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Excess Molar Enthalpies of 2-Methyl-2-butanol (1) + 1-Alkanols (C_1-C_5) (2) at 298.15 K

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The excess molar enthalpies, H^{E}_{m}, are reported for 1-alkanols (2), namely methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol, in 2-methyl-2-butanol (1) at 298.15 K and at ambient pressure over a range of mole fractions. The H^{E}_{m} data values were negative for all systems over the whole range of composition, and the magnitude of H^{E}_{m} decreases with increasing of chains length. The Redlich−Kister polynomial equation was used to correlate. H^{E}_{m} The excess partial molar enthalpies of 2-methyl-2-butanol, $H^{E}_{m,1}$, and excess partial molar enthalpies of 1-alkanols (C_1-C_5),$H^{E}_{m,2}$ were calculated. The experimental data were used to evaluated the intermolecular interaction functions such as $\partial H^{E}_{m,i}/\partial x_i$ and $\partial H^{E}_{m,i}/\partial x_j$.

Introduction

The thermophysical properties are important as quantitatively deviation from ideality of mixtures, which is due to molecular interactions. 1-alkanols (C_1-C_5) form complex structures because of creating of hydrogen bonding,[1] and the degree of association decreases with increasing of ring complexes due to the number of $-CH_2$ groups.[2]

This paper is a part of ongoing research to measure and characterize the excess enthalpy of mixtures containing organic solvent.[3−5] Excess partial molar enthalpies, $H^{E}_{m,i}$, were also calculated from the experimental data. This study is attempted to provide data to show the effect of chain length of 1-alkanols on the excess molar enthalpy. These data may provides information about molecular interaction between components in the mixture.

Composition derivatives of excess partial molar functions have been utilized to evaluate solute−solute and solute−solvent interactions.[6−8] In excess molar enthalpy, H^{E}_{m}, a situation where $\partial H^{E}_{m,i}/\partial x_i > 0$ implies that additional *i* makes the contribution (per mole) of *i* to the total enthalpy of the solution more positive; in other words, it makes the enthalpic situation of *i* in the solution less favorable. In such a case it may be said that *i*−*i* interactions are unfavorable or repulsive in terms of enthalpy. Similarly, if $\partial H^{E}_{m,i}/\partial x_i < 0$, *i*−*i* interactions make the enthalpic situation of *i* more favorable, and *i*−*i* interactions are denoted favorable or attractive in terms of enthalpy. In the present context, it is important to note that the above arguments are valid regardless of the number of components in the solution and that similar conclusions can be obtained for "heterogeneous" *i*−*j* interactions using the derivative $\partial H^{E}_{m,i}/\partial x_i$.

Experimental Section

Chemicals. 2-Methyl-2-butanol, methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol, were purchased from Merck with mass fraction higher than 99% and used without further purifications. The purity of reagents were checked by comparing the measured densities and refractive indices at 298.15 K with those reported in the literature.[9−12] The results are in good agreement with values found in the literature and reported in Table 1.

Table 1. Physical Properties of the Pure Compounds at T = 298.15 K

	ρ / $g\cdot cm^{-3}$		n_D	
compound	exp.	lit.	exp.	lit.
2-methyl-2-butanol	0.80460	0.80433[a]	1.4019	1.40238[d]
methanol	0.78658	0.78664[b]	1.3265	1.32750[b]
ethanol	0.78517	0.78523[b]	1.3587	1.35906[b]
1-propanol	0.79962	0.79962[c]	1.3827	1.3830[c]
1-butanol	0.80582	0.80576[c]	1.3969	1.3973[c]
1-pentanol	0.81101	0.81083[c]	1.4068	1.4080[c]

[a] Reference 9. [b] Reference 10. [c] Reference 11. [d] Reference 12.

Apparatus and Procedure. An Anton Paar digital densimeter (model DMA 4500) was used and operated in the static mode. The uncertainty of the density measurement was estimated to be $1 \cdot 10^{-5}$ $g\cdot cm^{-3}$. Refractive indices were measured using a high accuracy Abbe refractometer with an uncertainty of $2 \cdot 10^{-4}$. A Parr 1455 solution calorimeter was used to measure the excess molar enthalpies, H^{E}_{m}. The measurements were carried out in an isolated room at 298.15 K and at ambient pressure. The excess molar enthalpies of (water + ethanol) at 298.15 K and at ambient pressure were also measured to check the reliability of the apparatus used in this study. Excess molar enthalpy of three runs at different mole fractions for (water + ethanol) differed less than 1.8 % with the literature values.[13]

The temperature in calorimetric measurement can be read to an uncertainty of $2 \cdot 10^{-2}$K. Mole fractions of mixtures were determined by mass using a digital balance (model: Mettler AB 204-N) with an uncertainty of $1 \cdot 10^{-4}$ g.

The experimental excess molar enthalpies, H^{E}_{m}, values were presented in Table 2 and determined from the following equation:[14]

$$H^{E}_{m} = -\left(C_P + \frac{C_V}{n}\right)\Delta T \qquad (1)$$

where C_P, C_V, n, and ΔT represent the molar heat capacity of the mixture, heat capacity of the calorimeter, amount of substance in the Dewar vessel of calorimeter, and the temperature difference the calorimeter after the mixing process and initial temperature

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Table 2. Experimental Excess Molar Enthalpies, H^E_m, for Binary Systems at $T = 298.15$ K

x_1	H^E_m / $J \cdot mol^{-1}$	x_1	H^E_m / $J \cdot mol^{-1}$	x_1	H^E_m / $J \cdot mol^{-1}$	x_1	H^E_m / $J \cdot mol^{-1}$
2-methyl-2-butanol (1) + methanol (2)				2-methyl-2-butanol (1) + ethanol (2)			
0.0908	−256.3	0.5513	−1268.0	0.0898	−248.6	0.5507	−973.0
0.1814	−522.3	0.6416	−1215.6	0.1796	−471.9	0.6406	−911.4
0.2731	−803.6	0.7319	−1069.6	0.2807	−705.6	0.7306	−770.9
0.3644	−1044.7	0.8195	−799.7	0.3707	−853.0	0.8205	−544.6
0.4608	−1200.0	0.9101	−421.9	0.4607	−950.0	0.9103	−271.0
2-methyl-2-butanol (1) + 1-propanol (2)				2-methyl-2-butanol (1) + 1-butanol (2)			
0.0900	−254.3	0.5497	−853.8	0.0900	−267.6	0.5510	−787.4
0.1801	−458.5	0.6395	−803.7	0.1801	−477.9	0.6412	−730.4
0.2802	−656.1	0.7292	−671.5	0.2702	−649.7	0.7313	−606.7
0.3701	−786.0	0.8189	−473.2	0.3707	−750.0	0.8198	−426.7
0.4599	−858.8	0.9088	−232.8	0.4609	−800.0	0.9099	−212.8
2-methyl-2-butanol (1) + 1-pentanol (2)							
0.0899	−208.9	0.5468	−676.8				
0.1800	−412.8	0.6372	−634.0				
0.2700	−568.7	0.7278	−530.6				
0.3664	−649.0	0.8185	−386.4				
0.4566	−684.5	0.9091	−206.4				

before mixing process, respectively. Molar heat capacity of the mixture was calculated according to Venkatesulu et al.,[15] and the heat capacity of the calorimeter was determined by following the operating instruction manual.[16] For the intermediary mixture compositions, it was not possible to determine H^E_m directly from mixing pure reagents due to the limited volume of the cell and vessel. Hence, a mixture was used in Dewar vessel whose H^E_m was previously determined, and the value of H^E_m is calculated by

$$H^E_m = -\left(C_P + \frac{C_V}{n}\right)\Delta T + \frac{n_0}{n}H^E_{m_0} \tag{2}$$

where n_0 and $H^E_{m_0}$ are the amount of substance in the previous mixing process and its excess molar enthalpy, respectively. Their values are zero when pure reagent is used. The uncertainty of the excess molar enthalpy, H^E_m, measurement was estimated to $1 \cdot 10^{-1}$ $J \cdot mol^{-1}$.

Results and Discussion

The experimental excess molar enthalpies of the binary mixtures of 2-methyl-2-butanol (1) + 1-alkanols (C_1−C_5) (2) are listed in Table 2 as a function of the mole fraction (x_1) of the 2-methyl-2-butanol at 298.15 K. The experimental results are presented in Figure 1. The results can be compared with those published by D'Aprano et al.[17] For the mixture of 2-methyl-2-butanol (1) + 1-pentanol (2), our values are somewhat more negative than theirs. The measurement conditions were the same except for pressure, which our measurement pressure was ambient pressure (81.5 kPa against 101.33 kPa). Also, the type of instrument was different. Their measurements were carried out using a LKB 2107 flow microcalorimeter, but we used a Parr 1455 macrocalorimeter.

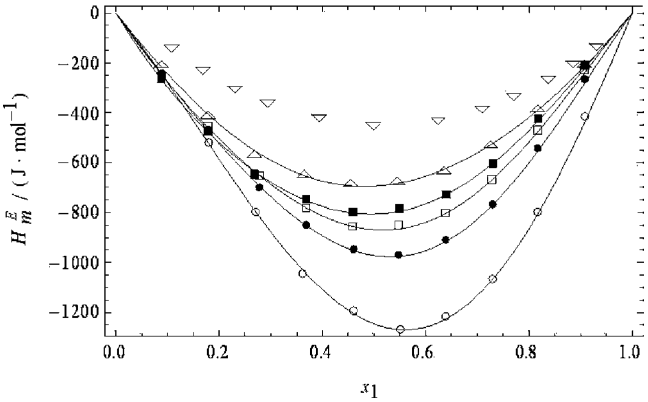

Figure 1. Experimental excess molar enthalpies of 2-methyl-2-butanol (1) + 1-alkanols (2) at 298.15 K. This work: ○, methanol; ●, ethanol; □, 1-propanol; ■, 1-butanol; Δ, 1-pentanol. D'Aprano et al.:[17] ∇, 1-pentanol. Solid lines were calculated from eq 3.

Table 3. Coefficients, A_k, and Standard Deviations, $\sigma(H^E_m)$ for Binary Systems at $T = 298.15$ K

system	A_0 / $J \cdot mol^{-1}$	A_1 / $J \cdot mol^{-1}$	A_2 / $J \cdot mol^{-1}$	A_3 / $J \cdot mol^{-1}$	$\sigma(H^E_m)$ / $J \cdot mol^{-1}$
2-methyl-2-butanol (1) + methanol (2)	−4980.9	−1573.51	1242.75	359.173	6.0
2-methyl-2-butanol (1) + ethanol (2)	−3884.05	−634.614	1024.27	657.705	3.0
2-methyl-2-butanol (1) + 1-propanol (2)	−3470.26	−288.689	761.495	630.272	4.5
2-methyl-2-butanol (1) + 1-butanol (2)	−3222.93	90.214	356.722	473.525	5.4
2-methyl-2-butanol (1) + 1-pentanol (2)	−2776.62	212.707	210.489	−195.034	7.9

Excess molar enthalpies are negative over the entire range of composition for all mixtures. These indicate that 2-methyl-2-butanol interacts more strongly with 1-alkanols (C_1−C_5). The magnitude of H^E_m for all the binary systems fall in the order: methanol > ethanol >1-propanol >1-butanol >1-pentanol. The H^E_m values increase as the chain length of the 1-alkanols is increased. The enthalpy of mixing H^E_m could be considered as being due to three effects: (i) the dissociation of 2-methyl-2-butanol, which is an endothermic effect, (ii) the dissociation of 1-alkanols (C_1−C_5), also causes an endothermic effect, (iii) the cross interaction of 2-methyl-2-butanol and 1-alkanols (C_1−C_5), which is an exothermic. It is well-known that alcohols are association by H-bonding in pure state that decreases with increasing of chain length.

Redlich−Kister Equation. The values of H^E_m for each binary mixture have been fitted to the Redlich−Kister polynomial equation[18]

$$H^E_m = x_1 x_2 \sum_{k=0}^{N} A_k (x_1 - x_2)^k \tag{3}$$

where x_1, x_2, and N are the mole fraction of 2-methyl-2-butanol, 1-alkanols (C_1−C_5), and order of polynomial, respectively. The coefficients, A_k, are adjustable parameters obtained by the method of least-squares are given in Table 3 together with their standard deviations, σ, determined from

$$\sigma(H^{E}_{m}) = \sum_{k=1}^{n}\left(\frac{(H^{E}_{m,exp} - H^{E}_{m,cal})^{2}}{n}\right)^{1/2} \qquad (4)$$

where n is the number of experimental data points.

The excess partial molar enthalpies, $H^{E}_{m,i}$, can be determined from excess molar enthalpies data using

$$H^{E}_{m,i} = H^{E}_{m} + (1 - x_i)(\partial H^{E}_{m}/\partial x_i)_{T,P} \qquad (5)$$

where $(\partial H^{E}_{m}/\partial x_i)_{T,P}$ is calculated from eq 3 using the parameters in Table 3 and x_i is mole fraction of component i.

Figure 2 represents graphically the excess partial molar enthalpies, $H^{E}_{m,i}$, of binary mixtures of 2-methyl-2-butanol (1) and 1-alkanols (C_1-C_5) (2) at 298.15 K. According to Figure 2, large negative values of $H^{E}_{m,i}$ at low x_1 have been ascribed to enhanced hydrogen bonding between solute−solvent molecules.

Intermolecular interactions in terms of enthalpy between 2-methyl-2-butanol (1), 1-alkanols (2), and 2-methyl-2-butanol (1) + 1-alkanols (2) were described as H^{E}_{1-1}, H^{E}_{2-2}, and H^{E}_{1-2}. H^{E}_{i-i} gives a measure of $i-i$ interaction in terms of enthalpy. Since $H^{E}_{m,i}$ is the actual contribution of i in terms of enthalpy, or the actual enthalpic situation of i component in the entire system, H^{E}_{i-i} shows the effect on the enthalpic situation of i when i is perturbed. Thus H^{E}_{i-i} and H^{E}_{i-j} are the enthalpic interaction functions[8] and can be determined from the following equations:

$$H^{E}_{i-i} = (1 - x_i)(\partial H^{E}_{m,i}/\partial x_i) \qquad (6)$$

$$H^{E}_{i-j} = (1 - x_j)(\partial H^{E}_{m,i}/\partial x_j) \qquad (7)$$

where i and j are the components in binary mixtures. The values of H^{E}_{i-i} and H^{E}_{i-j} for all binary mixture are negative so the intermolecular interaction are favorable in terms of enthalpy.

The thermodynamic properties of binary mixture containing polar and self-association components exhibit significant deviation from ideality, arising not only from the difference in size and shape but also from possible hydrogen bonding interaction between unlike molecules. The sign and magnitude of H^{E}_{m} show the deviation of mixture from ideality. If the sign of H^{E}_{m} is positive, the interaction between unlike molecules are repulsive, but if the sign of H^{E}_{m} is negative, it shows that the interaction between unlike molecules are attractive. For mixture of unlike alcohols the sign of H^{E}_{m} is negative due to existing of hydroxyl group and ability to creating of unlike hydrogen bonding. Cross-hydrogen bonding decreases with increasing of chain length of 1-alkanols due to steric hindrance effect so the magnitude of H^{E}_{m} decreases with the number of $-CH_2$ groups.

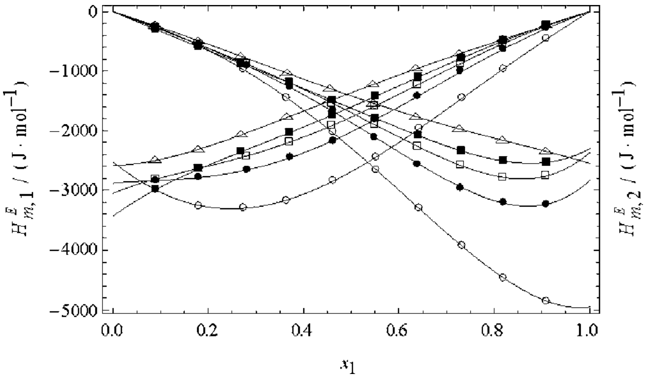

Figure 2. Excess partial molar enthalpies of 2-methyl-2-butanol (1) + 1-alkanols (2) at 298.15 K: ○, methanol; ●, ethanol; □, 1-propanol; ■, 1-butanol; Δ, 1-pentanol. Solid lines were calculated from eq 5.

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Literature Cited

(1) Bauer, B. A.; Patel, S. Condensed-phase properties of *n*-alkyl-amines from molecular dynamics simulations using charge equilibration force fields. *J. Mol. Liq.* **2008**, *142*, 32–40.
(2) Costas, M.; Patterson, D. Self-association of alcohols in inert solvents. Apparent heat capacities and volumes of linear alcohols in hydrocarbons. *J. Chem. Soc., Faraday Trans. I* **1985**, *81*, 635.
(3) Zarei, H. A.; Iloukhani, H. Excess molar enthalpies of methyl isobutyl ketone (MIBK) with alkan-1-ols (C1-C6) and their correlations at 298.15K. *Thermochim. Acta* **2005**, *427*, 201–205.
(4) Iloukhani, H.; Zarei, H. A. Excess Molar Enthalpies of N, N-Dimethylformamide + Alkan-1-ols (C_1-C_6) at 298.15 K. *J. Chem. Eng. Data* **2002**, *47*, 195–197.
(5) Zarei, H. A.; Iloukhani, H. Excess Molar Enthalpies of formamide + some Alkan-1-ols (C1-C6) and Their Correlations at 298.15 K. *Thermochim. Acta* **2003**, *405*, 123–128.
(6) Matsuo, H.; To, E. C. H.; Wong, D. C. Y.; Sawamura, S.; Taniguchi, Y.; Koga, Y. Excess Partial Molar Enthalpy of 1-Propanol in 1-Propanol-NaCl-H_2O at 25 °C: The Effect of NaCl on Molecular Organization of H_2O. *J. Phys. Chem. B* **1999**, *103*, 2981–2983.
(7) Westh, P.; Koga, Y. Intermolecular Interactions in 2-Butoxyethanol-DMSO-H_2O. *J. Phys. Chem.* **1996**, *100*, 433–438.
(8) Matthew, T. P.; Koga, Y. Interactions in 1-Propanol-(1,2- and 1,3-) Propanediol-H_2O: The Effect of Hydrophobic vs Hydrophilic Moiety on the Molecular Organization of H_2O. *J. Phys. Chem. B* **2002**, *106*, 7090–7095.
(9) Dzida, M. Study of the Effects of Temperature and Pressure on the Thermodynamic and Acoustic Properties of Pentan-1-ol, 2-Methyl-2-butanol, and Cyclopentanol in the Pressure Range from (0.1 to 100) MPa and Temperature from (293 to 318) K. *J. Chem. Eng. Data* **2009**, *54*, 1034–1040.
(10) Chen, H. W.; Wen, C. C.; Tu, C. H. Excess Molar Volumes, Viscosities, and Refractive Indexes for Binary Mixtures of 1-Chlorobutane with Four Alcohols at T = (288.15, 298.15, and 308.15) K. *J. Chem. Eng. Data* **2004**, *49*, 347–351.
(11) Jime’nez, E.; Casas, H.; Segade, L.; Franjo C. Surface Tensions, Refractive Indexes and Excess Molar Volumes of Hexane + 1-Alkanol Mixtures at 298.15 K. *J. Chem. Eng. Data* **2000**, *45*, 862–866.
(12) Iglesias, M.; Pineiro, M. M.; Marino, G.; Orge, B.; Domınguez, M.; Tojo, J. Thermodynamic properties of the mixture benzene + cyclohexane + 2-methyl-2-butanol at the temperature 298.15 K: excess molar volumes prediction by application of cubic equations of state. *Fluid Phase Equilib.* **1999**, *154*, 123–138.
(13) Landgren, M.; McEachern, D.; Olofsson, Q.; Randzio, S.; Sunner, S. Evaluation of excess enthalpies from flow-calorimetric measurements of enthalpies of dilution using local approximation by polynomials. *J. Chem. Thermodyn.* **1978**, *10*, 847.
(14) Checoni, R. F.; Francesconi, A. Z. Measurment and correlation of excess molar enthalpy at various temperatures acetonitrile + diethylamine or s-butylamine mixtures. *J. Thermal Anal. Calorim.* **2005**, *80*, 295–301.
(15) Venkatesulu, D.; Prabhakara Rao, M. V.; Veerana, D. Excess enthalpies of 2-alkoxyethanols with trichloroethylene and tetrachloroethylene at 298.15 K. *Thermochim. Acta* **1994**, *242*, 33–39.
(16) http://www.parrinst.com/doc_library/members/281m.pdf.
(17) D’Aprano, A.; De Lisi, R.; Donato, I. D. Thermodynamics of Binary Mixtures: Volumes, Heat Capacities, and Dilution Enthalpies for the n-Pentanol + 2-methyl-2-butanol System. *J. Sol. Chem.* **1983**, *12*, 383–400.
(18) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.

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