

# Excess Volume of the 1-Propanol + 1-Alkene Systems in Terms of an Equation of State with Association<sup>†</sup>

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The measurements of excess molar volume  $V^E$  at 298.15 K for binary mixtures formed by 1-propanol with 1-alkene ( $C_6$ ,  $C_7$ ) and excess molar volume  $V^E$  at (288.15, 298.15, and 308.15) K with 1-decene are reported. For the 1-decene system, the excess molar isobaric thermal expansion  $A_P^E$  at 298.15 K is estimated. These data together with  $V^E$  and  $A_P^E$  at 298.15 K for 1-propanol with 1-octene published previously (Treszczanowicz et al. *J. Solution Chem.* **2002**, *31*, 455–466 and **2004**, *33*, 275–285) are discussed and interpreted in terms of the Treszczanowicz and Benson (TB) model adapted for mixtures of self-associated component and active solvent. The model contains the Flory equation of state (EOS) combined with the association model proposed by Treszczanowicz and Kehiaian. The Flory EOS interaction interchange parameter is described in terms of the Kehiaian group contribution method taking into account the  $OH\cdots\pi$  interactions and nonspecific interactions. The model predicts qualitatively well the shape of the  $V^E$  and the partial molar excess volume as well as  $A_P^E$ .

## Introduction

The present paper reports excess volumes  $V^E$  of the binary mixtures formed by 1-propanol with 1-hexene and 1-heptene at 298.15 K and with 1-decene at (288.15, 298.15, and 308.15) K. For the 1-propanol + 1-decene system, the excess molar isobaric thermal expansion  $A_P^E = (\partial V^E/\partial T)_P$  at 298.15 K is estimated. The excess volume  $V^E$  and excess enthalpy  $H^E$  for mixtures formed by 1-propanol, ethanol, and methanol with 1-alkenes ( $C_6$ ,  $C_7$ ,  $C_8$ ) were investigated previously and discussed by Letcher et al.<sup>1</sup> using the ERAS model. They came to the conclusion that no cross-association  $OH\cdots\pi$  was necessary to describe these properties. Recently, Pawłowski<sup>2</sup> analyzed the prediction of  $H^E$  and  $V^E$  for 1-octanol + 1-alkene mixtures with the ERAS model with cross-association and with the Treszczanowicz and Benson (TB) model and confirmed Letcher's result. Therefore, to take into account  $OH\cdots\pi$  interactions without cross-association in the TB model, the interchange interaction parameter of the Flory equation of state contribution is described in terms of the Kehiaian<sup>3,4</sup> group contribution method (GCM). The GCM allows us to discuss weak H-bonding in the  $OH\cdots CH_2=CH-$  group and van der Waals interactions of the  $OH\cdots$ aliphatic group ( $CH_2$ ,  $CH_3$ ) and  $CH_2=CH\cdots$  aliphatic group in terms of the GCM.

The excess volumes for a series of binary systems 1-alkanol + 1-octene, including the 1-propanol + 1-octene system,<sup>5,6</sup> and for a series of 1-hexanol + 1-alkene systems<sup>7,8</sup> were investigated at (288.15, 298.15, and 308.15) K by Treszczanowicz et al. The  $V^E$ ,  $A_P^E$ , and partial molar excess volume  $V_i^E$  as well as partial molar excess thermal expansion  $A_{P,i}^E$  of the components were discussed and interpreted in terms of the Treszczanowicz and Benson model.<sup>9</sup> The TB model contains the Flory equation of state combined with the athermal associated mixture model of the Mecke–Kempter type proposed by Treszczanowicz and

Kehiaian.<sup>10,11</sup> The excess molar volume and excess molar isobaric thermal expansion in the TB model are given as a sum of the association and the Flory equation of state contributions<sup>8</sup>

$$V^E = \Delta V_H x_1 \left[ \frac{\ln(1 + K^{(\varphi)})}{K^{(\varphi)}} - \frac{\ln(1 + K^{(\varphi)}\varphi_1)}{K^{(\varphi)}\varphi_1} \right] +$$

association contribution  
 $V^*[ \bar{v} - (\bar{v}_1\varphi_1 + \bar{v}_2\varphi_2) ]$   
 EOS contribution

(1)

$$A_P^E = \frac{\Delta H_H \Delta V_H}{RT^2} x_1 \times$$

$$\left[ \frac{1}{1 + K^{(\phi)}} - \frac{\ln(1 + K^{(\phi)})}{K^{(\phi)}} - \frac{1}{1 + K^{(\phi)}\phi_1} + \frac{\ln(1 + K^{(\phi)}\phi_1)}{K^{(\phi)}\phi_1} \right] +$$

association contribution

$$V^* \left[ \frac{3\bar{v}^{7/3}}{T^*(4 - 3\bar{v}^{1/2})} - (\alpha_p^{(1)}\bar{v}_1\phi_1 + \alpha_p^{(2)}\bar{v}_2\phi_2) \right]$$

EOS contribution

(2)

where  $K^{(\phi)} = \exp[1 - \Delta H_H/RT + \Delta S_H/R]/r_1$ <sup>3,12</sup> is a self-association constant of 1-alkanol with a number of segments  $r_1 = 1 + n^{(1)}$ , where  $n^{(1)}$  is the number of C-atoms in 1-alkanol; and  $\Delta H_H$ ,  $\Delta S_H$ , and  $\Delta V_H$  are the enthalpy, entropy, and volume of H-bond formation. The remaining symbols are as follows:  $\phi_1 = r_1 x_1 / (r_1 x_1 + r_2 x_2)$  and  $\phi_2 = 1 - \phi_1$  are segment fractions;  $x_1$  and  $x_2 = 1 - x_1$  are mole fractions of components 1 and 2, respectively;  $r_2 = n^{(2)}$  is the number of C-atoms in the alkene molecule;  $\alpha_p^{(1)}$  and  $\alpha_p^{(2)}$  are isobaric thermal expansion coefficients;  $\bar{v}_1 = V_1/V_1^*$ ,  $\bar{v}_2 = V_2/V_2^*$ , and  $\bar{v} = V/V^*$  are reduced volumes of pure components 1, 2, and mixture, respectively; and  $V_1$ ,  $V_1^*$  and  $V_2$ ,  $V_2^*$  are molar volume and characteristic volume of components 1 and 2, respectively.  $V^* = V_1^* x_1 + V_2^* x_2$ , and  $T^* = T/\bar{T}$  is the characteristic temperature of the mixture

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$$T^* = \left( \sum_{i=1}^2 P_i^* \phi_i - X_{12} \phi_1 \theta_2 \right) / \sum_{i=1}^2 (P_i^* \phi_i / T_i^*) \quad (3)$$

where  $\tilde{T}$  is the reduced temperature of the mixture;  $P_i^*$  and  $T_i^*$  are characteristic pressure and temperature of component  $i = 1, 2$ ; and  $\theta_2 = \phi_2 / (\phi_1 r_{21}^{1/3} + \phi_2)$  is the site fraction of component 2, where  $r_{21} = V_2^*/V_1^*$ .

## Experimental Section

**Materials.** 1-Propanol (Aldrich, analytical grade) was further purified by distillation through a column packed with glass helices. 1-Hexene, 1-octene, and 1-decene (Sigma, > 99 %, analytical grade) and 1-heptene (Sigma, > 97 %, reagent grade) were distilled over sodium. All liquids were stored in the dark over type 3A molecular sieves. Densities  $\rho$  and coefficients of isobaric thermal expansion  $\alpha_p = -(\partial\rho/\partial T)_p/\rho$  of the pure components at 298.15 K are given in Table 1 together with the literature values and their purities determined by gas chromatography.

**Apparatus and Procedure.** Densities  $\rho$  were measured by an Anton Paar densimeter (model DMA 60/602) operated in the static mode; the estimated uncertainty was better than  $\pm 1 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$ . Conversion to molar quantities was based on the 1995 Table issued by IUPAC.<sup>15</sup> The uncertainty in mole fractions is estimated to be less than  $\pm 1 \cdot 10^{-4}$ . The temperature of the oscillator chamber in the densimeter was controlled by circulating thermostatted water supplied from a cascade thermostatic system and a UNIPAN 560 temperature controller. The temperature in the quartz cell was controlled to within  $\pm 0.001$  K by using a precision digital thermometer (Systemtechnik AB, type S 1220) with a thermistor probe. The temperature uncertainty was  $\pm 0.002$  K. Calibration of the apparatus at (288.15, 298.15, and 308.15) K was made by using twice distilled water deionized by using the Millipore Milli-Q system (Nihon Millipore Ltd.), standard benzene ( $x = 0.9997$  purity), and cyclohexane ( $x = 0.9995$  purity) both produced and supplied by CHEMIPAN (Warsaw, Poland). The pure liquids used for preparation synthetic mixtures were degassed. The operational procedure for measuring densities has been described elsewhere.<sup>5,6</sup> The densities measured and isobaric thermal expansion coefficient  $\alpha_p$  are compared in Table 1 with the literature data.<sup>13,14</sup>

## Results

The excess volume is calculated from densities by using the equation

$$V^E = \sum_{i=1}^2 M_i x_i \left( \frac{1}{\rho_m} - \frac{1}{\rho_i} \right) \quad (4)$$

where  $M_i$ ,  $x_i$ , and  $\rho_i$  are the molecular mass, mole fraction, and density of pure component  $i$ , respectively, and  $\rho_m$  is the density of a mixture. Experimental results of the molar excess volume in the binary systems of 1-propanol with 1-hexene and 1-heptene at 298.15 K and of 1-propanol with 1-decene at (288.15, 298.25, and 308.15) K are summarized in Table 2. The uncertainty in the excess volume is estimated to be less than  $\pm 0.003 \text{ cm}^3 \cdot \text{mol}^{-1}$ . The Neau smoothing equation<sup>16</sup> was found to be more suitable for the asymmetric excess volumes (cf. ref 17)

$$V^E / \text{cm}^3 \cdot \text{mol}^{-1} = x_1 (1 - x_1) \sum_{i=1}^k a_i Y^{i-1} \quad (5)$$

where  $a_i$  is the equation parameter assumed to be a square temperature function

$$a_i = \sum_{j=1}^3 [a_i^{(j-1)} (T/\text{K} - 298.15)^{j-1}] \quad (6)$$

$Y = x_1 - (1 + Dx_1)^{-1}$ , and the recommended<sup>16</sup> value of the parameter,  $D = 35$ , was assumed to be temperature independent. The coefficients  $a_i$  were obtained by the nonlinear least-squares method by using the Marquardt–Levenberg procedure<sup>18</sup> to fit eq 5 to the experimental results. The coefficients  $a_i$  for each  $V^E$  isotherm are listed in Table 3 along with the standard deviation defined as

$$\sigma_v = \left( \sum_{i=1}^m \frac{(V_i^{\text{E,exptl}} - V_i^{\text{E,calcd}})^2}{m - k} \right)^{1/2} \quad (7)$$

where  $k$  is the number of constants in the smoothing eq 5 and the sum is extended over all  $m$  data points. The data of the excess volume for the 1-propanol + 1-octene system at (288.15, 298.25, and 308.15) K given in the preceding papers<sup>5,6</sup> are presented in Table 3 in terms of the smoothing parameters. The smoothed experimental excess volume data at 298.15 K for the investigated series of mixtures are presented in Figure 1. The  $V^E$  in the investigated series of mixtures change from positive–negative for 1-hexene to positive over the whole mole fraction range for 1-decene. The results obtained agree reasonably well with Letcher et al.<sup>19</sup> results. This behavior is similar to that observed for the mixtures formed by alkanol with  $n$ -alkanes.<sup>9,17</sup>

The partial molar excess volume of 1-propanol in 1-alkenes,  $V_1^E$ , is calculated by means of the following relation

$$V_1^E = V^E + (1 - x_1) \left( \frac{\partial V^E}{\partial x_1} \right) \quad (8)$$

where  $V^E$  is given by eq 5 and by the parameters given in Table 3. The  $V_1^E$  at 298.15 K for 1-propanol in 1-hexene, 1-heptene, 1-octene, and 1-decene and  $V_2^E$  for these 1-alkenes in 1-propanol are presented in Figure 2. The  $V_1^E$  for 1-propanol in 1-hexene exhibits a positive–negative shape with a deep minimum in contrast to the positive over the whole concentration range for a longer molecule like 1-decene.

The excess molar isobaric thermal expansion  $A_p^E = (\partial V^E / \partial T)_p$  at 298.15 K is estimated by using eq 5 and 6 and the parameters  $a_i^{(1)}$  given in Table 3, by means of the relation

$$A_p^E / \text{cm}^3 \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = x_1 (1 - x_1) \sum_{i=1}^k a_i^{(1)} Y^{i-1} \quad (9)$$

The calculated values of  $A_p^E$  at 298.15 K for the 1-propanol + 1-decene system together with the results for the 1-propanol + 1-octene system<sup>6</sup> are presented graphically in Figure 3. The uncertainty in  $A_p^E$  does not exceed  $\pm 0.4 \cdot 10^{-3} \text{ cm}^3 \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  in the middle of the temperature range (298.15 K). The  $A_p^E$  values for these systems are positive over the whole concentration range with higher positive values at the maximum for the 1-decene system.

**Table 1.** Densities  $\rho$  and Thermal Expansion Coefficient  $\alpha_p$  at  $T = 298.15$  K, Refractive Indices  $n_D$  at  $T = 293.15$  K, and GLC Mole Purity

component $i$	$\rho/\text{g}\cdot\text{cm}^{-3}$		$n_D$		$10^3\alpha_p/\text{K}$		purity $x$
	obsd	lit. <sup>a</sup>	obsd	lit. <sup>a</sup>	obsd	lit. <sup>a</sup>	
1-propanol	0.79965	0.79970	1.38552	1.38556	1.002	0.995 <sup>b</sup>	0.998
1-hexene	0.66828	0.66848	1.38790	1.38788	1.390	1.410	0.998
1-heptene	0.69252	0.69267	1.39992	1.39980	—	1.275	0.995
1-octene	0.71088	0.71085	1.40874	1.40870	1.148	1.173	0.992
1-decene	0.73679	0.73693	1.42139	1.42146	1.026	1.054	0.995

<sup>a</sup> Ref 13. <sup>b</sup> Ref 14.**Table 2.** Experimental Results on the Excess Volume  $V^E$  of 1-Propanol (1) + 1-Alkene (2) Systems

$V^E$		$V^E$		$V^E$	
$x_1$	$\text{cm}^3\cdot\text{mol}^{-1}$	$x_1$	$\text{cm}^3\cdot\text{mol}^{-1}$	$x_1$	$\text{cm}^3\cdot\text{mol}^{-1}$
1-Hexene at $T = 298.15$ K					
0.0559	0.0747	0.3009	0.0722	0.6016	-0.0697
0.1058	0.0994	0.3520	0.0528	0.7038	-0.0951
0.1992	0.1002	0.3964	0.0317	0.8088	-0.1026
0.1507	0.1068	0.5009	-0.0220	0.8497	-0.0950
0.2544	0.0863	0.5518	-0.0520	0.8990	-0.0709
			0.9490		-0.0383
1-Heptene at $T = 298.15$ K					
0.0582	0.1151	0.3980	0.1791	0.6972	0.0655
0.1049	0.1526	0.4975	0.1439	0.7425	0.0421
0.1479	0.1764	0.5553	0.1204	0.7947	0.0250
0.2018	0.1954	0.5959	0.1026	0.8462	0.0124
0.2499	0.2022	0.6563	0.0783	0.8955	0.0013
			0.9510		-0.0009
1-Decene at $T = 288.15$ K					
0.0969	0.1597	0.2737	0.2707	0.6102	0.2550
0.1318	0.1939	0.3258	0.2857	0.6603	0.2441
0.1944	0.2342	0.3734	0.2932	0.7918	0.1740
0.2361	0.2551	0.5038	0.2845	0.8442	0.1401
		0.5598	0.2722	0.8939	0.1008
1-Decene at $T = 298.15$ K					
0.0564	0.1483	0.3551	0.3354	0.5977	0.2994
0.1090	0.2160	0.4028	0.3349	0.6479	0.2789
0.1582	0.2592	0.4501	0.3342	0.7980	0.1962
0.2550	0.3142	0.4961	0.3286	0.8500	0.1548
0.3028	0.3244	0.5495	0.3145	0.8943	0.1143
1-Decene at $T = 308.15$ K					
0.1008	0.2627	0.3286	0.4208	0.6632	0.3406
0.1436	0.3127	0.3713	0.4253	0.7473	0.2803
0.1972	0.3607	0.4631	0.4178	0.7900	0.2481
0.2342	0.3889	0.5207	0.4049	0.8432	0.1974
0.2701	0.3998	0.5637	0.3910	0.8935	0.1455
		0.6140	0.3630	0.9422	0.0872

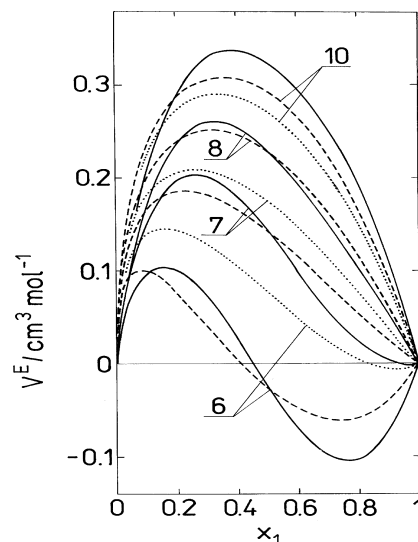
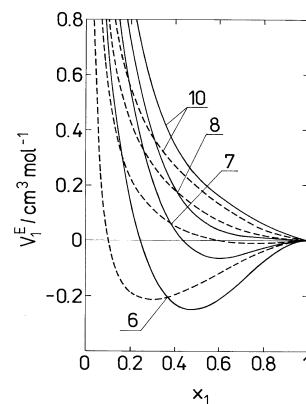
**Table 3.** Coefficients  $a_i$ , Standard Deviations  $\sigma_v$ , and Maximum Deviations  $\Delta$  for Least-Squares Representations of  $V^E$  Using Neau Equation 5 for (1-Propanol + 1-Alkene)

1-alkene	$T/\text{K}$	$a_1$	$a_2$	$a_3$	$\sigma_v$	$\Delta$
1-hexene	298.15	0.79557	-2.1680	0.38882	0.0027	0.0038
1-heptene	298.15	1.3810	-2.1074	0.66635	0.0028	0.0057
1-decene	288.15	1.6017	-1.4922	1.0236	0.0021	0.0040
	298.15	1.9624	-2.2041	1.6054	0.0030	0.0050
	308.15	2.4760	-2.7423	1.9187	0.0030	0.0059

## Discussion

The interpretation of the experimental  $V^E$  and  $A_p^E$  values is based on the Treszczanowicz and Benson model.<sup>9</sup> It should be emphasized that H-bond formation parameters were adopted from previous estimations for alkanol + inert solvent mixtures,<sup>9</sup> i.e., enthalpy  $\Delta H_H = -24.4 \text{ kJ}\cdot\text{mol}^{-1}$ , entropy  $\Delta S_H = -33 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , and volume  $\Delta V_H = -10 \text{ cm}^3\cdot\text{mol}^{-1}$  for H-bond formation. The interaction parameter  $X_{12}$  for the Flory equation of state contribution is described in terms of GCM<sup>8</sup> as

$$X_{12} = \omega[X_{o,a}^*(\alpha_o^{(1)})^2 + (X_{o,a}^* + X_{b,a}^* - X_{o,b}^*)\alpha_o^{(1)}\alpha_b^{(2)} + X_{b,a}^*(\alpha_b^{(2)})^2] \quad (10)$$

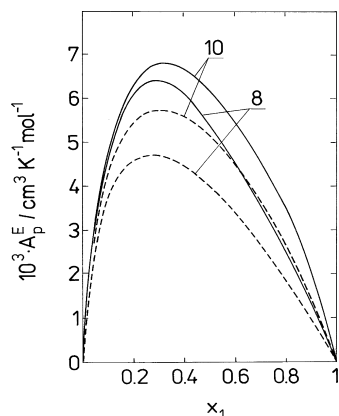
**Figure 1.** Excess molar volumes  $V^E$  of binary mixtures of 1-propanol + 1-alkene at  $T = 298.15$  K versus 1-propanol mole fraction  $x_1$ : —, smoothed experimental results from sources given in Table 3; ···, calculated from present theory using eq 10; ---, calculated from present theory using eq 11. Curves are labeled with  $n_C^{(2)}$ —number of C-atoms in the alkene molecule. Curve labeled with  $n_C^{(2)} = 8$  for the 1-propanol + 1-octene system is taken from ref 5, and both attempts by eqs 10 and 11 coincide.**Figure 2.** Excess partial molar volumes  $V_1^E$  of 1-propanol in homologous 1-alkenes at  $T = 298.15$  K versus 1-propanol mole fraction  $x_1$ : —, smoothed experimental results; ---, calculated from present theory using eq 11. Curves  $V_1^E$  are labeled with the number of carbon atoms in the alkene molecule.

where  $\omega = (cV_1^*)^{1/3}(cV_2^*)^{-2/3}$  is a dimensionless correction factor used for alkanol + alkane mixtures,<sup>8,9</sup>  $c = \text{cm}^3\cdot\text{mol}$ , and where  $\alpha_o^{(1)}$  and  $\alpha_b^{(2)}$  are the fractions of OH and  $\text{CH}_2=\text{CH}-$  groups in the molecules of alkanol (1) and alkene (2), respectively, calculated by using van der Waals volumes, as in Table 4. The interaction parameter between OH and the aliphatic group ( $X_{o,a}^* = 1.0135\cdot 10^5$ ) was used as before.<sup>9</sup> For the alkanol + alkene mixtures,<sup>5-8</sup> only two parameters were added:  $X_{o,b}^* = 1.41465\cdot 10^5$  for interaction of the OH and  $-\text{CH}=\text{CH}_2$  group and  $X_{b,a}^* = 8.621\cdot 10^3$  for interaction of the  $-\text{CH}=\text{CH}_2$  group and aliphatic ( $\text{CH}_2$  and  $\text{CH}_3$ ) group. The results of prediction

**Table 4. Molar Volume  $V$ , Coefficients of Isobaric Thermal Expansion  $\alpha_p$ , and Isothermal Compressibility  $\beta_T$ <sup>a</sup> at  $T = 298.15$  K, Characteristic Parameters Volume  $V^*$ , Pressure  $P^*$ , and Temperature  $T^*$ , and Fraction  $\alpha_k^{(i)c}$  of OH or  $-\text{CH}=\text{CH}_2$  Groups, Respectively, in Component Molecules**

component	$V^a$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$\alpha_p^a$ $\text{K}^{-1}$	$10^6 \beta_T^b$ $\text{atm}^{-1}$	$V^*$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$P^*$ $\text{J} \cdot \text{cm}^{-3}$	$T^*$ $\text{K}$	$\alpha_k^{(i)c}$
1-propanol	75.160	0.995	102.88	60.289	454.1	5245.6	0.19066
1-hexene	125.896	1.411	173.37	94.922	432.5	4401.7	0.31512
1-heptene	141.750	1.275	148.49	108.913	439.4	4614.5	0.27213
1-octene	157.858	1.173	131.45	123.121	443.15	4808.2	0.23947
1-decene	190.338	1.054	111.98	151.221	450.5	5083.7	0.19311

<sup>a</sup> Calculated from densities and molecular mass (see: ref 5 and ref 7). <sup>b</sup> Estimated by the Manzini and Crescenzi group method (see ref 5). <sup>c</sup> Fractions of the OH and  $-\text{CH}=\text{CH}_2$  groups are calculated by using the van der Waals volume (ref 5 and ref 7).



**Figure 3.** Excess molar isobaric thermal expansion  $A_p^E = (\partial V^E / \partial T)_p$  for binary mixtures of 1-propanol + 1-alkene at  $T = 298.15$  K versus 1-propanol mole fractions  $x_1$ : —, results from sources given in Table 5; ---, calculated from present theory, eq 11. Curves are labeled with  $n_C^{(2)}$ —number of C-atoms in the alkene molecule. Curve labeled with  $n_C^{(2)} = 8$  for the 1-propanol + 1-octene system is taken from ref 6.

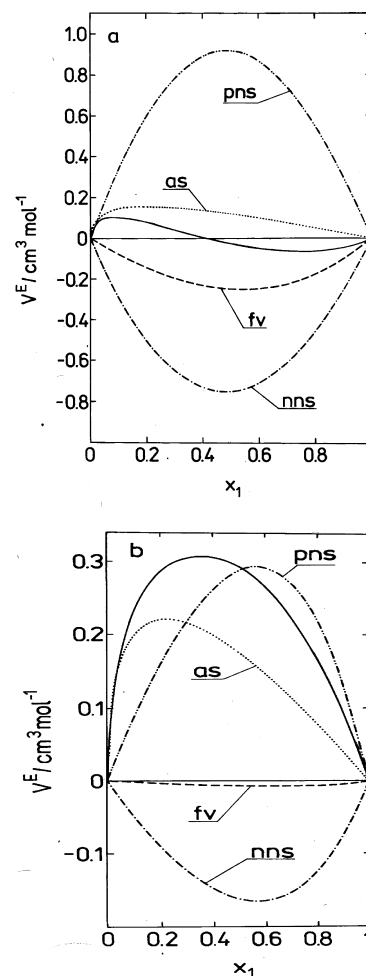
**Table 5. Coefficients  $a_i^{(1)}$  for Representations of the  $A_p^E$  at  $T = 298.15$  K Using Equation 6 for (1-Propanol + 1-Alkene) Systems**

$a_i^{(1)}$	component 2	
	1-octene <sup>a</sup>	1-decene
$a_1^{(1)}$	0.042425	0.043715
$a_2^{(1)}$	−0.06346	−0.062505
$a_3^{(1)}$	0.037264	0.044755

<sup>a</sup> Ref 6.

$V^E$  using eq 7 for 1-propanol + 1-hexene and 1-propanol + 1-decene systems presented in Figure 1 show rather poor results in contrast to the very satisfactory prediction for the mixtures formed by the larger molecules of alkene and alkanol.<sup>5–8</sup> In comparison with experimental data, the model predicts too high  $V^E$  values for 1-propanol + 1-hexene and lower  $V^E$  for the 1-decene system. The character of the deviation indicates a more negative effect of  $\text{OH} \cdots \pi$  interaction in the case of the 1-hexene system and also shows  $\text{OH} \cdots \pi$  interaction to change more rapidly with increase in the length of the 1-alkene molecule than described by eq 10 representing random mixing of the intermolecular contact surfaces (so-called zeroth approximation). This fact suggests a weak solvation effect occurs. Therefore, we modified eq 10 using a stronger dependence of  $\text{OH} \cdots \pi$  interchange interaction parameter  $X_{o,b}^*$  on the number of C-atoms in the 1-alkene molecule  $n_C^{(2)}$

$$X_{12} = \omega [X_{o,a}^* (\alpha_o^{(1)})^2 + (X_{o,a}^* + X_{b,a}^* - \varepsilon X_{o,b}^* \alpha_o^{(1)} \alpha_b^{(2)} + X_{b,a}^* (\alpha_b^{(2)})^2] \quad (11)$$



**Figure 4.** Contributions to excess molar volume of 1-propanol in (a) 1-hexene and (b) 1-decene at  $T = 298.15$  K versus the mole fraction of 1-propanol. Lines denote model calculations: —, total  $V^E$  curve and its contributions:  $\cdots$ , (as) alkanol self-association; ---, (fv) free volume; - · - · - · -, (pns) positive part of nonspecific interactions; - - - - -, (nns) negative (OH  $\cdots \pi$ ) part of nonspecific interactions.

where  $\varepsilon = 15/(n_C^{(2)} + 7)$ . The modified relation gives good qualitative results for  $V^E$  as presented in Figure 1 and for  $V_T^E$  in Figure 2.

Figure 4 shows an interpretation of the shape of the  $V^E$  curve for 1-propanol + 1-hexene and 1-propanol + 1-decene mixtures as a result of superposition of the contributions related to the negative effects of  $\text{OH} \cdots \pi$  interactions and of free volume and the positive effects of self-association of alkanol and residual nonspecific interactions (due to disruption of the pure liquid structure other than self-association). Similarly as for 1-alkanol + alkane systems, the negative free volume contribution and the relatively small positive but highly asymmetric alkanol self-



association contribution play a dominant role. For the short-chain 1-hexene, the highly asymmetric self-association contribution leads to a positive lobe in the 1-propanol diluted region. The negative lobe appearing for the remaining concentrations is due to the predominance of the negative contributions. For 1-decene, the 1-propanol self-association contribution slightly rises due to the higher ability of the longer chain to disrupt H-bonds; the positive nonspecific interaction contribution only slightly decreases; and the negative contributions (free volume,  $\text{OH}\cdots\pi$ ) are significantly less negative. Therefore, the observed  $V^E$  values are positive over the whole concentration range (Figure 1). These effects explain also changes of the partial molar excess volume of 1-propanol in 1-hexene and 1-decene,  $V_1^E$ . For 1-propanol in 1-hexene, the shape of  $V_1^E$  is characteristic for the potential type curve with very high positive values in a high dilution region and a deep minimum lowering at higher concentrations. The effects discussed above explain also the positive values in the whole concentration range  $V_1^E$  for 1-propanol in the 1-decene system. A similar behavior was observed for the 1-alkanol + n-alkane systems.<sup>9</sup>

The contributions were calculated in the following way:<sup>7,8</sup> (1) self-association contributions were calculated from the relation for  $V^E$ , where the equation of state contribution is neglected; (2) equation of state contributions were calculated by neglecting the self-association contribution; (3) packing (free volume) contribution was calculated by putting the Flory interaction parameter  $X_{12} = 0$  in the equation of state contribution and by neglecting the self-association contribution; (4) nonspecific interaction contribution was calculated as the difference between the equation of state contribution and the free volume contribution. The nonspecific interactions contribution (see eq 11) is divided into part (a) connected with  $\text{OH}\cdots\pi$  interactions related to interaction interchange parameter  $X_{\text{o,b}}^*$  and part (b) connected with the sum of positive nonspecific interaction contributions related to interaction interchange parameters  $X_{\text{o,a}}^*$  and  $X_{\text{b,a}}^*$ .

Results of  $A_p^E$  calculations at 298.15 K are compared with the model prediction for the series of systems in Figure 3. The model predicts a reasonably correct variation of the estimated  $A_p^E$  with the increase of length of the alkene molecule.

## Conclusion

The results indicate that the interchange interaction parameter for  $\text{OH}\cdots\pi$  interactions changes more extensively with the length of the alkene and alkanol molecules than it appears from the model representing random mixing of the intermolecular contact surfaces (so-called zeroth approximation). However, for mixtures formed by longer molecule alkanols and alkenes, the effect of the  $\text{OH}\cdots\pi$  interactions is relatively weaker and can be described qualitatively well by the zeroth approximation. The stronger dependence of the  $\text{OH}\cdots\pi$  interactions on the length of 1-alkene molecule, like it was assumed, allows us to interpret and qualitatively predict excess volume and partial molar excess volume for 1-propanol + 1-alkene mixtures as well as the excess molar isobaric thermal expansion.

Thermodynamic properties of the mixtures formed by alkanols with a weak active solvent like 1-alkene seem to be an apparently simple case to describe by the theory of nonelectrolyte solutions. However, as it was presented above, formation of the weak  $\text{OH}\cdots\pi$  cannot be excluded. Therefore, further study of weak coassociation of  $\text{OH}\cdots\pi$  in alkanol + alkene mixtures would be necessary, i.e., investigation on the excess molar isobaric heat capacity, as a thermodynamic function most sensitive to complex formation, and comparative IR and NMR studies.

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## Supporting Information Available:

Tables S1 and S2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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