Monatshefte für Chemie 136, 1171–1182 (2005)
DOI 10.1007/s00706-005-0323-x

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Apparent Specific Polarization and Dipole Moment of Some Poly(oxyethylene) Glycols in 1,4-Dioxane and Benzene Solutions at 298.15 K

Darja Rudan-Tasic and **Cveto Klofutar***

Biotechnical Faculty, University of Ljubljana, SI-1000 Ljubljana, Slovenia

Received July 6, 2004; accepted (revised) December 12, 2004
Published online June 13, 2005 © Springer-Verlag 2005

Summary. The electrical permittivity of 1,4-dioxane and benzene solutions of some poly(oxyethylene) glycols up to the average molecular weight of 1590 were measured at 298.15 K. From the experimental data the limiting apparent specific polarization and partial molar polarization were calculated. The electrical dipole moment of the investigated solutes was estimated according to the *Debye*, *Onsager*, and *Kirkwood* theoretical approaches. The calculated dipole moments increase linearly with the square root of the number of monomeric units. The group dipole moment of the polar monomeric unit was calculated from the corresponding limiting partial molar volume, the refraction and polarization of the solute. The factor g, which takes into account the degree of flexibility of the chain, was estimated and found to be greater than 0.92, which means that the lower members of the poly(oxyethylene) glycols possess almost free rotation within the chain backbone of polymer.

Keywords. Apparent specific polarization; Dipole moment; Poly(oxyethylene) glycols; 1,4-Dioxane solutions; Benzene solutions.

Introduction

Poly(oxyethylene) glycols of the general formula $HO–(CH_2–CH_2–O)_n–H$ are highly soluble in water and organic solvents over a large range of molecular weights and concentrations [1, 2]. These compounds are characterized by a very hydrophilic or water-soluble nature and have a relatively large electric permittivity. The hydrophilic property arises from the two end hydroxyl groups and the oxyethylene monomeric groups. Poly(oxyethylene) glycol molecules have a large degree of molecular freedom to rotation as a result of the considerable degree of rotational freedom about single bonds [3]. So, all these chain molecules are able to assume an enormous number of configurational arrays. Each configuration is characterized by

---

* Corresponding author. E-mail: darja.rudan.tasic@bf.uni-lj.si

a dipole moment equal to the vectorial sum of the moments of its *n* monomers. For such systems it was shown that the statistical mean dipole moment of the molecule as well as its mean displacement should be proportional to the square root of the degree of polymerisation. On the other hand, hindrance to free rotation tends to decrease the mean statistical dipole moment and to increase the mean statistical displacement. The dipole moment possesses some advantages over other more traditionally conformation-dependent properties such as the mean-square end-to-end distance. Thus, some of the skeletal bonds change much more in polarity than they do in length and consequently the dipole moment is more sensitive to structure than end-to-end distance [4].

Experimental studies of electric permittivity of non-aqueous solutions of low molecular poly(oxyethylene) glycols are scarce [5]. To obtain more information about the nature of 1,4-dioxane and benzene solutions of some lower members of the poly(oxyethylene) glycols an electric permittivity study was made. In the literature there are only some values for poly(oxyethylene) glycols in benzene solution [6–11] and for some lower members (up to the heptamer) in 1,4-dioxane solution [11, 12]. For these reasons we determined the dipole moments of some low molecular poly(oxyethylene) glycols (up to $n = 36$) in 1,4-dioxane and benzene solutions. Owing to strong polarization effects which arise from the very large dipole moments of the polymers, the *Debye* equation may not be valid even for dilute solutions in non-polar solvents [13–15]. Hence, we used the *Onsager* and *Kirkwood* methods to obtain more reliable values of the electric dipole moments of the investigated compounds. To compare the dipole moments obtained by the adopted procedure [11] with those given in the literature [6–12], we also calculated the *Debye* dipole moments.

Results and Discussion

The electrical permittivity of the investigated solutions is presented in Table 1 (1,4-dioxane solutions) and Table 2 (benzene solutions). The apparent specific polarization of solute, p_{app} is defined as shown by Eq. (1) [16] where p is the specific polarization of solution, p_1^0 is the specific polarization of pure solvent, and w is the mass ratio, *i.e.*, grams of solute per gram of solvent.

$$p_{app} = \frac{p - p_1^0}{w} \tag{1}$$

The dependence of p_{app} on mass ratio at a definite temperature and for a non-electrolyte solution can be conventionally given by Eq. (2) where p_{app}^0 represents the specific apparent polarization of the solute at infinite dilution, equal to the limiting partial specific polarization of solute, $\overline{p}_2^0$, and b_p, $b_{pp}, \ldots$ are constants which depend on the solute, solvent, and temperature.

$$p_{app} = p_{app}^0 + b_p w + b_{pp} w^2 + \cdots \tag{2}$$

By combining Eqs. (1) and (2), the following relation can be obtained (Eq. (3)) from which the value of p_{app}^0 and parameters b_p, $b_{pp}, \ldots$ can be calculated by least squares fitting to Eq. (3).

$$p = p_1^0 + p_{app}^0 w + b_p w^2 + b_{pp} w^3 + \cdots \tag{3}$$

Table 1. Electrical permittivity, ε, of 1,4-dioxane solutions of some poly(oxyethylene) glycols at 298.15 K

PEG-200		*PEG*-300		*PEG*-400		*PEG*-600	
w	ε	w	ε	w	ε	w	ε
0.002424	2.235	0.002640	2.229	0.002088	2.232	0.002449	2.235
0.014332	2.311	0.015720	2.311	0.013776	2.279	0.014540	2.283
0.028637	2.400	0.025907	2.354	0.024561	2.332	0.029199	2.337
0.039541	2.468	0.039675	2.428	0.038613	2.399	0.040626	2.395
0.053671	2.559	0.052934	2.498	0.052840	2.467	0.050622	2.437
0.066013	2.646	0.066389	2.570	0.065643	2.526	0.068172	2.524
0.080553	2.751	0.080338	2.648	0.079276	2.589	0.080308	2.572
0.096785	2.844	0.094449	2.718	0.094536	2.664	0.091873	2.612
0.1007892	2.913	0.109450	2.799	0.108516	2.735	0.108340	2.698

PEG-900		*PEG*-1000		*PEG*-1500	
w	ε	w	ε	w	ε
0.001865	2.243	0.002087	2.225	0.002597	2.221
0.011139	2.264	0.014922	2.274	0.013918	2.273
0.025976	2.342	0.026828	2.315	0.025702	2.312
0.039914	2.396	0.038981	2.368	0.038398	2.356
0.051804	2.441	0.053881	2.421	0.051505	2.403
0.067406	2.507	0.065222	2.467	0.063503	2.446
0.077378	2.559	0.074825	2.508	0.080154	2.504
0.091671	2.631	0.093278	2.578	0.091930	2.545
0.107550	2.706	0.107153	2.621	0.106157	2.595

The polarization of solution and consequently the apparent specific polarization of solute depends on the theoretical model used [17]. The *Debye* model, applied to homogeneous fluid mixtures, gives the following expression for the specific polarization of solution (Eq. (4)) where v is the specific volume of the solution.

$$p = \frac{(\varepsilon - 1)}{(\varepsilon + 2)} v \tag{4}$$

An analogous relation is valid for the specific polarization of pure solvent. This theory is quite successful for dilute solutions in non-polar solvents. The *Onsager* model, which can be used for solutions in polar solvents, and which takes into account a reaction field, yields for the specific polarization of solution p^* (Eq. (5)) and an analogous relation for the specific polarization of pure solvent.

$$p^* = \frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} v \tag{5}$$

The *Onsager* theory becomes inaccurate for solutions in which there is molecular complexing between solute and solvent. For such systems *Kirkwood* derived a general theory which allows for the coupling of dipoles due to molecular complexing. His expression for the polarization of solution, $p^\dagger$, is formally identical to *Onsager*'s equation, *i.e.* $p^* \equiv p^\dagger$ [17].

Table 2. Electrical permittivity, ε, of benzene solutions of some poly(oxyethylene) glycols at 298.15 K

PEG-200		*PEG*-300		*PEG*-400		*PEG*-600	
w	ε	w	ε	w	ε	w	ε
0.007883	2.325	0.012410	2.335	0.012149	2.326	0.010161	2.315
0.010341	2.344	0.022223	2.389	0.024300	2.381	0.020982	2.366
0.022559	2.430	0.047904	2.520	0.047047	2.488	0.046128	2.468
0.047502	2.588	0.070288	2.633	0.069080	2.585	0.067905	2.561
0.066163	2.714	0.099212	2.777	0.100385	2.750	0.095898	2.675
0.099252	2.924	0.122733	2.890	0.122535	2.813	0.117152	2.761
0.123049	3.087	0.153505	3.040	0.152109	2.936	0.158451	2.938
0.154533	3.291	0.181610	3.178	0.180981	3.056	0.176206	3.008
				0.216557	3.195	0.215293	3.161

PEG-900		*PEG*-1000		*PEG*-1500	
w	ε	w	ε	w	ε
0.020276	2.351	0.021397	2.350	0.023122	2.341
0.046046	2.446	0.047128	2.443	0.047236	2.430
0.071575	2.542	0.074337	2.538	0.071877	2.486
0.099318	2.644	0.099158	2.622	0.097625	2.568
0.122581	2.736	0.127093	2.728	0.123467	2.638
0.150983	2.832	0.156347	2.822	0.148385	2.715
0.178503	2.935	0.178325	2.896	0.177868	2.788
0.216423	3.079	0.212378	2.996	0.203079	2.854
0.238248	3.159	0.282304	3.225	0.238517	2.967

From the electric permittivity data, collected in Tables 1 and 2, and the density data [18], the apparent specific polarization of solute was calculated. The specific volume of solution was obtained from $v = (1 + w)/d$, where d is the density of the solution. For the *Debye* model (Eq. (4)) the simple linear form of Eq. (3) was used, whereas for the *Onsager* model (Eq. (5)) the data were treated by a quadratic form of Eq. (3) for 1,4-dioxane solutions and for some lower members of the poly(oxyethylene) glycols in benzene solutions. The values of p_1^0 obtained by the least squares treatment of the data *via* Eq. (3) do not differ by more than 0.2% for 1,4-dioxane solutions and 0.6% for benzene solutions from the corresponding values for pure 1,4-dioxane or benzene [19]. The values of p_{app}^0 are given in Table 3 together with some lower members of poly(oxyethylene) glycols, *i.e.* mono- (*MEG*), di- (*DEG*), tri- (*TEG*), and tetra- (*TTEG*) (oxyethylene) glycol determined earlier [11].

Irrespective of the model or solvent used, the p_{app}^0 values gradually decrease with increasing molecular weight of the poly(oxyethylene) glycol. It was shown previously that the limiting apparent specific values of a macromolecular solute, such as specific volume, specific refraction, and specific index of refraction increment [18], are proportional to the reciprocal value of the number average molecular weight, M_n, of a low molecular weight polymer solute. As an example in Fig. 1 this dependence is shown for the limiting apparent specific polarization of solute in 1,4-dioxane solutions treated by the *Debye* model. For such a dependence Eq. (6) is

Table 3. The mean number of oxyethylene units, *n*, and limiting apparent specific polarization of some poly(oxyethylene) glycols in 1,4-dioxane and benzene solution at 298.15 K

Solute	*n*	1,4-Dioxane		Benzene	
		Debye $p_{app}^{0}/\mathrm{cm}^3 \cdot \mathrm{g}^{-1}$	*Onsager* $p_{app}^{0*}/\mathrm{cm}^3 \cdot \mathrm{g}^{-1}$	*Debye* $p_{app}^{0}/\mathrm{cm}^3 \cdot \mathrm{g}^{-1}$	*Onsager* $p_{app}^{0*}/\mathrm{cm}^3 \cdot \mathrm{g}^{-1}$
MEG	1	1.883 ± 0.013[a]	2.491 ± 0.093[a]	–	–
DEG	2	1.545 ± 0.011[a]	2.261 ± 0.062[a]	1.552 ± 0.018[a]	2.314 ± 0.036[a]
TEG	3	1.324 ± 0.007[a]	1.910 ± 0.035[a]	1.388 ± 0.013[a]	1.937 ± 0.097[a]
TTEG	4	1.295 ± 0.007[a]	1.896 ± 0.020[a]	1.412 ± 0.013[a]	2.052 ± 0.065[a]
PEG-200	4.34	1.259 ± 0.009	1.826 ± 0.057	1.380 ± 0.012	1.955 ± 0.094
PEG-300	6.76	1.096 ± 0.007	1.526 ± 0.060	1.139 ± 0.009	1.752 ± 0.015
PEG-400	8.40	1.017 ± 0.004	1.367 ± 0.020	1.030 ± 0.015	1.660 ± 0.014
PEG-600	12.12	0.968 ± 0.010	1.273 ± 0.060	1.009 ± 0.005	1.614 ± 0.013
PEG-900	20.2	0.877 ± 0.040	1.154 ± 0.060	0.941 ± 0.003	1.508 ± 0.016
PEG-1000	22.8	0.886 ± 0.006	1.236 ± 0.035	0.889 ± 0.007	1.420 ± 0.011
PEG-1500	36.1	0.844 ± 0.005	1.177 ± 0.029	0.801 ± 0.005	1.234 ± 0.014

[a] Calculated from data given in Ref. [11]

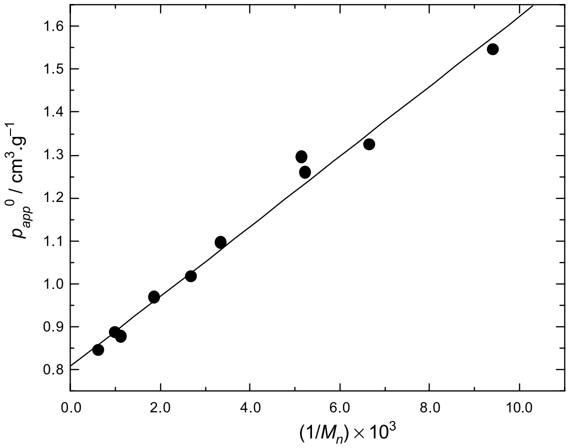

Fig. 1. Dependence of the limiting apparent specific polarization of solute on the reciprocal value of the number average molecular weight for some poly(oxyethylene) glycols in 1,4-dioxane solutions at 298.15 K; *Debye* method

valid except for the first member of the homologous series, *i.e.* for mono(oxyethylene) glycol. In Eq. (6) $p_{app(\infty)}^{0}$ is the limiting apparent specific polarization of solute whose number average molecular weight is infinity and L is a constant which depends primarily on the nature of the chain ends. In calculation of both constants of Eq. (6) for the *Debye* as well as for the *Onsager* model, the number average molecular weights were taken from Ref. [20]. The values of the respective constants are given in Table 4.

$$p_{app}^{0} = p_{app(\infty)}^{0} + \frac{L}{M_n} \tag{6}$$

Table 4. Values of constants $p^0_{app(\infty)}$ and L of Eq. (6) and limiting partial molar polarization of repeating unit, $\overline{P}^0_{mon}$, in 1,4-dioxane and benzene solution for the *Debye* and *Onsager* model at 298.15 K

Solvent	*Debye*		*Onsager*	
	$p^0_{app(\infty)}/\mathrm{cm}^3\cdot\mathrm{g}^{-1}$	$L/\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$	$p^{0*}_{app(\infty)}/\mathrm{cm}^3\cdot\mathrm{g}^{-1}$	$L/\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$
1,4-Dioxane	0.848 ± 0.024	81.3 ± 3.7	1.071 ± 0.039	132.4 ± 8.4
Benzene	0.830 ± 0.041	87.2 ± 8.9	1.343 ± 0.055	108.0 ± 12.0
Solvent	$\overline{P}^0_{mon}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$			
	Debye (Eq. (6))	*Debye* (Eq. (7))	*Onsager* (Eq. (6))	*Onsager* (Eq. (7))
1,4-Dioxane	37.4 ± 1.1	36.4 ± 2.6	47.2 ± 1.7	47.8 ± 2.8
Benzene	36.6 ± 1.8	35.4 ± 2.8	59.2 ± 2.4	57.8 ± 2.7

From the data collected in Table 4 it can be seen that both constants, *i.e.* $p^0_{app(\infty)}$ and L, are equal within experimental error for the *Debye* model and for the solvents used. On the other hand, the values of the constants obtained from the *Onsager* model are different and $p^{0*}_{app(\infty)}$ is greater for benzene solutions than for 1,4-dioxane solutions. Higher partial molar polarization of some lower members of the poly(oxyethylene) glycols (up to tetra(oxyethylene) glycol) in benzene solutions was also observed earlier [11]. From the $p^0_{app(\infty)}$ values given in Table 4, the limiting partial molar polarization of the repeating unit, $\overline{P}^0_{mon} = M_0 p^0_{app(\infty)}$, can be calculated where M_0 is the molecular weight of the monomeric unit. The values obtained are given in Table 4.

The limiting partial molar polarization of solutes, $\overline{P}^0_2$ were calculated from p^0_{app} and for the adopted model using the known average molecular weights [20]. It follows from Eq. (6) that the values of $\overline{P}^0_2$ for the investigated systems depend linearly on the number of monomeric units, n, as given by Eq. (7) (see Fig. 2) where $a_0 \equiv L$ and $a_1 \equiv M_0 p^0_{app(\infty)}$. Values of the $\overline{P}^0_{mon}$ for both solvents and

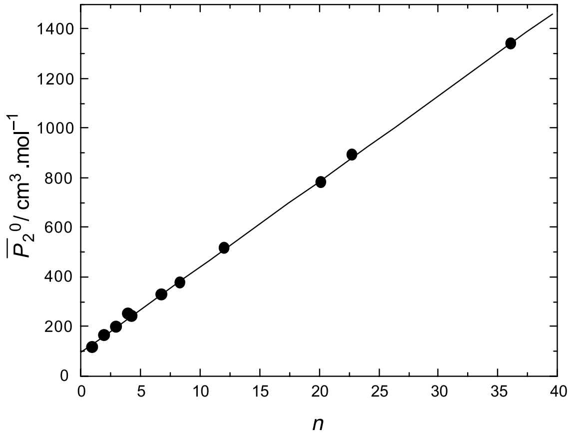

Fig. 2. Dependence of limiting partial molar polarization of some poly(oxyethylene) glycols in 1,4-dioxane solutions on the average degree of polymerisation at 298.15 K; *Debye* method

the adopted models, calculated by the weighted least square procedure using Eq. (7) are given in Table 4. The $\overline{P}^0_{mon}$ values for the *Debye* model and both solvents used are, within experimental error, equal and close to the values obtained by Eq. (6). For further calculation we used their weighted average value which amounts to (36.9 ± 0.3) $\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$. The average value of $\overline{P}^0_{mon}$ obtained from Eqs. (6) and (7) which we used for calculation of the dipole moment of the monomeric unit for the *Onsager* and *Kirkwood* model, are $47.5 \pm 3.3\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ in 1,4-dioxane and $58.5 \pm 3.6\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ in benzene solution.

$$\overline{P}^0_2 = a_0 + a_1 n \tag{7}$$

According to the *Debye* model, the partial molar polarization of solute at infinite dilution is given by Eq. (8) [17] where μ_2 is the permanent molecular electric dipole moment, k is *Boltzmann*'s constant, N_A is *Avogadro*'s number, α_e is the electronic polarizability of solute, and T is the absolute temperature. When calculating μ_2 *via* Eq. (8) the electronic polarizability of solute was multiplied by a factor of 1.05 to allow for atomic polarization [13]. The electronic polarizability was calculated from the limiting partial molar refraction of solute, $\overline{R}^0_2$, given in Ref. [18] as $\alpha_e = 3\overline{R}^0_2/(4\pi N_A)$. The values of μ_2 obtained are given in Table 5 together with those for some lower members of poly(oxyethylene) glycols calculated earlier [11] from the data given in Ref. [12].

$$\overline{P}^0_2 = \frac{4\pi N_A}{3}\left(\alpha_e + \frac{\mu_2^2}{3kT}\right) \tag{8}$$

Table 5. Dipole moments of some poly(oxyethylene) glycols and monomeric oxyethylene units, *OE*, determined in 1,4-dioxane and benzene solution at 298.15 K

Solute	1,4-Dioxane			Benzene		
	μ_2/D	μ_2^*/D	$g^{1/2}\mu_2^\dagger$/D	μ_2/D	μ_2^*/D	$g^{1/2}\mu_2^\dagger$/D
MEG	2.23 ± 0.01[a]	2.59 ± 0.05[a]	2.61 ± 0.05[a]	–	–	–
DEG	2.59 ± 0.01[a]	3.20 ± 0.05[a]	3.23 ± 0.04[a]	2.60 ± 0.02[a]	3.25 ± 0.02[a]	3.29 ± 0.02[a]
TEG	2.81 ± 0.01[a]	3.45 ± 0.04[a]	3.49 ± 0.04[a]	2.89 ± 0.02[a]	3.48 ± 0.10[a]	3.53 ± 0.10[a]
TTEG	3.14 ± 0.01[a]	3.90 ± 0.02[a]	3.95 ± 0.02[a]	3.32 ± 0.02[a]	4.09 ± 0.08[a]	4.13 ± 0.08[a]
PTEG	3.36 ± 0.05[a]	4.13 ± 0.03[a]	4.18 ± 0.03[a]	–	–	–
HXEG	3.39 ± 0.01[a]	4.19 ± 0.01[a]	4.25 ± 0.01[a]	–	–	–
HPEG	3.58 ± 0.01[a]	4.43 ± 0.01[a]	4.50 ± 0.01[a]	–	–	–
PEG-200	3.06 ± 0.01	3.79 ± 0.07	3.83 ± 0.07	3.24 ± 0.02	3.94 ± 0.11	3.99 ± 0.11
PEG-300	3.50 ± 0.02	4.24 ± 0.10	4.30 ± 0.10	3.59 ± 0.02	4.61 ± 0.03	4.67 ± 0.03
PEG-400	3.70 ± 0.02	4.40 ± 0.04	4.48 ± 0.04	3.73 ± 0.04	4.96 ± 0.03	5.03 ± 0.03
PEG-600	4.30 ± 0.03	5.15 ± 0.15	5.15 ± 0.15	4.44 ± 0.03	5.87 ± 0.04	5.96 ± 0.04
PEG-900	5.19 ± 0.17	6.11 ± 0.26	6.25 ± 0.26	5.47 ± 0.14	7.27 ± 0.17	7.39 ± 0.17
PEG-1000	5.54 ± 0.06	6.78 ± 0.14	6.92 ± 0.14	5.58 ± 0.06	7.43 ± 0.08	7.56 ± 0.07
PEG-1500	6.73 ± 0.19	8.25 ± 0.26	8.44 ± 0.25	6.53 ± 0.19	8.51 ± 0.23	8.70 ± 0.22
OE	1.13 ± 0.05	1.315 ± 0.004	1.341 ± 0.004	1.13 ± 0.05	1.51 ± 0.08	1.529 ± 0.08

[a] Given in Ref. [11]

Onsager's model leads to the partial polarization of solute at infinite dilution by Eq. (9) [17] where α_e^* is the effective polarizability of solute and μ_2^* the *Onsager*'s dipole moment.

$$\overline{P}_2^{0*} = \frac{4\pi N_A}{3}\left(\alpha_e^* + \frac{(\mu_2^*)^2}{3kT}\right) \tag{9}$$

Onsager's relationship between α_e^* and α_e (or between μ_2^0 and μ_2^*) is given by Eq. (10) [17] where $\overline{V}_2$ is the partial molar volume and μ_2^0 the dipole moment of solute in the gas phase.

$$\frac{\mu_2^0}{\mu_2^*} = \frac{\alpha_e}{\alpha_e^*} = 1 - \frac{4\pi N_A \alpha_e (2\varepsilon - 2)}{3\overline{V}_2(2\varepsilon + 1)} \tag{10}$$

Since the ratio α_e/α_e^* depends on the mass ratio of solute, we used its limiting value. So, when calculating α_e^* we used $\overline{V}_2^0$ [18] and the electric permittivity of pure solvent. The *Onsager*'s electric dipole moments μ_2^* are given in Table 5.

The partial molar polarization of solute at infinite dilution on the basis of *Kirkwood*'s theory is expressed by Eq. (11) [17] in which $\mu_2^\dagger$ is *Kirkwood*'s molecular dipole moment in solution, including any enhancement due to the reaction field, and g_2 is a correlation factor whose deviation from unity allows for coupling between the orientation of the given dipole and the surrounding dipoles. Generally, g_2 will deviate substantially from unity if such coupling is quite strong [21]; ordinary dipole–dipole coupling alone is not strong enough. Beyond that, g_2 is also a function of composition. However, in dilute solutions it is sufficient to assume that g_2 for the solute is constant [22]. From Eq. (11) it follows that the value of g_2 is characteristic of the molecular species. The calculated products $g^{1/2}\mu_2^\dagger$ are listed in Table 5.

$$\overline{P}_2^{0\dagger} = \frac{4\pi N_A}{3}\left(\alpha_e + \frac{g_2(\mu_2^\dagger)^2}{3kT}\right) \tag{11}$$

Because *Kirkwood*'s theory is exact and *Onsager*'s theory is approximate, the dipole moment μ_2^* calculated by *Onsager*'s method (Eq. (9)) is always at least somewhat approximate. μ_2^* is related to the exact value $\mu_2^\dagger$, given by *Kirkwood*'s theory, by Eq. (12) [22] in which V_1^0 denotes the molar volume, $\mu_1^\dagger$ the molecular dipole moment, g_1 *Kirkwood*'s correlation factor of the solvent, and c_2 is the concentration of solute in moles per cubic centimetre.

$$(\mu_2^*)^2 = g_2(\mu_2^\dagger)^2 + \frac{dg_1}{dc_2}\frac{(\mu_1^\dagger)^2}{V_1^0} \tag{12}$$

For non-polar solvents, such as 1,4-dioxane or benzene it follows from Eq. (12) that $(\mu_2^*)^2 = g_2(\mu_2^\dagger)^2$.

From Table 5 it can be seen that the dipole moments for a particular compound calculated on the basis of the *Debye* model for both solvents are smaller than those obtained by the *Onsager* or *Kirkwood* models. Irrespective of the model used, the dipole moment gradually increases with increasing average molecular weight of solute. It was observed earlier for the lower members of the poly(oxyethylene) glycols that *Onsager*'s dipole moments are within the experimental error equal to the *Kirkwood* products, $g^{1/2}\mu_2^{\dagger}$ which is in accordance with Eq. (12) [11]. The same can also be observed for the higher poly(oxyethylene) glycols from *PEG*-200 up to *PEG*-1500. Furthermore, the dipole moments determined on the *Debye* model do not show any appreciable solvent effect and are within experimental error equal in both solvents except for *PEG*-200 and *PEG*-300. As was stated earlier, the dipole moments of the polymers, determined by the *Debye* equation, may not be valid even for dilute polymer solutions in non-polar solvents [13–15]. In contrast, the dipole moments determined by the *Onsager* method are higher in benzene than in 1,4-dioxane solution, as was observed earlier [7, 11]. This proves that there is some interaction between the solvent and the polymer molecule. This interaction is a result of the influence of the solvent on the statistical dipole moment of the macromolecule which can be modified by a change in the configuration of the polymer molecule and due to the interactions between separated solute molecules and surrounding solvent molecules. In the case of 1,4-dioxane which is a non-polar compound, due to internal compensation of the strongly polar C–O groups, these groups must have considerable short-range interactions with the polar oxyethylene groups of the polymer as well as with the end –OH groups. On the other hand, in benzene, the π-electronic system of the aromatic benzene molecule may change the configuration of the polymer molecule influencing its statistical dipole moment. Furthermore, the dipole moment of a polar solute molecule at infinite dilution has associated with it a field which may be expected to induce dipoles in the surrounding solvent molecules. The electronic polarizability of the benzene molecule ($\alpha_e = 1.04\times10^{-23}\,\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$) is remarkably greater than in a 1,4-dioxane molecule ($\alpha_e = 0.86\times10^{-23}\,\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$) and so the solvent molecules can induce a moment on the solute molecule which is greater in benzene than in 1,4-dioxane solution [14].

Contrary to small molecules which adopt a reasonably well-defined geometric configuration, *e.g. MEG*, *i.e.*, 1,2-ethanediol [23], for the higher oligomers with mobile configurations, the measured dipole moment is the statistical average of the vector sums of dipoles located along the chain. It was found for such systems that the dipole moment is proportional to the square root of the number of polar groups in the polymer [15]. For the investigated poly(oxyethylene) glycols we found that the dipole moments, irrespective of the model or solvent used, depend linearly on the square root of the degree of polymerisation, as shown in Fig. 3. It is also clear from Table 5 that the dipole moments of poly(oxyethylene) glycols increase progressively with the molecular weight. This fact invalidates a configuration which is trans throughout, since for such forms the observed dipole moments should be zero or constant, depending on whether the number of repeating units is even or odd [7].

The dipole moment of a polymer is usually expressed by Eq. (13) [15] where μ_{mon} is the group dipole moment of the polar monomeric unit.

$$(\mu_2)^2 = gn(\mu_{mon})^2 \tag{13}$$

Thus, the mean-square dipole moment, $n(\mu_{mon})^2$, is the sum of the squares of the bond dipole moments for all bonds of the chain assuming that the skeletal bonds are freely jointed; g is a factor depending on the degree of flexibility of the chain and on the nature of the monomeric unit. In the polymer g is also a function of the energy barrier restricting rotation within the chain backbone. Experimental

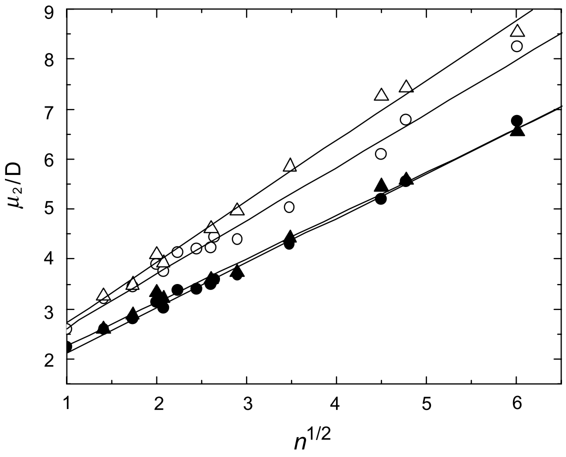

Fig. 3. Dependence of dipole moment of some poly(oxyethylene) glycols determined in 1,4-dioxane and benzene solutions on the square root of the mean number of oxyethylene units at 298.15 K; ● – *Debye* method, ○ – *Onsager* method (1,4-dioxane); ▲ – *Debye* method, △ – *Onsager* method (benzene)

determination of the g factor involves a knowledge of the dipole moment of the monomer unit. In the past it was supposed that the dipole moment of the monomeric unit, *i.e.*, oxyethylene group, is associated with the C–O ether bond. Thus *Marchal* and *Benoit* [10] for explanation of their experimental results for benzene solutions of some poly(oxyethylene) glycols at 293.15 K for the dipole moment of ether used a value of 1.22 D and for alcohol a value of 1.67 D, *Uchida et al.* [12] used a value of $\mu_{mon} = 1.20$ D for the C–O bond, *Svirbely* and *Lander* [24] calculated an average dipole moment of 0.117 D for the oxyethylenic unit on the basis of Eq. (13), assuming that $g = 1$ for a benzene solution of poly(oxyethylene) glycol at 317.15 K with a nominal molecular weight of 4000. Recently we calculated the group dipole moment of the monomeric oxyethylene unit which amounts to 1.5 D [11]. One can also calculate the dipole moment of the polar repeating unit, *OE*, from the partial molar volume and partial molar refraction [18], and partial molar polarization of the monomeric unit. The calculated value of μ_{mon} is given at the end of Table 5. From Table 5 can be seen that the dipole moment of the monomeric unit, determined on the basis of the *Debye* model, is within experimental error equal for both solvents and amounts to (1.13 ± 0.05) D. The corresponding dipole moment of the monomeric unit calculated on the basis of the *Onsager* or *Kirkwood* models shows a solvent effect; it is larger in benzene than in 1,4-dioxane. In further calculations of the factor g we used these data. The mean dipole moment of the polar repeating units varies from 0 *Debye* units for a hydrocarbon polymer to about 1 *Debye* unit for polyamides. These values are in general low compared with the dipole moments of the corresponding polar groups in liquid mixtures [25].

From Table 6 follows that μ_2^2/n rapidly decreases in both solvents and approaches a limiting value which is 1.13 for benzene solution [10]. Like the ratio of μ_2^2/n, the g factor depends on the molecular weight of the solute and rapidly decrease with increasing degree of polymerisation. The deviation of the experimentally determined g factor from that predicted for free rotation gives us a measure of the

Table 6. Ratio of μ_2^2/n and factor g for some poly(oxyethylene) glycols in 1,4-dioxane and benzene solutions at 298.15 K

Solute	1,4-Dioxane				Benzene			
	Debye		*Onsager*		*Debye*		*Onsager*	
	$\mu_2^2/n/\mathrm{D}^2$	g	$\mu_2^{*2}/n/\mathrm{D}^2$	g	$\mu_2^2/n/\mathrm{D}^2$	g	$\mu_2^{*2}/n/\mathrm{D}^2$	g
MEG	4.97	4.40	6.71	3.99	–	–	–	–
DEG	3.35	2.96	5.12	3.05	3.38	3.17	5.28	2.77
TEG	2.63	2.33	3.97	2.36	2.78	2.61	4.04	2.12
TTEG	2.46	2.18	3.80	2.26	2.76	2.59	4.18	2.19
PTEG	2.26	2.00	3.41	2.03	–	–	–	–
HXEG	1.92	1.70	2.93	1.74	–	–	–	–
HPEG	1.83	1.62	2.80	1.67	–	–	–	–
PEG-200	2.16	1.70	3.31	1.92	2.42	1.90	3.58	1.58
PEG-300	1.81	1.42	2.66	1.54	1.91	1.49	3.14	1.39
PEG-400	1.63	1.28	2.31	1.33	1.66	1.30	2.93	1.29
PEG-600	1.53	1.19	2.19	1.27	1.63	1.27	2.84	1.25
PEG-900	1.33	1.04	1.85	1.07	1.48	1.16	2.62	1.15
PEG-1000	1.35	1.05	2.02	1.17	1.36	1.07	2.42	1.07
PEG-1500	1.25	0.98	1.89	1.09	1.18	0.93	2.01	0.89

degree of hindrance to rotation within the polymer molecule. The predicted g factor, assuming free rotation within the chain backbone, is 0.92 for poly(oxyethylene) glycols [10]. From this it may be concluded that in the lower members of the poly(oxyethylene) glycol series molecular free rotation does exist (see Table 6). However, some authors [3, 8–10] pointed out that freedom of rotation of the elemental dipoles is not complete and that a steric hindrance potential barrier asymmetric around the "trans" conformation must be taken into account. These calculations are based upon a succession of gauche conformations. Recently *Riande* [26] used for such chains a rotational isomeric state model introduced by *Mark* and *Flory* [27]. The conformation of poly(oxyethylene) glycol in dilute solution has also been investigated by *Read* [3] using high resolution nuclear magnetic resonance. This study indicated that the gauche conformation is preferred.

Experimental

Materials

The specification of the solvents used, *i.e.*, 1,4-dioxane and benzene, were described previously [28]. The poly(oxyethylene) glycols, hereafter named *PEG*, of different molecular weights, ranging from 200 to 1500, were supplied by Fluka. The substances (pract.) were used as delivered and stored in a desiccator over P_2O_5. The investigated solutions were prepared on a mass ratio composition scale by precise weighing of the solute and solvent, to 1×10^{-5} g (AT 201 Mettler Toledo).

Electric Permittivity Measurements

Electric permittivities were measured by a WTW dipole meter (model DM 01) using a DFL 1 cell at a constant frequency of 2 MHz. The cell was previously calibrated with standard pure liquids, *i.e.*, carbon tetrachloride, benzene, and cyclohexane as standards [29]. The cell was thermostated with a temperature stability of better than ±0.01 K, using an external bath circulator (Haake, DC3-B3, Karlsruhe, Germany) and the temperature control was performed by means of a digital thermometer (Anton Paar, DT 100-20) with a precision of ±0.01 K. The reproducibility of permittivity data was within ±0.001 units.

References

[1] Bailey FE Jr, Koleske JV (1976) Poly(ethylene oxide). Plenum Press, New York, p 29

[2] Harris JM (1992) In: Harris JM (ed) Poly(Ethylene glycol) Chemistry. Biotechnical and Biomedical Applications. Plenum Press, New York, p 1

[3] Read BE (1965) Trans Faraday Soc **61**: 2140

[4] Debye P, Bueche F (1951) J Chem Phys **19**: 589

[5] Brandrup J, Immergut EH, Grulke EA (eds) (1999) Polymer Handbook, 4th edn. Wiley, New York, VII p 638

[6] Staudinger H (1932) Die Hochmolekulare organische Verbindungen. Springer, Berlin, pp 293, 301

[7] Aroney M, Le Fevre RJW, Parkins GM (1960) J Chem Soc 2890

[8] Magnasco V, Dellepiane G, Rossi C (1963) Makromol Chem **65**: 16

[9] Loveluck GD (1961) J Chem Soc 4729

[10] Marchal J, Benoit H (1955) J Chim Phys **52**: 818

[11] Rudan-Tasic D, Klofutar C (2003) J Mol Liq **103–104**: 187

[12] Uchida T, Kurita Y, Koizumi N, Kubo M (1956) J Polym Sci **21**: 313

[13] Böttcher C, Bordewijk P (1978) Theory of Electric Polarization, vol 2, 2nd ed. Elsevier, Amsterdam, pp 285, 387

[14] De Brouckere L, Mandel M (1958) Adv Chem Phys **1**: 77

[15] Hill EN, Vaughan WE, Price AH, Davies M (1969) Dielectric Properties and Molecular Behaviour. Van Nostrand Reinhold, London, p 264

[16] Klotz IM (1964) Chemical Thermodynamics. Benjamin, New York, p 241

[17] Grunwald E, Highsmith S, Ting-Po I (1974) In: Szwarc M (ed) Ions and Ion Pairs in Organic Reactions, vol 2. Wiley, New York, p 447

[18] Rudan-Tasic D, Klofutar C (2004) Monatsh Chem **135**: 1209

[19] Riddick JA, Bunger WB, Sakano TK (1986) Organic Solvents. Physical Properties and Methods of Purification, 4th ed. Wiley, New York, pp 135, 263, 312, 694

[20] Rudan-Tasic D, Klofutar C (2004) Monatsh Chem **135**: 773

[21] Oster G (1946) J Am Chem Soc **68**: 2036

[22] Grunwald E, Effio A (1973) J Solution Chem **2**: 373

[23] Tourkey AR, Rizk HA, Elanwar JM (1962) Z Physik Chem **31**: 161

[24] Svirbely WJ, Lander JJ (1945) J Am Chem Soc **67**: 2189

[25] Van Krevelen DW (1990) Properties of Polymers. Elsevier, Amsterdam, p 320

[26] Riande E (1976) J Polym Sci, Polym Phys Ed **14**: 2231

[27] Mark JE, Flory PJ (1966) J Am Chem Soc **88**: 3702

[28] Rudan-Tasic D, Klofutar C (2003) Monatsh Chem **134**: 1185

[29] Oehme F, Wirth H, Die Bestimmung des molekularen Dipolmoments. Wissenschaftlich-Technische Werkstätten GmBH, Weilheim, Oberbayern 4/70