

A Comparative Study of Sorption of Water Vapor by Oligomeric Triblock Copolymers of Ethylene and Propylene Oxides

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SYNOPSIS

Equilibrium sorption of water vapor by oligomeric block copolymers (PEP) of ethylene and propylene oxides was measured at 23°C at five values of the relative vapor pressure, $0.32 \leq p/p_o \leq 0.90$. Sorption isotherms were described by a simple empirical two-parameter equation. The effect of the copolymer composition on the parameters was established. The Lundberg-Zimm clustering function, the mean size of clusters of water molecules, and the Flory-Huggins interaction parameters were estimated. Their dependencies on copolymer composition and water content in the system are discussed.

INTRODUCTION

Low-molecular-weight copolymers of ethylene and propylene oxides have recently attracted attention as "soft" components of segmented polyurethanes because they significantly increase their hydrophilicity.¹⁻³ The sorption capacity of polyurethanes was found to depend on the proportion and arrangement of the ethylene oxide and propylene oxide units in the soft segment. However, no information exists about the sorption behavior of oligomeric block copolymers of ethylene and propylene oxides (cf. ref. 4).

The present paper summarizes results on the sorption of water by the triblock copolymers (type PEP) where the central block is formed by a sequence of ethylene oxide units.

EXPERIMENTAL

Polymers

Oligomers of ethylene and propylene oxides (PEO, PPO, respectively) were commercial products (Table I). Oligomeric triblock copolymers (POP) were

provided by the Petrochemical Research Institute, Prievidza (Czechoslovakia). All of them were deionized to the "urethane grade" purity level. The content of potassium and sodium ions as determined by atomic absorption spectroscopy was lower than 0.05 wt %. The number average molecular weights, M_n , were calculated from the total content of hydroxyl end groups (Table I) determined by the acetylation method. The composition of copolymers is expressed in weight fractions (w_E , w_P) of the ethoxamer (E) or propoxamer (P) units, respectively.

Sorption Measurement by the Desiccator Method

About 2 g of polymer samples were poured into weighed Petri dishes (diameter 40 mm, which corresponds to a layer thickness of about 0.25 mm) and dried over P_2O_5 to constant weight (about 24 h). The entire set of measured samples was then stored in a 20-L desiccator, maximum 50 mm above the level of a saturated electrolyte solution with defined activity.⁵ The desiccator was stored in a room conditioned at $23 \pm 1^\circ\text{C}$. In 24-h intervals, the samples were quickly closed and weighed. The equilibrium was reached when the weight did not change by more than 0.3 mg after 24 h. Afterwards, the samples were transferred into another desiccator containing an electrolyte solution with a higher water activity. The time necessary to reach the equilibrium was 170 h

Table I Properties of Polyethers

Sample Code	w_E^a	w_{OH}^a	M_n^a	t_m
PPO 1000 ^b	0	3.27	1040	—
PEP 10 ^c	0.143	3.43	990	—
PEP 20 ^c	0.210	3.93	865	—
PEP 30 ^c	0.343	3.12	1090	—
PEP 50 ^c	0.502	3.27	1040	-2.5°C
PEP 70 ^c	0.688	3.17	1280	23–23.8°C
PEO 300 ^d	1.00	11.76	290	< 0°C
PEO 1000 ^e	1.00	3.41	995	39–40°C

^a w_E weight fraction of ethoxamer units, w_{OH} weight fraction of hydroxyl end groups, M_n number-average molecular weight.

^b Polyurax 1000 (British Petroleum, UK).

^c Petrochemical Research Institute, Prievidza (Czechoslovakia).

^d Breox PEG 300 (Hythe Chemicals Ltd., Southampton, UK).

^e Plurion E-1000 (BASF, FRG).

with PPO and PEP 10, and 360 h with the other samples.

Sorption data were obtained at five values of the relative vapor pressure, p/p_0 : 0.32, 0.43, 0.52, 0.79, and 0.90. The activity of water was set equal to p/p_0 .

Treatment of Data

The quantity obtained by experiments is the weight sorption W , i.e., the weight (in grams) sorbed by 1 g of polymer at equilibrium. By means of the equations

$$w_1 = W/(1 + W) \quad (1)$$

$$\rho_1 = W/(W + \bar{v}_2/\bar{v}_1) \quad (2)$$

the weight sorption is converted into the weight or volume fractions (w_1 , ρ_1) of water in the water-polymer system.

The partial specific volumes of copolymers and water (\bar{v}_2 and \bar{v}_1) are unknown at concentrations corresponding to the sorption experiments. However, measurements of the specific volumes carried out at $1 < w_1 < 0.6$ indicate⁶ that the \bar{v}_i values ($i = 1, 2$) do not differ from the specific volumes of the pure components, v_i , by more than 3%. Therefore, the replacement of \bar{v}_2/\bar{v}_1 in eq. (2) by v_2/v_1 introduces an error which is lower than the error of estimation of W .

RESULTS AND DISCUSSION

The desiccator method used in the present work has several disadvantages⁷ (e.g., presence of an air bar-

rier, interruption of the sorption process at each weighing, low sensitivity in the low pressure region, long time intervals required to achieve the equilibrium, and temperature variation due to the latent heat of condensation being given up) which are serious at short and low sorption levels. In long-term experiments with strongly sorbing substances, such as polymers and copolymers of ethylene oxide, these disadvantages are less relevant and are outweighed by the simplicity of the method and by the fact that it allows a simultaneous measurement of several samples under identical conditions.

Sorption Isotherms

Sorption isotherms, i.e., plots of W vs. p/p_0 , presented in Figure 1 in a semilogarithmic form, show that the effect of copolymer composition becomes very strong at higher p/p_0 values. As can be expected with water soluble polymers, the uptakes by PEO, PEP 50, and PEP 70 rise to approach the $p/p_0 = 1$ axis at high p/p_0 values only asymptotically.

The weight sorption by PPO amounts to about 5% of the value for PEO 1000. If the results are converted to the molar scale (moles of water sorbed by 1 mol of ethoxamer or propoxamer unit), the sorption capacity of PPO is raised to about 10% of the value for PEO.

The effect of molecular weight is small but not negligible. The W values for PEO 300 are about 10–15% higher than those for PEO 1000.

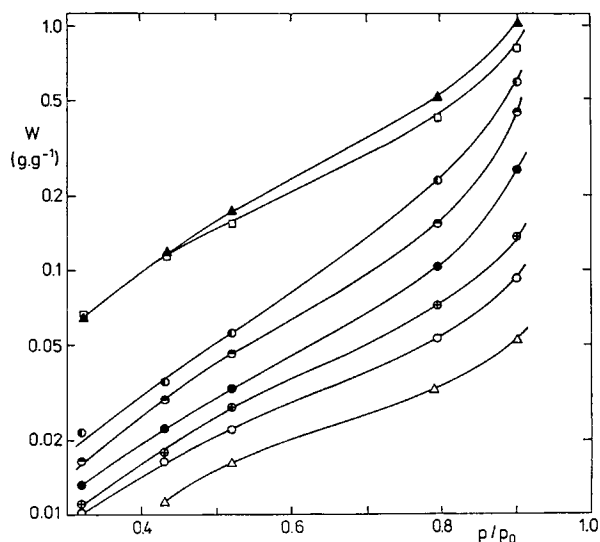


Figure 1 Sorption isotherms (W vs. p/p_0) for polyethers at 23°C. Data points: (Δ) PPO; (\circ) PEP 10; (\oplus) PEP 20; (\bullet) PEP 30; (\odot) PEP 50; (\ominus) PEP 70; (\square) PEO 300; (\blacktriangle) PEO 1000.

The effect of the copolymer composition on sorption can be seen more clearly in Figure 2 where the weight sorption measured at a chosen value of p/p_o is plotted against the weight fraction of ethoxamer units w_E . Broken lines correspond to the assumption that the contributions to sorption by chemically dissimilar monomeric units are additive. The values obtained by interpolation, W_{cal} , serve as a reference basis.

Quite generally, the W values for copolymers PEP 10, 20, and 30 are lower than W_{cal} over the whole range of p/p_o . With copolymers having a higher content of ethoxamer units (PEP 50 and 70), this rule holds at low pressures only; at high values of p/p_o , the weight sorption approaches W_{cal} .

We have found empirically (Fig. 3) that the plots of a_1/ρ_1 vs. a_1 (where $a_1 = p/p_o$) are linear (at least for $0.32 \leq a_1 \leq 0.9$) so that we can write

$$a_1/\rho_1 = A + Ba_1 \quad (3a)$$

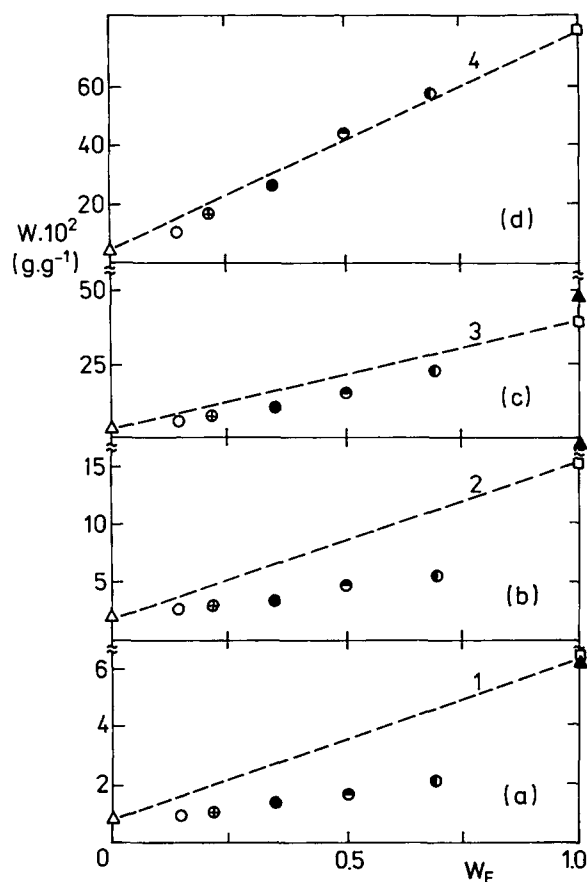


Figure 2 Sorption data, W , at constant p/p_o plotted against composition of polyethers. $p/p_o =$ (a) 0.32, (b) 0.52, (c) 0.79, (d) 0.90. Notation of points as in Figure 1. Broken curves give W_{cal} values (see text).

or

$$\rho_1 = a_1/(A_1 + Ba_1) \quad (3b)$$

By substituting for ρ_1 from eq. (2) we have

$$W = (\bar{v}_2/\bar{v}_1)a_1/[A + (B - 1)a_1] \quad (4)$$

The ratio \bar{v}_2/\bar{v}_1 can be replaced by v_2/v_1 . It follows from eq. (3a) that the B parameter is the slope value of the linear dependence of a_1/ρ_1 vs. a_1 , i.e.,

$$B = [d(a_1/\rho_1)/da_1]_{M,T} \quad (5)$$

For $a_1 \rightarrow 0$, we obtain from eq. (4)

$$\lim_{a_1 \rightarrow 0} (dW/da_1) = (v_2/v_1)A^{-1} \quad (6)$$

For $a_1 \rightarrow 1$, we have

$$\lim_{a_1 \rightarrow 1} W \equiv W_{max} = (v_2/v_1)(A + B - 1)^{-1} \quad (7)$$

or

$$\lim_{a_1 \rightarrow 1} \rho_1 \equiv \rho_{1,max} = (A + B)^{-1} \quad (8)$$

According to eq. (6), A is inversely proportional to the initial slope of the isotherms, and according to eqs. (7) and (8), $(A + B)$ is related to the maximum value of sorption at $a_1 \rightarrow 1$.

Though these values provide useful information, they must be taken with caution if the sum $(A + B)$ is very low. With strongly sorbing or soluble polymers, the sum should be close or equal to zero. Since B is always negative, $(A + B)$ can be equal to zero only if $A = |B|$. Inaccuracy in the parameters may make the sum differ from zero even with soluble polymers, which may be misleading.

Eqs. (3) and (4) do not fit sorption isotherm having an inflexion point (e.g., the BET II type curve⁸). This follows from the fact that for $A \neq 0$ and $B \neq 0$, the second derivative of a_1 with respect to ρ_1

$$(\partial^2 a_1 / \partial \rho_1^2)_{p,T} = 2AB(1 - B\rho_1)^{-3} \quad (9)$$

cannot be zero. The plots of a_1/ρ_1 vs. ρ_1 for polyethers at $0.32 \leq p/p_o \leq 0.9$ are not nonlinear. This makes us assume that the isotherms have no inflexion points even at very low pressures.

The parameter A is a decreasing function of w_E (Fig. 4). A low value of $1/A$ for PPO and a high one for PEO (i.e., a low initial slope of the isotherm

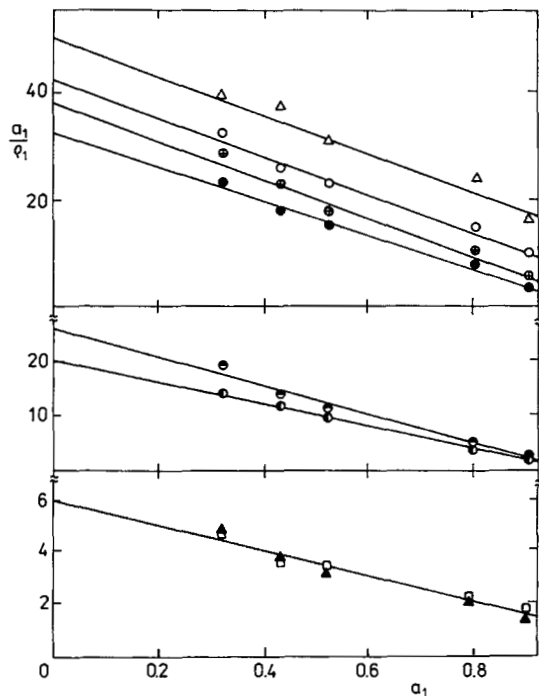


Figure 3 Plot of sorption data for polyethers according to eq. (3). Notation of points as in Figure 1.

in the former case and a high one in the latter) are in line with the hydrophobicity of PPO and hydrophilicity of PEO.

The B parameter (Fig. 4) is independent of the copolymer composition at $w_E \leq 0.25$ whereupon its absolute value $|B|$ decreases. With PEP 50 and 70 and with PEO, $|B|$ is close to A so that $(A + B)$ is practically zero. This is in agreement with the unlimited miscibility⁹ of these polymers with water at 23°C. The $(A + B)$ values for PEP 10 and 20 (as well as for PPO) are high, which implies limited

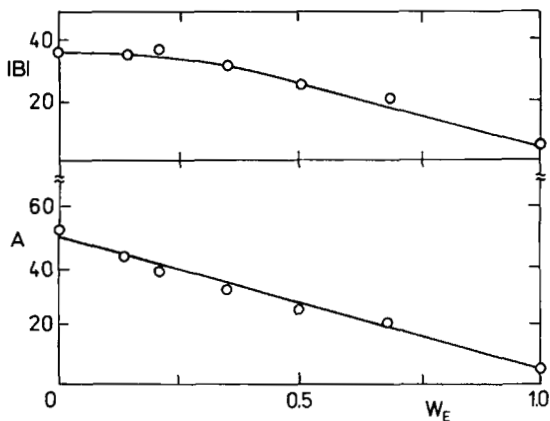


Figure 4 Dependence of parameters of eq. (3) on the polyether composition.

sorption at $a_1 \rightarrow 1$ or, in other words, limited miscibility at 23°C.^{4,9}

The Zimm-Lundberg Clustering Function

The Zimm-Lundberg treatment¹⁰⁻¹² defines the cluster integral, G_{11}/\bar{V}_1 , which gives a measure of the clustering trend of the solvent molecules, $\rho_1 G_{11}/\bar{V}_1$. The sum

$$f = 1 + \rho_1 (G_{11}/\bar{V}_1) \quad (10)$$

which is another characteristic of the system, measures the size of clusters, i.e., the mean number of solvent molecules per cluster.

The cluster integral is calculated as

$$G_{11}/\bar{V}_1 = - (1 - \rho_1) [\partial(a_1/\rho_1)/\partial a_1]_{p,T} - 1 \quad (11)$$

The estimation of the quotient $[\partial(a_1/\rho_1)/\partial a_1]_{p,T}$ is usually difficult. Fortunately, eq. (5) simplifies the evaluation of G_{11}/\bar{V}_1 . By substituting B for the quotient into eqs. (10) and (11) we obtain

$$G_{11}/\bar{V}_1 = - [(1 - \rho_1)B + 1] \quad (12)$$

and

$$f = (1 - \rho_1)(1 - \rho_1 B) \quad (13)$$

Clustering functions calculated according to eq. (12) for several typical values of $|B|$ are presented in Figure 5. Whereas the values of G_{11}/\bar{V}_1 (and the

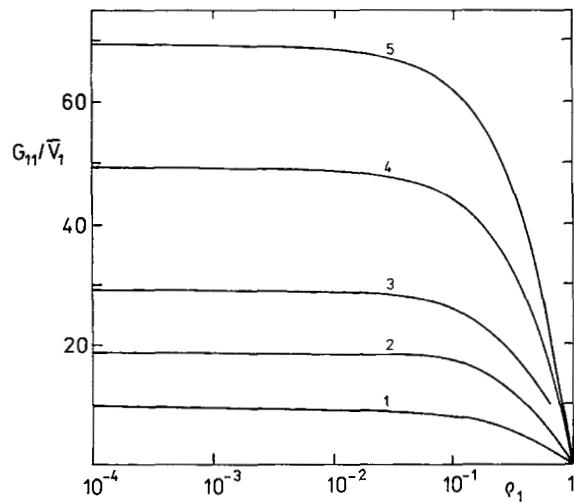


Figure 5 Cluster function G_{11}/\bar{V}_1 of water molecules in the polyether-water mixtures. Curves 1 to 5 calculated by means of eq. (11) for $|B|$: 10, 20, 40, 50, and 70, respectively.

clustering tendency) are almost constant and high at $\rho_1 \leq 0.05$, they decrease at higher water concentrations.

The cluster size has an opposite trend. Figure 6 shows that, in spite of a strong clustering tendency at low ρ_1 values, the clusters are small. This is due to the low water concentration in the system. As the water concentration increases, the clustering tendency becomes somewhat smaller but the clusters are larger. While this increase is small, if any, with PEO, it is pronounced with the PEP samples, particularly those containing large blocks of propylene oxide units. Clustering of water molecules is promoted by the hydrophobic character of these units and is limited by the strong interaction with water of the ethylene oxide units.

Interaction Parameters of Water with the PEP Copolymers

The sorption equilibria can also be discussed in terms of the solution theory, treating the sorption process as mixing of the solvent and polymer.^{7,13} This approach has proved useful with many systems, particularly at higher vapor pressures. It makes use of the Flory-Huggins equation.¹³

$$\ln a_1 = \ln \rho_1 + (1 - r^{-1})\rho_2 + \chi\rho_2^2, \quad (14)$$

where a_1 is the solvent activity, ρ_1 and ρ_2 are volume fractions of solvent and polymer, respectively, and χ is the empirical polymer-solvent interaction parameter. The symbol r stands for the ratio of molar volumes of both components and, in the first approximation, may be replaced by the ratio of molecular weights. The term $(1 - r^{-1})$ is usually ne-

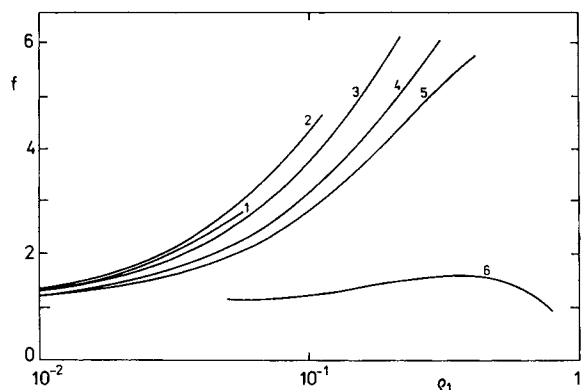


Figure 6 Mean size of clusters of water molecules in the polyether-water mixtures. Curves 1 to 6 calculated according to eq. (13) for PPO, PEP 10, PEP 30, PEP 50, PEP 70 and PEO, respectively.

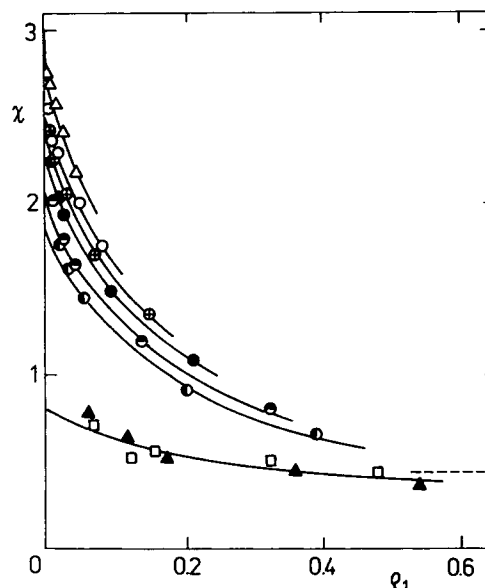


Figure 7 Dependence of the Flory-Huggins interaction parameter on composition of the polyether-water mixtures. Notation of points as in Figure 1. Broken line corresponds to $\chi = 0.43$ for PEO (ref. 4).

glected with high-molecular weight polymers but cannot be omitted with oligomers.

The interaction parameters χ calculated by means of eq. (14) are decreasing functions of the water content (Fig. 7). This trend is common with many polymer systems, including those with water as solvent. It also has been found with high-molecular weight PEO (cf. ref. 4).

After correcting the data by $(1 - 1/r)$ in eq. (14), the χ values for PEO 300 and PEO 1000 give a common plot against ρ_1 . Two different curves would be obtained without the correction. At $\rho_1 > 0.25$ the χ parameter for PEO is almost constant and very close to the value ($\chi = 0.43$) estimated from osmometric data at high dilution (cf. ref. 4).

The concentration dependence of χ can be described by the equation

$$\chi = \chi' - k_1\rho_1 + k_2\rho_1^2 \quad (15)$$

with three parameters (χ' , k_1 , k_2) which decrease with increasing content of ethoxamer groups in the copolymer chain. It is to be noted that eq. (15), with the parameter values given in Figure 8, is valid only over a limited range of ρ_1 and must not be used for extrapolation to higher water concentrations.

In Figure 9, broken line 1 connects the χ' values for PPO and PEO. Those corresponding to copolymers are higher. The difference (more than 10%) is significant for samples with a higher content of

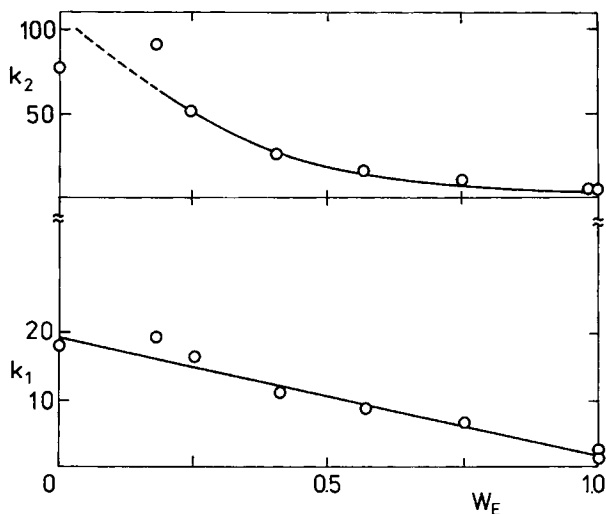


Figure 8 Dependence of parameters k_1 and k_2 of eq. (15) on the polyether composition.

ethoxamer units. A similar picture is obtained for the χ values corresponding to $\rho_1 = 0.05$ (line 2).

According to Stockmayer et al.¹⁴ the interaction parameter of a copolymer can be written as a sum of three terms

$$\chi = \chi_A \rho_A + \chi_B \rho_B - \chi_{AB} \rho_A \rho_B, \quad (16)$$

where χ_A and χ_B characterize the interaction of the solvent with the A and B segments, respectively, χ_{AB} is a characteristic of the A - B interactions (which may depend on the solvent), and ρ_A and ρ_B are volume fraction of the copolymer components. This equation is currently used to interpret properties of dilute solutions but can provide a guideline for a qualitative discussion of concentrated systems.

In the absence of the A - B interactions ($\chi_{AB} = 0$, broken lines in Fig. 9), χ is a linear function of composition. If the interaction is an attractive one ($\chi_{AB} < 0$), the χ parameter is higher than in the previous case, and vice versa.

Positive deviation from additivity observed with the PEP copolymers may indicate a favorable interaction of ethoxamer and propoxamer units ($\chi_{AB} < 0$). This interpretation is seemingly supported by results of some papers^{9,15} but rebutted by others.¹⁶⁻¹⁹

We have recently found that the lower critical solution temperatures of PEP in water are lower by 30°C to 50°C than those obtained by interpolation between those for PEO and PPO of equal molecular weights.⁹

Highly negative values of χ_{AB} (-5 to -0.87) were estimated by Shilov et al.¹⁵ from the melting point depression of crystalline oligomeric PEO ($M_n = 10^3$)

in blends with amorphous PPO ($M_n = 10^3$) at $0.7 < \rho_{PEO} < 1$.

On the other hand, it has been recently shown¹⁶ that the possibility of estimating χ_{AB} from the melting point depression in blends of crystalline and amorphous oligomers is severely restricted and the method need not provide reliable results.

Furthermore, positive heats of mixing of PEO and PPO were found by calorimetry¹⁷ and positive values of χ_{AB} (about 0.1) were obtained by gas-liquid chromatography¹⁸ and by studying liquid-liquid equilibria in mixtures of oligomers of ethylene and propylene oxides.¹⁹ These were shown to phase-separate on cooling and to display an upper critical solution temperature at about 30°C.

With respect to the findings of the latter group of papers one would expect lower χ_{AB} values than those estimated by interpolation in Figure 9 but the opposite is true. One can think of a solvent effect on χ_{AB} . This has been established with many copolymers (cf. ref. 20) and may be very significant with aqueous systems. However, no explanation has been advanced so far for this effect, even with less-complicated systems.

CONCLUSION

The discussion in terms of the clustering functions or interaction parameters is to be considered an attempt to interpret sorption data for PEP copoly-

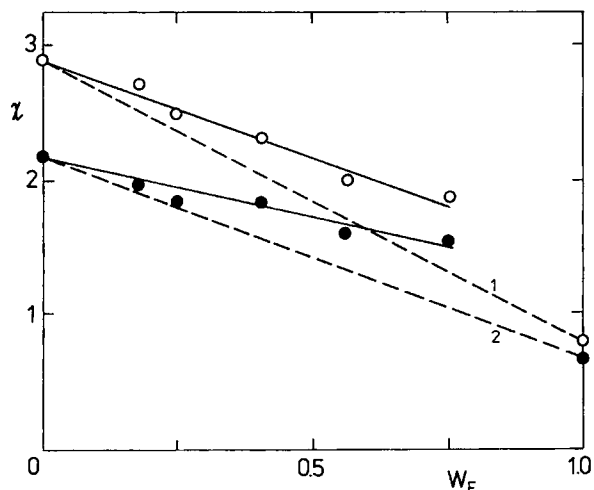


Figure 9 Dependence of the Flory-Huggins interaction parameters on the polyether composition. Data points: (○) χ' at $\rho_1 \rightarrow 0$; (●) χ [calculated for $\rho_1 = 0.05$ by means of eq. (15)]. Reference lines 1 and 2 connect the values for PPO and PEO.

mers. Experimental studies by other methods, e.g., light scattering, would, no doubt, contribute to a better understanding of these involved systems.

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