Gas chromatographic evaluation of thermodynamic interaction parameters for the water–poly(ethylene oxide) system

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Flory-Huggins χ interaction parameters for the mixing of water and n-propanol in poly(ethylene oxide) of molecular weights 20 000 and 1 000 daltons are calculated from gas chromatographic retention data. The values obtained for infinite dilution of water in the polymer agree well with extrapolated literature data. The high values of χ for water confirm the existence of a highly structured water–poly(ethylene oxide) complex in concentrated solution; no such association was detected in propanol solution.

Keywords Poly(ethylene oxide); water; n-propanol; interaction parameter; gas chromatography

INTRODUCTION

The high solubility of poly(ethylene oxide) (PEO) in water has led to its wide industrial use. As a result, the solution properties of this polymer in both aqueous and non-aqueous media[1] have been studied in detail. In particular, thermodynamic studies have shown[2,3] that at high polymer concentration, the aqueous solution properties of PEO are controlled by negative entropies of dilution. Such values indicate that a high degree of orientation of water molecules with respect to the polymer chain must exist. Indeed, results obtained from n.m.r. and i.r.[4,5], calorimetric[6] and Raman[7,8] studies have shown that in aqueous solution the PEO molecule forms a hydrogen bonded complex in which three water molecules are associated with each repeat unit. Evidence for a 1:1 complex has also been reported[9] based on neutron scattering studies.

One of the main advantages of using gas chromatography as a means of obtaining thermodynamic information is that we can obtain data at effectively infinite dilution of the low molecular weight species in the polymer. The aim of the present work is to extend the measurements of water–PEO interactions at high water concentrations to infinite dilution of water in this polymer. These experiments will also determine the applicability of the gas chromatographic method to the measurement of the interactions between polar polymers and polar solvents.

EXPERIMENTAL

Samples of poly(ethylene oxide) (Carbowax 1,000 and Carbowax 20,000, Union Carbide Company) were used as received. The PEO was coated onto a fluorocarbon support (Fluoropak 80, Fluorocarbon Co.) and packed in a polypropylene column, as previously described[10]. The Carbowax 1000 column characteristics are summarized in *Table 1*. The Carbowax 20 M column characteristics and the measurement of specific retention volumes on these columns for water and n-propanol have also been discussed previously[10].

At temperatures more than 5° above the melting point, symmetrical peaks were obtained for all injections of water and n-propanol. The retention time was found to be unaffected when the size of the injected sample was increased by about an order of magnitude. Thus it was considered safe to assume that the water and n-propanol were at effectively infinite dilution in the stationary phase. Injections consisted of 1–2 μl of air saturated with required vapour, which corresponds to liquid volumes in the order of 50 nanolitres.

RESULTS AND DISCUSSION

The specific retention volumes for water and propanol on Carbowax 1000 as a function of reciprocal temperature are shown in *Figure 1*. The retention volume is seen to increase as the loading of PEO decreases, as was found for the higher molecular weight compound[10], due to a surface excess concentration of vapour at the polymer surface. The retention volume also decreases at lower temperatures as the polymer goes through its melting transition. (The melting point of Carbowax 1000 is 37°–40°C.) In order to obtain a measure of the bulk PEO–vapour interaction, it is necessary to separate the measured retention volume into its separate bulk and

Table 1 Characteristics of Carbowax 1000 columns

Column % loading	Weight of support, *s* (g)	Weight of PEO, *w* (g)
2.5	21.890	0.561
5.0	24.883	1.318
7.8	24.220	2.042

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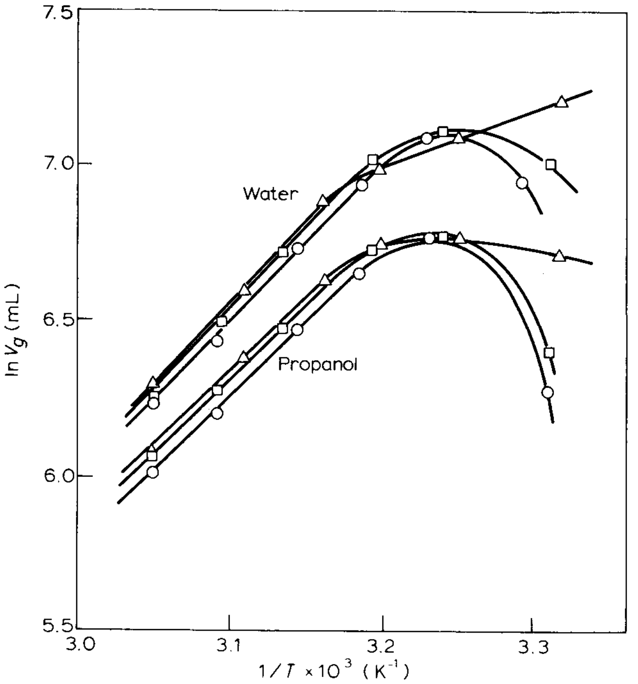

Figure 1 Specific retention volume *versus* reciprocal temperature for water and n-propanol on Carbowax 1000 at loadings of 2.5 (△), 5.0 (□) and 7.8% (○)

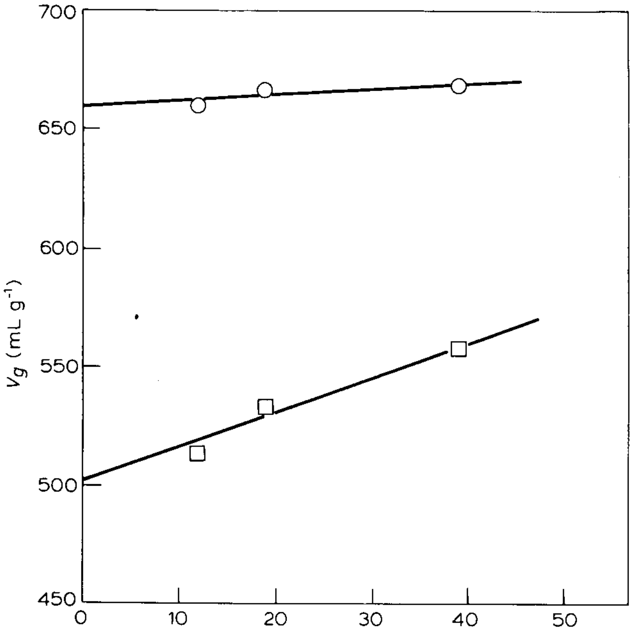

Figure 2 Specific retention volume, V_g, *versus* reciprocal loading, *s/w*, for water (○) and n-propanol (□) on Carbowax 1000 at 50.0°C

surface components. In previous work[10] we have shown that the specific retention volume V_g above the melting point of the polymer can be written in the form:

$$V_g = V_g^b + V^s A(s/w) \tag{1}$$

where V_g^b is the specific retention volume due solely to bulk interactions. V^s is the retention volume measured at 0°C, per square centimetre of stationary phase surface, A is the area of the stationary phase per gram of support and s and w are the number of grams of support and stationary phase, respectively, in the column. The retention data of *Figure 1* gave reasonably good linear plots of V_g against s/w shown in *Figure 2*, which, when extrapolated to $s/w = 0$, yielded the desired bulk retention volumes. A comparison of the bulk retention volumes for water and propanol on Carbowax 20 M and 1000 at 70°C is shown in *Table 2*. The bulk retention volumes at 70.0°C for the 1000 dalton polymer were calculated by extrapolating the V_g^b values at 50.0°C obtained from *Figure 2* to 70°C using the slopes of the ln V_g vs. $1/T$ plots of *Figure 1*. Retention volumes on the 1000 Dalton polymer were measured at a maximum temperature of 55°C in this work as this gave sufficient data to calculate the partial molar enthalpies of vapourization. Correlation of retention data at 70°C for both 1000 and 20 000 Dalton polymer is useful as it permits comparisons to be made between the two polymers and comparisons with the retention data of other workers[11–13]. The retention data for Carbowax 20 M was taken from reference 10. The retention volumes for n-propanol listed in *Table 2* are in good agreement with those obtained by other researchers[11,12]. However, Chang and Bonner[13] measured a retention volume of 283.9 ml g^{-1} for water at 70.2°C on a poly(ethylene oxide) of much higher molecular weight (4 × 10^6 Daltons) than our samples. The reasons for the differences between our data and those of Chang and Bonner may be related to the polymer degradation observed by these researchers.

The polymer–solvent interaction can be measured by means of the Flory–Huggins χ parameter. According to Patterson *et al.*[14], this parameter can be related to the bulk specific retention volume V_g^b by equation (2):

$$\chi = \ln\left(\frac{273.2\,Rv_2}{p_1^0 V_g^b V_1}\right) - \left(1 - \frac{V_1}{\bar{V}_2}\right) - \frac{p_1^0}{RT}(B_{11} - V_1) \tag{2}$$

where R is the gas constant; V_1, p_1^0 and B_{11} are the molar volume, vapour pressure and second virial coefficient, respectively, of the pure liquid probe and v_2 and $\bar{V}_2$ are the specific volume and average molar volume, respectively, of the polymer. If it is assumed that the probe vapour behaves as an ideal gas and we further assume that $\bar{V}_2 \gg V_1$, equation (2) simplifies to:

$$\chi = \ln\left(\frac{273.2\,Rv_2}{p_1^0 V_g^b V_1}\right) - 1 \tag{3}$$

The values of χ calculated using equation (3) for water and propanol are listed in *Table 2*. The χ values for water in poly(ethylene oxide) are clearly much higher than the propanol values, which are typical of most organic solvent–polymer systems. However, they are consistent with the trends shown by Malcolm and Rowlinson[2], as shown in *Figure 3* and are in accord with the model of a highly ordered polymer–solvent complex in aqueous solution. That the solution properties at high polymer

Table 2 Summary of extrapolated retention volumes and interaction parameters at 70°C on poly(ethylene oxide)

	Sample	Water	Propanol
V_g^b (ml^{-1})	Carbowax 20 M	171	170
χ	Carbowax 20 M	2.06	0.58
V_g^b (ml g^{-1})	Carbowax 1000	244	198
χ	Carbowax 1000	1.70	0.43

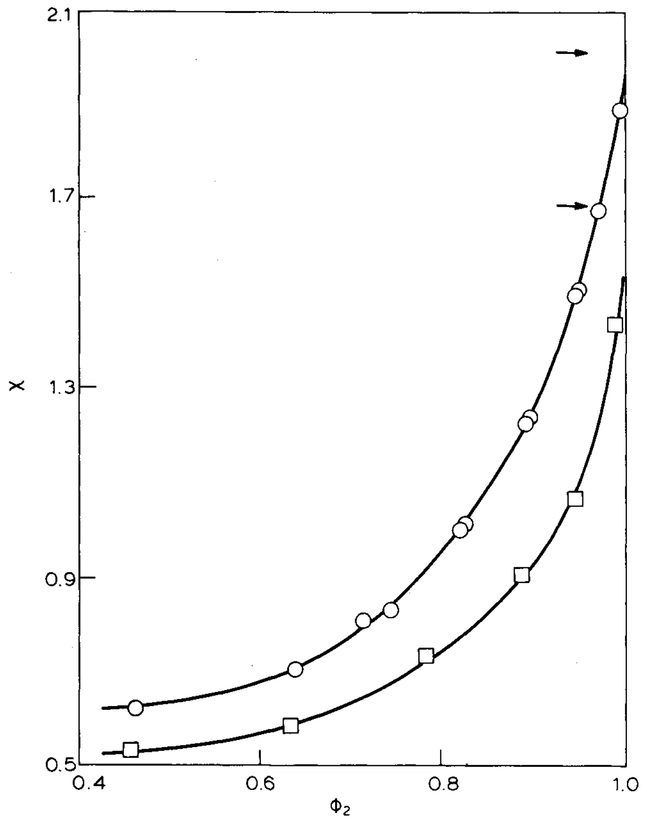

Figure 3 The χ interaction parameter as a function of polymer volume fraction ϕ_2 for water–poly(ethylene glycol) solutions at 65°C as determined by Malcolm and Rowlinson[2]. Polymer molecular weights were 5000 (○) and 300 (□) Daltons. Top arrow indicates the value obtained in these experiments for Carbowax 20 M, bottom arrow for Carbowax 1000

concentration are controlled by negative entropies of mixing is also indicated by the heats of mixing. The partial molar enthalpy of vapourization from infinitely dilute solution, $\bar{\Delta}H^{\infty}$ may be estimated from the ln V_g^b *versus* $1/T$ plots.

$$\frac{\partial(\ln V_g^b)}{\partial(1/T)} \cong \frac{\bar{\Delta}H^{\infty}}{R} \tag{4}$$

It is clear from *Figure 1* that the plots of ln V_g vs. $1/T$ above the melting point are parallel within experimental error. Thus the temperature dependence of the surface contribution to V_g is negligible and hence in equation (4) $\partial(\ln V_g^b)\partial(1/T)$ may be taken as equal to $\partial(\ln V_g)1/\partial(1/T)$. The average value of $\bar{\Delta}H^{\infty}$ for water on the three Carbowax 1000 columns was 43 ± 3 kJ mol^{-1}, and for n-propanol the corresponding value was 41 ± 2 kJ mol^{-1}. The enthalpies are the average from each of the three column loadings and the errors are the 90% confidence limits. The literature values[15] for the latent heat of vapourization, ΔH_{vap}, of pure water and n-propanol at 70°C are 42.0 kJ mol^{-1} and 45.3 kJ mol^{-1}, respectively. For water, the value for $\bar{\Delta}H^{\infty}$ is equal to the latent heat, within rather large experimental error, and thus the excess enthalpy of mixing (the difference between $\bar{\Delta}H^{\infty}$ and the latent heat of vapourization) for water and PEO should be small at infinite dilution. Similar results were observed on the higher *MW* PEO sample (10). The excess enthalpy of mixing of an aqueous solution of a poly(ethylene oxide) sample with *MW* of 5000, estimated from calorimetric data at 80°C, also tends to a low value at high polymer concentrations[2]. The large values for χ in these systems is thus not due to an unfavourable enthalpic contribution, but to an entropic contribution, presumably associated with an increase in order or structuring when water molecules become associated with poly(ethylene oxide) segments. If the mixing is assumed to be completely athermal, then the excess entropy of mixing, S^E can be calculated from[14]:

$$S^E = -g^E/T = -R\ln\left(\frac{273.2\,Rv_2}{p_1^0 V_g^b V_1}\right) \tag{5}$$

where g^E is the excess free energy of mixing for water at essentially zero concentration. For Carbowax 20 M at 70°C, the value of S^E calculated from equation (5) is about -1 J g^{-1} K^{-1}.

Neglect of the third term in equation (3), which accounts for vapour non-ideality, is a point which requires justification. Indeed it has been shown[16] that when the vapour pressure of the pure liquid is greater than 25 kPa, inclusion of this term is necessary if accuracy of better than 5% in the calculation of thermodynamic parameters is required. However, at 70°C, $(p_1^0/RT)(B_{11} - V_1) = 7.5 \times 10^{-3}$ and over the range 50°–70°C the term $R\,\partial[p_1^0(B_{11} - V_1)/RT]/\partial(1/T)$ is estimated to be 0.09 kJ mol^{-1} for water. Thus, considering the error limits on the values of $\bar{\Delta}H^{\infty}$, neglect of vapour non-ideality appears to be justified in this case.

In contrast to the high values of χ obtained for water in poly(ethylene oxide), the lower values for n-propanol are typical of the results generally obtained for most polymers in organic solvents. Although the poly(ethylene oxide) molecule has been shown to retain a certain degree of ordering when dissolved in organic solvents[8], the kind of highly structured complex formed in aqueous solutions apparently does not exist, presumably due to the much lower hydrogen bonding capacity of propanol. The lower values of χ obtained in these experiments are therefore due to a more regular mixing process which occurs when PEO is dissolved in propanol. It is also clear that the values of χ for the 1000 Dalton polymer are lower than for the 20000 Dalton polymer, particularly for water. This lowering of χ indicates that aqueous solutions of the latter polymer are more highly structured. The higher concentration of end groups in the 1000 Dalton sample is the most likely cause of this difference. The decrease of χ with molecular weight of polymer is also seen to occur over the whole concentration range studied by Malcolm and Rowlinson, as seen from *Figure 2.*

The major factor affecting the experimental accuracy of the χ parameters measured by this method is the reliability of the retention volume data. The largest error in this data is undoubtedly due to the extrapolation procedures required to obtain V_g^b, the bulk retention volume. The limits of accuracy of the values of V_g^b listed in *Table 2* for Carbowax 1000 are therefore of the order of ±10% (estimated by combining the error in the extrapolation to $s/w = 0$ with the error in the extrapolation to 70°C) which corresponds to an uncertainty of ±0.1 in the values of the χ parameters. We note that the numerical values of the χ parameters are based on the assumption that the combinatorial entropy of the mixing process at very high polymer concentrations follows Flory–Huggins theory. This may not be an appropriate general assumption. (It certainly is incorrect for solvent mixing with high concentrations of stiff polymer chains[17].) Furthermore, care must be exercized in comparing our results for mixing above the PEO melting point with room temperature studies[3,6] in which the destruction of crystalline portions of PEO must complicate the thermodynamic changes occuring on solution.

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