

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

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Summary. The density and refractive index of 1,4-dioxane and benzene solutions of poly(oxyethylene) glycols of the type $\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{H}$ (n varying from 4 to 36) were measured at 298.15 K. From the experimental data the apparent specific volume and the apparent specific refraction at infinite dilution were calculated. The limiting apparent specific volume and the limiting apparent specific refraction were found to be inversely proportional to the number average molecular weight of solute. From the limiting apparent specific values at the infinite degree of polymerization, the partial molar volume and partial molar refraction of the monomeric unit were calculated. The partial molar volume as well as the partial molar refraction of the investigated compounds at infinite dilution are additive and depend linearly on the number of oxyethylene groups. The volumetric data were analyzed in terms of the intrinsic volume of solute molecules and by a void partial molar volume. The packing density of the investigated compounds approaches a uniform value as the size of the molecules increases and in both solvents limiting values are reached.

Keywords. Apparent specific volume; Apparent specific refraction; Poly(oxyethylene) glycols; 1,4-Dioxane solutions; Benzene solutions.

Introduction

In recent years poly(oxyethylene) glycols have found wide-spread applications in many branches of industry such as pharmaceuticals, food, and cosmetics. These compounds are soluble in water and most organic solvents and are used as solvents, carriers, humectants, lubricants, and binders [1]. Poly(oxyethylene) glycols are linear polymers whose chains are made up of oxyethylene units and terminated by hydroxyl groups at both ends. The commercial poly(oxyethylene) glycols are not homogeneous with respect to molar mass, but are polydisperse. Information collected on their physical properties should, therefore, be an average. Correlations

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between molecular weight and physical properties of polymer solutions have been extensively investigated, mostly in the high molecular range, while studies on low molecular weight polymers are less frequent. For such solutes the effect of end-groups may be predominant whereas for the high molecular weight range intramolecular segment–segment contacts within the coil prevail.

Great interest has been focused on the measurement, correlation, and prediction of the thermodynamic properties of solutions with a macromolecular solute. A detailed understanding of such solutions requires information on a variety of chemical and physical parameters. The apparent specific volume and the apparent specific refraction are two such parameters which may be helpful in the identification of solute–solute as well as solute–solvent interactions. The apparent specific volume of a macromolecular solute reflects not only the intrinsic volume of the solute molecules, but the extent to which they interact with the solvent. Furthermore, when the solute is made up of flexible chain molecules, the limiting apparent specific volume depends on the extent to which the molecules are extended or coiled in solution [2]. Therefore, studies of such solution properties are important since the parameters obtained are useful, for example in the application of characterization methods and physicochemical techniques.

In the literature there are many characterizations reported of water solutions of poly(oxyethylene) glycols of various average molecular weight but few data have been reported for mixtures of poly(oxyethylene) glycol with organic solvents, *e.g.* Refs. [3–6]. The present work deals with solutions of some lower molecular weight members of the poly(oxyethylene) glycol series in 1,4-dioxane and benzene. The densities and refractive indices of these solutions were measured and the apparent specific volume and the apparent specific refraction of solutes with nominal molecular weights of 200 up to 1500 were calculated.

Results and Discussion

The density and refractive index of the investigated solutions are presented in Tables 1 and 2.

The apparent specific quantity, y_{app} , is defined by Eq. (1) [7] where y is the specific volume (v), or specific refraction (r) of the solution, y_1^0 is the corresponding property of an appropriate amount of the pure solvent (v_1^0, r_1^0), and w is the mass ratio of solute, *i.e.* grams of solute per gram of solvent.

$$y_{app} = \frac{(y - y_1^0)}{w} \quad (y = v, r) \quad (1)$$

The apparent specific quantity is not seriously influenced by the uncertainties in the determination of mass ratio, but it is very sensitive to experimental uncertainties in the specific volume or specific refraction of solution at high dilutions. The error in y_{app} due to uncertainties in the mass ratio is given by Eq. (2) and due to uncertainties of y and y_1^0 , *i.e.* δy and δy_1^0 , as described in Eq. (3).

$$(\delta y_{app})_w^2 = \left(-\frac{y_{app}}{w} \right)^2 (\delta w)^2 \quad (2)$$

$$(\delta y_{app})_y^2 = \frac{1}{w^2} [(\delta y)^2 + (\delta y_1^0)^2] \quad (3)$$

The total error in y_{app} is $(\delta y_{app})_{tot}^2 = (\delta y_{app})_y^2 + (\delta y_{app})_w^2$.

Table 1. Density, d , and refractive index, n_D , of 1,4-dioxane solutions of some poly(oxyethylene) glycols at 298.15 K

<i>PEG-200</i>			<i>PEG-300</i>		
w	$d/\text{g} \cdot \text{cm}^{-3}$	n_D	w	$d/\text{g} \cdot \text{cm}^{-3}$	n_D
0.002424	1.02832	1.42009	0.002640	1.02837	1.42007
0.014332	1.02932	1.42049	0.015720	1.02948	1.42061
0.028637	1.03046	1.42094	0.025907	1.03034	1.42101
0.039541	1.03128	1.42137	0.039675	1.03150	1.42154
0.053671	1.03244	1.42181	0.052934	1.03255	1.42207
0.066013	1.03336	1.42216	0.066389	1.03363	1.42254
0.080553	1.03445	1.42264	0.080338	1.03470	1.42307
0.096785	1.03563	1.42312	0.094449	1.03576	1.42350
0.107892	1.03643	1.42346	0.109450	1.03690	1.42401
<i>PEG-400</i>			<i>PEG-600</i>		
w	$d/\text{g} \cdot \text{cm}^{-3}$	n_D	w	$d/\text{g} \cdot \text{cm}^{-3}$	n_D
0.002088	1.02828	1.42010	0.002449	1.02845	1.42006
0.013776	1.02930	1.42059	0.014540	1.02946	1.42065
0.024561	1.03021	1.42104	0.029199	1.03068	1.42117
0.038613	1.03138	1.42163	0.040626	1.03161	1.42178
0.052840	1.03253	1.42219	0.050622	1.03245	1.42219
0.065643	1.03353	1.42266	0.068172	1.03382	1.42286
0.079238	1.03457	1.42315	0.080308	1.03478	1.42329
0.094536	1.03575	1.42371	0.091873	1.03565	1.42381
0.108516	1.03672	1.42423	0.108340	1.03691	1.42445
<i>PEG-900</i>			<i>PEG-1000</i>		
w	$d/\text{g} \cdot \text{cm}^{-3}$	n_D	w	$d/\text{g} \cdot \text{cm}^{-3}$	n_D
0.001865	1.02829	1.42010	0.002087	1.02838	1.42009
0.011139	1.02915	1.42049	0.014922	1.02941	1.42070
0.025976	1.03056	1.42113	0.026828	1.03046	1.42126
0.039914	1.03182	1.42173	0.038981	1.03145	1.42179
0.051804	1.03296	1.42219	0.053881	1.03264	1.42242
0.067409	1.03427	1.42283	0.065222	1.03360	1.42289
0.077378	1.03515	1.42323	0.074825	1.03430	1.42348
0.091671	1.03631	1.42376	0.093278	1.03571	1.42399
0.107550	1.03775	1.42433	0.107153	1.03674	1.42454
<i>PEG-1500</i>					
w	$d/\text{g} \cdot \text{cm}^{-3}$	n_D			
0.002597	1.02836	1.42014			
0.013918	1.02935	1.42068			
0.025702	1.03037	1.42123			
0.038398	1.03146	1.42180			
0.051505	1.03255	1.42236			
0.063503	1.03356	1.42286			

(continued)

Table 1 (continued)

<i>PEG-1500</i>		
<i>w</i>	<i>d/g · cm⁻³</i>	<i>n_D</i>
0.080154	1.03487	1.42358
0.091930	1.03574	1.42402
0.106157	1.03689	1.42464

Table 2. Density, *d*, and refractive index, *n_D*, of benzene solutions of some poly(oxyethylene) glycols at 298.15 K

<i>PEG-200</i>			<i>PEG-300</i>		
<i>w</i>	<i>d/g · cm⁻³</i>	<i>n_D</i>	<i>w</i>	<i>d/g · cm⁻³</i>	<i>n_D</i>
0.007883	0.87506	1.49740	0.012410	0.87597	1.49733
0.010341	0.87551	1.49733	0.022223	0.87787	1.49690
0.022559	0.87781	1.49690	0.047904	0.88266	1.49620
0.047502	0.88239	1.49612	0.070288	0.88671	1.49562
0.066163	0.88574	1.49561	0.099212	0.89186	1.49491
0.099252	0.89146	1.49460	0.122733	0.89592	1.49442
0.123049	0.89550	1.49392	0.153505	0.90095	1.49383
0.154533	0.90052	1.49303	0.181610	0.90533	1.49330
<i>PEG-400</i>			<i>PEG-600</i>		
<i>w</i>	<i>d/g · cm⁻³</i>	<i>n_D</i>	<i>w</i>	<i>d/g · cm⁻³</i>	<i>n_D</i>
0.012149	0.87593	1.49755	0.010161	0.87560	1.49730
0.024300	0.87825	1.49731	0.020982	0.87765	1.49702
0.047047	0.88250	1.49681	0.046128	0.88249	1.49631
0.069080	0.88657	1.49641	0.067905	0.88673	1.49590
0.100385	0.89212	1.49575	0.095898	0.89162	1.49533
0.122535	0.89589	1.49537	0.117152	0.89534	1.49492
0.152109	0.90071	1.49485	0.158451	0.90229	1.49430
0.180981	0.90526	1.49431	0.176206	0.90522	1.49411
0.216557	0.91073	1.49379	0.215293	0.91135	1.49381
<i>PEG-900</i>			<i>PEG-1000</i>		
<i>w</i>	<i>d/g · cm⁻³</i>	<i>n_D</i>	<i>w</i>	<i>d/g · cm⁻³</i>	<i>n_D</i>
0.020276	0.87766	1.49720	0.021397	0.87788	1.49723
0.046046	0.88270	1.49662	0.047128	0.88290	1.49660
0.071575	0.88750	1.49601	0.074337	0.88793	1.49622
0.099318	0.89253	1.49551	0.099158	0.89238	1.49571
0.122581	0.89658	1.49500	0.127093	0.89740	1.49510
0.150983	0.90148	1.49453	0.156347	0.90217	1.49470
0.178503	0.90596	1.49412	0.178325	0.90564	1.49432
0.216423	0.91188	1.49350	0.212378	0.91081	1.49380
0.238248	0.91531	1.49321	0.282304	0.92083	1.49291

(continued)

Table 2 (continued)

PEG-1500		
w	$d/\text{g} \cdot \text{cm}^{-3}$	n_D
0.023122	0.87819	1.49758
0.047236	0.88290	1.49723
0.071877	0.88754	1.49689
0.097625	0.89222	1.49659
0.123467	0.89677	1.49625
0.148385	0.90091	1.49593
0.177868	0.90559	1.49547
0.203079	0.90954	1.49529
0.23852	0.91495	1.49480

From the density data given in Tables 1 and 2, the apparent specific volume of solute, v_{app} , was calculated from Eq. (1), where $y = v = (1 + w)/d$ and $y_1^0 = v_1^0 = 1/d_1^0$; d and d_1^0 are the density of solution and pure solvent, respectively. For 1,4-dioxane we used a value of $d_1^0 = 1.02816 \text{ g} \cdot \text{cm}^{-3}$, and for benzene, $d_1^0 = 0.87360 \text{ g} \cdot \text{cm}^{-3}$ which are close to the literature values [8]. The uncertainty of v_{app} was 0.1% at the highest w values and 2% at the lowest w values.

It was found that for some low molecular weight solutes v_{app} varies linearly with the mass ratio in accordance for a non-electrolyte solution and can be given as shown in Eq. (4) where v_{app}^0 represents the apparent specific volume of the solute at infinite dilution, equal to the limiting partial specific volume of solute, \bar{v}_2^0 , and b_v is a constant which depends on the solute, solvent, and temperature.

$$v_{app} = v_{app}^0 + b_v w \quad (4)$$

Both parameters were calculated by a weighted least square procedure using the square of the reciprocal value of δv_{app} as weight. For other solutes which do not show a concentration dependence a weighted average using $1/(\delta v_{app})^2$ as weight was used. The values of v_{app}^0 are given in Tables 3 and 4 together with v_{app}^0 of some lower molecular weight members of the poly(oxyethylene) glycols, *i.e.* mono(oxyethylene) glycol, *MEG*, di(oxyethylene) glycol, *DEG*, tri(oxyethylene) glycol, *TEG*, tetra(oxyethylene) glycol, *TTEG*, penta(oxyethylene) glycol, *PTEG*, hexa(oxyethylene) glycol, *HXEG*, and hepta(oxyethylene) glycol, *HPEG*, respectively [9]. The values of constant b_v are given in Table 5. In analyzing the experimental density data *via* Eq. (4) we found that recalculated d values are within experimental errors equal to those given in Tables 1 and 2. In Table 6 the v_{app}^0 data for aqueous solutions of some poly(oxyethylene) glycols determined previously [9, 10] are given.

From Tables 3, 4, and 6 a decrease in the apparent specific volume of the investigated poly(oxyethylene) glycols at infinite dilution with increasing molecular weight of solute can be observed. This dependence was attributed to the end groups attached to the polymer chain or to the spatial configuration of the macromolecule [11] and is supposed to be negligible in systems of a sufficiently high degree of polymerization [12, 13]. As was shown previously, the dependence of v_{app}^0 against the reciprocal number average molecular weight, M_n [12] or reciprocal

Table 3. Apparent specific volume and partial molar volume of some poly(oxyethylene) glycols in 1,4-dioxane solution at infinite dilution, the fraction of void space of the limiting partial molar solute volume, and the packing density at 298.15 K

Solute	$v_{app}^0/\text{cm}^3 \cdot \text{g}^{-1}$	$\bar{V}_2^0/\text{cm}^3 \cdot \text{mol}^{-1}$	$\frac{\bar{V}_2^0 - V_W}{V_2^0}$	$\frac{V_W}{V_2^0}$
MEG	0.8926 ± 0.0002^a	55.40 ± 0.01^b	0.378	0.62
DEG	0.8983 ± 0.0006^a	95.30 ± 0.06^b	0.369	0.63
TEG	0.8929 ± 0.0001^a	134.09 ± 0.02^b	0.360	0.64
TTEG	0.8940 ± 0.0002^a	173.64 ± 0.04^b	0.358	0.64
PTEG	0.8937 ± 0.0009^a	212.95 ± 0.21^b	0.358	0.64
HXEG	0.8905 ± 0.0004^a	251.43 ± 0.11^b	0.353	0.65
HPEG	0.8977 ± 0.0009^a	292.99 ± 0.30^b	0.357	0.64
PEG-200	0.8952 ± 0.0009	171.0 ± 0.9	0.294	0.71
PEG-300	0.8911 ± 0.0009	265.5 ± 0.9	0.304	0.70
PEG-400	0.8911 ± 0.0011	329.7 ± 2.0	0.315	0.68
PEG-600	0.8887 ± 0.0007	474.6 ± 4.0	0.325	0.68
PEG-900	0.8824 ± 0.0024	785.3 ± 29	0.327	0.67
PEG-1000	0.8900 ± 0.0010	894.5 ± 13	0.334	0.67
PEG-1500	0.8884 ± 0.0012	1412.6 ± 55	0.337	0.66

^a Calculated from data given in Ref. [9]; ^b given in Ref. [9]

Table 4. Apparent specific volume and partial molar volume of some poly(oxyethylene) glycols in benzene solution at infinite dilution, the fraction of void space of the limiting partial molar solute volume, and the packing density at 298.15 K

Solute	$v_{app}^0/\text{cm}^3 \cdot \text{g}^{-1}$	$\bar{V}_2^0/\text{cm}^3 \cdot \text{mol}^{-1}$	$\frac{\bar{V}_2^0 - V_W}{V_2^0}$	$\frac{V_W}{V_2^0}$
DEG	0.8985 ± 0.0003^a	95.35 ± 0.03^b	0.370	0.63
TEG	0.8901 ± 0.0004^a	133.67 ± 0.06^b	0.358	0.64
TTEG	0.8928 ± 0.0005^a	173.41 ± 0.10^b	0.358	0.64
PEG-200	0.8945 ± 0.0010	170.8 ± 0.9	0.293	0.71
PEG-300	0.8877 ± 0.0008	264.5 ± 0.9	0.302	0.70
PEG-400	0.8868 ± 0.0007	328.1 ± 2.0	0.312	0.69
PEG-600	0.8824 ± 0.0007	471.2 ± 4.0	0.320	0.68
PEG-900	0.8775 ± 0.0006	780.9 ± 29	0.323	0.68
PEG-1000	0.8775 ± 0.0006	881.9 ± 12	0.325	0.68
PEG-1500	0.8764 ± 0.0006	1393.5 ± 54	0.328	0.67

^a Calculated from data given in Ref. [9]; ^b given in Ref. [9]

value of the degree of polymerization, n [11] are almost linear in low molecular solvents, where the high molecular weight effect becomes unimportant. Sarazin and Francois [14] were able to explain this dependence by the intramolecular density of the macromolecular segments inside the coil and by the size of the solvent molecules, *i.e.* by their molar volume, V_s .

For the solutes investigated in this work a linear dependence of v_{app}^0 on the reciprocal value of the degree of polymerization, $1/n$, was also observed and for benzene solutions of poly(oxyethylene) glycols it is shown in Fig. 1. The degree of

Table 5. The values of constant b_v (Eq. (4)) of some poly(oxyethylene) glycols in 1,4-dioxane and benzene solution at 298.15 K

Solute	b_v	
	1,4-Dioxane	Benzene
PEG-200	-0.0213 ± 0.0099	-0.0379 ± 0.0081
PEG-300	-0.0138 ± 0.0098	-0.0245 ± 0.0057
PEG-400		-0.0196 ± 0.0038
PEG-600		-0.0253 ± 0.0039
PEG-900		-0.0156 ± 0.0030
PEG-1000		
PEG-1500		

Table 6. Apparent specific volume and partial molar volume of some poly(oxyethylene) glycols in aqueous solution at infinite dilution, the fraction of void space of the limiting partial molar solute volume, and the packing density at 298.15 K

Solute	$v_{app}^0 / \text{cm}^3 \cdot \text{g}^{-1}$	$\bar{V}_2^0 / \text{cm}^3 \cdot \text{mol}^{-1}$	$\frac{\bar{V}_2^0 - V_w}{\bar{V}_2^0}$	$\frac{V_w}{\bar{V}_2^0}$
MEG	0.8790 ^a	54.56 ± 0.01^c	0.369	0.63
DEG	0.8681 ^a	92.12 ± 0.03^c	0.348	0.65
TEG	0.8599 ^a	129.13 ± 0.08^c	0.336	0.66
TTEG	0.8557 ^a	166.20 ± 0.05^c	0.330	0.67
PEG-300	0.8505 ^b	253.5 ± 0.9	0.271	0.73
PEG-400	0.8485 ^b	314 ± 2	0.281	0.72
PEG-600	0.8452 ^b	451 ± 3	0.289	0.71
PEG-900	0.8432 ^b	750 ± 28	0.296	0.70
PEG-1000	0.8426 ^b	847 ± 12	0.297	0.70
PEG-1500	0.8410 ^b	1337 ± 52	0.299	0.70

^a Calculated from data given in Ref. [9]; ^b given in Ref. [10]; ^c given in Ref. [9]

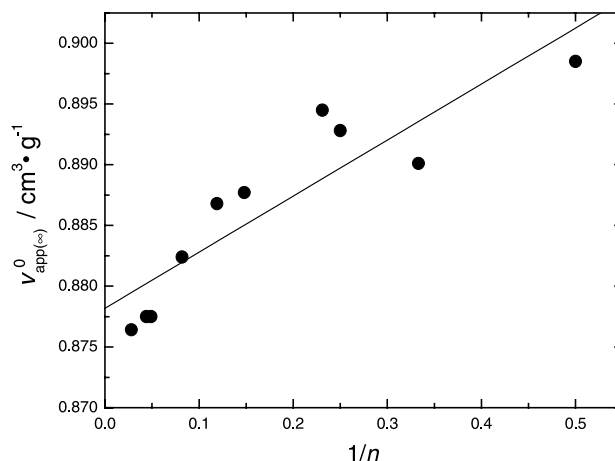
**Fig. 1.** Dependence of $v_{app(\infty)}^0$ of some poly(oxyethylene) glycols determined in benzene solution on the reciprocal value of the degree of polymerization, $1/n$, at 298.15 K

Table 7. Molar volume of solvent, V_s , apparent specific volume at infinite dilution, $v_{app(\infty)}^0$, constant K , and volume of the monomeric unit, V_m , for some poly(oxyethylene) glycols at 298.15 K

Solvent	$V_s/\text{cm}^3 \cdot \text{mol}^{-1}$	$v_{app(\infty)}^0/\text{cm}^3 \cdot \text{g}^{-1}$	$K/\text{cm}^3 \cdot \text{g}^{-1}$	$V_m/\text{cm}^3 \cdot \text{mol}^{-1}$	
				Eq. (4)	Eq. (9)
Water	18.068	0.8374 ± 0.0003^a	5.9 ± 0.3	36.90 ^a	36.50 ^a
1,4-Dioxane	85.700	0.891 ± 0.002	0.233 ± 0.005	39.2	38.55
Benzene	89.416	0.877 ± 0.002	2.75 ± 0.01	38.60	38.13

^a Calculated from data in Ref. [10]

polymerization, n , for the investigated solutes was calculated from the known number average molecular weight of solute, determined by the cryoscopic method [15]. As illustrated in Fig. 1, the v_{app}^0 values vary almost linearly with $1/n$ and approach a limiting value of $v_{app(\infty)}^0$ as n increases to infinity. Thus, according to *Schulz* and *Hoffmann* [12], one may write as shown in Eq. (5) where $v_{app(\infty)}^0$ is the apparent specific volume at infinite dilution of a solute whose degree of polymerization is infinity, M_0 is the molecular weight of the monomeric unit, and K is a constant which depends on the solvent and the nature of the end groups.

$$v_{app}^0 = v_{app(\infty)}^0 + \frac{K}{M_n} = v_{app(\infty)}^0 + \frac{K}{nM_0} \quad (5)$$

The values of $v_{app(\infty)}^0$ and K were obtained by a least squares procedure from the data collected in Tables 3 and 4. These values, together with the value for aqueous solution [10] are presented in Table 7.

From Table 7 follows that $v_{app(\infty)}^0$ depends on the molecular volume of the solvent. So, $v_{app(\infty)}^0$ has its lowest value in water, whereas with increasing molar volume of solvent the reverse can be observed. Such anomalous behavior was also found by *Sarazin* and *Francois* [14] for poly(oxyethylene) glycol dissolved in formamide ($V_s = 39.85 \text{ cm}^3 \cdot \text{mol}^{-1}$) in which $v_{app(\infty)}^0$ has a higher value than in benzene.

From $v_{app(\infty)}^0$ the volume of the monomeric unit, $\text{CH}_2\text{CH}_2\text{O}$, V_m , was calculated. The value of $36.90 \text{ cm}^3 \cdot \text{mol}^{-1}$ determined in water, agrees well with the value of $36.10 \text{ cm}^3 \cdot \text{mol}^{-1}$ given by *Zana* [16] for repeating monomeric units of non-ionic polymers in aqueous solution. The V_m values for 1,4-dioxane and benzene are close together and considerably greater than in water (see Table 7).

Equation (5) is supported by the thermodynamic theory, based on the *McMillan-Mayer* theory of solutions [17], developed by *Kobataka* and *Inagaki* [18] for the density of polymer solutions. According to this theory it is supposed that the end-groups in the polymer molecule are different from the monomer units. So, the constants in Eq. (5) can be correlated with the parameters of the intramolecular potential as follows in Eqs. (6)–(8) where B_{12} is the excluded volume between solvent and polymer molecules, β_{12} is the excluded volume between solvent molecule and repeating unit, β'_{12} is the excess excluded volume representing the end group effect,

Table 8. The parameters of Eqs. (6)–(8) for aqueous, 1,4-dioxane, and benzene solutions of some poly(oxyethylene) glycols at 298.15 K

Solvent	$kT\kappa_T/\text{cm}^3 \cdot \text{g}^{-1}$	$-\beta_{12}/M_0/\text{cm}^3 \cdot \text{g}^{-1}$	$-\beta'_{12}/\text{cm}^3 \cdot \text{g}^{-1}$	$-B_{12} \times 10^{-3}/\text{cm}^3 \cdot \text{g}^{-1}$
Water	0.0623	0.8374 ± 0.0003^a	2.9 ± 0.2	0.843
1,4-Dioxane	0.0208	0.891 ± 0.002	0.106 ± 0.005	0.891
Benzene	0.0307	0.877 ± 0.002	1.36 ± 0.01	0.879

^a Calculated from data in Ref. [10]

κ_T is the isothermal compressibility of the solvent, k is the Boltzman constant, and T is the absolute temperature.

$$v_{app(\infty)}^0 = -\frac{\beta_{12}}{M_0} \quad (6)$$

$$K = -2\beta'_{12} + kT\kappa_T \quad (7)$$

$$B_{12} = 2\beta'_{12} + n\beta_{12} \quad (8)$$

From Eq. (7) follows that the constant K depends not only upon the physical properties of the solvent, *i.e.* on its isothermal compressibility, but also upon the end-groups and that $v_{app(\infty)}^0$ corresponds to a monomer unit in the sense of interaction between solute and solvent. The excluded volume between solvent and polymer molecule, given by Eq. (8), depends on both end groups and increases linearly with the degree of polymerization. The parameters of Eqs. (6)–(8) are given in Table 8. The values of the isothermal compressibility of the solvents were taken from Ref. [8]. The excluded volume between solvent and polymer molecule was calculated for $M_n = 1000$.

From Table 8 can be seen that the excess excluded volume of the end-groups differs markedly from the excluded volume between solvent molecule and repeating unit only in 1,4-dioxane. The conspicuously greater value of β'_{12} for aqueous solution may be ascribed to intense H-bonding between water molecules and terminal hydroxyl groups of the poly(oxyethylene) glycol molecule. Furthermore, it follows from Eq. (8) that the excluded volume between solvent molecules and polymer molecules depends almost entirely on the “free volume” of the poly(oxyethylene) glycol molecule per monomer unit and much less on the excess excluded volume of the end groups. Similar results were obtained earlier by *Nakanishi* and *Kurata* [11] for aqueous solutions of polyvinyl alcohol.

The partial molar volume of the solute at infinite dilution, \bar{V}_2^0 (Tables 3, 4, and 5), depends linearly on the number of $\text{CH}_2\text{CH}_2\text{O}$ -units (see Fig. 2) as described in Eq. (9) where a_0 is an empirical constant and a_1 is equal to the volume of the monomeric unit.

$$\bar{V}_2^0 = a_0 + a_1n \quad (9)$$

Both values depend on solvent and temperature. The calculated values of V_m are given in Table 7. These values in both non-aqueous solvents are close to the value of $38.34 \text{ cm}^3 \cdot \text{mol}^{-1}$ calculated by the group contribution method given by

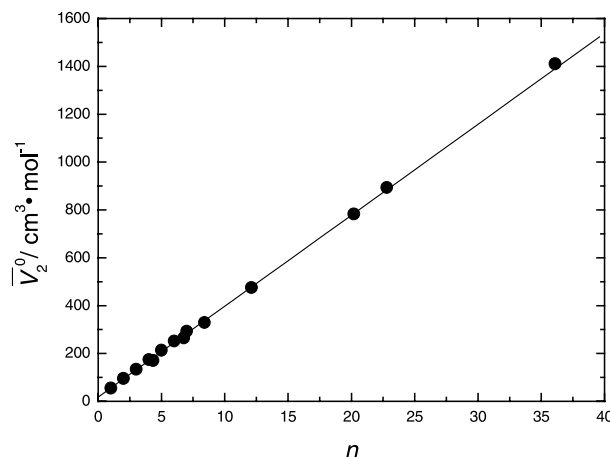


Fig. 2. Dependence of limiting partial molar volume, \bar{V}_2^0 , of some poly(oxyethylene) glycols in 1,4-dioxane solution on the degree of polymerization, n , at 298.15 K

Cabani et al. [19] for aqueous solution and for the values obtained earlier for the lower molecular weight members of poly(oxyethylene) glycols in 1,4-dioxane and benzene [9]. The smallest value of V_m determined in water can be ascribed to the formation of hydrogen bonds between oxygen atoms of poly(oxyethylene) glycols and water molecules. Such an effect results in a decrease in the partial molar volume due to shortening the interatomic distances [20].

It was shown by *Teresawa et al.* [21] that the limiting partial molar volume for a series of hydrocarbons, alkanols and glycols depends linearly on the *van der Waals* volume of the solute. Such a linear dependence was also observed for the investigated systems, as well as for aqueous solutions of poly(oxyethylene) glycols. The *van der Waals* volume, V_W , was calculated by the *Bondi* approach, corrected for hydrogen bonding for each terminal $-\text{OH}$ group [22]. For the dependence given in Eq. (10) where a and b are constants, the following values of the constants were obtained: $a = 1.500$ and $b = 1.12 \text{ cm}^3 \cdot \text{mol}^{-1}$ for 1,4-dioxane, $a = 1.484$ and $b = -0.82 \text{ cm}^3 \cdot \text{mol}^{-1}$ for benzene, and $a = 1.420$ and $b = 1.82 \text{ cm}^3 \cdot \text{mol}^{-1}$ for water.

$$\bar{V}_2^0 = aV_W + b \quad (10)$$

Thus the constant b , which can be related to the covolume [2], depends on the solvent used, while the constant a is somewhat lower for an aqueous solution than for other solvents. It is interesting to compare the obtained values of constants a and b obtained with those for glycols in aqueous solution where $a = 1.585$ and $b = -2.3 \text{ cm}^3 \cdot \text{mol}^{-1}$ [21].

If it is assumed that V_W does not change in solution, then the difference, $\bar{V}_2^0 - V_W$, may be the volume of the actual void space, \bar{V}_{void} [21], as can be seen in Eq. (11).

$$\bar{V}_2^0 = V_W + \bar{V}_{\text{void}} \quad (11)$$

From Eq. (11) follows that \bar{V}_2^0 consists of the intrinsic volume of solute molecules, *i.e.* V_W , and the void partial molar volume. \bar{V}_{void} may be the volume of the actual

void space created by the addition of 1 mol of the solute to the solvent. In Tables 3, 4, and 6 the fraction of the void partial molar volume of the limiting partial molar volume of solute is given. From these tables can be seen that after some lower molecular weight members of the poly(oxyethylene) glycols the fraction of void space becomes nearly constant and amounts to 0.333 ± 0.022 for 1,4-dioxane, 0.324 ± 0.022 for benzene, and 0.289 ± 0.011 for water. It is concluded from these results that the fraction of partial void space depends primarily on the hydration of solute molecules. As was shown previously, poly(oxyethylene) glycol molecules are intensively hydrated by water molecules [23]. On the other hand, in both non-aqueous solvents the fraction of void space is, within experimental error, equal.

In Tables 3, 4, and 6 the packing density, *i.e.* the ratio of the *van der Waals* volume to the limiting partial molar volume of solute, is given [24]. The packing density gives us some information about how solute molecules are accommodated in the cavities of the solvent. It has been shown that for a given class of molecular solute the packing density approaches a uniform value as the size of the molecules increases. From the results given in Tables 3, 4, and 6 it can be seen that the packing density of the investigated poly(oxyethylene) glycols gradually increases with the number of $\text{CH}_2\text{CH}_2\text{O}$ units for all solvents and approaches a plateau which is greater for water than for the other two solvents. *Bernal* and *Finney* [25] found that in a random close packed collection of spheres the packing density was an average of the densities around individual molecules, the extreme values being 0.57 and 0.70. So, the investigated compounds adopt the extreme value of packing density, as can be seen from the data collected in Tables 3, 4, and 6.

The refractive index of a polymer solution provides fundamental information on a physical property that can be used in characterization and description of a macromolecular system. So, for example the specific index of refraction increment, ν , as given in Eq. (12) where $c_2 = wd/(1 + w)$ denotes the concentration of the polymer in solution ($\text{g} \cdot \text{cm}^{-3}$), is required to determine the weight average molecular weight and the second virial coefficient, A_{22} , for a polymer in solution, using a light scattering method.

$$\nu = \frac{\partial n_D}{\partial c_2} \quad (12)$$

In Tables 9 and 10, besides the specific index of refraction increments of the investigated compounds, the limiting apparent specific refraction and limiting partial molar refraction of some lower members of poly(oxyethylene) glycols taken from the literature are given. The specific refraction index increment was calculated from the simple linear relation of n_D versus c_2 which suffices for the investigated systems. From the collected data given in Tables 9 and 10 it can be seen that ν is positive for 1,4-dioxane solutions, while for benzene solutions it is negative. The negative values of the specific index of refraction increments was also obtained by *Rempp* [26] for benzene solutions of some lower molecular weight members of the poly(oxyethylene) glycols (from di- to octadeca(oxyethylene) glycols) at a wavelength of 435.8 nm at 298 K. In both solvents ν rises with increasing molecular weight of the polymeric compound.

It was shown by *Huglin* [27] that a linear relationship exists between the specific index of refraction and the reciprocal molecular weight. *Lorimer* and *Jones*

Table 9. Specific index of refraction increment, limiting apparent specific refraction, and limiting partial molar refraction of some poly(oxyethylene) glycols in 1,4-dioxane solution at 298.15 K

Solute	$\nu/\text{cm}^3 \cdot \text{g}^{-1}$	$r_{app}^0/\text{cm}^3 \cdot \text{g}^{-1}$	$\bar{R}_2^0/\text{cm}^3 \cdot \text{mol}^{-1}$
MEG	0.0120 ± 0.0005^a	0.2322 ± 0.003^a	14.41 ± 0.02^b
DEG	0.0237 ± 0.0003^a	0.2402 ± 0.002^a	25.49 ± 0.02^b
TEG	0.0311 ± 0.0002^a	0.2423 ± 0.002^a	36.39 ± 0.02^b
TTEG	0.0339 ± 0.0002^a	0.2441 ± 0.001^a	47.42 ± 0.02^b
PEG-200	0.0343 ± 0.0005	0.2442 ± 0.0004	46.6 ± 0.3
PEG-300	0.0396 ± 0.0003	0.2461 ± 0.0002	73.3 ± 0.2
PEG-400	0.0414 ± 0.0003	0.2477 ± 0.0004	91.6 ± 0.5
PEG-600	0.0441 ± 0.0005	0.2478 ± 0.0007	132.3 ± 1.1
PEG-900	0.0430 ± 0.0004	0.2462 ± 0.0007	219.1 ± 8.0
PEG-1000	0.0456 ± 0.0008	0.2496 ± 0.0006	250.8 ± 4.0
PEG-1500	0.0462 ± 0.0002	0.2496 ± 0.0007	396.9 ± 16.0

^a Calculated from data given in Ref. [9]; ^b given in Ref. [9]

Table 10. Specific index of refraction increment, limiting apparent specific refraction and limiting partial molar refraction of some poly(oxyethylene) glycols in benzene solution at 298.15 K

Solute	$-\nu/\text{cm}^3 \cdot \text{g}^{-1}$	$r_{app}^0/\text{cm}^3 \cdot \text{g}^{-1}$	$\bar{R}_2^0/\text{cm}^3 \cdot \text{mol}^{-1}$
DEG	0.0478 ± 0.0015^a	0.2394 ± 0.0009^a	25.41 ± 0.10^b
TEG	0.0397 ± 0.0007^a	0.2410 ± 0.0003^a	36.19 ± 0.05^b
TTEG	0.0364 ± 0.0002^a	0.2430 ± 0.0005^a	47.20 ± 0.10^b
PEG-200	0.0384 ± 0.0003	0.2436 ± 0.0023	46.5 ± 0.5
PEG-300	0.0309 ± 0.0008	0.2425 ± 0.0007	72.3 ± 0.3
PEG-400	0.0250 ± 0.0003	0.2484 ± 0.0021	91.9 ± 0.9
PEG-600	0.0235 ± 0.0001	0.2430 ± 0.0014	129.8 ± 1.2
PEG-900	0.0251 ± 0.0005	0.2434 ± 0.0002	216.6 ± 8.0
PEG-1000	0.0235 ± 0.0004	0.2451 ± 0.0008	246.3 ± 3.5
PEG-1500	0.0177 ± 0.0001	0.2498 ± 0.0011	397.2 ± 16

^a Calculated from data given in Ref. [9]; ^b given in Ref. [9]

[28] deduced a relation which predicts that the specific index of refraction increment of a polymer solution is inversely proportional to the number average molecular weight of the solute as given in Eq. (13) where ν_∞ and ν_0 are constants which depend on the refractive index of the solvent, on the specific refraction of the pure polymer, and on the specific volume of the polymer in solution.

$$\nu = \nu_\infty + \frac{\nu_0}{M_n} = \nu_\infty + \frac{\nu_0}{nM_0} \quad (13)$$

The collected data in Tables 9 and 10 satisfy the requirements of Eq. (13). As an example, in Fig. 3 the specific index of refraction increment as a function of $1/n$ for 1,4-dioxane solution is given. The values of the specific index of refraction increment of a solute whose degree of polymerization is infinity, ν_∞ and constant ν_0 were calculated and found to be: $\nu_\infty = (0.0468 \pm 0.0005) \text{cm}^3 \cdot \text{g}^{-1}$, $\nu_0 =$

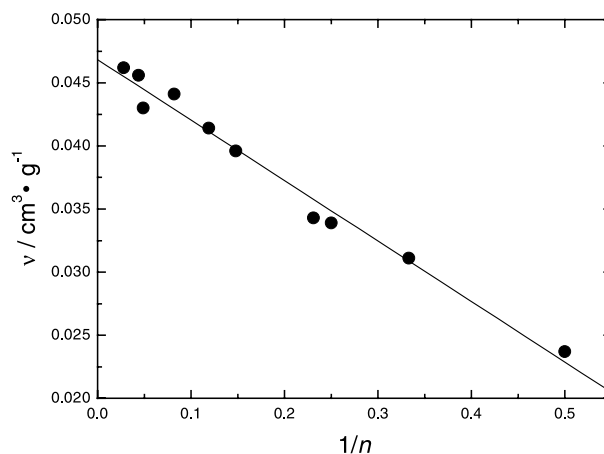


Fig. 3. Dependence of the specific index of refraction increments, ν , on the reciprocal value of the degree of polymerization, $1/n$, for 1,4-dioxane solutions of some poly(oxyethylene) glycols at 298.15 K

$-(2.11 \pm 0.10) \text{ cm}^3 \cdot \text{mol}^{-1}$ for 1,4-dioxane solution and $\nu_\infty = -(0.020 \pm 0.01) \text{ cm}^3 \cdot \text{g}^{-1}$, $\nu_0 = -(2.64 \pm 0.26) \text{ cm}^3 \cdot \text{mol}^{-1}$ for benzene solution. The effect of molecular weight on the specific index of refraction increment has been investigated in the past [26, 29]. From these references it is evident that a significant molecular weight dependence vanishes around a molecular weight of 4000 and that the specific index of refraction increment becomes essentially constant at a molecular weight of 20000 [30].

From the density and refractive index given in Tables 1 and 2, the specific refraction of the solution, *i.e.* $y = r = (n_D^2 - 1)v/(n_D^2 + 2)$, was calculated and the apparent specific refraction of solute by Eq. (1). The uncertainties of r_{app} value, calculated by Eqs. (2) and (3), are at the lowest mass ratio 4% and at the highest mass ratio 0.2%. In calculation of the r_{app} values we used a value of $n_D^0 = 1.42000$ for 1,4-dioxane and $n_D^0 = 1.49762$ for pure benzene [8]. For the investigated systems the apparent specific refraction of solute does not show any concentration dependence so we calculated a weighted average using a reciprocal value of the squared error of r_{app} , *i.e.* $1/(\delta r_{app})^2$ as a weight. The values of the limiting apparent specific refraction, r_{app}^0 , are given together with some lower molecular weight members of the poly(oxyethylene) glycol series [9] in Tables 9 and 10. In both solvents used, r_{app}^0 increases with increasing molecular weight of the polymeric compound.

Like the limiting apparent specific volume (Eq. (5)) and the specific index of refraction increment (Eq. (13)), the limiting apparent specific refraction of solute can be represented as shown in Eq. (14) where $r_{app(\infty)}^0$ is the limiting apparent specific refraction of solute at an infinite degree of polymerization and L is a constant.

$$r_{app}^0 = r_{app(\infty)}^0 + \frac{L}{M_n} = r_{app(\infty)}^0 + \frac{L}{nM_0} \quad (14)$$

In Fig. 4 the dependence of the limiting apparent specific refraction on the reciprocal value of the degree of polymerization for some poly(oxyethylene) glycols

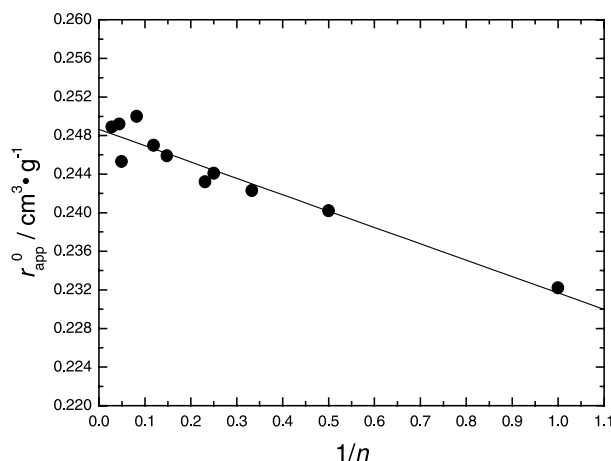


Fig. 4. Dependence of the limiting apparent specific refraction, r_{app}^0 , on the reciprocal value of degree of polymerization, $1/n$, for 1,4-dioxane solutions of some poly(oxyethylene) glycols at 298.15 K

in 1,4-dioxane solutions is presented. The calculated values of constant $r_{app(\infty)}^0$ and L are: $r_{app(\infty)}^0 = (0.2489 \pm 0.0004) \text{ cm}^3 \cdot \text{g}^{-1}$, $L = -(0.76 \pm 0.05) \text{ cm}^3 \cdot \text{mol}^{-1}$ for 1,4-dioxane solution and $r_{app(\infty)}^0 = (0.2466 \pm 0.0012) \text{ cm}^3 \cdot \text{g}^{-1}$, $L = -(0.66 \pm 0.22) \text{ cm}^3 \cdot \text{mol}^{-1}$ for benzene solution. From the limiting apparent specific refraction at infinite polymerization the following values of partial molar refraction of the monomeric unit were obtained: $\bar{R}_m^0 = (9.68 \pm 0.08) \text{ cm}^3 \cdot \text{mol}^{-1}$ in 1,4-dioxane solution and $\bar{R}_m^0 = (9.46 \pm 0.07) \text{ cm}^3 \cdot \text{mol}^{-1}$ for benzene solution. \bar{R}_m^0 determined in 1,4-dioxane solution is about 2% greater than in benzene solution.

From the limiting apparent specific refraction and the number average molecular weight of the investigated solutes, the limiting partial molar refraction, \bar{R}_2^0 was calculated. The values of \bar{R}_2^0 are given in Tables 9 and 10 together with the values for some lower molecular weight members of the poly(oxyethylene) glycols [9]. The investigated compounds show good additivity when \bar{R}_2^0 is plotted against the number of monomeric units. The data for both solvents lie on a straight line with a correlation coefficient better than 0.9998 and of a slope of $(10.89 \pm 0.06) \text{ cm}^3 \cdot \text{mol}^{-1}$ for 1,4-dioxane solutions and of $(10.86 \pm 0.09) \text{ cm}^3 \cdot \text{mol}^{-1}$ for benzene solutions. These values, *i.e.* the molar refraction of the monomeric unit, are not appreciably affected by the solvent effect. Taking into account the value of \bar{R}_m^0 obtained from $r_{app(m)}^0$, we calculated the weighted average of \bar{R}_m^0 and obtained a value of $(10.22 \pm 0.76) \text{ cm}^3 \cdot \text{mol}^{-1}$ which is close to the value of $(10.93 \pm 0.03) \text{ cm}^3 \cdot \text{mol}^{-1}$ determined earlier for some lower molecular weight poly(oxyethylene) glycols [9]. The limiting molar refraction of the monomeric unit, calculated from the atomic refraction for the sodium *D*-line [31] is $10.879 \text{ cm}^3 \cdot \text{mol}^{-1}$, which means that self-association of solute molecules does not take place. This can be confirmed by the recently determined excess molar volumes and excess molar refraction for solutions of PEG-200 and PEG-400 in 1,4-dioxane which are small and negative [5].

Experimental

Materials

The specification of the solvents used, *i.e.* 1,4-dioxane and benzene, were described previously [9]. The poly(oxyethylene) glycols, hereafter named *PEG*, of different molecular weights, ranging from 200 to 1500, were supplied by Fluka. The substances were used as delivered and stored in a desiccator over P₂O₅. The investigated solutions were prepared on a mass ratio concentration scale by precise weighing of the solute and solvent, to 1×10^{-5} g (AT 201 Mettler Toledo).

Density Measurements

The solution density was measured at (298.15 ± 0.01) K using an *A. Paar* digital densimeter (Model DMA 601) with a reproducibility of 3×10^{-5} g · cm⁻³. The thermal stability of the measuring cell was monitored by a digital thermometer (DT 100-20, *A. Paar*) and was better than 0.01 K. The densimeter was calibrated with water and dry air [9].

Refractive Index Measurements

The refractive index was measured with a model DUR-W2 *Schmidt-Haensch* refractometer with a precision of 1×10^{-5} . All measurements were performed at 298.15 K and at a wavelength of 589 nm.

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