

THERMODYNAMIC INTERACTION OF POLY(2-HYDROXYETHYL METHACRYLATE) WITH 2-METHYL-2-PROPANOL*

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The concentration dependence of the interaction parameter χ in the system poly(2-hydroxyethyl methacrylate-co-ethylene dimethacrylate)-tert-butyl alcohol was determined by measuring the equilibrium degree of swelling. The enthalpic component of the parameter was calculated from the heats of dilution of the polymer and compared with the heats of mixing for the model system 2-hydroxyethyl pivalate-tert-butyl alcohol. The factor responsible for the good dissolving power of tert-butyl alcohol for poly(2-hydroxyethyl methacrylate) is the negative sign of enthalpic changes. Similarly to mixtures of tert-butyl alcohol with primary alcohols, the explanation can be sought in that the molecules of tert-butyl alcohol form hydrogen bonds with those of poly(2-hydroxyethyl methacrylate) more readily than between themselves.

The solubility of poly(2-hydroxyethyl methacrylate) in a monohydric alcohol depends on the size and structure of the molecule of the alcohol. While the linear polymer is unlimitedly miscible with methanol even at room temperatures, it is dissolved in the homologs of the latter only at elevated temperatures. Dušek¹ found for 1% polymer solutions having the molecular weight 233 000 the following cloud points: in 1-propanol 42.3°C, in 1-butanol 69.1°C, in 2-methyl-1-propanol 68.8°C, in 2-butanol 13.5°C. Fiedlerová and Hudeček² determined by extrapolating cloud temperatures according to Cornet and van Ballegooijen the following theta temperatures: for a solution in 1-propanol 51.1°C, in 1-butanol 77.1°C, and in 2-propanol 32.7 to 34.1°C. According to Tuzar and Bohdanecký³, n-alcohols starting with ethanol dissolve the given polymer only in cosolvent mixtures with another liquid, such as dioxan; the composition of the cosolvent mixture varies over a much broader range for 1-propanol than for 1-butanol. The swelling of the poly(2-hydroxyethyl methacrylate-co-ethylene dimethacrylate) in n-alcohols decreases with increasing number of carbon atoms⁴; however, according to Wichterle and Chromeček⁵, 2-methyl-2-propanol (tert-butyl alcohol) has a considerably higher swelling capacity for the respective gel than any other monohydric alcohol.

The data gathered so far can be summarized by stating that the miscibility of poly(2-hydroxyethyl methacrylate) with primary alcohols decreases with molecular weight of the alcohol. The branching of the alkyl group itself is of no great importance,

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but the miscibility steeply increases in the series primary < secondary < tertiary alcohol, so that of all alcohols from C_1 to C_4 tert-butyl alcohol is the best solvent for the polymer. We therefore concentrated our attention on some thermodynamic properties of systems containing a polymer based on 2-hydroxyethyl methacrylate and tert-butyl alcohol, and of its low-molecular weight model system, 2-hydroxyethyl pivalate-tert-butyl alcohol.

EXPERIMENTAL

Materials

2-Methyl-2-propanol (tert-butyl alcohol), produced by Reanal, Hungary, was crystallized four times and finally distilled with sodium on a packed column with c. 40 TP. The experimentally determined physical constants were in accordance with the literature: m.p. 25.58°C (in ref.^{6,7} 25.60°C), d_4^{25} 0.78083 (in ref.⁸ 0.78086) and n_D^{25} 1.3830 (in ref.⁵ 1.38231). Tert-butyl alcohol was freshly distilled with sodium before each measurement. Hydroxyethyl pivalate was synthesized¹⁰ at the Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences. The purity of the product used was 99.98% (by gas chromatography). The soluble poly(2-hydroxyethyl methacrylate), $M_w = 3.2 \cdot 10^5$ was identical with the polymer used in ref.³.

Poly(2-hydroxyethyl methacrylate-co-ethylene dimethacrylate). A mixture of monomeric components with 0.5% wt. of 2,2'-azo-bis(isobutyronitrile) was flushed with nitrogen, sealed into glass ampoules and kept at 50°C for 12 h. For swelling, cylinders 10 mm in diameter and 1.5 mm high were turned from the copolymer and freed from the unreacted monomer by boiling ten hours with water in a Soxhlet extractor. (The elasticity modulus was measured on prisms milled from the polymer, $100 \times 10 \times 1$ mm in size.) Drying to constant weight *in vacuo* of the oil pump at 115°C took approximately 4 weeks. Before measurements the samples were kept in a desiccator over phosphorus pentoxide.

Procedures Used

The elasticity modulus of the copolymer swollen to equilibrium was determined by measuring tensile strain for a relative elongation $\lambda \leq 1.1$ in the force range 24–440 g. Gel strips, $100 \times 10 \times 1$ mm in size, swollen to equilibrium in tert-butyl alcohol, used for measurements with an Instron dynamometer, were placed in tert-butyl alcohol thermostated to 30°C during the measurements. The size of the sample was measured by means of a micrometer and a centesimal indicator. The elasticity modulus, G , was determined by using the equation

$$f l^2 = (G/l_0) l^3 - G l_0^2, \quad (1)$$

where l is the length of the sample at a stress f and l_0 is the length of an undeformed sample. G was calculated from the slope and the intercept of the linearized $f l^2$ vs l^3 plot.

The volume degree of swelling was calculated from the weight degree by using densities of the dry gel and of the liquid tert-butyl alcohol assuming additivity of volumes. The samples were preswollen in sealed ampoules in an autoclave at 115°C ($> T_g$) for 24 h and swollen to equilibrium with the alcohol in weighing bottles closed in ground cells over silicagel in an aqueous thermostat. The swollen gel was dried with filter paper and weighed. The weight not changing after another two days of swelling was taken to be the equilibrium one.

The heat of dilution of poly(2-hydroxyethyl methacrylate) with tert-butyl alcohol (H_{dil}) was measured in Calvet's microcalorimeter, manufactured by Setaram, Lyon, France, in a stainless steel vessel c. 10 ml in volume with an aluminium diaphragm separating the cells with a volume ratio c. 1 : 6. The polymer solution (3% wt. of the polymer) was introduced into the lower (smaller) cell, alcohol was introduced into the upper one. Anhydrous tert-butyl alcohol identical with that used for the preparation of the polymer solution was used for the measurements; the effect of air moisture was limited as much as possible during all operations, because of the

TABLE I

Equilibrium Volume Degree of Swelling q , for Gels Based on 2-Hydroxyethyl Methacrylate in Alcohols

ν_c^* Effective degree of crosslinking (mol l^{-1}), ρ_2 density of unswollen copolymer.

ν_c^*	ρ_2	q (30°C)	q (50°C)
Methanol			
0.125	1.2883	2.63	—
2-Propanol			
0.125	1.2883	2.36	—
2-Methyl-2-propanol			
0.125	1.2883	3.73	3.43
0.242	1.2886	2.44	2.38
0.779	1.2891	1.76	1.76
0.930	1.2895	1.56	1.56
3.443	1.2899	1.22	1.22

TABLE II

Heat of Dilution (J/ml) of the Polymer of 2-Hydroxyethyl Methacrylate in Tert-butyl Alcohol and the Enthalpic Interaction Parameter χ_H at 26°C

ϕ_2, ϕ_2' Initial and final volume fractions of the polymer.

ϕ_2	ϕ_2'	$1/2(\phi_2 + \phi_2')$	H_{dil}/V_2	χ_H
0.0219	0.0027	0.0123	-0.044	-0.09
0.0219	0.0025	0.0122	-0.064	-0.13
0.0329	0.0036	0.0183	-0.069	-0.09
0.0475	0.0053	0.0264	-0.085	-0.07

hygroscopicity of tert-butyl alcohol. The large relative experimental error should be assigned at the expense of the very small value of the effect measured and of the large heat of dilution of water in tert-butyl alcohol.

The heats of mixing of 2-hydroxyethyl pivalate with tert-butyl alcohol (H^E) were measured similarly¹¹. The vapour space at the margins of the concentration range was reduced as much as possible by means of mercury.

RESULTS AND DISCUSSION

The swelling measurements (Table I) carried out in this work confirmed that tert-butyl alcohol exhibited a greater swelling capacity toward copolymer than methanol and 2-propanol. The interaction parameter was calculated from the equilibrium value of the volume degree of swelling, q , by using the equation

$$\ln(1 - q^{-1}) + q^{-1} + \chi q^{-2} + v_e^* \mathcal{V}_1 (q^{-1/3} - q^{-1}/2) = 0, \quad (2)$$

where \mathcal{V}_1 is the molar volume of the swelling agent and v_e^* is the effective degree of swelling; the latter quantity was calculated from the elasticity modulus G and the degree of swelling of an undeformed sample q by means of the equation

$$v_e^* = Gq^{1/3}/RT. \quad (3)$$

Similarly to most polymer-liquid systems, the parameter χ increases with the volume fraction of the polymer φ_2 (Fig. 1) in our case too. In the limit for a dilute polymer solution ($\varphi_2 \rightarrow 0$), χ probably will become lower than 0.5. For 1-butanol (from 70° to 88°C) Dušek¹ gives the dependence of χ on φ_2 and T which after extrapolation to 30°C would become $\chi = 0.511 + 0.640\varphi_2$. Even admitting that the extrapolation may be subjected to error one still may state with certainty that the χ values for tert-butyl alcohol are considerably lower than for its n-isomer (Fig. 1).

The dependence of q on temperature leads to a conclusion that the swelling of poly-(2-hydroxyethyl methacrylate-co-ethylene dimethacrylate) and dissolution of poly-(2-hydroxyethylmethacrylate) in tert-butyl alcohol are (at least in the region of lower φ_2 values) an exothermal process. In order to verify this we carried out calorimetric measurements of the heats of dilution of a linear polymer, the results of which are given in Table II. The heats of dilution H_{d11} thus determined were used for calculating the enthalpic part of the interaction parameter χ_H by means of the equation

$$H_{d11}/V_2 = RT\chi_H(\varphi_2 - \varphi_2')/V_1, \quad (4)$$

where V_2 is the volume of the polymer present in the measuring cell, φ_2 and φ_2' indicate the volume fractions of the polymer at the beginning and at the end of the measurement respectively. If χ_H is not constant but depends linearly on concentration,

the functional dependence $\chi_H(\varphi_2)$ may be obtained by assigning the experimental value χ_H to the concentration $(\varphi_2 + \varphi_2')/2$. (If the dependence is not linear, the assignment is not unequivocal, but in the range of low φ_2 in which the measurements were carried out the linear approximation is satisfactory.) As is confirmed by the data in the fourth and fifth columns of Table II, the heat of dilution of the polymer solution in tert-butyl alcohol is negative; on the other hand, alcohols investigated in papers^{1,2} form mixtures with the polymer having the upper critical dissolution temperature, which indicates a negative temperature coefficient of the parameter χ and a positive heat of mixing.

In order to get a better insight into the nature of interaction in the system under study we measured the heat of mixing of the system tert-butyl alcohol (1)-2-hydroxyethyl pivalate(2) regarding pivalate as the low-molecular model of poly(methyl methacrylate). As can be seen in Fig. 2, in the region of large dilution of 2-hydroxyethyl pivalate, similarly to dilute solutions of poly(2-hydroxyethyl methacrylate), the heat of mixing is negative, but for $\varphi_2 = 0.2$ the sign changes, so that the curve becomes S-shaped.

The very good dissolving power of tert-butyl alcohol for poly(2-hydroxyethyl

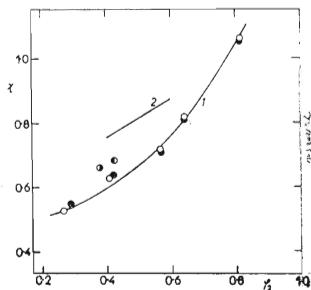


FIG. 1

Dependence of the Interaction Parameter χ on the Volume Fraction of the Polymer φ_2

Polymer based on 2-hydroxyethyl methacrylate in mixture 1 with tert-butyl alcohol at 30°C. 2 with 1-butanol¹ recalculated to 30°C. Polymer in mixture with tert-butyl alcohol ○ at 30°C, ● at 50°C, ⊙ with methanol at 30°C, ⊖ with 2-propanol at 30°C

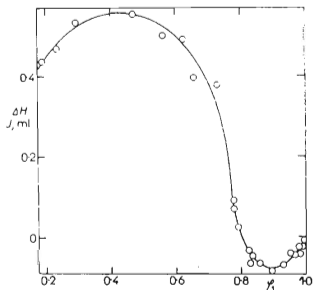


FIG. 2

Heat of Mixing (J/ml) of the System Tert-Butyl Alcohol (1)-2-Hydroxyethyl Pivalate (2) as a Function of the Alcohol Volume Fraction at 26°C

methacrylate) and 2-hydroxyethyl pivalate has its parallel for mixtures of the tert-alcohol with primary alcohols. Polák and coworkers¹² determined the thermodynamic parameters G^E , H^E and V^E of all four isomers of butanol in a mixture with methanol; recently Geiseler and coworkers¹³ studied all binary combinations of isomeric butyl alcohols. The results may be summarized into the following rules: Excess thermodynamic quantities of mixtures of a tertiary and a primary alcohol are always negative; the same holds for mixtures of a tertiary and a secondary alcohol, and of a secondary and a primary alcohol, but the absolute value of the additional quantities is lower and the rule has its exceptions; mixtures of two primary alcohols have positive signs. The determining factor for the sign of G^E in almost all cases considered here is H^E which reflects the energetic balance of mixing. In mixtures of two alcohols the main terms of this balance are represented by the energy consumed for breaking hydrogen bonds between like molecules, and by the energy released due to hydrogen bond formation between unlike molecules. The positive sign of H^E regularly appearing in mixtures of n-alcohols is a consequence of the former term prevailing over the latter. On the other hand, for tert-butyl alcohol (and to a lesser extent for secondary alcohols) the energy and the equilibrium constant of the bonding with like molecules are smaller than for a similar interaction with molecules of primary alcohols, probably owing to the effect of steric hindrances. As a consequence, the energy released by the formation of a new hydrogen bond during the mixing of tert-butyl alcohol with n-alcohol is larger than that consumed by the partial breaking of the existing bonds^{12,13}.

It is obvious that in this way one can explain — in principle at least — also the differences in the dissolving behaviour of primary, secondary, and tertiary alcohols with respect to poly(2-hydroxyethyl methacrylate). Also the S-shaped dependence of the heat of mixing of 2-hydroxyethyl pivalate with tert-butyl alcohol on composition is consistent with the above views if we consider that: 1) The negative heat of mixing of tert-butyl alcohol with primary alcohols exhibits an asymmetrical dependence on composition with the minimum shifted to the region $x_{TB} > 0.5$; 2) differences in the composition of the molecules of tert-butyl alcohol and 2-hydroxyethyl pivalate must lead to the existence of a positive nonspecific interaction term. The sum of the specific and nonspecific terms yields the resulting thermal effect which is numerically small and the sign of which varies with composition as described above. We have not mentioned yet in this discussion the possibility of hydrogen bonding between the hydroxyl groups and the ester group of poly(2-hydroxyethyl methacrylate) or 2-hydroxyethyl pivalate. As shown by the existing experimental results¹⁴, this interaction is weaker than that between two hydroxyl groups, and in the first approximation it may be included into the second nonspecific term.

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