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Osmotic Coefficients of Aqueous Solutions of Some Poly(oxyethylene) Glycols at the Freezing Point of Solution

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Summary. The freezing temperatures of dilute aqueous solutions of some poly(oxyethylene) glycols (*PEG*, HO–$(CH_2CH_2O)_n$–H, n varying from 4 to 117) were measured over a solute to solvent mass ratio from 0.0100 to 0.3900. The second and third osmotic virial coefficient (A_{22} and A_{222}) of poly(oxyethylene) glycols in aqueous solution were determined. The molecular weight dependence of the second virial coefficient can be described by a simple relation $A_{22} = 2 \times 10^{-5} M_n^{1.86}$, and the third virial coefficient is $A_{222} = 0.038\, A_{22}^2$. The activity coefficients of the solute were calculated using the *Gibbs-Duhem* equation as applied by *Bjerrum*. From the osmotic and activity coefficients the excess *Gibbs* energies of solution, as well as the respective partial molar functions of solute and solvent and the virial pair interaction coefficients for the excess *Gibbs* energies were estimated. The second and the third osmotic virial coefficients are correlated with the *Mc-Millan-Mayer* virial coefficients.

Keywords. Poly(oxyethylene) glycols; Water solutions; Excess *Gibbs* energy; Solute activity coefficients.

Introduction

In recent years water-soluble polymers have found increasing industrial applications such as additives to pharmaceuticals, detergents, cosmetics, and food [1]. They have for many years received less than their share of the considerable scientific effort which has been devoted to the study of the structure and properties of the broad mass of macromolecular systems. In the literature many theoretical studies describing polymer solutions can be found, *e.g.* [2]. Most of these theories are not useful for a description of aqueous polymer systems [3, 4]. All polymer solution theories mentioned so far neglect the highly ordered structure of water. Non-ionic water-soluble polymers exhibit solution properties which differ greatly from those of other polymers in organic solvents. The solution properties of water-soluble

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polymers are governed by interactions between the macromolecules, by the polymer conformation, and by intramolecular interactions between solute and solvent molecules. The relevant parameters to describe such systems can be obtained, for example, by measurement of the thermodynamic activity of the solvent.

Among water-soluble polymers poly(oxyethylene) glycol, *PEG*, is the most studied compound. Its simple molecular structure, HO–$(CH_2CH_2O)_n$–H, makes *PEG* a good model system for studying water structuring effects in macromolecular solutions. The properties of dilute aqueous solutions of *PEG* have been studied by various authors. Most of these investigations were based on experimental methods which yield the thermodynamic activity of the solvent. A comprehensive survey of the literature data is given in Ref. [5]. No association of *PEG* in water was found by *Elias* and *Lys* [6] by vapour pressure osmometry. On the other hand, *Burchard* [7] observed the presence of large aggregates by light scattering measurements of aqueous solutions of *PEG*. The aggregation was explained by hydrophobic interaction which drives the polymers together. A layer of strongly bound water, about two molecules of water for each monomeric unit, was postulated [8]. However, estimates of the hydration numbers found in literature vary from less than one to more than five [9]. The only exception are hydration numbers estimated by viscometry. Thus in aqueous solutions *PEG* may in fact be considered as water-coated chains, which are now provided with the functional groups for aggregation via H-bonds [10].

In the present work, the osmotic coefficients of dilute aqueous solutions of *PEG* were measured by a cryoscopic method to describe their thermodynamic properties. The experimental results are evaluated to determine second and third osmotic virial coefficients. The osmotic coefficient of dilute aqueous solutions of *PEG* was measured in the past. Thus, *Alexandrowicz* [11] determined the osmotic coefficient of an aqueous *PEG* solution with a molecular weight of 8000 at 298.15 K. Recently, *Gao et al.* [12] measured the monomer glycol and some *PEG*'s with molecular weights from 200 to 2000 in the temperature range from 313 to 333 K with a vapour pressure osmometer. They found that at a definite temperature the osmotic coefficients of aqueous solutions increased with increasing molecular weight of *PEG*.

Results and Discussion

In an aqueous dilute polymer solution, the chemical potential of water, μ_1, is related to its rational osmotic coefficient, g, by

$$\mu_1 = \mu_1^0 + gRT \ln x_1 \tag{1}$$

where superscript ^{0} designates the standard state, here taken as pure water, T is the absolute temperature, R the gas constant, and x_1 is the mole fraction of water. The experimental variable obtained is usually the practical molal osmotic coefficient, ϕ, which for polydispersed polymers may be given as [13]

$$\phi = g\left[1 - \frac{1}{2}\sum_{i=2}^{N} m_i M_1 + \frac{1}{3}\left(\sum_{i=2}^{N} m_i M_1\right)^2 - \cdots\right] \tag{2}$$

where M_1 is the molecular weight of water ($\mathrm{kg\,mol^{-1}}$) and $\sum_{i=2}^{N} m_i$ is the sum of the molalities of the oligomers i equal to the polymer molality m, *i.e.* $m = \sum_{i=2}^{N} m_i$. The indices 2 to N refer to the oligomers. The practical molal osmotic coefficient can also be related to [14]

$$\phi = \frac{\pi}{\pi_{id}} \tag{3}$$

where π and π_{id} are the osmotic pressures of a real and ideal solution. A different way of representing the concentration-dependent non-ideality of a polymer solution is through the molal activity coefficient of the macromolecular component. The molal activity coefficient of a polymer solute, γ, can be obtained from *Bjerrum*'s relation in the form

$$d[(1-\phi)m] + md\ln\gamma = 0 \tag{4}$$

The practical molal osmotic coefficient of aqueous solutions of poly(oxyethylene) glycols was calculated from the freezing point depression, ΔT_f, using the relation [15]

$$\phi = \frac{\Delta T_f}{1.8560\,m} \tag{5}$$

Higher terms in relation (5) were ignored as they contribute less than 0.001 to ϕ at the highest molality used.

The experimental values for the practical molal osmotic coefficient are given in Table 1. They are accurate within 0.5%. From Table 1 it can be seen that the practical molal osmotic coefficients increase with increasing mass ratio and that their values strongly depend on the molecular weight of the polymer solute. They are well represented by the equation

$$\phi = 1 + A_{22}m + A_{222}m^2 \tag{6}$$

where A_{22} ($\mathrm{kg\,mol^{-1}}$) and A_{222} ($\mathrm{kg^2\,mol^{-2}}$) are the second and third virial osmotic coefficients. For some of the polymer solutes even a linear form of Eq. (6) is sufficient. The coefficients in Eq. (6) are measures of the solute–solute interactions at the freezing temperatures of the solutions [16]. The values of the virial osmotic coefficients of Eq. (6) and the standard deviation of the fit, s, calculated by the method of least squares, are given in Table 2.

The values of ϕ against mass ratio, r_m, for some of the investigated solutes are shown in Fig. 1. The solid lines were drawn on the basis of Eq. (6) using the corresponding virial osmotic coefficient given in Table 2.

From Table 2 it can be seen that the virial osmotic coefficients A_{22} and A_{222} depend on the molecular weight of the polymer solutes. In Fig. 2 $\log A_{22}$ is plotted against $\log M_n$. It can be seen that this relation is linear with an intercept of -4.702 ± 0.084 and a slope of 1.858 ± 0.027. Thus A_{22} can be given as $A_{22} = 2\times10^{-5}\,M_n^{1.86}$. This relation is in accordance with the theory of dilute polymer solutions [3], from which follows that the second virial osmotic coefficient depends not only on the molecular weight of the solute, but also on the thermodynamic interaction parameters which characterize the segment–solvent interaction and also the configuration or "size" of the macromolecule in solution. In contrast

Table 1. Freezing point depression, practical molal osmotic coefficient, logarithm of molal activity coefficient of solute, excess *Gibbs* free energy, and partial molal excess *Gibbs* energy of solute and solvent at the freezing point of solution

r_m	$\Delta T_f/\mathrm{K}$	ϕ	$\ln\gamma$	$\Delta G^{ex}/\mathrm{J\,kg^{-1}}$	$\Delta\bar{G}_2^{ex}/\mathrm{J\,mol^{-1}}$	$-\Delta\bar{G}_1^{ex}/\mathrm{J\,mol^{-1}}$
PEG-200						
0.01016	0.100	1.017	0.0421	2.5	96	0.05
0.03464	0.363	1.079	0.1399	29	318	0.5
0.06138	0.666	1.116	0.2411	90	548	1.6
0.09811	1.125	1.180	0.3706	224	842	3.8
0.11557	1.360	1.211	0.4282	307	972	5.1
0.13497	1.616	1.232	0.4892	413	1111	6.7
0.16620	2.056	1.273	0.5809	612	1319	9.7
0.19345	2.436	1.296	0.6545	812	1486	12.5
PEG-300						
0.01412	0.091	1.036	0.0790	4	54	0.08
0.04642	0.326	1.128	0.2564	46	582	0.8
0.08242	0.626	1.220	0.4463	142	1014	2.5
0.11602	0.938	1.298	0.6167	278	1401	4.8
0.14738	1.259	1.371	0.7698	444	1748	7.6
0.18033	1.630	1.451	0.9242	657	2099	11.0
0.21590	2.043	1.519	1.0837	930	2461	15.3
0.23999	2.341	1.566	1.1875	1138	2697	18.6
PEG-400						
0.02135	0.113	1.057	0.1159	8	263	0.14
0.05553	0.320	1.148	0.3033	52	689	0.9
0.08498	0.529	1.241	0.4663	121	1059	2.2
0.11013	0.729	1.319	0.6065	204	1377	3.7
0.15182	1.084	1.424	0.8417	389	1911	7.1
0.18463	1.407	1.519	1.0288	577	2337	10.6
0.20851	1.649	1.577	1.1661	738	2649	13.6
0.23174	1.925	1.656	1.3008	914	2954	16.9
PEG-600						
0.03038	0.119	1.123	0.2316	15	526	0.3
0.06790	0.294	1.244	0.5177	75	1176	1.3
0.11367	0.563	1.426	0.8666	210	1968	3.8
0.14823	0.807	1.566	1.1299	356	2566	6.4
0.17520	1.019	1.673	1.3354	498	3033	9.0
0.22729	1.480	1.873	1.7323	837	3934	15.1
0.26572	1.865	2.019	2.053	1144	4600	20.6
0.28487	2.057	2.077	2.1715	1316	4932	23.7
PEG-900						
0.04535	0.123	1.296	0.6855	34	1325	0.6
0.09279	0.308	1.590	1.4121	142	2733	2.6
0.14622	0.603	1.979	2.2424	354	4347	6.5
0.18688	0.874	2.242	2.8837	581	5595	10.7

(*continued*)

Table 1 (*continued*)

r_m	$\Delta T_f/\mathrm{K}$	ϕ	$\ln\gamma$	$\Delta G^{ex}/\mathrm{J\,kg^{-1}}$	$\Delta\bar{G}_2^{ex}/\mathrm{J\,mol^{-1}}$	$-\Delta\bar{G}_1^{ex}/\mathrm{J\,mol^{-1}}$
0.23696	1.295	2.622	3.6829	939	7155	17.4
0.28307	1.708	2.893	4.4312	1349	8619	25.0
0.32710	2.226	3.263	5.1526	1809	10032	33.8
PEG-1000						
0.04338	0.108	1.343	0.6540	32	1485	0.6
0.09080	0.280	1.668	1.3671	140	3105	2.5
0.13666	0.509	2.016	2.0590	318	4676	5.7
0.18911	0.841	2.409	2.8493	609	6471	11.0
0.23230	1.174	2.738	3.4988	918	7946	16.5
0.27780	1.575	3.071	4.1846	1313	9504	23.7
0.32520	2.079	3.461	4.8992	1800	11126	32.4
0.37124	2.623	3.826	5.5926	2346	12701	42.3
PEG-1500						
0.03403	0.058	1.451	0.8290	20	1883	0.4
0.09151	0.224	2.096	2.2106	145	5021	2.6
0.15459	0.513	2.842	3.7305	412	8472	7.4
0.20359	0.815	3.430	4.9126	714	11156	12.9
0.26827	1.344	4.292	6.4746	1240	14704	22.3
0.32699	1.914	5.013	7.8947	1844	17929	33.2
0.38896	2.578	5.679	9.3877	2607	21320	47.0
PEG-2000						
0.03274	0.044	1.521	0.9288	17	2109	0.3
0.06272	0.104	1.871	1.7960	61	4079	1.1
0.08940	0.185	2.330	2.5836	124	5868	2.3
0.12417	0.315	2.855	3.6434	242	8275	4.5
0.15439	0.464	3.387	4.5796	376	10400	7.1
0.18813	0.653	3.913	5.6508	563	12833	10.6
0.21511	0.834	4.370	6.5277	742	14825	14.1
0.24965	1.096	4.948	7.6735	1008	17427	19.3
0.31167	1.662	6.010	9.8042	1596	22266	31.0
PEG-3000						
0.03332	0.035	1.632	1.2678	16	2879	0.3
0.06898	0.104	2.374	2.6685	71	6060	1.3
0.10369	0.201	3.053	4.0663	161	9235	3.0
0.12525	0.278	3.497	4.9646	237	11275	4.4
0.16923	0.485	4.512	6.8492	439	15555	8.3
0.20492	0.696	5.352	8.4227	651	19128	12.4
0.24307	0.965	6.259	10.149	924	23049	17.8
0.27550	1.230	7.035	11.664	1200	26489	23.3
PEG-4000						
0.03947	0.035	2.156	2.3181	23	5265	0.4
0.07230	0.096	3.264	4.3441	77	9866	1.4

(*continued*)

Table 1 (*continued*)

r_m	$\Delta T_f/\mathrm{K}$	ϕ	$\ln\gamma$	$\Delta G^{ex}/\mathrm{J\,kg^{-1}}$	$\Delta\bar{G}_2^{ex}/\mathrm{J\,mol^{-1}}$	$-\Delta\bar{G}_1^{ex}/\mathrm{J\,mol^{-1}}$
0.10936	0.197	4.405	6.7531	180	15336	3.4
0.14689	0.347	5.794	9.2767	329	21068	6.3
0.17295	0.475	6.735	11.098	461	25205	8.9
0.20828	0.698	8.207	13.681	681	31071	13.4
0.24274	0.942	9.508	16.297	939	37013	18.7
0.28168	1.289	11.219	19.340	1283	43924	25.9
PEG-6000						
0.05540	0.056	2.788	3.4728	42	7887	0.8
0.08468	0.116	3.786	5.4664	100	12414	1.9
0.12041	0.222	5.090	8.0179	207	18209	4.0
0.15731	0.378	6.615	10.805	361	24540	7.1
0.18238	0.514	7.762	12.785	492	29037	9.8
0.21402	0.712	9.171	15.384	690	34938	13.9
0.25581	1.024	11.026	18.998	1009	43146	20.7
0.28808	1.339	12.807	21.921	1302	49785	27.0

Table 2. Values of the number average molecular weights and virial osmotic coefficients for aqueous solutions of some poly(oxyethylene) glycols at the freezing point of solution

Solute	M_n	$A_{22}/\mathrm{kg\,mol^{-1}}$	$A_{222}/\mathrm{kg^2\,mol^{-2}}$	s
PEG-200	191 ± 1	0.400 ± 0.008	-0.100 ± 0.010	0.006
PEG-300	298 ± 1	0.843 ± 0.006	-0.175 ± 0.011	0.003
PEG-400	370 ± 2	1.001 ± 0.020	0.079 ± 0.050	0.01
PEG-600	534 ± 4	2.04 ± 0.07	–	0.01
PEG-900	890 ± 33	5.67 ± 0.09	1.221 ± 0.4	0.02
PEG-1000	1005 ± 14	7.6 ± 0.2	–	0.02
PEG-1500	1590 ± 62	19.2 ± 0.3	–	0.04
PEG-2000	2092 ± 84	29.2 ± 0.6	33.2 ± 6	0.05
PEG-3000	2925 ± 107	54.7 ± 0.3	101.5 ± 5	0.02
PEG-4000	4547 ± 321	129.8 ± 1.6	568.6 ± 40	0.05
PEG-6000	5113 ± 590	152.8 ± 1.6	989 ± 43	0.06

to non-aqueous dilute polymer solutions, *e.g.* polyisobutylene fractions in cyclohexane or polystyrene fractions in toluene, where $\log A_{22}$ decreases linearly with increasing $\log M_n$, the aqueous solutions of poly(oxyethylene) glycols show an opposite trend. According to *Berry* and *Cassasa* [17] the second virial coefficient for a polydisperse system of i solute components may be given in terms of the composition of the solute mixture and $i(i+1)/2$ virial coefficients, A_{ij}, for interactions between solute components. So A_{22} is given by

$$A_{22} = \sum_i \sum_j A_{ij} w_i w_j \tag{7}$$

with sums running over all solutes $2, \ldots i$ and w_i is the mass fraction of the solute of the species with molecular weight M_i. The molecular weight dependence of A_{22}

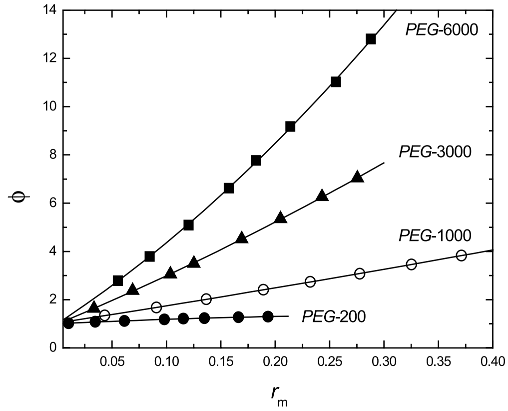

Fig. 1. Dependence of the practical molal osmotic coefficient on mass ratio for some poly(oxyethylene) glycols at the freezing point of solution

was explained by the excluded volume effect caused by the intermolecular interactions of the polymers [18].

The dependence of A_{22} on the molecular mass of the poly(oxyethylene) glycol was also found earlier by many authors [2, 6, 19–22]. So, for example the molecular weight dependence of the second osmotic coefficients of *Gaube et al.* [19] can be described by a function of the type $A_{22} = f(M_n^{-0.31})$ and those of *Elias* and *Lys* [6] by $A_{22} = f(M_n^{-0.5})$. In contradiction to these literature data, *Hasse et al.* [5] found that neither A_{22} nor A_{222} depends on the molecular mass of poly(oxyethylene) glycol. According to these authors the observed differences in A_{22} values can be explained by the lack of accuracy in the measurements of the activity of water at low polymer concentrations. The activity of water in the polymer solution hardly differs from that of pure water. Like the second virial osmotic coefficient, the A_{222} values increase with molecular weight of solute where for the lower members of the investigated poly(oxyethylene) glycols, A_{222} values are even negative. In Fig. 2 the dependence of $\log A_{222}$ against $\log M_n$ is shown. From this figure can be seen

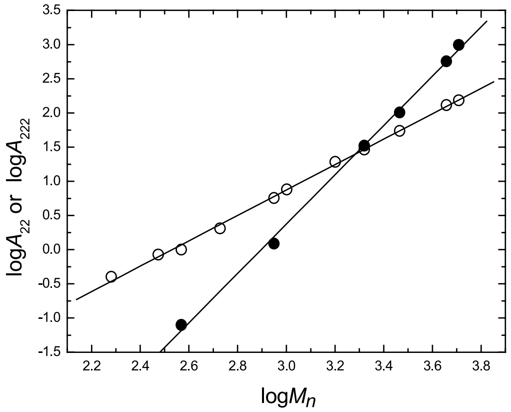

Fig. 2. Dependence of $\log A_{22}$ and $\log A_{222}$ on $\log M_n$ for aqueous solutions of poly(oxyethylene) glycols at the freezing point of solution; ○ – $\log A_{22}$, ● – $\log A_{222}$

that beyond a nominal molecular weight of *PEG*-900 this dependence is linear with an intercept of -11.09 ± 0.19 and a slope of 3.79 ± 0.06. It can be shown that the third virial osmotic coefficient depends on A_{22} as $A_{222} = 0.038 A_{22}^2$. This result is indicative of a strong dependence of the third virial osmotic coefficient on the second one. The important conclusion remains that A_{222} rapidly vanishes as A_{22} decreases toward zero (see Table 2). Such behaviour was predicted by *Flory* [3] who gives the following relation between the two virial osmotic coefficients

$$A_{222} = g A_{22}^2 \tag{8}$$

where g is a slowly varying function whose value equals $5/8$ for a good solvent.

The molal activity coefficient of a macromolecular solute, $\ln \gamma$, was calculated using Eq. (4) and considering Eq. (6) as

$$\ln \gamma = \sum_{i=2}^{N} \ln \gamma_i = 2 A_{22} m + \frac{3}{2} A_{222} m^2 \tag{9}$$

From Eq. (9) it follows that the solute molal activity coefficient γ, for a macromolecular solute, containing i macromolecular components, each of molecular weight M_i and concentration m_i is given by the product of the γ_i values

$$\gamma = \prod_{i=2}^{N} \gamma_i \tag{10}$$

The values of $\ln \gamma$ for the systems investigated are given in Table 1. The dependence of $\ln \gamma$ on mass ratio of solute is similar to that observed for the molal osmotic coefficients (see Table 1); $\ln \gamma$ values increase with increasing mass ratio and with increasing molecular weight of solute. In Fig. 3 the dependence of $\ln \gamma$ on mass ratio of some poly(oxyethylene) glycols is presented.

At normal pressure the virial osmotic coefficients A_{22} and A_{222} are functions only of temperature and the nature of the solvent and solute. The first application of the *McMillan-Mayer* theory to solutions of flexible chain polymers was made by *Zimm* [23] and recently by *Döbert et al.* [24]. The calculations led to a dependence of the second virial coefficient on the molecular weight in

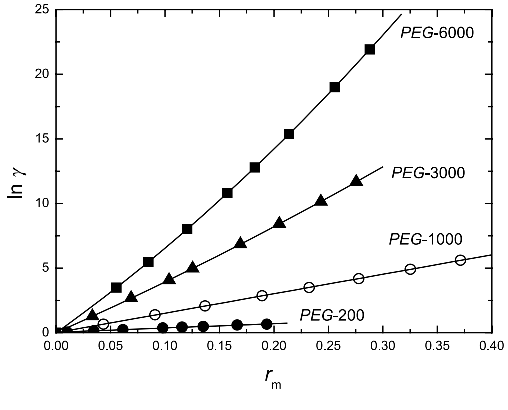

Fig. 3. Dependence of $\ln \gamma$ on mass ratio of some poly(oxyethylene) glycols at the freezing point of solution

contradiction with the early lattice theory. According to the *McMillan-Mayer* theory of solutions [25], the excess thermodynamic functions should be separated formally into contributions arising from pairs, triplets, *etc.* of the solute particles in a definite medium. So, the dependence of the practical molal osmotic coefficient on molality may be given by Eq. (11) where g_{22} and g_{222} are the average virial coefficients which characterize the contributions to the excess *Gibbs* free energy due to the two-body and three-body polymer interactions in aqueous solution containing $1\,\mathrm{mol\,kg^{-1}}$ of polymer.

$$\phi = 1 + \frac{g_{22}}{RT}m + \frac{2g_{222}}{RT}m^2 \tag{11}$$

Comparing Eq. (6) with Eq. (11), it follows that $g_{22} = A_{22}RT$ and $g_{222} = \frac{1}{2}A_{222}RT$. The values of g_{22} and g_{222} are positive, except of g_{222} for *PEG*-200 and *PEG*-300, and increase with increasing molecular weight of solute, as was also observed earlier for some lower members of the poly(oxyethylene) glycols [26]. The large and positive values of g_{22} and g_{222} indicate predominantly repulsive forces between oligomeric units when they come close together with the expulsion of water. In such a case the volume exclusion effects apparently dominate over the interactions [27]. According to the values of the virial coefficients obtained, it may be concluded that associative solute phenomena are not much favoured in these systems and that interactions between solute molecules are nearly negligible relative to solute-solvent interactions on account of the good structural fit between water and poly(oxyethylene) glycol molecules [8].

To represent the deviation from ideality of the investigated solutions, the excess *Gibbs* free energy of solution per kg of solvent, ΔG^{ex} ($\mathrm{J\,kg^{-1}}$) was calculated making use of Eqs. (9) and (11) [28]

$$\Delta G^{ex} = mRT(1 - \phi + \ln\gamma) = g_{22}m^2 + g_{222}m^3 \tag{12}$$

The calculated values are given in Table 1. Their average relative error calculated from Eq. (12), considering only the standard error of the virial coefficients, is less than 2%. The values of ΔG^{ex} are positive and increase with increasing mass ratio and with the chain length of the solute molecule, *i.e.* they show the same tendency in non-ideal behaviour as the osmotic and activity coefficients. We assume that the variation of the excess function with the content of ethylene oxide units is a superimposition of two effects: promotion of the supramolecular structure of water by apolar groups (–CH_2–) and its destruction by the polar groups of the solute (–O– and terminal –OH), and/or formation of hydrogen bonds between water and polar groups [26]. The excess *Gibbs* free energy of solution can also be given by Eq. (13) where n_1 is the number of moles of water, equal to $1/M_1$ and $\Delta\bar{G}_i^{ex}$ is the partial molal excess *Gibbs* free energy of component i of solution ($i = 1$ for solvent; $i = 2$ for solute) as defined by Eq. (14)

$$\Delta G^{ex} = n_1\Delta\bar{G}_1^{ex} + m\Delta\bar{G}_2^{ex} \tag{13}$$

and

$$\Delta\bar{G}_i^{ex} = \left(\frac{\partial\Delta G^{ex}}{\partial n_i}\right)_{T,P,n_j\neq n_i} \tag{14}$$

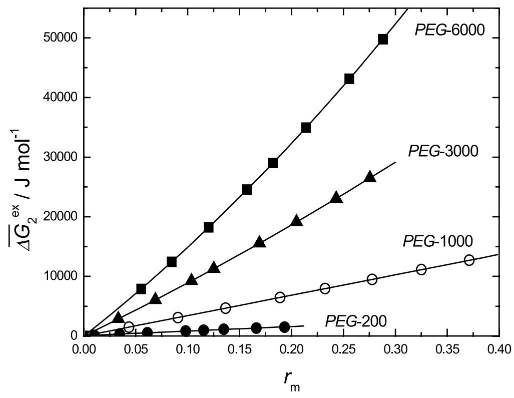

Fig. 4. Dependence of $\Delta\bar{G}_2^{ex}$ on mass ratio of some poly(oxyethylene) glycols at the freezing point of solution

The partial molal excess *Gibbs* free energy of solute and solvent, respectively, are calculated from

$$\Delta\bar{G}_2^{ex} = RT\ln\gamma = 2g_{22}m + 3g_{222}m^2 \tag{15}$$

and

$$\Delta\bar{G}_1^{ex} = M_1 mRT(1-\phi) = -M_1 g_{22}m^2 - 2M_1 g_{222}m^3 \tag{16}$$

and are given in Table 1. Their average relative errors are less than 2%. The $\Delta\bar{G}_2^{ex}$ values are high and positive and they increase with increasing molecular weight of the polymer solute, in contrast to the $\Delta\bar{G}_1^{ex}$ values which are small and negative and only slightly dependent on the molecular weight of the polymer solute. So, for example, the average value of $\Delta\bar{G}_1^{ex} = -6.9 \pm 0.6\,\mathrm{J\,mol^{-1}}$ at $r_m = 0.15$ and $-19.3 \pm 0.5\,\mathrm{J\,mol^{-1}}$ at $r_m = 0.25$. The same was observed earlier by *Kjellander* and *Florin* [8] for the excess partial *Gibbs* free energy of the system defined as $(\Delta G_1')^{ex} = \mu_1 - \mu_0$, which is also practically independent of the chain length, at least in the temperature interval 35–69.5°C. The negative value of $\Delta\bar{G}_1^{ex}$ may be ascribed to hydrogen bonding of the polymer and water molecules. The dependence of $\Delta\bar{G}_2^{ex}$ on mass ratio for some poly(oxyethylene) glycols is shown in Fig. 4. This dependence is analogous to that given in Fig. 3 for logarithms of solute activity coefficients. The relatively high and positive value of $\Delta\bar{G}_2^{ex}$ may be ascribed, as mentioned before, to repulsive forces between oligomeric units, *i.e.* to volume exclusion effects. Furthermore, at low temperature the structuring of water is enhanced around poly(oxyethylene) glycol molecules [8, 27].

Experimental

Materials

Samples of poly(oxyethylene) glycols (*PEG*) of different molecular weights, ranging from 200 to 6000, were supplied from Fluka Chemica (pract.). The compounds were dried at 120°C and stored in a desiccator over P_2O_5. Doubly distilled water was used in preparation of solutions. The concentration of solute was expressed as mass ratio, r_m, *i.e.* in grams of poly(oxyethylene) glycol per gram of water. The aqueous solutions were prepared gravimetrically using an electronic balance (Mettler Toledo) with a precision of 1×10^{-5} g.

Freezing Point Measurements

The freezing point depression of the solutions, ΔT_f, was measured with a Knauer cryoscopic unit, Model 7312400000, equipped with a strip chart recorder (Knauer Model 733.41). The freezing point depression was recorded as the difference in resistance of the thermistor ($\varDelta R$, arbitrary scale) between solvent and solution. The reproducibility of $\varDelta R$ measurements was better than 0.25% of the measuring scale.

The instrument was calibrated using aqueous sodium chloride solutions of accurately known weight fraction and freezing temperatures [29]. The following calibration curve was obtained

$$\varDelta T_f = \alpha_0 \varDelta R \tag{17}$$

where $\alpha_0 = 0.007756 \pm 0.000077$. The absolute uncertainty in the smallest values of the freezing point depression was 0.001 K. The measured highest value of $\varDelta T_f$ did not exceed 2.5 K.

Determination of Number Average Molecular Weight

The number average molecular weight of the investigated poly(oxyethylene) glycols, M_n, was determined by depression of the freezing point of solution using the relation

$$\frac{\varDelta T_f}{r_m} = \frac{k_f \times 10^3}{M_n} + Br + Cr^2 \tag{18}$$

where k_f is the cryoscopic constant and B and C are empirical constants. The cryoscopic constant can be calculated from known solvent properties, but it is more normal practice to employ comparative methods using polymers of known molecular weight as reference standards [30]. For this reason we used some lower members of the poly(oxyethylene) glycol series, namely mono-, di-, tri-, and tetra(oxyethylene) glycols as reference standards. The cryoscopic constant obtained amounts to $k_f = (1.8560 \pm 0.0003)$ K mol^{-1} kg [26]. The calculated values of the number average molecular weights are given in Table 2.

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