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Apparent Molar Volume and Apparent Molar Refraction of Mono-, Di-, Tri-, and Tetra(oxyethylene) Glycol in Aqueous, 1,4-Dioxane, and Benzene Solutions at 298.15 K

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Summary. The density and refractive index of aqueous, 1,4-dioxane, and benzene solutions of poly (oxyethylene) glycols of the type HO–$(CH_2CH_2O)_n$–H (n varying from 1 to 4) were measured at 298.15 K. From these experimental data the apparent molar volume and the apparent molar refraction at infinite dilution were calculated. The limiting apparent molar volume of the investigated compounds in a definite solvent depends linearly on the number of oxyethylene groups. From these data, the volume of the monomeric unit was evaluated and found to be greater in non-aqueous solvents than in water. The limiting apparent molar refraction of the solute for the investigated systems, within the experimental uncertainties, is equal to the molar refraction of the pure solute. The electronic polarizability of the solute molecule depends linearly on the number of monomeric units and the ratio of the electronic polarizability to the molecular *van der Waals* volume is constant and independent of the number of oxyethylene groups.

Keywords. Limiting partial molar volume; Limiting partial molar refraction; Poly(oxyethylene) glycols.

Introduction

Poly(oxyethylene) glycols (*PEG*) of the general formula HO–$(CH_2CH_2O)_n$–H are highly soluble in water and organic solvents [1, 2]. For this reason solutions of poly(oxyethylene) glycols have been studied as model systems for macromolecular solutions [3]. A detailed understanding of the solution behaviour of non-electrolyte solutes requires information on a variety of chemical and physical parameters. The limiting partial molar volume is an important thermodynamic property, which may

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be helpful in the identification of solvent-solute and solute-solute interactions. In the past limiting partial molar volumes of mono-, di-, tri-, and tetra(oxyethylene) glycols in aqueous solution were reported [4–6] but no data seem to have been reported for non-aqueous solutions. It is therefore the object of this contribution to present the limiting partial molar volumes and the limiting partial molar refraction of some lower members of the poly(oxyethylene) glycol series in aqueous, 1,4-dioxane, and benzene solutions and to discuss and analyze them on the basis of the general solution behaviour related to their chemical structure.

Results and Discussion

The density and refractive index of the investigated solutions are presented in Table 1 (aqueous solutions), Table 2 (1,4-dioxane solutions), and Table 3 (benzene solutions).

The apparent molar quantity, Y_{app}, is defined by Eq. (1) [7]

$$Y_{\mathrm{app}} = \frac{(y - y_1^0)}{m} \quad (Y \equiv V, R, P) \tag{1}$$

where y is the volume (v) or refraction (r) of the solution, y_1^0 is the corresponding property of the appropriate amount of pure solvent (v_1^0, r_1^0) and m is molality. The dependence of Y_{app} on solute molality at a definite temperature and for a non-electrolyte solution can be conventionally given as

$$Y_{\mathrm{app}} = Y_{\mathrm{app}}^0 + b_y m + b_{yy} m^2 + \cdots \tag{2}$$

Table 1. Density, *d*, and refractive index, n_D, of aqueous solutions of *MEG*, *DEG*, *TEG*, and *TTEG* at 298.15 K

$m/\mathrm{mol \cdot kg^{-1}}$	$d/\mathrm{g \cdot cm^{-3}}$	n_D	$m/\mathrm{mol \cdot kg^{-1}}$	$d/\mathrm{g \cdot cm^{-3}}$	n_D
MEG			*DEG*		
0.0575	0.99747	1.33280	0.0438	0.99766	1.33298
0.2628	0.99904	1.33397	0.2263	1.00021	1.33497
0.4517	1.00050	1.33506	0.4043	1.00260	1.33690
0.6442	1.00199	1.33617	0.6268	1.00554	1.33923
0.8906	1.00392	1.33759	0.7959	1.00773	1.34091
1.0561	1.00522	1.33862	1.0190	1.01048	1.34312
1.2364	1.00664	1.33961	1.2075	1.01276	1.34498
1.4681	1.00848	1.34098	1.4132	1.01519	1.34679
TEG			*TTEG*		
0.0514	0.99812	1.33332	0.0461	0.99834	1.33355
0.1898	1.00101	1.33567	0.1684	1.00170	1.33626
0.3499	1.00423	1.33821	0.3276	1.00592	1.33973
0.5229	1.00759	1.34089	0.4726	1.00962	1.34265
0.6954	1.01083	1.34351	0.5582	1.01175	1.34435
0.8497	1.01366	1.34577	0.6873	1.01486	1.34681
1.0321	1.01690	1.34830	0.8210	1.01797	1.34937
1.1598	1.01904	1.34999	0.9264	1.02034	1.35120

Table 2. Density, d, and refractive index, n_D, of 1,4-dioxane solutions of *MEG*, *DEG*, *TEG*, and *TTEG* at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	$d/\text{g}\cdot\text{cm}^{-3}$	n_D	$m/\text{mol}\cdot\text{kg}^{-1}$	$d/\text{g}\cdot\text{cm}^{-3}$	n_D
MEG			*DEG*		
0.0477	1.02846	1.41983	0.0280	1.02847	1.42005
0.2238	1.02935	1.42009	0.1499	1.02932	1.42034
0.4461	1.03046	1.42019	0.2628	1.03040	1.42061
0.6230	1.03138	1.42035	0.3468	1.03104	1.42082
0.8379	1.03238	1.42047	0.4999	1.03224	1.42119
1.0753	1.03350	1.42071	0.6190	1.03314	1.42149
1.2901	1.03451	1.42079	0.7391	1.03396	1.42174
1.5369	1.03562	1.42098	0.8886	1.03500	1.42207
1.7604	1.03659	1.42103	1.0091	1.03584	1.42234
TEG			*TTEG*		
0.0178	1.02835	1.42004	0.0100	1.02829	1.42006
0.0912	1.02925	1.42039	0.0693	1.02923	1.42048
0.1795	1.03033	1.42078	0.1404	1.03034	1.42089
0.2625	1.03131	1.42112	0.1946	1.03115	1.42129
0.3508	1.03235	1.42155	0.2768	1.03242	1.42182
0.4430	1.03340	1.42197	0.3432	1.03335	1.42218
0.5365	1.03443	1.42236	0.4108	1.03429	1.42259
0.6405	1.03557	1.42279	0.4856	1.03536	1.42302
0.7175	1.03639	1.42306	0.5586	1.03632	1.42344

Table 3. Density, d, and refractive index, n_D, of benzene solutions of *DEG*, *TEG*, and *TTEG* at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	$d/\text{g}\cdot\text{cm}^{-3}$	n_D	$m/\text{mol}\cdot\text{kg}^{-1}$	$d/\text{g}\cdot\text{cm}^{-3}$	n_D
DEG			*TEG*		
0.0224	0.87393	1.49779	0.0229	0.87410	1.49770
0.0564	0.87459	1.49761	0.1074	0.87652	1.49725
0.0962	0.87538	1.49744	0.2053	0.87923	1.49671
0.1374	0.87623	1.49728	0.3066	0.88203	1.49628
0.1768	0.87700	1.49709	0.4087	0.88484	1.49582
0.2159	0.87793	1.49687	0.5164	0.88767	1.49530
0.2763	0.87886	1.49666	0.6140	0.89018	1.49487
0.3192	0.87966	1.49651	0.7200	0.89280	1.49445
0.3639	0.88052	1.49632	0.8399	0.89572	1.49371
TTEG					
0.0153	0.87415	1.49779			
0.0865	0.87673	1.49731			
0.1599	0.87933	1.49687			
0.2393	0.88210	1.49637			
0.3170	0.88476	1.49594			
0.3968	0.88732	1.49556			
0.5139	0.89131	1.49489			
0.5649	0.89295	1.49461			
0.6781	0.89656	1.49407			

where Y^0_{app} represents the apparent molar quantity of the solute at infinite dilution, equal to the limiting partial molar quantity of solute, $\overline{Y}^0_2$, and $b_y, b_{yy}\ldots$ are constants which depend on the solute, solvent and temperature. By combining Eqs. (1) and (2), the following relation can be obtained

$$y = y^0_1 + Y^0_{\mathrm{app}} m + b_y m^2 + b_{yy} m^3 + \cdots \tag{3}$$

from which the values of Y^0_{app} and parameters $b_y, b_{yy}\ldots$ can be calculated by least squares fitting to Eq. (3).

From the density data given in Tables 2, 3, and 4, the apparent molar volume of solute at infinite dilution, $V^0_{\mathrm{app}} \equiv \overline{V}^0_2$, and parameter b_v were calculated from Eq. (3), where $y = v = (10^3 + mM_2)/d^a$ and $y^0_1 = v^0_1 = 10^3/d^{0\mathrm{a}}_1$; v and v^0_1 are the volume of the solution and solvent and M_2 is the molecular weight of solute. For aqueous solutions a quadratic form of Eq. (3) was employed, while for 1,4-dioxane and benzene solutions a linear form of Eq. (3) is sufficient. The values of $\overline{V}^0_2$ and b_v are given in Table 4. The limiting apparent molar volumes are represented to within $\pm 0.10\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$. In analysing the experimental density data via Eq. (3), v^0_1 values differ by less than 0.01% from the values of the pure solvents calculated from the respective density data [8]. The limiting apparent molar volumes, determined in aqueous solution, are in good agreement with published data [4–6]. The difference is smaller than 0.15%. The volume of the aqueous

Table 4. Molar volume, *van der Waals* volume, surface ratio, limiting partial molar volume, coefficient of Eq. (3), ratio $V_{\mathrm{void}}/V_{\mathrm{W}}$ and packing density for the investigated compounds at 298.15 K

Comp.	$V^0_2/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$	$V_{\mathrm{W}}/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$	$\frac{A_{\mathrm{W,OH,O}}}{A_{\mathrm{W,t}}}$	Water				
				$\overline{V}^0_2/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$	$\overline{V}^0_2/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1\mathrm{b}}$	$-b_v$	$\frac{V_{\mathrm{void}}}{V_{\mathrm{W}}}$	$\frac{V_W}{\overline{V}^0_2}$
MEG	55.907	34.44	0.52	54.56 ± 0.01		0.042 ± 0.009	0.58	0.63
DEG	95.325	60.10	0.40	92.12 ± 0.03		0.197 ± 0.024	0.53	0.65
TEG	134.070	85.76	0.35	129.13 ± 0.08		0.394 ± 0.063	0.51	0.66
TTEG	173.322	111.42	0.32	166.20 ± 0.05		0.642 ± 0.054	0.49	0.67
				1,4-Dioxane				
MEG				55.40 ± 0.01	55.52 ± 0.23		0.61	0.62
DEG				95.33 ± 0.06	95.15 ± 0.13		0.59	0.63
TEG				134.09 ± 0.02	132.84 ± 0.20		0.56	0.64
TTEG				173.64 ± 0.04	173.82 ± 0.32		0.56	0.64
				Benzene				
DEG				95.35 ± 0.03			0.59	0.63
TEG				133.67 ± 0.06			0.56	0.64
TTEG				173.41 ± 0.10			0.56	0.64

[b] Calculated from the density data in Ref. [12]

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[a] The numerical value 10^3, which is in a strict sense not consistent with quantity calculus, originates from the use of different mass units for molality (1 kg), molar mass (1 g) and density (1 g)

solutions investigated, v, show a distinctive concentration dependence. The value of the parameter b_v almost linearly decreases with an increasing number of –CH_2–CH_2–O– units in the molecule of poly(oxyethylene) glycol (slope equals -0.20), i.e. with increasing hydrophobic character of the solute, as was also found by *Harada et al.* [4]. The values of b_v are generally thought to be proportional to the volume change of the hydrated molecules with increasing solute concentration [9]. This is assumed to be a consequence of the overlap of the hydration co-spheres of the solute pair or to the redistribution of water among the solute molecules when pairing does not occur. Thus, the values of b_v could yield some information on solute–solute as well as solute-solvent interactions. For the investigated solutes the values of g_{22} characterise the contributions to the excess Gibbs energy due to the two-body solute interactions in solution containing $1\,\mathrm{mol \cdot kg^{-1}}$ of solute [10]. Since g_{22} values are positive [11], the solutes can be classified as hydrophylic structure-making solutes for which associative phenomena are not favoured. For such a solute, according to *Wurzburger et al.* [9], the distribution of water between the hydration co-spheres occurs in such a way that a hydrated solute molecule of volume V releases water molecules occupying a volume V_R in the co-sphere to a volume of αV_R in the bulk. Thus, the total volume change for such a process is given by Eqs. (4) and (5)

$$\Delta V = V_R(\alpha - 1) \tag{4}$$

$$b_v = KV_R(\alpha - 1) \tag{5}$$

where K is a constant of proportionality. Since for the investigated systems (aqueous solutions) $b_v < 0$, from Eq. (5) it follows that $\alpha < 1$, which means that water molecules in the bulk occupy a volume smaller than in the co-sphere. If $b_v = 0$, from Eq. (5) it follows that $\alpha = 1$, which means that in the solvation process there is no volume change; *i.e.* the same number of solvent molecules occupy the same volume in the co-sphere as in the bulk. Such behaviour was found for 1,4-dioxane and benzene solutions (see Table 4).

The limiting apparent molar volumes of the investigated compounds, determined in 1,4-dioxane, are within experimental uncertainties equal to those values calculated from the density data given in Ref. [12] by the above procedure, except for *TEG* where the difference is rather large, *i.e.* $1.25\,\mathrm{cm^3 \cdot mol^{-1}}$ (see Table 4). For the 1,4-dioxane system we extended the homologous series up to the heptamer by calculation of their $\overline{V}_2^0$ values from the density data [12] and obtained the following values: penta(oxyethylene) glycol (*PTEG*): 212.95 ± 0.21; hexa(oxyethylene) glycol (*HXEG*): 251.43 ± 0.11, and for hepta(oxyethylene) glycol (*HPEG*): $292.99 \pm 0.30\,\mathrm{cm^3 \cdot mol^{-1}}$.

The value of $\overline{V}_2^0$ for the investigated systems depends linearly on the number of –CH_2–CH_2–O– units, n, as shown in Eq. (6)

$$\overline{V}_2^0 = a_0 + a_1 n \tag{6}$$

where a_0 and a_1 are empirical constants given in Table 5 together with the statistical parameters, *i.e.* the correlation coefficient, r, and the standard error of the estimate, s. In calculation of constants a_0 and a_1 we used both values of $\overline{V}_2^0$, *i.e.* our own and literature values [4, 5, 12], except for *TEG* in 1,4-dioxane solutions where

Table 5. Values of constants a_0 and a_1 in Eq. (6)

Solvent	a_0	a_1	r	s
water	17.6 ± 0.1	37.21 ± 0.04	0.9999	0.2
1,4-dioxane	16.1 ± 0.4	39.41 ± 0.09	0.9999	0.6
benzene	17.0 ± 1.3	39.03 ± 0.41	0.9999	0.6

we omitted the value of $\overline{V}_2^0$ for *TEG*. Both of the constants of Eq. (6) are solvent dependent. The volume of the –CH_2–CH_2–O– unit is practically equal for non-aqueous solvents ($39.22 \pm 0.42\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$) and smaller for the aqueous solution ($37.21 \pm 0.04\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$). This value is close to the value of $37.08\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ obtained by *Harada et al.* [4]. The experimental volume of the –CH_2–CH_2–O– unit in aqueous solution is considerably less than the value of $38.83\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ calculated by the group contribution method given by *Cabani et al.* [13]. It is interesting to note that a value of $36.9\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ was obtained from the dependence of partial specific volume at infinite dilution of some poly(oxyethylene) glycols on the degree of polymerisation [4, 14, 15]. This value is close to the value of $36.1\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ which was calculated from the group contribution data given by *Zana* [16] for the repeating units of non-ionic polymers in aqueous solution.

In Table 4 the molar volume, V_2^0, and the *van der Waals* molar volume, V_W, are also given. The *van der Waals* volume was calculated by the *Bondi* approach corrected for hydrogen bonding for each –OH group [17]. From the collected data of $\overline{V}_2^0$ given in Table 4 it is evident that the values of $\overline{V}_2^0$ determined in 1,4-dioxane or benzene solutions are practically equal to the molar volume, while the values of $\overline{V}_2^0$ determined in aqueous solution are considerably smaller due to intensive hydrogen bonding of terminal –OH groups and ether oxygen atoms with water molecules. It was shown by *Teresava et al.* [18] that the limiting partial molar volume for a series of hydrocarbons and alkanols depends linearly on the *van der Waals* volume of the solute. Such a linear dependence was also observed for the investigated systems. If it is assumed that V_W does not change in solution, then $\overline{V}_2^0 - V_W$ should be the volume of the void space created by the addition of 1.0 mol of solute to the solvent [19]. Thus, the partial molar volume at infinite dilution can be described by Eq. (7)

$$\overline{V}_2^0 = V_W + \overline{V}_{\mathrm{void}} \tag{7}$$

From Table 4 it may be seen that the ratio of $\overline{V}_{\mathrm{void}}$ to V_W decreases almost linearly for aqueous solutions with increasing hydrophobicity of the solute molecule and with the fraction of the surface of the molecule, which can act as a proton acceptor or proton donor (surface of the –OH group and O atom), $A_{W,OH,O}$, to the total surface of the molecule, $A_{W,t}$, calculated from the *Bondi* values [17]. In Table 4 the packing densities of the investigated glycols are also given. The packing density of a solute in solution is defined as the ratio of its *van der Waals* volume to its limiting partial molar volume [20]. It has been shown that for a given class of molecular solute the packing density approaches a uniform value as the size of the molecule increases. From the results given in Table 4 it can be seen that the packing density of the investigated glycols gradually increases with the number of –CH_2–CH_2–O– units for all the solvents used and approaches a plateau which is substantially greater for water than for the other two solvents. *Bernal* and *Finney* [21] 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. The packing density plateaus for 1,4-dioxane and benzene solutions (0.64) are somewhat higher for example than for amines [13].

The density and refractive index given in Tables 1–3 were used to calculate the refraction of the solutions, *i.e.* $y = r = (n_D^2 - 1)v/(n_D^2 + 2)$. For the investigated systems the refraction of the solution can be adequately represented by the linear form of Eq. (3). The values of $R^0_{\mathrm{app}} \equiv \overline{R}^0_2$ are given in Table 6. The parameter $y^0_1 \equiv r^0_1 = [(n^0_{D_1})^2 - 1]v^0_1/[(n^0_{D_1})^2 + 2]$ in Eq. (3), obtained by fitting the experimental data to Eq. (3), differ by less than 0.01% from the corresponding values of pure solvents calculated from the respective density and refraction data [8]. The values of $\overline{R}^0_2$ given in Table 6 and presented to within $0.10\,\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$, do not show an appreciable solvent effect. Such behaviour is a generally expected property of infinite dilution data. Then, we calculated their weighted averages using as weighting factors the reciprocal of the square of the uncertainties, $\delta\overline{R}^0_2$. These averages are

Table 6. Molar and calculated refraction of solute, partial molar refraction of solute at infinite dilution, and electronic polarizability of solute at 298.15 K

Comp.	$R^0_2/\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$	$R_{\mathrm{cal}}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$	Solvent $\overline{R}^0_2/\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$				$\alpha_e\cdot 10^{23}/\mathrm{cm}^3\cdot\mathrm{molecule}^{-1}$
			Water	1,4-Dioxane	Benzene	Average values	
MEG	14.46	14.49	14.41 ± 0.01	14.41 ± 0.02	–	14.41 ± 0.02	0.5712
DEG	25.42	25.37	25.29 ± 0.02	25.49 ± 0.02	25.41 ± 0.10	25.37 ± 0.01	1.0056
TEG	36.36	36.22	36.16 ± 0.01	36.39 ± 0.02	36.19 ± 0.05	36.24 ± 0.01	1.4368
TTEG	47.32	47.12	47.04 ± 0.03	47.42 ± 0.02	47.20 ± 0.10	47.26 ± 0.02	1.8735

Table 7. Comparison of density, *d*, and refractive index, n_D, of compounds used at 298.15 K

Compound	$d/\mathrm{g}\cdot\mathrm{cm}^{-3}$		n_D	
	Exp.	Lit.	Exp.	Lit.
1,4-dioxane	1.02821	1.02803[a]	1.41998	1.42025[a]
benzene	0,87357	0,87360[a]	1.49790	1.49792[a]
MEG	1.11020	1.10999[b] 1.1100[a]	1.43048	1.4306[a]
DEG	1.11326	1.11297[b]	1.44590	1.4461[a]
TEG	1.12012	1.11991[b] 1.1195[a]	1.45479	1.4541[a]
TTEG	1.12061	1.12030[b]	1.45833	

[a] Ref. [8]; [b] Ref. [24]

taken to represent the molar refractions of the solute at infinite dilution and are used for further calculation. From the density and refractive index of the pure compounds given in Table 7, the molar refraction of pure solute, R_2^0, was calculated by the *Lorenz–Lorentz* relation [22]. The values of R_2^0 differ by less than $0.10\,\mathrm{cm^3\cdot mol^{-1}}$ from the corresponding average values of $\overline{R}_2^0$. In Table 6 values of R_{cal}, *i.e.* the molar refraction of solute, calculated from the atomic and atomic group contribution data [23] are given. The values obtained are within $0.20\,\mathrm{cm^3\cdot mol^{-1}}$ equal to the values of the experimental molar refraction of the solute, R_2^0. Usually the molar refraction of the solute is obtained from the group contributions and very few experimental values have been reported. The present study provides such data from the measurements of the refractive index and density of the pure compounds as well as their solutions. Although values of R_{app} can in principle depend on the solvent and the concentration of solute because of self-association of solute molecules, no evidence for such behaviour of the investigated compounds can be detected from the above refraction data (see Table 6).

The electronic polarizability of solute molecule, α_e, was calculated from the values of $\overline{R}_2^0$ using the *Clausius-Mossotti* relation [22]. The values of α_e are given in Table 6 and depend linearly on the number of $-CH_2-CH_2-O-$ units, with an increment of $(0.43381 \pm 0.00071)\cdot 10^{-23}\,\mathrm{cm^3\cdot molecule^{-1}}$. The ratio of electronic polarizability to the molecular *van der Waals* volume is constant and amounts to 0.1007 ± 0.0005 independent of the number of $-CH_2-CH_2-O-$ units in the solute molecule. A review of experimental results for the *Lorenz–Lorentz* expression showed that satisfactory additivity in a given homologous series exists [23]. For the investigated compounds we found good additivity when we plotted $\overline{R}_2^0$ against the number of $-CH_2-CH_2-O-$ units. The data lie on a straight line with a correlation coefficient of 0.99996 and a slope of $10.93 \pm 0.03\,\mathrm{cm^3\cdot mol^{-1}}$ and an intercept of $3.50 \pm 0.09\,\mathrm{cm^3\cdot mol^{-1}}$. So, the molar refraction of $-CH_2-CH_2-O-$ units is $10.93\,\mathrm{cm^3\cdot mol^{-1}}$. The corresponding plots of R_2^0 or R_{cal} *vs.* the number of $-CH_2-CH_2-O-$ units give data which, within experimental uncertainties, are close to the above values.

Experimental

Materials

1,4-Dioxane (Kemika, p.a.) and benzene (Fluka, A.G., for HPLC) were used directly without further purification. Ethylene glycol (*MEG*), di(oxyethylene) glycol (*DEG*), tri(oxyethylene) glycol (*TEG*), and tetra(oxyethylene) glycol (*TTEG*) (all supplied by Fluka, A.G.) were used as delivered and stored in a desiccator over P_2O_5. The purity of each compound was checked by comparing its density and refractive index with data reported earlier. Experimental values of density and refractive index of the pure compounds, along with literature values at 298.15 K, are given in Table 7.

Density Measurements

The density was measured with a vibrating tube digital densimeter (model DMA 601, Anton Paar, Graz, Austria), calibrated with air and water at a temperature of 298.15 K. The thermal stability of the measuring cell was checked by an Anton Paar digital thermometer (DT 100-20) and was better than ±0.01 K. The accuracy of the density measurements was estimated as $2\cdot 10^{-5}\,\mathrm{g\cdot cm^{-3}}$.

Refractive Index Measurements

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

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