Study on Dipole Moments of Macromolecules I. Apparatus for Dielectric Measurements and Dipole Moment of Poly(p-methoxystyrene)

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ABSTRACT: A three-terminal cell for the dielectric measurement of liquid was made and the cell capacitance was determined using a capacitance bridge. The accuracy of the dielectric constant measurement with the apparatus was examined by measuring standard materials such as benzene and cyclohexane. The mean square dipole moments of poly(p-methoxystyrene) in benzene were determined by accurate measurements of dielectric constants on the polymer dilute solutions and the values were estimated according to two procedures, *i.e.*, one based on Debye and Halverstadt-Kumler equations (DHK method) and the other on Guggenheim and Smith equations (G-S method). The average dipole moments per repeat unit μ were obtained as 1.214 (25°C) and 1.221 (40°C) by the DHK method and 1.204 (25°C) and 1.209 (40°C) by the G-S method (in debye unit). The slight disagreement in μ values obtained by two different procedures was interpreted as arising from differences in assumptions used in the DHK method and the G-S method.

KEY WORDS Dipole Moment / Dielectric Constant / Molecular Polarization / Electronic Polarization / Atomic Polarization / Molecular Refraction / Poly(p-methoxystyrene) / Dielectric Cell / Dilute Solution /

Dipole moment is a configuration-dependent property of polymer chains carrying polar groups in their monomer units and the observed dipole moment is the statistical average of molecular conformations. Theory predicts that the dipole moments of polymer molecules cannot be affected greatly by long-range excluded volume interactions when the molecules have the dipole components perpendicularly attaching to the chain axis.[1,2] The probable absence of the effect of the excluded volume on dipole moments, in contrast with its pronounced effect on chain dimensions, is of great advantage in investigating the influence of intramolecular interactions on the conformation of polar polymers.

We have been studying since early in the 1960's the dipole moments μ of polar vinyl polymers to investigate configurational prop-erties such as the stereochemical structure of the vinyl chains and the monomer sequence distribution in the copolymers.[3-10] Since the conformational analysis of the polymer chains was developed by Flory *et al.* on the basis of a rotational isomeric model (RIS model),[11] a number of studies on the dipole moments of various polymers have been carried out theoretically and experimentally. The dipole moment ratio, $D_r = \langle \mu^2 \rangle / xm^2$, and the temperature coefficient, $d \ln \langle \mu^2 \rangle / dT$, are important parameters in the investigation of the conformational properties of a polymer, where $\langle \mu^2 \rangle$ is the mean square dipole moment of the polymer with x bond dipoles of magnitude m in the chains. The quantities of D_r and $d \ln \langle \mu^2 \rangle / dT$ for polystyrene derivatives in various solvents were reported by many workers.[6,9,10,12-16] Theoretical calculations of

these quantities were carried out for poly(*p*-chlorostyrene) (PClSt) by Mark and Saiz on the basis of the RIS model.[17] There is, however, much scattering in the experimentally observed values of D_r and $d\ln\langle\mu^2\rangle/dT$ and conclusive results have not been obtained. D_r values for PClSt at 25°C range from 0.4 to 0.7 ($m = 1.90$ debye was used) in which there is no obvious correlation with the solvent type employed in the measurements; the negative values of $-8 \times 10^{-3} \sim -1.6 \times 10^{-3}$ were observed for $d\ln\langle\mu^2\rangle/dT$ of PClSt,[9,12,13,16] while an increasing tendency of μ with temperature and/or an inflection of the temperature dependence at a certain temperature has been reported.[6,12,14,16] These facts do not permit a quantitative comparison with theoretical results.

In this paper, we report a new dielectric apparatus with a capacitance bridge and a three-terminal cell prepared to improve the accuracy of dielectric measurements and present some data on the dielectric constants of organic solvents such as benzene and cyclohexane. We then report the dipole moments determined by two procedures for poly(*p*-methoxystyrene) in benzene and discuss the underlying assumptions for determining the dipole moments. μ is usually estimated according to the conventional procedure known as Debye's method,[18] by measuring the dielectric constant and the density of polymer solutions. On the other hand, in many recent papers μ is determined by the use of the Guggenheim-Smith method,[19] by measuring the dielectric constant and the refractive index instead of the density. It is important to clarify the adequancy of approximations in each procedure.

EXPERIMENTAL

Apparatus for Dielectric Measurements

A three-terminal cell with main, counter and guard electrodes for a liquid was constructed following the report by Hartshown *et al.*[20] The capacitance cell with a guard electrode is adequate to get higher accuracy in measurements of smaller capacitances (with air, vacuum, and non-polar organic solvent), because of the adequate screening of the stray capacitance of leads or solid insulators. The cell consists of platinum electrodes of two coaxial cylinders and double-walled cylindrical Pyrex glass as shown in Figure 1. The outer platinum cylinder having an inner diameter $r_2 = 21.0$ mm is divided by circumferential narrow gaps into three parts, the central portion (A) with a length $L = 60.0$ mm forming the main electrode and two end portions (C), each about 8.3 mm in length, serving as the guard electrode. The inner platinum cylinder (B) 84.0 mm long is the counter electrode having an outer diameter $r_1 = 18.4$ mm. The cell capacitance in vacuum was calculated as $C_v = 25.3$ pF using the relation, $C_v = 0.2416L/\log(r_2/r_1)$ (pF).[21]

Capacitance measurement was made on a cell with a capacitance bridge (General Radio
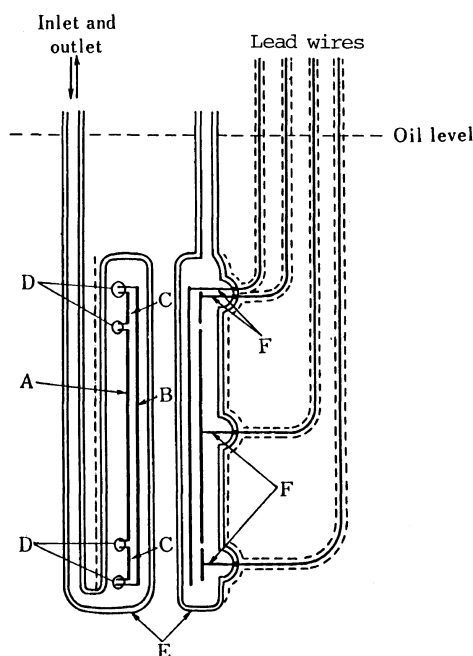

Figure 1. Three-terminal cell. A, B, and C, main, counter and guard platinum electrodes of cylindrical form; D, glass beads; E, a double-walled cylindrical Pyrex glass cell; F, platinum lead wires. The dotted lines indicate screens.

Co., Type 1620) at a frequency of 10 kHz. The bridge is a type of transformer-ratio bridge that uses a single decade of a transformer voltage and multiple, fixed standard capacitors to provide six decades of resolution in capacitance. The cell capacitance with air C_0 was obtained as, $C_0 = 26.5650 \pm 0.0005 \, \text{pF}$ at 25.0°C. The observed value was consistent with the calculated one. The constancy of the cell capacitance measurements was found to be satisfactory through the course of the measurements over a month in which the cell was cleaned with benzene and evacuated and dried by the passage of dry air in each case. In these measurements, the cell was shielded by surrounding it with a stainless mesh and immersed in a silicone oil bath where the temperature was thermostatically controlled to ± 0.01°C. The deviation of the cell capacitance from the mean value was ± 2 parts in 10^5.

Materials

Benzene and cyclohexane were repeatedly purified by distillation. The solvents were dried by passage through a molecular sieve 4A prior to each distillation. Poly(p-methoxystyrene) (PMeOSt) was prepared by radical polymerization by the use of benzoyl peroxide as the initiator at 80°C. The crude product of PMeOSt was purified by reprecipitation using benzene and methanol and dried in vacuum. The number average molecular weight of the PMeOSt was 4.1×10^4, as determined by osmotic pressure measurements of toluene solutions with a Hewlett-Packard high speed membrane osmometer, Type 502.

Measurements of Dielectric Constant, Density, and Refractive Index

The capacitances of the cell with benzene and cyclohexane were measured by using the capacitance bridge at a frequency of 10 kHz over the temperature range from 25 to 55°C. The dielectric constants ε relative to vacuum, i.e., not to air, were calculated by the relation,

$\varepsilon = C_s/(C_0/\varepsilon_{\text{air}})$, where C_s is the capacitance of the cell with the solvent, C_0 is the cell capacitance with air and ε_{air} is the dielectric constant of air ($\varepsilon_{\text{air}} = 1.0005364$ at 20°C[22]). The dielectric constants of the benzene solutions of PMeOSt were determined in a similar manner as above at a frequency of 10 kHz at 25 and 40°C. The concentrations of solutions were in the range of 1.9 to 5.5 weight percent. The densities of the benzene solutions of PMeOSt were determined with a flask type capillary pycnometer of 10 ml in volume at 25 and 40°C, from which the partial molar volumes of the polymer at each temperature were estimated. The refractive indices of the solutions were obtained at 546 nm wavelength using a Shimadzu differential refractometer at 25 and 40°C.

RESULTS AND DISCUSSION

Dielectric Constants of Benzene and Cyclohexane

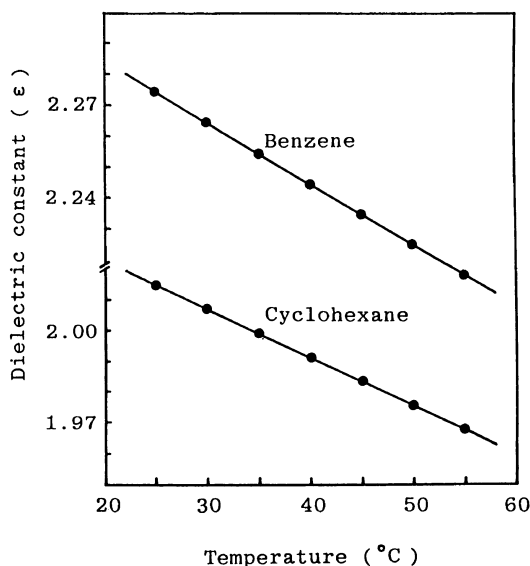The dielectric constants ε for benzene and cyclohexane are plotted against temperature in Figure 2. In the calculation of ε with the

Figure 2. Plots of dielectric constant ε vs. temperature for benzene and cyclohexane.

relation, $\varepsilon = \varepsilon_{air} \cdot C_s/C_0$, the values of ε_{air} and C_0 were assumed to be constant. These assumptions should be rather adequate, because the temperature dependence of ε_{air} should be negligibly small and the change in the C_0 value was actually found to be negligibly small over the temperature range from 25 to 55°C. As shown in Figure 2, linear relationships were obtained between ε and temperature t for benzene and cyclohexane. The relations obtained by the least-squares method are as follows,

$$\varepsilon = 2.2741_0 - 0.00197(t - 25)$$

for benzene ,

$$\varepsilon = 2.0147_7 - 0.00157(t - 25)$$

for cyclohexane .

In Table I, the observed values of ε at 25 and 30°C and the temperature coefficient $d\varepsilon/dt$ for both solvents are listed. In Table II, the values of ε and $d\varepsilon/dt$ reported for benzene and cyclohexane[20,23-25] are shown. Studies on accurate measurements of dielectric constant for or-

ganic solvents are rather few. Hartshown et al.[20] carried out dielectric measurements of organic solvents with an objective of providing values of higher accuracy than had been available. The measurements were performed on well purified, i.e., carefully dried and moisture free, solvents such as benzene, cyclohexane etc. by using the apparatus composed of a Schering bridge and a three-terminal cell at a frequency covering the range 50 Hz to 10 kHz at several temperatures between 20 and 30°C. The Office of Standard Reference Materials of the National Bureau of Standards (NBS) has recently reported the standard reference materials for use in the calibration of cells for determination of dielectric constants, in which cyclohexane is the standard with a small value of ε.[25] The dielectric constant of cyclohexane was measured by using a capacitance bridge (General Radio Co., Type 1615-A) with the three-terminal cell at a frequency of 0.75 to 12 kHz over the temperature range of 10 to 40°C. The maximum deviation of observed values from the mean in the measurements is listed as ± 0.00004. These results are shown in Table II.

Our results for the dielectric constants and temperature coefficients for benzene and cyclohexane agree well with those reported in the literature. The standard deviation calculated from the values obtained in three independent measurements of freshly purified benzene at 25°C was ± 0.00005. These facts suggest that the dielectric measurements in the present

Table I. Dielectric constants and temperature coefficients of benzene and cyclohexane

Solvent	ε		$-d\varepsilon/dt$
	25°C	30°C	
Benzene	2.2741_0	2.2642_5	0.00197
Cyclohexane	2.0147_7	2.0069_2	0.00157

Table II. Lists of dielectric constants and temperature coefficients of benzene and cyclohexane

Solvent	ε			$-d\varepsilon/dt$	Reference
	20°C	25°C	30°C		
Benzene	2.282_6	2.272_5	2.262_8	0.0019_8	23
	2.284	2.274	2.264	0.0020	24
	2.2836	2.2741	2.2646	0.00190	20
Cyclohexane	2.023	2.015	2.007	0.0016	24
	2.0250	2.0173	2.0095	0.00155	20
	2.02280	2.01517	2.00730	0.00154	25

study were carried out satisfactorily. The results also suggest that the dielectric constant of organic solvent with a small value of ε can be obtained without using any standard substance as the ratio of the capacitance of the cell filled with the sample solvent and that of the empty cell.

Dipole Moment of Poly(p-methoxystyrene)

The dielectric constant ε, density ρ, and refractive index n observed for the benzene solutions of PMeOSt at 25 and 40°C are
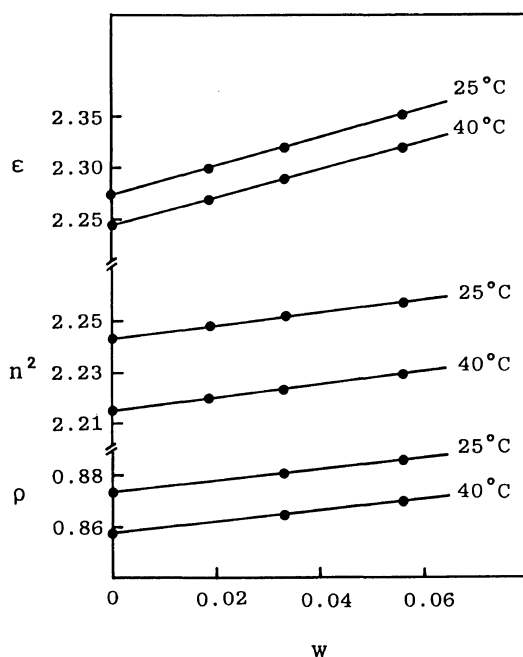

Figure 3. Plots of dielectric constant ε, refractive index squared n^2, and density ρ against weight fraction w for poly(p-methoxystyrene) in benzene at 25 and 40°C.

shown in Table III. Plots of ε, ρ, and n^2 against the weight fraction w gave linear relations as shown in Figure 3.

The dipole moment μ of a polar solute in a non-polar solvent is usually determined in two different procedures, both of which are based on Debye's theory for dielectric polarization.[18] According to the theory, the molecular polarization of a solute P_2 is given by:

$$P_2 = \frac{\varepsilon-1}{\varepsilon+2}\frac{M}{\rho} = \frac{4\pi N}{3}\left(\gamma + \frac{\mu^2}{3kT}\right) \quad (1)$$

$$P_2 = P_O + P_E + P_A$$

$$P_O = \frac{4\pi N}{9kT}\mu^2, \qquad P_E + P_A = \frac{4\pi N}{3}\gamma$$

where, ε and ρ are the dielectric constant and density, M is the molecular weight, γ is the polarizability, P_O, P_E, and P_A are the orientation, electronic, and atomic polarizations, respectively, k is the Boltzmann constant, N is the Avogadro's number and T is temperature.

For the determination of μ, the orientation polarization P_O must be known. One of the procedures is a conventional method, that is, the molecular polarization P_2 is determined by the dielectric constant and the density of the polymer solution and P_O is calculated by subtracting P_E and P_A from P_2.

The specific polarization of the solution of a polar solute in a non-polar solvent p_{12} is expressed by using the weight fraction w of the solute as follows,

$$p_{12} = \frac{\varepsilon_{12}-1}{\varepsilon_{12}+2}\frac{1}{\rho_{12}} = (1-w)p_1 + wp_2 \quad (2)$$

Table III. Dielectric constants, densities, and refractive indices of poly(p-methoxystyrene) in benzene solution at 25 and 40°C

w	25°C			40°C		
	ε	ρ	n	ε	ρ	n
0	2.2741	0.87368	1.4979	2.2446	0.85762	1.4883
0.018967	2.3012	—	1.4995	2.2702	—	1.4900
0.033330	2.3211	0.88102	1.5007	2.2893	0.86515	1.4912
0.056135	2.3539	0.88615	1.5025	2.3207	0.87052	1.4932

where

$$p_1 = \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \frac{1}{\rho_1} \quad \text{and} \quad p_2 = \frac{\varepsilon_2 - 1}{\varepsilon_2 + 2} \frac{1}{\rho_2}$$

in which suffixes 1, 2, and 12 refer to the solvent, solute and solution, respectively. The specific polarization of the solute p_2 is evaluated by using Halverstadt–Kumler equation[26] in place of the direct extrapolation by eq 2

$$p_2 = p_1 \left(1 + \frac{3\alpha}{(\varepsilon_1 - 1)(\varepsilon_1 + 2)} - \frac{\beta}{\rho_1} \right) \quad (3)$$

where α and β are the specific increments at infinite dilution as,

$$\alpha = \frac{d(\varepsilon_{12} - \varepsilon_1)}{dw} \quad (4)$$

and

$$\beta = \frac{d(\rho_{12} - \rho_1)}{dw} \quad (5)$$

The molecular polarization P_2 is obtained by the relation,

$$P_2 = p_2 \cdot M \quad (6)$$

The electronic polarization P_E is equal to the molecular refraction found for the light of infinite wavelength, so that P_E is a quantity possible to determine experimentally. There is no appropriate method to determine P_A. In general, P_A is small compared with P_E,[27] except for a molecule whose atoms or atom groups are easily displaced relative to each other in the presence of a field.[28] Therefore, P_A has been neglected or roughly estimated as 5—15% of the related P_E. One plausible assumption is that the molecular refraction for the D-line is taken as the sum of P_E and P_A,

$$P_E + P_A = \frac{n_D^2 - 1}{n_D^2 + 2} \frac{M}{\rho} = [MR]_D \quad (7)$$

where n_D is the refractive index of the solute for the D-line. $[MR]_D$ is a little larger than the molecular refraction for infinite wavelength.

The value of $[MR]_D$ is generally estimated as the sum of the appropriate atomic or bond refractions of the constituent atoms or bonds. By the use of the approximation, the dipole moment is expressed by:

$$\mu = \left\{ \frac{9kT}{4\pi N} (P_2 - [MR]_D) \right\}^{1/2}$$

$$= 0.01281 \sqrt{(P_2 - [MR]_D)T} \quad (8)$$

This procedure, hereafter, is refered to as the DHK method.

Another procedure is the one proposed by Guggenheim and Smith[19] in which the dipole moment is determined by measuring the dielectric constant and refractive index of the solutions. Debye's equation is written for a dilute solution of a polar solute in a non-polar solvent with mole fraction x as follows,

$$\frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} V_{12} = \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} V_1 (1 - x) + x P_2 \quad (9)$$

$$\frac{n_{12}^2 - 1}{n_{12}^2 + 2} V_{12} = \frac{n_1^2 - 1}{n_1^2 + 2} V_1 (1 - x) + x P_E \quad (10)$$

where, V_{12} is the mean molar volume calculated by the relation, $V_{12} = (1 - x)V_1 + xV_2$, V_1 and V_2 are the partial molar volumes of the solvent and solute, respectively. If the atomic polarization of the solute is assumed to be given by the fictitious atomic polarization,

$$P_A = \left(\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} - \frac{n_1^2 - 1}{n_1^2 + 2} \right) V_2 \quad (11)$$

the equation for the orientation polarization is derived as follows,

$$P_O = \frac{3M}{\rho_1} \left(\frac{\alpha}{(\varepsilon_1 + 2)^2} - \frac{v}{(n_1^2 + 2)^2} \right) \quad (12)$$

where, α is given by eq 4 and v is defined by:

$$v = \frac{d(n_{12}^2 - n_1^2)}{dw} \quad (13)$$

The dipole moment μ is expressed as:

$$\mu^2 = \frac{27kTM}{4\pi N \rho_1} \left(\frac{\alpha}{(\varepsilon_1 + 2)^2} - \frac{v}{(n_1^2 + 2)^2} \right) \quad (14)$$

This procedure is refered to as the G-S method.

The specific increments at infinite dilution α, β, and v were obtained from plots of ε, ρ, and n^2 against w, respectively, and the resulting lines were located by least-squares analysis (see Figure 3). The orientation polarization P_0 and dipole moment μ were estimated in the following manner. In the DHK method, the molecular polarization P_2 was calculated from eq 3 and 6 with α and β, and $[MR]_D$ was estimated from the bond refractions of the constituent bonds.[22] P_O was obtained as the difference between P_2 and $[MR]_D$. μ was determined by eq 8. In the G-S method, P_O and μ were calculated from eq 12 and 14, respectively, using the values of α and v. The average dipole moments per repeat unit for poly(p-methoxystyrene) in benzene were obtained as 1.214 (25°C), 1.221 (40°C) by the DHK method and 1.204 (25°C), 1.209 (40°C) by the G-S method (in debye unit). The results are summarized in Table IV.

The values of μ for PMeOSt in benzene previously reported in the literature are 1.21 (20°C),[6] 1.24 (50°C),[6] 1.25 (25°C),[13] and 1.17 (25°C)[16] (in debye unit). The results of the present study are very close to the values of 1.21 (20°C) and 1.24 (50°C) which were previously reported by one of the authors. The values of μ obtained in the present study are considered to be correct to ± 2 parts in 10^3, since the measurements of ε, ρ, and n can be done very accurately and errors in these values were less than ± 2 parts in 10^4, respectively.

The results show that the μ values of PMeO-St obtained by the two different methods were in fair agreement at the respective temperatures of 25 and 40°C and increased slightly with increase in temperature. Closer examination of the results indicated that μ obtained by the DHK method is about 1% larger than the one by the G-S method, which is more than the experimental error. We will now discuss the differences in μ values.

As mentioned before, in the DHK method, the sum of electronic and atomic polarization is assumed to be equal to the molecular refraction for the D-line and it is generally calculated as the summation of the appropriate atomic or bond refractions[22] of the constituent atoms or bonds. As the molecular refraction is an additive and constitutive property, the summation seems to be reasonable

Table IV. Results for dipole moments of poly(p-methoxystyrene) in benzene at 25 and 40°C

Temp °C	α	β	v	DHK method		G-S method	
				P_O/ml	μ (debye)	P_O/ml	μ (debye)
25	1.4204	0.22202	0.24288	30.116	1.213_9	29.610	1.204_0
40	1.3542	0.22952	0.25928	29.020	1.221_2	28.430	1.209_1

Table V. Electronic, Atomic, and molecular polarizations of poly(p-methoxystyrene) in benzene

Temp °C	DHK method		G-S method		
	$[MR]_D$/ml	P_2/ml	P_E/ml*	P_A/ml*	P_2/ml*
25	39.856	69.972	39.998	0.488	69.951
40	39.856	68.876	39.951	0.475	68.681

* The partial molar volumes of poly(p-methoxystyrene) in benzene used to calculate the polarizations with an asterisk were calculated from the density of the polymer solution as $V_2 = 115.13$ ml at 25°C and 115.10 ml at 40°C.

but the $[MR]_D$ value is altered slightly depending on whether it is calculated from the atomic refraction or bond refraction. This means that in the DHK method, it is unavoidable to bring some uncertainty into a final dipole moment. The molecular refraction for the structural unit of PMeOSt is calculated as 39.604 ml from the atomic refraction and 39.856 ml from the bond refraction. This small difference brings a difference of 0.005 debye into the μ value. μ in Table IV were calculated with $[MR]_D$ value obtained from the bond refraction. In the G-S method, P_E is the molecular refraction of a solute as similar as in the DHK method, but it was estimated from eq 10 by using the experimental data of the refractive index and the partial molar volume. P_A was obtained from eq 11 with ε and n for the solvent and the partial molar volume of the solute. These values are listed in Table V, as well as the values of P_2 obtained by the DHK and the G-S methods.

P_E values obtained from eq 10 are very close to the $[MR]_D$ value calculated from the bond refractions. This agreement is rather reasonable, since the refractive index measurements for the estimation of P_E were made at the finite wavelength of 546 nm, which is almost the same for the D-line. The G-S method is usually thought to be a fairly good approximation if the solvent used in the measurements has a small value of $(\varepsilon - n^2)$ such as benzene. $(\varepsilon - n^2)$ for benzene are 0.0304 at 25°C and 0.0296 at 40°C. The P_A value assumed by eq 11 is a quantity proportional to $(\varepsilon - n^2)$ and is 0.488 ml (25°C) and 0.477 ml (40°C) for PMeOSt in benzene, which correspond to ca. 0.01 debye unit in μ. It is evident that the slight disagreement between the μ values obtained by the two different procedures resulted from the different approaches to estimate P_E and P_A. The exact value of P_E is able to be estimated from eq 10 by using the refractive index at infinite wavelength instead of the widely used method of obtaining it with the refractive index at a finite wavelength, while the estimation of P_A is not exact but based on a fictitious assumption in both the DHK and the G-S methods. Therefore, it is unavoidable that the uncertainty arising from the fictitious assumptions of P_A is brought into the final value of μ, even if the exact value of P_E is obtained.

Fortunately, P_A for many substances is not large compared to the related P_E, so both procedures can give appropriate results in the study on comparison of dipole moments of series of molecules in a given solvent or in the study on temperature dependence in a given solvent. Nevertheless, in the study on solvent effect of μ, it should be noted that P_A assumed in the G-S method is a solvent dependent quantity.

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