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Excess Molar Enthalpies of Benzyl Alcohol + Alkanols (C_1-C_6) and Their Correlations at 298.15 K and Ambient Pressure

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Excess molar enthalpies, H_m^E, for the binary mixtures of benzyl alcohol + methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, and hexan-1-ol were measured over the entire range of composition at 298.15 K and ambient pressure using a Parr 1455 solution calorimeter. From the experimental results the excess partial molar enthalpies, H_i^E, and excess partial molar enthalpies at infinite dilution, $H_i^{\mathrm{E},\infty}$, were calculated. While the excess molar enthalpies are negative for the methanol mixture, those for ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, and hexan-1-ol mixtures are positive over the entire range of composition of benzyl alcohol. The experimental data were correlated by the Redlich−Kister equation and the two thermodynamics models (Wilson and nonrandom two-liquid, NRTL).

Introduction

The purpose of this excess molar enthalpy study is to provide information about molecular interactions in the liquid state. Benzyl alcohol and alkanol are widely used solvents in chemical industry. Benzyl alcohol has been used as a good solvent in chemical processes such as extraction distillation.[1,2] We have previously measured the excess molar enthalpies of some organic solvents with alkanols.[3−8] In continuation of our earlier work we present experimental data on excess molar enthalpies, H_m^E, for benzyl alcohol + methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, and hexan-1-ol over the entire range of composition at 298.15 K and ambient pressure. From the experimental results the excess partial molar enthalpies, H_i^E, and excess partial molar enthalpies at infinite dilution, $H_i^{\mathrm{E},\infty}$, were calculated. These data help to obtain some insight into the intermolecular interactions, particular hydrogen bonding properties, between the benzyl alcohol and an alcohol with a different extent of chain length.

Experimental Section

Materials. The solvents used in this study, suppliers, and purities are listed in Table 1. These liquids were used without further purification with the exception of hexan-1-ol, which was purified by the standard method of Perrin and Armarego.[9] The purities of the solvents were also checked by their densities and refractive indices, and comparisons with literature values[10,11] are shown in Table 1.

Densities. The densities of pure components, ρ, were determined at 298.15 K by means of an Anton Paar DMA 4500 oscillating U-tube density meter, provided with automatic viscosity correction. The temperature in the cell was regulated to ± 0.01 K with a solid state thermostat. Before measurements, the apparatus was calibrated using double-distilled fresh water and dry air. The uncertainty in the density was $\pm\ 1\cdot10^{-5}$ $\mathrm{g\cdot cm^{-3}}$.

Refractive Index Measurements. Refractive indices were measured at 298.15 K using a thermostatted Abbe refractometer. Water was circulated into the prism of the refractometer by a circulation pump connected to an external thermostatted water bath. The uncertainty of the refractive index is in the order of ± 0.0002 units, and for the temperature it was ± 0.1 K.

Table 1. Sources, Purity Grades, Densities, ρ, and Refractive Indices, n_D, of the Pure Components at 298.15 K

			$\rho/(\mathrm{g\cdot cm^{-3}})$		n_D	
component	source	purity	exptl	lit.	exptl	lit.[11]
benzyl alcohol	Merck	0.99	1.04199	1.0416[10]	1.5381	1.53837
methanol	Merck	0.995	0.78650	0.78664[11]	1.3266	1.3265
ethanol	Merck	0.998	0.78515	0.78504[11]	1.3595	1.3594
propan-1-ol	Merck	0.998	0.79951	0.79975[11]	1.3833	1.3837
butan-1-ol	Merck	0.998	0.80575	0.80575[11]	1.3974	1.3973
pentan-1-ol	Fluka	0.99	0.81088	0.81080[11]	1.4088	1.4079
hexan-1-ol	Merck	0.99	0.81520	0.81534[11]	1.4165	1.4161

Calorimetric Measurements. A Parr 1455 solution calorimeter was used to measure the excess molar enthalpies, H_m^E. The measurements were carried out in an isolated room at 298 K and ambient pressure. In the measurement of excess enthalpies, the known weight of 100 mL of component A is taken into Dewar vessel, and about 20 mL of component B is weighted in a sealed glass rotating cell. Both of the components are kept in thermal contact with each other in the Dewar mixing chamber at 298.15 K. After attaining the thermal equilibrium component B in the rotating cell is mixed with component A in the Dewar vessel by pushing the glass rod. These experiments were continued until the concentration reached 50 to 60 in volume fraction. This procedure was repeated by taking component A as component B and component B as component A. Details of the equipment and its operation procedure have been described previously.[6,7] The miscibility of the components was tested prior to calorimetric measurements, and the two components were found to be completely miscible over the whole concentration range. The temperature in calorimetric measurement can be read to an uncertainty of $\pm\ 2\cdot10^{-3}$ K.

Mole fractions of mixtures were determined by mass using a digital balance (model: Mettler AB 204-N) with an uncertainty of $\pm\ 1\cdot10^{-4}$ g. The uncertainty in the mole fraction is estimated to be lower than $\pm\ 2\cdot10^{-4}$. The estimated relative uncertainty in the excess enthalpy measurements is $\pm\ 1\cdot10^{-2}$ of the determined value.

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Table 2. Excess Molar Enthalpies, H_m^E, and Excess Partial Molar Enthalpies for the Binary Mixtures of Benzyl Alcohol (1) + Alkan-1-ols (2) at 298.15 K

x_1	H_m^E J·mol^{-1}	H_2^E J·mol^{-1}	H_1^E J·mol^{-1}	x_1	H_m^E J·mol^{-1}	H_2^E J·mol^{-1}	H_1^E J·mol^{-1}
Benzyl Alcohol (1) + Methanol (2)							
0.0000		0	−140.3	0.4995	−140.8	−69.6	−208.7
0.0700	−15.2	3.7	−249.5	0.5964	−144.5	−150.4	−142.4
0.1388	−33.4	10.4	−309.6	0.6972	−135.8	−262.6	−81.3
0.2057	−57.0	15.0	−332.6	0.7998	−108.1	−401.0	−34.8
0.2728	−79.2	13.6	−328.9	0.9028	−61.5	−555.3	−7.8
0.3404	−100.6	3.0	−305.5	1.0000		−703.9	0
0.3992	−119.8	−15.4	−274.4				
Benzyl Alcohol (1) + Ethanol (2)							
0.0000		0	1113.4	0.4855	223.2	243.0	197.6
0.0746	73.4	9.3	864.7	0.5857	207.9	333.6	118.9
0.1514	130.6	33.9	669.6	0.6883	176.7	437.5	59.5
0.2275	171.4	68.6	520.1	0.7915	129.3	545.2	21.3
0.3029	198.4	110.9	402.4	0.8949	71.7	638.8	3.5
0.3785	214.4	160.5	306.3	1		688.7	0
Benzyl Alcohol (1) + Propan-1-ol (2)							
0		0	522.4	0.5993	107.2	207.7	40.1
0.0984	48.6	4.5	443.1	0.6983	86.7	250.3	16.7
0.1964	84.7	22.5	340.7	0.7996	61.4	282.9	5.6
0.2873	106.5	52.7	246.0	0.8988	32.3	306.3	1.3
0.3999	123.6	104.6	146.6	1		331.9	0
0.4987	119.0	156.5	82.6				
Benzyl Alcohol (1) + Butan-1-ol (2)							
0		0	937.8	0.6029	212.1	357.2	117.8
0.0976	84.9	8.6	775.5	0.7039	179.0	466.3	59.7
0.1973	148.9	37.7	607.8	0.8026	132.8	574.3	24.1
0.2950	196.1	87.7	454.8	0.9017	72.6	680.9	5.4
0.3960	221.1	160.2	317.4	1		783.8	0
0.4931	231.1	246.3	209.7				
Benzyl Alcohol (1) + Pentan-1-ol (2)							
0		0	938.3	0.5999	271.2	403.3	186.5
0.1044	95.7	4.9	869.7	0.6988	240.9	548.8	107.9
0.1968	168.5	27.8	743.9	0.7995	185.7	720.0	50.6
0.2902	226.0	76.1	594.9	0.8992	105.7	927.2	14.2
0.3864	265.5	153.0	444.8	1		1204.5	0
0.4838	284.8	255.4	311.8				
Benzyl Alcohol (1) + Hexan-1-ol (2)							
0		0	1121.3	0.5980	342.2	453.6	266.6
0.0954	104.5	4.9	1041.7	0.6996	309.7	645.2	163.2
0.1959	198.1	31.7	888.4	0.8022	241.1	896.5	80.4
0.2910	270.8	85.8	721.6	0.8986	145.4	1218.2	24.5
0.3901	324.2	173.1	552.9	1		1701.0	0
0.5072	343.8	314.9	378.8				

Results and Discussion

The experimental excess molar enthalpies at 298.15 K of the binary mixtures of benzyl alcohol + alkan-1-ols (C_1-C_6) are listed in Table 2 as a function of the mole fraction (x_1) of the benzyl alcohol. The experimental results are presented in Figure 1.

The excess molar enthalpies are positive over the entire range of composition for all mixtures except in the system of benzyl alcohol + methanol, for which H_m^E is negative. This indicates that benzyl alcohol interacts more strongly with methanol than with other alkanols. The H_m^E values at $x_1 = 0.5$ are in the order methanol < propan-1-ol < ethanol < butan-1-ol < pentan-1-ol < hexan-1-ol. The H_m^E values increase as the chain length of the alkan-1-ol is increased, except for ethanol which is more positive than propan-1-ol. The heat of mixing of these systems may be influenced by factors such as (i) absorption of heat due to dissociation of self-associated benzyl alcohol or alkanols and (ii) liberation of heat as a result of possible hydrogen bonding interaction between benzyl alcohol and alkanols. The actual value of H_m^E would depend upon the relative strength of the two opposing effects.

The excess molar enthalpies were correlated by the Redlich−Kister equation and two kinds of local composition models. The Wilson and nonrandom two-liquid (NRTL) models can be used to predict the ternary data using interaction parameters obtained from the binary data.

Redlich−Kister Equation. The excess molar enthalpies were correlated by the Redlich−Kister[12] equation:

$$H_m^E/\mathrm{J\cdot mol^{-1}} = x_1 x_2 \sum_{r=1} A_r (x_1 - x_2)^{r-1} \qquad (1)$$

where x_1 is the mole fraction of benzyl alcohol and A_r represents the adjustable parameters. The parameters in eq 1 were estimated by the least-squared fit method, and in each case the optimum number of coefficients is ascertained from the examination of the variation in the standard deviation, $\sigma(H_m^E)$, as given by:

$$\sigma(H_m^E)/\mathrm{J\cdot mol^{-1}} = [\sum_{k=1}^{n} \{H_{m,cal}^E - H_{m,exp}^E\}_k^2/(n-p)]^{1/2} \qquad (2)$$

where n is the number of experimental points and p is the number of adjustable parameters A_r. The adjustable

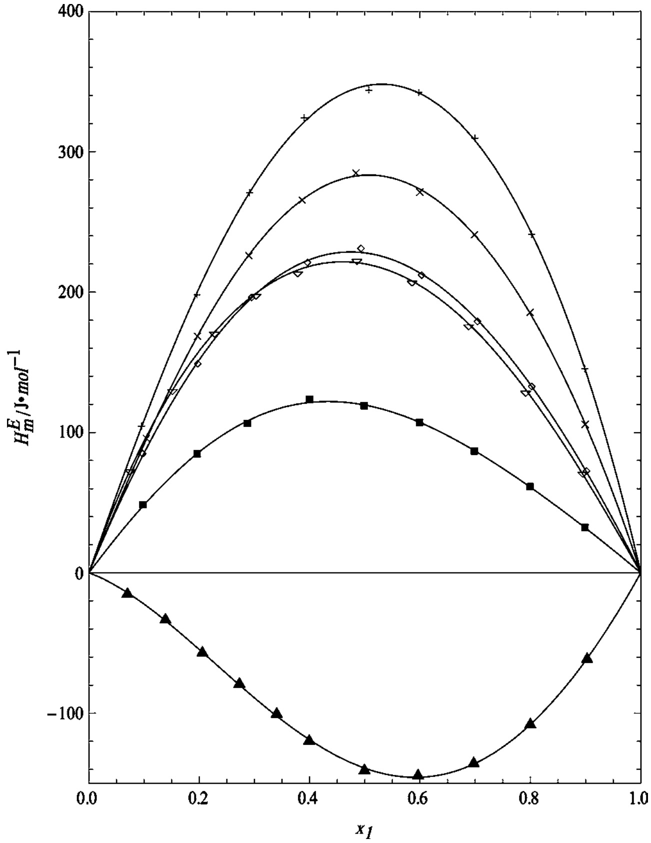

Figure 1. Experimental excess molar enthalpies of benzyl alcohol (1) + alkan-1-ols (2) at 298.15 K: ▲, methanol; ▽, ethanol; ■, propan-1-ol; ◇, butan-1-ol; ×, pentan-1-ol; +, hexan-1-ol. Solid lines were calculated with eq 1 at ambient pressure.

parameters A_r and the standard deviation σ are given in Table 3.

Wilson Model. The model proposed by Wilson[13] is based on the concept of local composition. The explicit form of excess molar enthalpies of binary mixtures developed through Wilson's model is

$$H_m^E/J\cdot mol^{-1} = x_1x_2\left(\frac{\lambda_{12}\Lambda_{12}}{x_1 + \Lambda_{12}x_2} + \frac{\lambda_{21}\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \quad (3)$$

where $\Lambda_{12} = (V_2/V_1)\exp(-\lambda_{12}/RT)$ and $\Lambda_{21} = (V_1/V_2)\exp(-\lambda_{21}/RT)$; λ_{12} and λ_{21} are model parameters; and V_i is molar volume. The adjustable parameters λ_{21} and λ_{12} in the Wilson equation were obtained by a nonlinear least-squares fit and along with the standard deviation, $\sigma(H_m^E)$, are given in Table 4.

NRTL Equation. Renon and Prausnitz[14] modified Wilson's model for local mole fraction by introducing the constant α_{ij} to account for the nonrandomness of liquid solutions. The nonrandomness parameter, α_{ij}, is an empirical constant. According to the modification the explicit form of excess molar enthalpies is

$$H_m^E/J\cdot mol^{-1} = -x_1x_2 \left[\frac{Z_1N_1\alpha_{12}\Delta g_{21} - \Delta g_{21}G_{21}N_1 - Z_1x_2G_{21}\alpha_{12}\Delta g_{21}}{N_1^{\,2}} + \frac{Z_2N_2\alpha_{12}\Delta g_{12} - \Delta g_{12}G_{12}N_2 - Z_2x_1G_{12}\alpha_{12}\Delta g_{12}}{N_2^{\,2}}\right] \quad (4)$$

where $G_{21} = \exp(-\alpha_{12}\Delta g_{21}/RT)$, $N_1 = x_1 + x_2G_{21}N_2 = x_2 + x_1G_{12}$, $G_{12} = \exp(-\alpha_{12}\,\Delta g_{12}/RT)$, $Z_1 = (\,\Delta g_{21}/RT)G_{21}$, and $Z_2 = (\,\Delta g_{12}/RT)G_{12}$; Δg_{12} and Δg_{21} are the two adjustable parameters remaining, because the nonrandomness parameter, α_{ij}, was taken to be constant for each binary mixture. The adjustable parameters (Δg_{21}, Δg_{12}) and the randomness parameter (α_{ij}) in the NRTL equation were obtained by a nonlinear least-squares fit and along with the standard deviation, $\sigma(H_m^E)$, are given in Table 4.

Analyses of experimental data of all binary systems using the Wilson and NRTL models show that both models were generally satisfactory.

The excess partial molar enthalpies, H_i^E, can be determined from excess molar enthalpy data using:

$$H_i^E/J\cdot mol^{-1} = H_m^E + (1 - x_i)(\partial H_m^E/\partial x_i)_{T,P} \quad (5)$$

where $(\partial H_m^E/\partial x_i)_{T,P}$ is calculated from eq 1 using the parameters in Table 3.

The excess partial molar enthalpy at infinite dilution $H_i^{E,\infty}$ can be determined from the following equation:

$$H_i^{E,\infty}/J\cdot mol^{-1} = (\partial H_m^E/\partial x_i)_{x_i=0,T,P} \quad (6)$$

The excess partial molar enthalpy at infinite dilution, $H_i^{E,\infty}$, appears to be of particular interest. The properties of the solute at infinite dilution reflect, at least to a good approximation, how the solute interacts with the solvent. The values of H_i^E and $H_i^{E,\infty}$

Table 3. Redlich−Kister Equation Fitting Coefficients, A_r, in Equation 1 and Standard Deviation, $\sigma(H_m^E)$, in Equation 2 for Benzyl Alcohol (1) + Alkan-1-ols (2) at 298.15 K

system	A_1	A_2	A_3	A_4	$\sigma(H_m^E)$ / J•mol^{-1}
benzyl alcohol (1) + methanol (2)	−556.554	−276.921	134.459	−4.885	1.2
benzyl alcohol (1) + ethanol (2)	880.382	−140.835	20.668	−71.510	1.4
benzyl alcohol (1) + propan-1-ol (2)	478.105	−150.589	−50.965	55.317	1.4
benzyl alcohol (1) + butan-1-ol (2)	911.702	−99.829	−50.901	22.878	1.8
benzyl alcohol (1) + pentan-1-ol (2)	1133.130	35.134	−61.730	97.956	1.4
benzyl alcohol (1) + hexan-1-ol (2)	1387.080	167.185	24.083	122.658	2.3

Table 4. Parameters λ_{21}, λ_{12}, Δg_{21}, Δg_{12}, and $\alpha_{12} = \alpha_{21}$ Used in Equations 3 and 4 for Calculating H_m^E Derived at 298.15 K

	λ_{21}	λ_{12}	Δg_{21}	Δg_{12}		σ/(J•mol^{-1})	
system	J•mol^{-1}				α_{ij}	Wilson	NRTL
benzyl alcohol (1) + methanol (2)	1394.86	−2234.08	−707.469	461.08	1.0	3.0	11.2
benzyl alcohol (1) + ethanol (2)	631.955	216.302	920.077	169.094	0.6	1.6	1.6
benzyl alcohol (1) + propan-1-ol (2)	40.4436	574.89	2675.91	−1789.87	0.1	3.5	2.8
benzyl alcohol (1) + butan-1-ol (2)	392.95	634.081	910.97	93.524	0.3	2.9	2.6
benzyl alcohol (1) + pentan-1-ol (2)	754.219	544.352	−126.54	132.31	0.1	3.6	3.1
benzyl alcohol (1) + hexan-1-ol (2)	1064.96	659.975	213.19	1422.44	0.2	3.1	2.8

are given in Table 2. The H_1^E and H_2^E of methanol are negative and for other alkanols are positive over the entire range of benzyl alcohol composition.

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