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Thermodynamic Study of Binary Mixtures Containing Glycols or Polyethylene Glycols + Benzyl Alcohol at 308.15 K

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Excess molar enthalpies and excess molar volumes of binary mixtures containing ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, or poly(ethylene glycol)s (PEG200, PEG300, PEG400, and PEG600) + benzyl alcohol were determined at 308.15 K and at atmospheric pressure using a flow microcalorimeter and a digital density meter. Results were fitted to the Redlich−Kister polynomial to estimate the binary interaction parameters. The results are interpreted in terms of molecular interactions between the components.

Introduction

Binary liquid mixtures containing monodisperse glycols and poly(ethylene glycol)s are widely used in the pharmaceutical, chemical, cosmetic, and food industries,[1] for purification of biological materials[2] and as additives in the production of films for food coating.[3]

As a continuation of our previous studies,[4−6] we present here the excess molar volumes and the excess molar enthalpies of binary mixtures containing different compounds as component 1 [ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol (TETG), or poly(ethylene glycol)s of different molecular weights (PEG200, PEG300, PEG400, or PEG600)] and the same component 2 [benzyl alcohol]. Benzyl alcohol was chosen as solvent for the present study because its properties were the subject of considerable interest, due to the versatility of this compound as a solvent for gelatin, cellulose acetate, and shellac and for pharmaceutical aid as an antimicrobial agent.[7] Benzyl alcohol is also used in perfumery, in microscopy as embedding material, and in veterinary applications for relief from purities.[8] All the experiments were carried out at 308.15 K and at atmospheric pressure. The formula of component 1 has been expressed as $HOCH_2-[OP]_p-CH_2OH$, where OP is the repeating ethereal unit CH_2OCH_2. The values of p are reported in Table 1 and range between zero (EG) and 11.17 (PEG600).

Moreover, we are not aware of any physical property data in the literature on these mixtures. The V_m^E and H_m^E values were fitted to the Redlich−Kister polynomial to obtain the binary adjustable parameters and to estimate the standard deviations. Our aim is to obtain information about the effect of the alcoholic group of benzyl alcohol on the interaction between the oxyethylene units of glycols or PEGs, which are self-associated through hydrogen bonding.[9]

Experimental Section

Materials. The chemical substances employed were supplied by Aldrich and Fluka, and used without further purification other than drying with molecular sieves (Union Carbide, type 4A), to eliminate residual traces of water, and degassing by an ultrasonic technique (ultrasonic bath, Hellma, type 460, Milan, Italy). The purities of the chemicals were ≥ 99%. Molecular weights of PEGs were obtained by gel permeation chromatography (GPC), as described in a previous paper.[5] Both the number average, M_n $(=\sum N_iM_i/\sum N_i)$, and the weight average, M_w $(=\sum N_iM_i^2/\sum N_iM_i = \sum w_iM_i)$, molecular weights were determined. In the above equalities, N_i is the number of moles of species i, having molecular weight M_i and weight fraction w_i. A polydispersity index was obtained as the ratio M_w/M_n. Values of M_n and M_w/M_n are reported in Table 1, where also density values in comparison with literature data[9−14] are shown.

Calorimetric Measurements. A flow-type isothermal microcalorimeter (LKB, model 2107, Producer AB, Bromma, Sweden) operating under constant flow conditions was employed in this study to measure the enthalpy changes of mixing. The apparatus consists of a flow-mixing cell, a reference cell, a thermostatic water bath, a data acquisition system, and two automatic pumps (ABU, Radiometer, Copenhagen, Denmark) necessary to pump continuously, at given rates, the required amounts of pure liquids into the mixing cell. The volume of the cylinder was 2.5 cm^3. Mole fractions were computed from fluxes, and the flow rates were selected to cover the entire mole fraction range. In general, the total flow rates were kept at about 0.4 cm^3·min^{-1}. The accuracy of the LKB bath temperature was ±0.01 K. The experimental uncertainties in H_m^E and mole fraction, x_1, are estimated to be <1% and 2×10^{-4}, respectively. More details of the operating procedure are described elsewhere.[15,16] Before measurements, the apparatus was checked using the test systems cyclohexane + hexane, benzene + cyclohexane, and methanol + water. Agreement with literature data[17] was better than 0.5% at the maximum of the thermal effect.

Density Measurements. Binary mixtures were prepared by weight using a digital balance (Mettler, model AE 160, Switzerland). Precautions were taken such as using samples recently prepared and reducing to a minimum the vapor space in the vessel. Glycols and PEGs were weighted as the first component. The accuracy in the determination of the mole fraction of the measured samples

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Table 1. Data of Pure Components

				ρ/g·cm^{-3}	
compound	M_n	p	T/K	exptl	lit.
ethylene glycol		0	298.15	1.109 80	1.109 82[10]
			308.15	1.102 93	1.102 9[9]
diethylene glycol		1	298.15	1.112 38	1.112 33[11]
			308.15	1.105 88	1.105 7[12]
triethylene glycol		2	298.15	1.119 78	1.119 76[11]
			308.15	1.112 61	1.112 0[9]
tetraethylene glycol		3	298.15	1.120 09	1.120 05[11]
			308.15	1.112 31	1.112 28[12]
PEG200	$M_n = 192$; $M_w/M_n = 1.16$	2.95	308.15	1.113 001	1.112 4[9]
PEG300	$M_n = 274$; $M_w/M_n = 1.11$	4.81	308.15	1.113 91	1.113 2[9]
PEG400	$M_n = 365$; $M_w/M_n = 1.10$	6.88	308.15	1.114 13	1.113 72[12]
PEG600	$M_n = 554$; $M_w/M_n = 1.06$	11.17	308.15	1.114 40	
benzyl alcohol			298.15	1.041 46	1.041 6[13]
			298.15		1.041 3[14]
			308.15	1.033 70	1.033 0[13]

was $\pm 1 \times 10^{-4}$. Excess molar volumes, V_m^E, were determined from the densities of the pure liquids and mixtures. The measurements were carried out using a vibrating-tube density meter (Anton Paar, model DMA 60/602, Graz, Austria) operating under static mode. The temperature inside the vibrating-tube cell was measured using a digital thermometer (Anton Paar, type CTK 100) and was regulated to better than ±0.01 K, using a water circulating bath (Heto, type 01 DBT 623, Birkeròd, Denmark). The technique of the apparatus was described previously.[18] The uncertainty in the densities was $\pm 1.5 \times 10^{-5}$ g·cm^{-3}. Before each series of measurements, the apparatus was calibrated at atmospheric pressure using double-distilled water and dry air. Density data were taken from the literature.[19,20] Excess volumes were also checked by determining the V_m^E value of the test mixture benzene + cyclohexane at 298.15 K. A discrepancy of ±0.5% in the central range of the mole fraction of benzene[21] was found. The uncertainty in excess molar volume measurements is estimated as better than 1%.

Results and Discussion

Values of V_m^E and H_m^E of all mixtures are reported in Tables 2 and 3 for different values of x_1. The excess molar volumes were computed by the following equation:

$$V_m^E = (x_1 M_1 + x_2 M_2)/\rho - x_1 M_1/\rho_1 - x_2 M_2/\rho_2 \qquad (1)$$

where x_i, M_i, ρ_i (i = 1, 2), and ρ are the mole fractions, molecular weights, and densities of the pure components and of the mixture, respectively.

The variation of V_m^E and H_m^E with composition is expressed by the Redlich–Kister polynomial

$$Q_m^E(\text{calc}) = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \qquad (2)$$

where Q_m^E(calc) refers to V_m^E or H_m^E.

The adjustable parameters, a_k, were determined by a least-squares method with all points weighted equally, fitting the experimental values to eq 3, and the results are given in Table 4. The standard deviations, $\sigma(Q_m^E)$, reported in Table 4 were defined as

$$\sigma(Q_m^E) = |\phi_{\min}/(N - n)|^{0.5} \qquad (3)$$

with N and n the number of experimental points and parameters, respectively, whereas $\phi_{\min}$ is the minimum value of the objective function ϕ, defined as

$$\phi = \sum_{k=1}^{N} [Q_m^E(\text{calc}) - Q_m^E]_k^{\,2} \qquad (4)$$

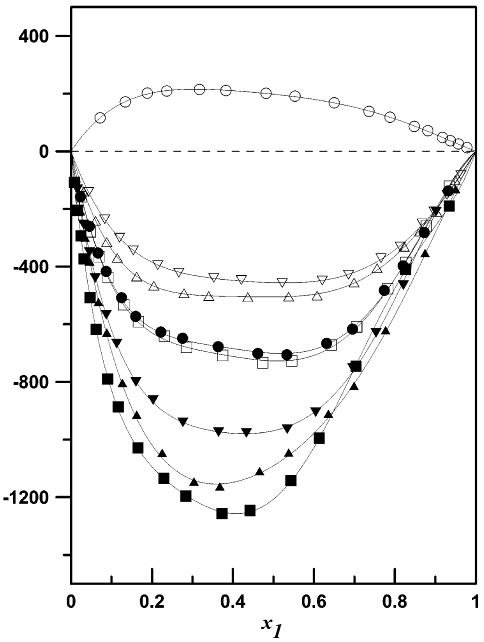

Figure 1. Excess molar enthalpies, H_m^E, for binary mixtures at 308.15 K: ○, EG (1) + benzyl alcohol (2); ▽, DEG (1) + benzyl alcohol (2); △, TEG (1) + benzyl alcohol (2); □, TETG (1) + benzyl alcohol (2); ●, PEG200 (1) + benzyl alcohol (2); ▼, PEG300 (1) + benzyl alcohol (2); ▲, PEG400 (1) + benzyl alcohol (2); ■, PEG600 (1) + benzyl alcohol (2); solid curves, Redlich–Kister equation.

Q_m^E is the experimental value H_m^E or V_m^E. These excess quantities are reported in Figures 1 and 2 as a function of x_1 (the full lines correspond to the Redlich–Kister polynomials). The plots show decreasing values of H_m^E or V_m^E as a function of increasing molecular weight of component 1. Moreover, the H_m^E and V_m^E values of mixtures with EG (p = 0) are positive, whereas those of other mixtures ($p \geq 1$) are negative. As a consequence, the curves of Figures 1 and 2 show that the number of ethereal groups present in the glycol molecules is significant in the 1–2 interactions.

Considering the approximated expression $H_m^E \propto E_{11} + E_{22} - 2E_{12}$, where the terms E_{ij} are the interaction energies between molecules i and j, the excess molar enthalpy reflects the overall hydrogen-bonding structure present in

Table 2. Densities, ρ, and Excess Molar Volumes, V_m^E, for Binary Mixtures Containing Ethylene Glycol, Propylene Glycol, Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol, PEG200, PEG300, PEG400, or PEG600 (Component 1) + Benzyl Alcohol (Component 2) at 308.15 K

x_1	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}
		EG + Benzyl Alcohol			
0.0395	1.035 06	0.0131	0.6090	1.065 04	0.0151
0.1313	1.038 54	0.0345	0.6863	1.071 03	0.0059
0.2622	1.044 29	0.0451	0.7371	1.075 32	0.0001
0.3189	1.047 10	0.0445	0.8097	1.081 99	−0.0075
0.4645	1.055 28	0.0348	0.8790	1.088 96	−0.0080
0.5057	1.057 90	0.0283	0.9638	1.098 48	−0.0039
		DEG + Benzyl Alcohol			
0.0719	1.038 79	−0.0315	0.6035	1.076 60	−0.0790
0.1308	1.042 93	−0.0485	0.7277	1.085 70	−0.0669
0.2285	1.049 76	−0.0644	0.8237	1.092 77	−0.0495
0.3115	1.055 63	−0.0743	0.8597	1.095 43	−0.0406
0.4139	1.062 92	−0.0806	0.8984	1.098 29	−0.0300
0.5312	1.071 36	−0.0824	0.9539	1.102 43	−0.0143
		TEG + Benzyl Alcohol			
0.0519	1.039 48	−0.0619	0.6320	1.089 43	−0.1897
0.1740	1.051 93	−0.1519	0.7533	1.097 60	−0.1526
0.2411	1.058 18	−0.1752	0.8256	1.102 12	−0.1171
0.3373	1.066 69	−0.2027	0.8572	1.104 07	−0.1037
0.4327	1.074 57	−0.2127	0.9337	1.108 50	−0.0511
0.5295	1.082 04	−0.2091	0.9610	1.110 01	−0.0294
		TTEG + Benzyl Alcohol			
0.0793	1.044 72	−0.1151	0.5786	1.090 24	−0.2385
0.1126	1.048 88	−0.1493	0.6885	1.096 97	−0.1962
0.2056	1.059 34	−0.2113	0.7489	1.100 31	−0.1630
0.2511	1.063 96	−0.2314	0.8169	1.103 87	−0.1258
0.3592	1.073 84	−0.2544	0.9226	1.108 94	−0.0587
0.4688	1.082 58	−0.2578	0.9433	1.109 85	−0.0412
		PEG200 + Benzyl Alcohol			
0.0394	1.039 67	−0.0687	0.4083	1.079 44	−0.2972
0.0824	1.045 70	−0.1307	0.4486	1.082 59	−0.2952
0.1018	1.048 28	−0.1562	0.5918	1.092 46	−0.2586
0.1938	1.059 30	−0.2391	0.6793	1.097 71	−0.2214
0.2702	1.067 18	−0.2703	0.8576	1.106 82	−0.1060
0.3627	1.075 67	−0.2954	0.8972	1.108 60	−0.0739
		PEG300 + Benzyl Alcohol			
0.0558	1.046 16	−0.1892	0.4879	1.093 51	−0.4388
0.1263	1.058 62	−0.3473	0.6004	1.099 66	−0.3771
0.1943	1.068 09	−0.4329	0.6867	1.103 56	−0.3121
0.3128	1.080 58	−0.4786	0.8014	1.107 90	−0.2023
0.4220	1.089 22	−0.4642	0.9037	1.111 20	−0.0994
0.4711	1.092 47	−0.4456	0.9499	1.112 53	−0.0486
		PEG400 + Benzyl Alcohol			
0.0474	1.047 64	−0.2441	0.6369	1.104 35	−0.4011
0.1096	1.061 26	−0.4539	0.7126	1.106 99	−0.3380
0.2116	1.076 37	−0.5985	0.7858	1.109 14	−0.2522
0.3034	1.085 59	−0.6125	0.8295	1.110 32	−0.2064
0.4034	1.093 02	−0.5827	0.8727	1.111 37	−0.1507
0.5205	1.099 46	−0.5003	0.9490	1.113 07	−0.0557
		PEG600 + Benzyl Alcohol			
0.0365	1.049 10	−0.2802	0.5946	1.106 48	−0.5449
0.1095	1.069 13	−0.6419	0.6934	1.109 11	−0.4351
0.2151	1.085 00	−0.8065	0.7812	1.110 98	−0.3222
0.3053	1.093 00	−0.7899	0.8418	1.112 05	−0.2295
0.4443	1.100 92	−0.6789	0.9075	1.113 11	−0.1371
0.5465	1.104 94	−0.5897	0.9111	1.113 14	−0.1173

Table 3. Excess Molar Enthalpies, H_m^E, for Binary Mixtures Containing Ethylene Glycol, Propylene Glycol, Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol, PEG200, PEG300, PEG400, or PEG600 (Component 1) + Benzyl Alcohol (Component 2) at 308.15 K

x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}
		EG + Benzyl Alcohol			
0.0719	115.7	0.4817	201.0	0.8815	71.2
0.1341	171.2	0.5533	191.2	0.9177	47.7
0.1886	201.7	0.6502	168.0	0.9370	36.6
0.2365	209.0	0.7361	138.3	0.9571	25.2
0.3173	214.3	0.7880	118.0	0.9781	12.5
0.3826	210.5	0.8480	86.0		
		DEG + Benzyl Alcohol			
0.0434	−141.3	0.3528	−439.4	0.8135	−330.9
0.0833	−235.9	0.4208	−447.1	0.8674	−250.5
0.1199	−300.1	0.5216	−457.4	0.8970	−209.5
0.1537	−344.1	0.6206	−448.8	0.9290	−151.3
0.2142	−395.4	0.6856	−428.7	0.9632	−82.6
0.2665	−421.6	0.7658	−371.2		
		TEG + Benzyl Alcohol			
0.0313	−139.2	0.2792	−492.0	0.7560	−405.0
0.0606	−240.9	0.3405	−501.9	0.8230	−331.1
0.0883	−314.5	0.4366	−505.5	0.8613	−278.1
0.1143	−369.5	0.5376	−504.2	0.9029	−210.1
0.1623	−434.1	0.6078	−500.1	0.9490	−100.0
0.2047	−466.0	0.6992	−455.2		
		TTEG + Benzyl Alcohol			
0.0244	−157.9	0.2305	−640.6	0.7056	−609.4
0.0475	−279.3	0.2853	−680.5	0.7824	−476.8
0.0697	−366.0	0.3747	−708.0	0.8274	−385.6
0.0908	−437.9	0.4734	−733.9	0.8778	−258.8
0.1303	−532.6	0.5451	−727.3	0.9349	−121.2
0.1665	−591.5	0.6425	−672.3		
		PEG200 + Benzyl Alcohol			
0.0232	−157.8	0.2220	−627.1	0.6954	−617.0
0.0454	−260.5	0.2756	−648.6	0.7740	−482.6
0.0666	−353.0	0.3635	−678.0	0.8203	−397.4
0.0869	−417.0	0.4613	−701.3	0.8726	−281.7
0.1249	−507.9	0.5330	−705.9	0.9320	−137.7
0.1598	−572.7	0.6313	−666.2		
		PEG300 + Benzyl Alcohol			
0.0157	−132.1	0.1604	−800.2	0.6045	−905.2
0.0309	−253.6	0.2029	−863.3	0.6963	−752.5
0.0456	−350.1	0.2764	−940.4	0.7535	−629.9
0.0599	−439.7	0.3644	−974.4	0.8210	−464.7
0.0872	−567.2	0.4332	−977.2	0.9017	−209.7
0.1130	−667.4	0.5341	−964.3		
		PEG400 + Benzyl Alcohol			
0.0120	−112.6	0.1269	−807.9	0.5376	−1049.7
0.0236	−213.5	0.1623	−918.5	0.6356	−915.0
0.0351	−304.3	0.2252	−1050.3	0.6993	−818.3
0.0462	−386.6	0.3037	−1149.8	0.7772	−625.3
0.0677	−527.6	0.3676	−1167.2	0.8746	−357.7
0.0883	−633.4	0.4658	−1114.0		
		PEG600 + Benzyl Alcohol			
0.0082	−108.1	0.0902	−789.5	0.4423	−1245.8
0.0163	−205.2	0.1167	−886.5	0.5433	−1142.3
0.0242	−293.8	0.1655	−1029.2	0.6133	−994.8
0.0320	−373.0	0.2293	−1134.1	0.7041	−745.8
0.0472	−507.9	0.2839	−1195.8	0.8264	−409.3
0.0620	−618.4	0.3730	−1256.5		

pure components and in the binary mixtures. As a consequence, negative values of H_m^E correspond to $2E_{12} > E_{11} + E_{22}$.

Monodisperse and polydisperse glycols (PEGs) contain two terminal hydroxyl groups and, except for the case of EG, an increasing number p of ethereal groups (Table 1). According to Jeffrey and Saenger,[22] the H-bonds can involve infinite or finite chains and isolated bonds, such as (a) ...OH···OH···OH···OH... ($p \geq 0$), (b) ...OH···OH···OH···O(ethereal) ($p > 0$), (c) ...OH···O(ethereal) ($p > 0$).

It is evident that as p increases, pattern a must compete more and more with patterns b and c. Since the cooperative effect shortens and strengthens the OH···OH hydrogen bonds,[22] E_{11} decreases as the number of ethereal groups in the chain increases.

Benzyl alcohol is a flexible molecule. However, the conformational properties are not fully clear despite a large

Table 4. Least-Squares Parameters, a_k, for Eq 8 and Standard Deviations, $\sigma(Q^E_m)$, of Binary Mixtures Containing Ethylene Glycol, Propylene Glycol, Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol, PEG200, PEG300, PEG400, or PEG600 (Component 1) + Benzyl Alcohol (Component 2) at 308.15 K

function	a_0	a_1	a_2	a_3	a_4	$\sigma(Q^E_m)$
			EG + Benzyl Alcohol			
V^E_m/cm^3·mol^{-1}	0.11718	−0.25012				0.001
H^E_m/J·mol^{-1}	791.58665	−293.39486	531.38913	−486.61162		1.5
			DEG + Benzyl Alcohol			
V^E_m/cm^3·mol^{-1}	−0.32833	−0.00611	−0.09304	0.12022		0.001
H^E_m/J·mol^{-1}	−1823.69558	−74.64071	−1242.64927	828.53997		2.5
			TEG + Benzyl Alcohol			
V^E_m/cm^3·mol^{-1}	−0.84009	0.11079	−0.22461	0.14268		0.002
H^E_m/J·mol^{-1}	−2020.63148	16.53018	−1577.96829	1425.05288		4.7
			TTEG + Benzyl Alcohol			
V^E_m/cm^3·mol^{-1}	−1.00774	0.29082	−0.21822	0.24331		0.003
H^E_m/J·mol^{-1}	−2908.70250	−79.27736	−1224.5871	2932.66504		5.8
			PEG200 + Benzyl Alcohol			
V^E_m/cm^3·mol^{-1}	−1.14654	0.40140	−0.17127	0.24100		0.003
H^E_m/J·mol^{-1}	−2802.45745	−141.3512	−1381.5951	2883.19439		6.2
			PEG300 + Benzyl Alcohol			
V^E_m/cm^3·mol^{-1}	−1.73274	0.96317	−0.76294	0.63336		0.107
H^E_m/J·mol^{-1}	−3877.74429	614.1973	1207.62943	3431.11887		6.8
			PEG400 + Benzyl Alcohol			
V^E_m/cm^3·mol^{-1}	−2.05801	1.43094	−1.49357	1.12618		0.115
H^E_m/J·mol^{-1}	−4363.69877	1700.6489	1659.90839	1798.35303		8.3
			PEG600 + Benzyl Alcohol			
V^E_m/cm^3·mol^{-1}	−2.51651	1.82336	−2.52154	2.20005		0.120
H^E_m/J·mol^{-1}	−4826.71721	2283.079	1945.82818	2605.39708	6006.50297	4.1

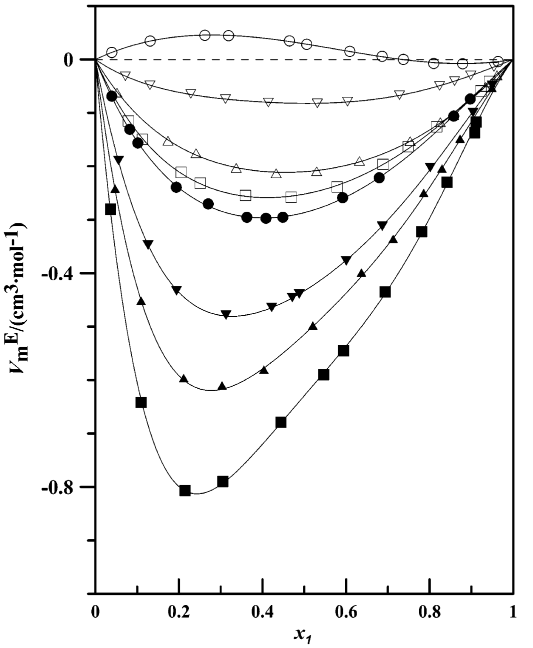

Figure 2. Excess molar volumes, V^E_m, for binary mixtures at 308.15 K: ○, EG (1) + benzyl alcohol (2); ▽, DEG (1) + benzyl alcohol (2); △, TEG (1) + benzyl alcohol (2); □, TETG (1) + benzyl alcohol (2); ●, PEG200 (1) + benzyl alcohol (2); ▼, PEG300 (1) + benzyl alcohol (2); ▲, PEG400 (1) + benzyl alcohol (2); ■, PEG600 (1) + benzyl alcohol (2); solid curves, Redlich−Kister equation.

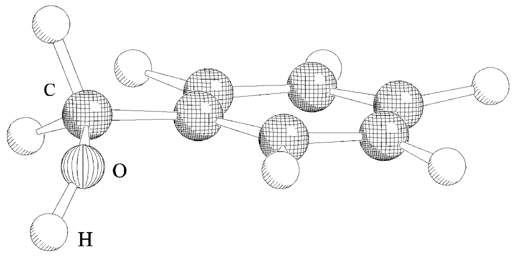

Figure 3. Molecular conformation of benzyl alcohol (crystallographic coordinates from ref 25).

number of experimental and theoretical investigations. The minimum energy structure of benzyl alcohol found in ab initio calculations[23,24] has a gauche conformation about the C−O bond. The hydrogen bonding interactions formed by benzyl alcohol have still been the subject of numerous investigations.[23,24] Actually, both spectroscopic and ab initio data give evidence of the association of benzyl alcohol with formation of dimers stabilized by both OH···O and OH···π H-bonds and by a weak O···CH$_{ring}$ interaction.[23,24] These results support the role of the term E_{22} that can be considered significant in the heat of mixing of the binary systems studied in the present work. The qualitative analysis of the term E_{12} appears to be more complex. In the solid-state X-ray structure of the β-cyclodextrin benzyl alcohol clathrate,[25] benzyl alcohol has the OH group out-of-the-plane of the benzene ring with a CCOH torsion angle of −112.47° (Figure 3). The hydroxyl group of benzyl alcohol forms three intermolecular hydrogen bonds with adjacent acceptor oxygen atoms with consequent disruption of the O−H···π interaction. While benzyl alcohol might display varying behavior in polymer solutions, it is clear that the number of intermolecular H-bonds will increase with the increase of the number of ethereal oxygen atoms present in the chain of glycols and PEGs. The curves V^E_m versus x_1 (Figure 2), showing a trend quite similar to that of H^E_m, seem to confirm the prevailing of E_{12} interactions over E_{11} and E_{22} interactions, since volume decreases after mixing and in the same order given by enthalpy. In conclusion, the progressive decrease of H^E_m and V^E_m as a function of increasing molecular weight of component 1 can be qualitatively attributed both to a lowering of the cooperative effect between the terminal OH groups of glycols and PEGs

(E_{11}) and to an increase of the number of intermolecular H-bonds between the components (E_{12}).

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