk Cotton-Mouton constant C^b of the sample defined as

$$C^b = \Delta n\, \mu_0^2/\lambda B^2 \qquad (1)$$

with λ being the wavelength of the laser and μ_0 the permittivity of the vacuum. For a given solute, the molar Cotton-Mouton constant $_mC$ can be defined by (cf. ref 13)

$$_mC = \frac{2}{3}\frac{n_{solution}}{(n_{solution}^2 + 2)^2}\frac{V_m\,\Delta n_{solute}\,\mu_0^2}{B^2} \qquad (2)$$

where Δn_{solute} is the birefringence of the solute in solution, $n_{solution}$ is the refractive index of the solution, and $V_m = M/\rho$ is the molar volume of the dissolved compound of molecular weight M in solution the density of which is given by ρ.

Following Le Fèvre and co-workers,[22,23] the molar CM constant at infinite dilution may be evaluated from the experimental data according to

$$_\infty(_mC) = M\left[_sC_1(1 - \beta + \gamma - H\gamma) + \frac{2\lambda n_1 D}{3(n_1^2 + 2)^2\rho_1}\right] \qquad (3)$$

Here n_1 is the refractive index of the solvent, $_sC_1$ is the specific
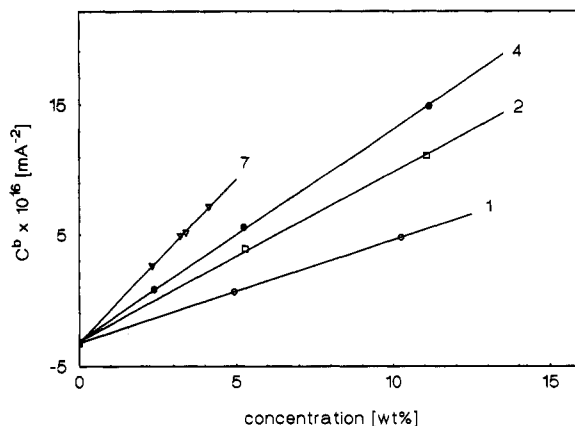
Figure 2. Plot of the bulk Cotton-Mouton constant C^b (eq 1) versus weight concentration of solute for compounds **1**, **2**, **4**, and **7**. For the definition of compounds, see Chart 1 and Table 1.

TABLE 1: Comparison of Measured and Calculated Cotton-Mouton Constants $_\infty(_mC)$[a]

compd	R_1	R_2	$_\infty(_mC)$	
			exp	theor
1	phenyl acetate		28.5	28.1
2	methyl benzoate		48.0	43.5
3	H	H	83.6	87.0
4	OCH$_3$	H	101	107
5	H	OCH$_3$	91.8	100
6	OCH$_3$	OCH$_3$	109	119
7	OCH$_3$	H	240	250
8	H	OCH$_3$	219	241
9	OCH$_3$	OCH$_3$	249	269

[a] Units of 10^{-27} m^5 A^{-2} mol^{-1}.

CM constant of the solvent, and β and γ are derived from incremental densities and refractive indices,[22] respectively. The quantity H is defined[22] by $H = 4n_1^2/(n_1^2 + 2)$; D describes the dependence of the bulk CM constant C^b of the solution on the weight concentration of the solute.[22] As it turns out for the dilute systems investigated herein, the corrections β and γ can be safely dismissed within given limits of error. The increments D were determined by plotting the bulk CM constant of the solution versus the weight concentration of the solute. Figure 2 displays several examples of such a plot. The good linearity over the given range of concentration indicates the absence of association or other effects disturbing the measurements. Also, the bulk Cotton-Mouton constant of benzene agreed within a few percent with the literature value[22] recalculated for the wavelength used here. Table 1 contains the experimental Cotton-Mouton constants at infinite dilution $_\infty(_mC)$ of all compounds thus obtained.

Results and Discussion

Conformational Analysis. For a system of noninteracting diamagnetic molecules, a theoretical expression for $_mC$ has been given by Buckingham and Pople,[26] which may be rendered in SI units as[21,27,18]

$$_mC = (N_L\mu_0/270\epsilon_0)[\Delta\eta + (1/kT)\,\text{tr}(\hat{\alpha}\hat{\kappa})] \qquad (4)$$

where N_L is Avogadro's number, k the Boltzmann constant, T the absolute temperature, $\Delta\eta$ the hyperpolarizability term arising from the distortions of the optical polarizability by the magnetic field, and $\hat{\alpha}$ and $\hat{\kappa}$ are the traceless tensors of the polarizability α and the magnetic susceptibility κ, respectively:

$$\hat{\alpha} = \alpha - (1/3)\,\text{tr}(\alpha)\,E \qquad (5)$$

$$\hat{\kappa} = \kappa - (1/3)\,\text{tr}(\kappa)\,E \qquad (6)$$

with $E = \text{diag}(1,1,1)$. Evaluation of $_mC$ thus requires knowledge

Figure 3. Definition of the torsional angles of the oxybenzoate unit together with the group contributions $\Delta\alpha$ (cylindrical terms) and $\Delta\alpha^+$ (acylindrical terms) of the traceless tensor α of the optical polarizability.[7]

of $\hat{\alpha}$ and $\hat{\kappa}$ in a molecular coordinate system. The hyperpolarizability $\Delta\eta$ is usually found to be small for aromatic systems as compared to the temperature-dependent term.[21,27,28] For the molecules under consideration here, $\Delta\eta$ is therefore expected to be a minor contribution to $_mC$ and is omitted in the following calculation of $_mC$. Careful measurements on molecules with small CM constants such as cyclopropane, ethane, ethene, and ethyne over a wide range of temperatures[29,30] revealed, however, that in these cases $\Delta\eta$ must not be disregarded.

Tensor of the Optical Polarizability α. The traceless tensor $\hat{\alpha}$ of the optical polarizability is calculated according to the method devised previously.[7] The definition of the various group contributions of $\hat{\alpha}$ together with the torsional angles Φ_1, Φ_2, and Ψ for the oxybenzoate unit is displayed in Figure 3.

As outlined previously,[6,7] the tensor $\hat{\alpha}$ is decomposed into a cylindrical and an acylindrical part by

$$\hat{\alpha} = \Delta\alpha\, J + \Delta\alpha^+ J^+ \tag{7}$$

with

$$J = \mathrm{diag}(2/3, -1/3, -1/3) \tag{8}$$

$$J^+ = \mathrm{diag}(0, 1/2, -1/2) \tag{9}$$

where

$$\Delta\alpha = \alpha_{xx} - (\alpha_{yy} + \alpha_{zz})/2 \tag{10}$$

$$\Delta\alpha^+ = \alpha_{yy} - \alpha_{zz} \tag{11}$$

The tensor of the entire molecule is thus formulated as the sum of suitably chosen group contributions. The previous analysis[6,7] showed that large entities like phenyl or ester groups must be taken to render this scheme valid. The respective values for the various contributions $\Delta\alpha$ and $\Delta\alpha^+$ defined in Figure 3 are[7] (all in angstroms[3]) (1) cylindrical terms, $\Delta\alpha_{ph}' = 3.40$ (unsubstituted), 5.45 (substituted in para position); $\Delta\alpha_{ph}'' = 5.05$ (unsubstituted), 7.97 (substituted in para position); $\Delta\alpha_{ph}''' = 7.00$ (unsubstituted); $\Delta\alpha_E = 1.02$ and (2) acylindrical terms, $\Delta\alpha_{ph}^+ = 2.63$; $\Delta\alpha_E^+ = 0.87$. Following Flory and Navard,[31] the contribution of terminal methoxy groups is given by

$$\hat{\alpha}(\mathrm{OCH_3}) = (2/9)\Gamma A \tag{12}$$

with

$$A = \begin{vmatrix} 2 & -(2)^{1/2} & 0 \\ -(2)^{1/2} & 1 & 0 \\ 0 & 0 & -3 \end{vmatrix} \tag{13}$$

and $\Gamma\ (= 0.072\ \text{Å}^3)$ being the optical anisotropy of the oxymethyl group.

The geometry of the oxybenzoate unit as depicted in Figure 3 is assumed to be strictly colinear. Therefore the x axes x, x', x'' (see Figure 3) of the subsequent phenyl groups are parallel to each other. The small deviation expressed in terms of an angle

TABLE 2: Eigenvalues of the Local Group or Bond Susceptibilities[5] (10^{-12} m^3/mol)

	κ_{xx}	κ_{yy}	κ_{zz}
C—C[a]	−99.3	−2.5	−2.5
C—H[a]	−70.4	−39.0	−39.0
C—O[b]	−90.5	−84.2	−47.8
C=O[c]	−16.3	+27.6	−163
benzene[d]	−439	−439	−1189
phenyl[e]	−298	−361	−1111

[a] Axis 1 along the bond. [b] Axis 1 along the bond and axis 2 in the plane of the pendant oxygen bond. [c] Axis 1 along the bond and axis 2 in the plane of the pendant carbon bond. [d] Axis 1 and 2 in plane of the benzene ring. [e] Axis 1 along the bond to the pendant group and axis 3 perpendicular to the ring.

δ between subsequent x axes ($\delta \approx 5°$) has been shown[6] to effect only negligible alterations of $\hat{\alpha}$. Also, within the limits of error, the angle C(carbonyl)–O–CH$_3$ in methyl benzoate (compound **2**) and the angle C(aryl)–O–C(carbonyl) of phenyl acetate (compound **1**) could be assumed to be 120° (see the discussion of this point in ref 6).

The above geometry therefore only requires[7] the introduction of conformers generated through the different angles Φ_1, Φ_2 ($\pm 60°$), and Ψ (0, 180°). Since rotations of the ester group alone, i.e. rotation of Ψ from 0 to 180° while Φ is kept constant, are inconsequential due to the absence of off-diagonal elements, compounds **7–9** are characterized by two conformers[7] (1: $\Phi_1 = +60°$, $\Phi_2 = +60°$. 2: $\Phi_1 = +60°$, $\Phi_2 = -60°$). For phenyl benzoate (compound **3**), e.g., we obtain[6,7]

$$\hat{\alpha} = (\Delta\alpha_{ph}'' + \Delta\alpha_{ph}' + \Delta\alpha_E)J + (\Delta\alpha_{ph}^+ + \Delta\alpha_E^+)J^+ +$$
$$\Delta\alpha_{ph}^+ \, RJ^+ R^T \tag{14}$$

where R effects the rotation about the x axis:

$$R = \begin{vmatrix} 1 & 0 & 0 \\ 0 & c & -s \\ 0 & s & c \end{vmatrix} \tag{15}$$

with $s = \sin 60°$ and $c = \cos 60°$. As an example, the traceless $\hat{\alpha}$ tensor of compound **3** (phenyl benzoate) results in

$$\hat{\alpha} = \begin{vmatrix} 7.02 & 0 & 0 \\ 0 & -2.30 & \pm 1.27 \\ 0 & \pm 1.27 & -4.73 \end{vmatrix} \tag{16}$$

in units of 10^{-40} A s m^2 V^{-1} (SI units[32]).

Molecular Tensor of Diamagnetic Susceptibility κ. The calculation of $\hat{\kappa}$ (cf. also ref 3) was performed in the same coordinate system as defined in Figure 3 using the local bond and group susceptibilities of Flygare.[5] Table 2 gathers the values used in the calculations. All angles of the ester group were set at 120°. As an example, the traceless tensor for compound **3** (phenyl benzoate) follows as

$$\hat{\kappa} = \begin{vmatrix} 8.52 & \pm 0.3 & 0 \\ \pm 0.3 & -0.5 & \pm 5.48 \\ 0 & \pm 5.48 & -8.07 \end{vmatrix} \tag{17}$$

in units of 10^{-34} m^3. Insertion of both $\hat{\alpha}$ and $\hat{\kappa}$ into eq 4 leads to the calculated value of the molar Cotton–Mouton constant.

Comparison with Experimental Data. As can be seen from Table 1, measured and calculated values of $_mC$ compare favorably for all compounds. It is obvious that for all compounds the CM constant can be predicted with an accuracy of approximately 10%, i.e., within the limits of error of group contribution schemes.

From the above conformational analysis and the construction of the tensors $\hat{\alpha}$ and $\hat{\kappa}$, it becomes obvious that the Cotton–Mouton constant is mainly determined by the cylindrical parts of both tensors. This holds true in particular for the trimeric compounds **7–9** and facilitates the analysis of the Cotton–Mouton constant in terms of a group contribution scheme. It furthermore

demonstrates that in the case of even longer chains, i.e., substituted oligomers of p-hydroxybenzoic acid, the acylindrical terms may be neglected in good approximation (cf. the discussion of the α tensor in ref 6).

The foregoing analysis rests fully on the data obtained in refs 6 and 7, where a second-power Lorentz factor had been used to evaluate the optical anisotropies. The good agreement found here is in clear contradiction to the arguments[10] in favor of the use of the fourth-power Lorentz factor for the evaluation of the α tensor. Also, the present data are not compatible with the definition of the CM constant according to Hüttner and co-workers.[14] It may appear that the good agreement of theory and experiment could be due to cancellation of errors through the use of an incremental scheme. The analysis of the traceless tensors $\hat{\alpha}$ and $\hat{\kappa}$ has shown, however, that the cylindrical terms will dominate the CM constant as well as the quantity γ^2 evaluated from DRS measurements,[6,7] in particular for the trimeric compounds 7–9. Thus[6,7] for these particular compounds,

$$\gamma^2 = (3/2)\mathrm{tr}(\hat{\alpha}\hat{\alpha}) = (\Delta\alpha)^2 + (3/4)(\Delta\alpha^+)^2 \simeq (\Delta\alpha)^2 \quad (18)$$

Therefore the cylindrical part $\Delta\alpha \approx (\gamma^2)^{1/2}$ is directly available from DRS data without recourse to the above incremental scheme. Here, as well as in the work of Madden et al.,[11,12] it is assumed that DRS intensity and the CM constant contain the same effective $\Delta\alpha$. Therefore, a fourth-order Lorentz correction for the DRS intensity data immediately leads to a decrease of the calculated CM constant (see Table 1) by a factor of $(n^2 + 2)/3$. Similarly, the application of the linear Lorentz factor according to Hüttner et al.[14] is followed by an increase of the experimental value of $_\infty(_mC)$ by the same factor. Both modifications are therefore in clear disagreement with the present experimental data.

Conclusion

The foregoing analysis has shown that the measured CM data of the compounds under consideration here are in good agreement with values deduced from Flygare's increments[5] and the optical anisotropies supplied by the tensorial scheme of refs 6 and 7. The discussion of the local field problem for both the DRS and the CM data has demonstrated that other approaches to the local field problem do not lead to agreement between theory and experiment. This discrepancy is not due to possible shortcomings of the incremental schemes used herein. It appears that further investigations of the local field problem would be clearly desirable to clarify this point. Besides these problems, the incremental schemes appear to provide a sound base for the calculation of the Cotton–Mouton data of stiff-chain polymers.

References and Notes

(1) Vertogen, G.; de Jeu, W. H. *Thermotropic Liquid Crystals, Fundamentals*; Springer Verlag: Berlin, 1988.
(2) de Gennes, P. G. *The Physics of Liquid Crystals*; Clarendon Press: Oxford, U.K., 1974.
(3) Dries, Th.; Fuhrmann, K.; Fischer, E. W.; Ballauff, M. *J. Appl. Phys.* **1991**, *69*, 7539.
(4) Philo, J. S.; Fairbank, W. M. *Rev. Sci. Instrum.* **1977**, *48*, 1529 and further literature cited there.
(5) Flygare, W. H. *Chem. Rev.* **1974**, *74*, 653.
(6) Irvine, P. A.; Erman, B.; Flory, P. J. *J. Phys. Chem.* **1983**, *87*, 2929.
(7) Floudas, G.; Patkowski, A.; Fytas, G.; Ballauff, M. *J. Phys. Chem.* **1990**, *94*, 3215.
(8) Keyes, T.; Ladanyi, B. M. *Mol. Phys.* **1977**, *34*, 765.
(9) Keyes, T.; Ladanyi, B. M. *Mol. Phys.* **1979**, *38*, 605.
(10) Keyes, T.; Ladanyi, B. M. *Adv. Chem. Phys.* **1984**, *56*, 411.
(11) Battaglia, M.; Cox, T. I.; Madden, P. A. *Mol. Phys.* **1979**, *37*, 1413.
(12) Madden, P. A.; Battaglia, M. R.; Cox, T. I.; Pierens, R. K.; Champion, J. *Chem. Phys. Lett.* **1980**, *76*, 604.
(13) Burnham, A. K.; Gierke, T. D. *J. Chem. Phys.* **1980**, *73*, 4822.
(14) Müller, H.; Köder, T.; Hüttner, W. *Chem. Phys. Lett.* **1986**, *125*, 473. Hüttner, W.; Köder, T.; Müller, H. To be published.
(15) Schröer, W. *Chem. Phys. Lett.* **1986**, *131*, 500.
(16) Ballauff, M. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 253.
(17) Maret, G.; Dransfeld, K. In *Topics in Applied Physics*; Herlach, F., Eds.; Springer: Berlin, 1985; Vol. 57, p 143.
(18) Maret, G.; Weill, G. *Biopolymers* **1983**, *22*, 2727.
(19) Organikum, Deutscher Verlag der Wissenschaften, 10. Auflage, Berlin, 1971.
(20) Ballauff, M.; Wu, D.; Flory, P. J.; Barrall, E. M., II. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 524.
(21) Battaglia, M. R.; Ritchie, G. L. D. *J. Chem. Soc. Faraday Trans. 2* **1977**, *73*, 209.
(22) Le Fèvre, R. J. W.; Williams, P. H.; Eckert, J. M. *Aust. J. Chem.* **1965**, *18*, 1133.
(23) Le Fèvre, R. J. W.; Murthy, D. S. N.; Stiles, P. J. *Aust. J. Chem.* **1969**, *22*, 1421.
(24) Weast, R. C.; Melvin, J. A.; Beyer, W. H. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1985.
(25) Measured with an Abbé refractometer.
(26) Buckingham, A. D.; Pople, J. A. *Proc. Phys. Soc. B* **1956**, *69*, 1133.
(27) Lukins, P. B.; Buckingham, A. D.; Ritchie, G. L. D. *J. Phys. Chem.* **1984**, *88*, 2414.
(28) Geschka, H.; Pferrer, S.; Häussler, H.; Hüttner, W. *Ber. Bunsen-Ges. Phys. Chem.* **1982**, *86*, 790.
(29) Lukins, P. B.; Laver, D. R.; Buckingham, A. D.; Ritchie, G. L. D. *J. Phys. Chem.* **1985**, *89*, 1309.
(30) Kling, H.; Geschka, H.; Hüttner, W. *Chem. Phys. Lett.* **1983**, *96*, 631.
(31) Flory, P. J.; Navard, P. *J. Chem. Soc. Faraday Trans. 1* **1986**, *82*, 3381.
(32) Conversion of α from cgs units (Å^3) to SI units (A s m^2 V^{-1}): $\alpha(\text{SI}) = (10^6/4\pi\epsilon_0)^{-1} \alpha(\text{cgs})$, see ref 29.