Colloid & Polymer Science Colloid Polym Sci 272:872–875 (1994)

Solubility characteristics of poly(ethylene oxide): Effect of molecular weight, end groups and temperature

P. Sakellariou[1], M. H. Abraham[2], and G. S. Whiting[2]

[1] ICI Paints, Research Department, Slough, United Kingdom
[2] Department of Chemistry, University College London, London, United Kingdom

Abstract: The general solvation equation

$$\text{Log}\,L = c + r \cdot R_2 + s \cdot \pi_2^H + a \cdot \alpha_2^H + b \cdot \beta_2^H + l \cdot \log L^{16}$$

has been used to evaluate the effect of molecular weight, hydroxyl end groups and temperature on the solubility characteristics of poly(ethylene oxide), PEO. In this equation L is the gas-liquid partition coefficient of a series of probes on PEO, and the explanatory variables are solute properties describing the excess molar refraction, R_2, the probe dipolarity-polarisability, π_2^H, and the probe hydrogen-bond acidity and basicity, α_2^H and β_2^H. L^{16} is the gas-liquid partition coefficient of the probe on n hexadecane at 298 K. The $r \cdot R_2$ and $l \cdot \log L^{16}$ terms increased with increase in molecular weight whereas the $s \cdot \pi_2^H$ and a α_2^H terms decreased; in all cases the $b \cdot \beta_2^H$ term was not significant. Since the s-constant is a measure of polymer polarity-polarisability, and the a-constant a measure of polymer basicity, we deduce that these polymer properties decrease with increasing molecular weight. Chains with molecular weight below 3000 showed a more rapid decrease in basicity compared to the higher molecular weight species. The $s \cdot \pi_2^H$, $a \cdot \alpha_2^H$ and $l \cdot \log L^{16}$ terms all decreased with increase in temperature. Finally, the contribution of the terminal hydroxyl groups to the total polymer basicity was evaluated and discussed.

Key words: Poly(ethylene oxide) – solubility – basicity – hydroxyl end groups – polymer – solute interactions

Introduction

Abraham and co-workers [1–6] have introduced a general solvation equation [1], based on a simple cavity model of solvation. On this theory, dissolution of a gaseous solute involves the formation of a cavity in the polymer, requiring work in an endoergic process. The probe is then inserted into the cavity, thus setting up various exoergic polymer/probe interactions. Since the polymer is a constant feature, the magnitude of these interactions will depend on the probe properties as follows: R_2 is the excess molar refraction, π_2^H is the probe dipolarity-polarisability, and α_2^H and β_2^H are the probe hydrogen-bond acidity and basicity. The endoergic cavity term cannot be isolated, and the $\log L^{16}$ parameters includes both this term and an exoergic general dispersion interaction term; L^{16} is the gas-liquid partition coefficient of the probe on hexadecane at 25 °C.

$$\text{Log}\,L = c + r \cdot R_2 + s \cdot \pi_2^H + a \cdot \alpha_2^H + b \cdot \beta_2^H + l \cdot \log L^{16} \quad , \quad (1)$$

Each explanatory variable of Eq. (1) refers to some particular interaction and the constants characterize the complementary polymer property. The r-constant indicates the propensity of the polymer to interact with probe π- and n-electron pairs and is usually slightly positive, except with fluorinated polymers. The s-constant characterizes the interactions of the polymer with dipolar-polarisable probes. The a-constant relates to the polymer hydrogen-bond basicity and the

b-constant to the polymer hydrogen-bond acidity. The $l \cdot \log L^{16}$ term contains information on both the exoergic cavity formation and the endoergic polymer general dispersion interactions, and is invariably positive. The terms $s \cdot \pi_2^H$, $a \cdot \alpha_2^H$, and $b \cdot \beta_2^H$ describe also exoergic interactions and, therefore, lead always to positive s, a and b constants. The method leads to a set of characteristic constants c, r, s, a, b and l which describe quantitatively the specific polymer/probe interactions and reflect fundamental physico-chemical properties of polymers rather than being simply empirical constants. Equation (1) has already been applied to the solubility characteristics of polymers [1, 3]. Furthermore, the polymer-solvent interaction parameters and weight fraction activity coefficients can be predicted by the same methodology [6].

This paper utilises the general solvation Eq. (1) to determine the effect of molecular weight, the terminal hydroxyls and temperature on the solubility of poly(ethylene oxide), PEO.

Experimental

The gas-liquid partition coefficient was determined by means of inverse gas liquid chromatography (IGC). Stationary phases were prepared from dilute solutions (typically 5% w/v) of the polymer in chloroform on Chromosorb W acid-washed and dichlorodimethyl silane-treated (mesh 100–120), supplied from Phase Separations Ltd. The solvent was removed slowly by rotary evaporation followed by vacuum drying at 60 °C overnight. The loading was maintained between 8–10% so that flow rate and interfacial adsorption contributions to the specific volume are balancing out [7]. The stationary phase was packed in 2m-long 3mm-i.d. glass columns and conditioned above the glass transition and melting point of the polymer (typically at 120 °C) under helium overnight. The carrier gas was helium at a flow rate of 20 $\mathrm{mL\,min^{-1}}$. The flow rate was determined by means of a thermostatted (25 °C) bubble flowmeter. The temperature dependence of the polymer behaviour was measured with a Model 93 Gas Chromatograph, AI Cambridge, equipped with thermal conductivity detector (TCD) and helium as the carrier gas. The chromatograph was interfaced to an IBM XT computer via a JCL6000 interface card and software for data acquisition and reduction. The molecular weight dependence was obtained through a recalculation of experimental results [8] using Eq. (1).

Different grades of monodisperse ($\bar{M}_w/\bar{M}_n < 1.1$) Carbowax poly(ethylene glycols) were used as received. The higher molecular weight poly(ethylene oxide), $\bar{M}n = 46700$ and $\bar{M}_w/\bar{M}_n = 2$, was supplied by Aldrich (quoted molecular weight 10^5) and was also used as received. The molecular weight of PEO was determined by g.p.c with respect to poly(styrene) standards and, therefore, the value determined is only approximate. The probes were all HPLC grades and were used without any further purification.

Data analysis

The gas-liquid partition coefficient, L, is calculated from the specific retention volume of the probe at the column temperature (V_g) and the polymer density at the same temperature:

$$L = V_g\, d_{Tc} \,. \tag{2}$$

The specific retention volume at the column temperature was calculated from standard chromatographic equations including all the necessary corrections for pressure drop, water vapour pressure and methane marker retention (9).

The constants in the general solvation Eq. (1) were determined by the method of multilinear regression analysis (MLRA), care was taken to ensure that the various descriptors or explanatory variables were not colinear. Tests based on the Student's t-test and the Fisher F-statistic were used to assess the significance of each term in Eq. (1).

Results and discussion

In all regressions, the acidity term, b, was not significant, as expected from the chemical structure of the polymer. Table 1 shows the solvation constants and the multilinear regression parameters for a range of PEO with varying molecular weights. The r and l constants increased with molecular weight, suggesting a similar dependence of the propensity of the macromolecules to

Table 1. Solvation constants of PEO of varying molecular weights ($\bar{M}_n$) at 120 °C

$\bar{M}_n$	c	r	s	a	l	n	p	sd	F
300	– 0.769	0.144	1.518	2.253	0.434	163	0.9975	0.039	7826
400	– 0.737	0.162	1.482	2.120	0.437	164	0.9981	0.035	10254
600	– 0.805	0.186	1.472	2.119	0.455	166	0.9976	0.040	8459
1000	– 0.726	0.217	1.372	1.942	0.449	163	0.9978	0.035	8883
1540	– 0.722	0.217	1.350	1.895	0.453	165	0.9974	0.039	7566
4000	– 0.728	0.241	1.321	1.846	0.462	160	0.9969	0.039	6268
6000	– 0.714	0.252	1.309	1.801	0.462	161	0.9970	0.040	7447
20000	– 0.723	0.260	1.301	1.782	0.462	164	0.9976	0.039	8336

n: number of solutes (probes); p: overall correlation coefficient; sd: overall standard deviation; F: F-statistic

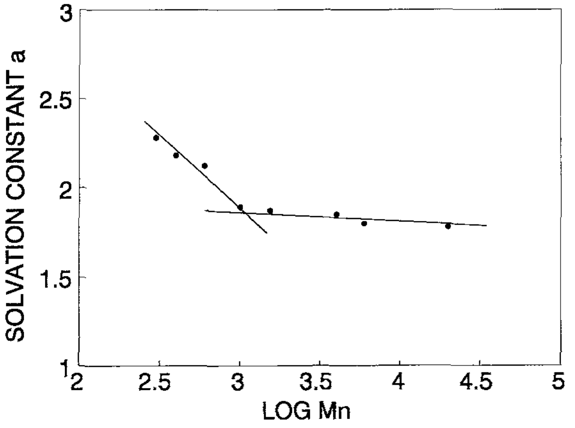

Fig. 1. Variation of the basicity constant, a, with PEO molecular weight

participate in interactions involving π and n electrons on chain length. The term which contributes to the $l \cdot \log L^{16}$ term would be expected to show some small dependence on the size of the macromolecule. The s constant decreased with increasing molecular weight as did the basicity constant in line with the decreasing number of terminal hydroxyl groups and with earlier calculations of the Hildebrand solubility parameters (10). Closer inspection of the a constants (Fig. 1) revealed a two-step change with a faster decrease for molecular weights below 3000 than for higher molecular weights. This behaviour is not fully understood at present but its implication is that PEG oligomers with molecular weight below 3000 are characterised by an increased basicity.

To establish the contribution of the terminal hydroxyl groups to the solubility characteristics of PEO and, also, to demonstrate the sensitivity of our method in describing and quantifying such contributions, we compare the PEO solvation constants to those calculated from the V_g values reported by Galin (11) on a comparable molecular weight methoxy-terminated PEO (Table 2). The data demonstrate that methyl end-capping of PEO affects the excess molar refraction and the basicity constants. The biggest effect, however, a decrease by 0.17 units, was observed for the basicity indicating a significant part of the overall basicity of the uncapped molecule is due to the terminal hydroxyl groups.

The effect of temperature on the solubility characteristics of a high molecular weight PEO is summarised in Fig. 2. The constants were comparable to those of the Carbowax series, any deviations arising from the polydispersity of PEO relative to the monodisperse PEGs. Only the

Table 2. Comparison of solvation constants of hydroxyl-terminated (PEO) and methoxy-terminated MeOPEG AT 120 °C

Polymer	t(°C)	r	s	a	l	n	p	sd
PEO*)	120	0.26	1.30	1.80	0.46	16	0.9980	0.036
MeOPEG**)	120	0.14	1.35	1.63	0.40	11	0.9931	0.051

*) $\bar{M}_n$ (PEO) = 20000
**) $\bar{M}n$ (MeOPEG) = 10700

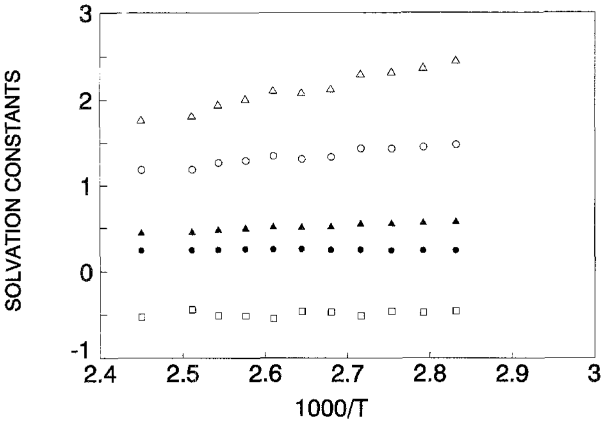

Fig. 2. Variation of the solvation constants with temperature (●) *r*; (○) *s*; (△) *a*; (▲) *l*; (□) *c*

dipolarity-polarisability and basicity constants, *s* and *a*, showed significant temperature dependence. They decreased with increasing temperature in agreement with experimental [12] data and the theoretical trend in the Hildebrand solubility parameters (δ). In the latter case, the behaviour was rationalised in terms of the increase of the molar volume, *V*, and the decrease in the enthalpy of vapourization, ΔH_V:

$$\delta^2 = (\Delta H_V - RT)/V\,. \tag{3}$$

Our data seem to indicate that the free energy of acid-base and dipolar interactions of PEO decreases with increasing temperature.

Conclusions

The effect of molecular weight and terminal end groups of macromolecules can be assessed quantitatively through the new solvation Eq. (1). In the case of PEO, the excess molar refraction and $l \cdot \log L^{16}$ terms increased with molecular weight whereas the dipolarity and basicity constants decreased. The basicity was shown to exhibit a critical point at 3000 below which a stronger dependence on the molecular weight was observed. End-capping the terminal hydroxyls by methyl groups decreased the excess molar refraction and, particularly, the basicity constants, as expected from replacing the polar and basic hydroxyls with methyl groups. The dipolarity-polarisability and basicity constants decreased with increasing temperature in line with the expected behaviour.

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Received August 18, 1993;
accepted October 1, 1993

Authors' address:

Dr P Sakellariou
ICI Paints
Research Department
Wexham Road
Slough SL5 2DS
United Kingdom