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# Excess Molar Enthalpies for Binary Mixtures of Benzyl Alcohol and Heptanone Isomers at Different Temperatures

**Xia Zhao, Zhi-Wu Yu,* Rui Zhou, and Yun Liu**

Department of Chemistry, Tsinghua University, Beijing 100084, China

Excess molar enthalpies for the binary mixtures of benzyl alcohol + 2-heptanone, + 3-heptanone, + 5-methyl-2-hexanone, and + 2,4-dimethyl-3-pentanone were measured over the entire composition range at (298.65, 303.55, and 308.50) K using a Calvet-type microcalorimeter. The excess molar enthalpies are positive for all the mixtures with their maximums between (300 and 500) J·mol$^{-1}$. The Redlich−Kister polynomial was used to correlate the experimental results. The experimental results are discussed in terms of intermolecular interactions, particularly hydrogen-bonding interactions between like and unlike molecules.

## Introduction

Because of its strong polarity and limited water solubility, benzyl alcohol has long been used as a good solvent in chemical processes such as extraction distillation. Thermodynamic properties of binary liquid mixtures containing benzyl alcohol and another compound such as butanone,[1] chloroalkanes or chloroalkenes,[2] ethylene glycol,[3] or benzyl benzoate[4] have been investigated recently. In this paper, we report the excess enthalpies of benzyl alcohol with four isomers of heptanone at (298.65, 303.55, and 308.50) K. This study also aims to understand the intermolecular interactions, particularly hydrogen-bonding properties, between the aromatic alcohol and a ketone with a different extent of branching. Their close molecular weights make them good candidates for such examination, because contributions to the enthalpy of mixing from the nonspecific interactions should be insignificant in this case.

## Experimental Section

Benzyl alcohol (A.R. grade) was purchased from Tianjin Chemical Reagent Co., and 2-heptanone (>95%), 3-heptanone (>95%), 5-methyl-2-hexanone (>98%), and 2,4-dimethyl-3-pentanone (>97%) were from Beijing Chemical Ind. They were all purified either by normal or fractional distillation. Then they were stored over 5 Å molecular sieves and were degassed right before measurements. The purity of these chemicals was found to be better than 99% by gas chromatography. Comparison of the measured densities and refractive indexes and the literature data is shown in Table 1. They were found to be in good agreement.

A Calvet-type C-80 microcalorimeter (SETARAM, France)[9] was used to measure the excess enthalpies of the binary liquid systems. Briefly, the two components were transferred into the inner and outer chambers of the mixing cell, separately. Concentrations of the mixture were determined by weighing both components with an uncertainty of 0.1 mg. The cell was then placed in the calorimeter body for thermal equilibration. After a flat and smooth baseline was recorded, the calorimeter was allowed to rotate to achieve a thorough mixing of the two liquids. Calorimeter constants at the measuring temperatures, that is, 298.65 K, 303.55 K, and 308.50 K, were determined by electric calibration, or the so-called Joule effect. The performance of the calorimeter was checked by measuring the dissolving enthalpy of potassium chloride in water, in a mole ratio of 1 to 200. The result at 298.65 K was determined to be 17.79 kJ·mol$^{-1}$. The literature value at 298.15 K, 17.556 kJ·mol$^{-1}$, was derived from the standard molar enthalpies of formation of KCl (crystal) and KCl (1 in 200 $H_2O$), that is, −436.747 kJ·mol$^{-1}$ and −419.191 kJ·mol$^{-1}$, respectively.[10] Using its temperature dependence of −145 J·mol$^{-1}$·K$^{-1}$,[11] the expected literature value at 298.65 K is 17.48 kJ·mol$^{-1}$. This is in good agreement with the experimental results.

**Table 1. Experimental and Literature Values of Densities *d* at 25 °C and Refractive Indices $n_D$ at 20 °C**

| compound | *d*(expt)/(g·cm$^{-3}$) | *d*(lit)/(g·cm$^{-3}$) | $n_D$ (expt) | $n_D$ (lit) | purity[e] |
|---|---|---|---|---|---|
| benzyl alcohol | 1.0416 | 1.04156[a] | 1.5342 | 1.53648[d] | 99.5 |
| 2-heptanone | 0.8110 | 0.81158[b] | 1.4085 | 1.40869[b] | 99.8 |
| 3-heptanone | 0.8145 | 0.8140[c] | 1.4090 | 1.4088[b] | 99.7 |
| 5-methyl-2-hexanone | 0.8074 | 0.808[b] | 1.4078 | 1.4069[b] | 99.8 |
| 2,4-dimethyl-3-pentanone | 0.7988 | 0.8012[c] | 1.4000 | 1.3999[b] | 99.3 |

[a] Value from Windholz.[5] [b] TRC d-5870, a-5870, a-5940, a-5940, and a-5940, respectively.[6] [c] Data calculated from the Francis-1 type of equation compiled by Smith and Srivastava.[7] [d] TRC B-1880 (average of three values: 1.546 06, 1.534 02, and 1.529 37).[8] [e] Determined by gas−liquid chromatography.

## Results and Discussion

Excess enthalpies of binary systems of benzyl alcohol and various ketones were determined at 298.65 K, 303.55 K, and 308.50 K. The results are listed in Table 2 and are shown in Figure 1. The measured data were fitted to the Redlich−Kister polynomial[12] in the form of eq 1 using the least-squares procedure as employed previously.[13]

$$H_m^E/(\mathrm{J\cdot mol^{-1}}) = x(1 - x)\sum_{i=0}^{3} A_i(1 - 2x)^i \qquad (1)$$

Values of $A_i$ are listed in Table 3, together with the

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* To whom correspondence should be addressed. Telephone: (+86) 10-62781177. Fax: (+86) 10-62771149. E-mail: yuzhw@tsinghua.edu.cn.

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**Table 2. Experimental Excess Molar Enthalpies $H_m^E$ of {($x$)Benzyl Alcohol + (1 − $x$)Heptanone} Systems**

| system | $x$ | $H_m^E/(J \cdot mol^{-1})$ | $x$ | $H_m^E/(J \cdot mol^{-1})$ |
|---|---|---|---|---|
| {($x$)Benzyl Alcohol + (1 − $x$)2-Heptanone} | | | | |
| 298.65 K | 0.0603 | 77.4 | 0.5271 | 313.1 |
| | 0.1442 | 229.1 | 0.5970 | 271.3 |
| | 0.1769 | 266.8 | 0.6675 | 231.7 |
| | 0.2499 | 331.8 | 0.7326 | 159.3 |
| | 0.3305 | 359.6 | 0.8018 | 102.6 |
| | 0.3934 | 364.4 | 0.8517 | 68.1 |
| | 0.4431 | 350.5 | 0.9414 | 24.8 |
| 303.55 K | 0.0400 | 70.7 | 0.5262 | 284.2 |
| | 0.0890 | 154.7 | 0.5952 | 241.2 |
| | 0.1877 | 267.3 | 0.6521 | 209.7 |
| | 0.2490 | 301.4 | 0.7428 | 140.7 |
| | 0.3297 | 330.4 | 0.8213 | 81.4 |
| | 0.4017 | 325.9 | 0.9204 | 30.0 |
| | 0.4515 | 310.4 | | |
| 308.50 K | 0.0400 | 72.0 | 0.5557 | 278.5 |
| | 0.1431 | 216.9 | 0.6392 | 223.0 |
| | 0.2396 | 289.8 | 0.7219 | 153.0 |
| | 0.3374 | 325.2 | 0.8024 | 91.1 |
| | 0.4361 | 320.0 | 0.8788 | 35.9 |
| {($x$)Benzyl Alcohol + (1 − $x$)3-Heptanone} | | | | |
| 298.65 K | 0.0398 | 82.4 | 0.5494 | 348.3 |
| | 0.1013 | 198.6 | 0.6287 | 293.5 |
| | 0.1803 | 310.7 | 0.7092 | 215.4 |
| | 0.2600 | 375.0 | 0.7871 | 145.2 |
| | 0.3399 | 404.4 | 0.8650 | 74.4 |
| | 0.4203 | 400.0 | 0.9510 | 18.4 |
| | 0.4951 | 384.1 | | |
| 303.55 K | 0.0400 | 84.5 | 0.4963 | 345.8 |
| | 0.0991 | 190.4 | 0.5406 | 332.7 |
| | 0.1809 | 290.1 | 0.6220 | 261.8 |
| | 0.2592 | 357.0 | 0.6892 | 202.2 |
| | 0.3398 | 388.3 | 0.7919 | 117.4 |
| | 0.4000 | 385.3 | 0.8658 | 58.7 |
| 308.50 K | 0.0346 | 69.7 | 0.5001 | 340.9 |
| | 0.0963 | 174.9 | 0.5835 | 290.5 |
| | 0.1780 | 281.9 | 0.6754 | 223.2 |
| | 0.2708 | 361.2 | 0.7601 | 141.0 |
| | 0.3395 | 364.7 | 0.8402 | 72.1 |
| | 0.4155 | 357.9 | 0.9192 | 17.8 |
| {($x$)Benzyl Alcohol + (1 − $x$)5-Methyl-2-hexanone} | | | | |
| 298.65 K | 0.0395 | 81.0 | 0.4796 | 409.7 |
| | 0.1020 | 192.2 | 0.5499 | 380.7 |
| | 0.1700 | 289.2 | 0.6407 | 300.2 |
| | 0.2386 | 356.7 | 0.7177 | 232.7 |
| | 0.3193 | 402.4 | 0.7943 | 152.8 |
| | 0.3195 | 411.7 | 0.8679 | 78.3 |
| | 0.3992 | 421.7 | 0.9513 | 23.8 |
| 303.55 K | 0.0078 | 12.1 | 0.4186 | 400.6 |
| | 0.0725 | 131.8 | 0.5143 | 359.4 |
| | 0.1399 | 252.3 | 0.6329 | 279.9 |
| | 0.1999 | 311.3 | 0.7016 | 226.5 |
| | 0.2680 | 377.6 | 0.8044 | 128.2 |
| | 0.3248 | 394.4 | 0.8689 | 71.4 |
| | 0.3791 | 399.9 | 0.9460 | 16.6 |
| 308.50 K | 0.0423 | 82.2 | 0.5208 | 356.5 |
| | 0.1199 | 217.2 | 0.6004 | 308.5 |
| | 0.2012 | 314.7 | 0.6771 | 236.5 |
| | 0.2799 | 380.3 | 0.7597 | 162.3 |
| | 0.3591 | 391.1 | 0.8472 | 72.1 |
| | 0.4380 | 393.2 | | |
| {($x$)Benzyl Alcohol + (1 − $x$)2,4-Dimethyl-3-pentanone} | | | | |
| 298.65 K | 0.0426 | 102.7 | 0.4268 | 474.4 |
| | 0.0999 | 240.7 | 0.5209 | 432.4 |
| | 0.1600 | 328.4 | 0.5958 | 383.2 |
| | 0.2134 | 397.4 | 0.6868 | 310.7 |
| | 0.2197 | 398.1 | 0.7699 | 218.2 |
| | 0.2800 | 439.6 | 0.8506 | 117.6 |
| | 0.3523 | 468.2 | 0.9298 | 48.7 |
| 303.55 K | 0.0171 | 38.5 | 0.4840 | 442.2 |
| | 0.0511 | 124.1 | 0.5625 | 381.7 |
| | 0.1312 | 293.4 | 0.6627 | 309.2 |
| | 0.2480 | 434.5 | 0.7653 | 188.0 |
| | 0.3200 | 462.8 | 0.8700 | 82.7 |
| | 0.3899 | 468.3 | 0.8967 | 57.4 |
| | 0.3949 | 457.2 | 0.9394 | 28.4 |
| 308.50 K | 0.0400 | 86.1 | 0.5805 | 382.7 |
| | 0.0997 | 219.7 | 0.6602 | 335.3 |
| | 0.1894 | 368.4 | 0.7361 | 235.6 |
| | 0.2716 | 440.0 | 0.8197 | 145.4 |
| | 0.3403 | 468.1 | 0.8967 | 66.6 |
| | 0.4219 | 454.4 | 0.9493 | 24.5 |
| | 0.5002 | 425.0 | | |

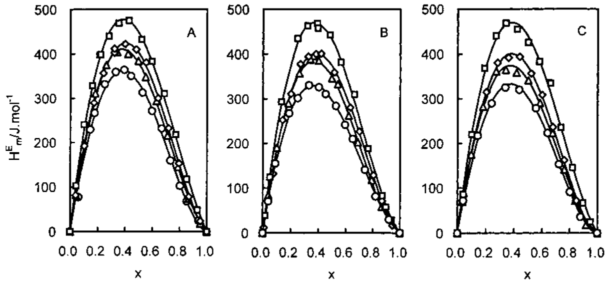

**Figure 1.** Excess enthalpy for {($x$)benzyl alcohol + (1 − $x$)ketone} mixtures at 298.65 K (A), 303.55 K (B), and 308.50 K (C). Solid lines represent the Redlich−Kister fitting results. The ketones used are 2-heptanone (○), 3-heptanone (△), 5-methyl-2-hexanone (◇), and 2,4-dimethyl-3-pentanone (□).

**Table 3. Parameters of Eq 1 and the Standard Deviations of the Binary Systems {($x$)Benzyl Alcohol + (1 − $x$)Ketone}**

| system | $T$/K | $A_0$ | $A_1$ | $A_2$ | $\sigma^{a}$ |
|---|---|---|---|---|---|
| 2-heptanone | 298.65 | 1336.74 | 921.03 | −317.25 | 11.3 |
| | 303.55 | 1182.46 | 904.42 | −47.17 | 3.4 |
| | 308.50 | 1211.45 | 890.78 | −261.35 | 5.0 |
| 3-heptanone | 298.65 | 1512.00 | 1010.33 | −218.76 | 3.6 |
| | 303.55 | 1397.79 | 1066.92 | −224.73 | 4.1 |
| | 308.50 | 1359.35 | 1010.95 | −239.65 | 7.4 |
| 5-methyl-2-hexanone | 298.65 | 1604.68 | 906.16 | −395.56 | 3.9 |
| | 303.55 | 1490.93 | 966.56 | −272.93 | 5.8 |
| | 308.50 | 1481.01 | 1006.18 | −356.10 | 5.4 |
| 2,4-dimethyl-3-pentanone | 298.65 | 1786.94 | 1024.20 | −103.49 | 7.6 |
| | 303.55 | 1722.10 | 1193.63 | −154.07 | 7.7 |
| | 308.50 | 1752.23 | 1057.16 | −190.41 | 11.0 |

[a] In units of $J \cdot mol^{-1}$.

regression standard deviation $\sigma$ of each curve as calculated with eq 2,[14]

$$\sigma = [\sum_{i=1}^{N}(H_{m,expt}^{E} - H_{m,calc}^{E})^2]/(N - r) \qquad (2)$$

where $N$ is the number of experimental points and $r = 3$ is the number of coefficients in eq 1. Calculated values of the excess volumes according to eq 1 are also shown in Figure 1 as solid lines.

As illustrated in Figure 1, values of excess enthalpy of all the systems are positive in the entire mole fraction range. The predominant contribution to the positive enthalpies is most likely from the net weakening of hydrogen-bonding interactions upon mixing. In contrast to ketone molecules, benzyl alcohol molecules are able to form hydrogen-bonding structures, either in cyclic or chain forms. This is the main reason benzyl alcohol, though with a smaller molecular weight, shows a higher density (1.0419 g·cm$^{-3}$ at 20 °C) and boiling point (205.3 °C) than those of the ketones examined in the present study. The densities of the ketones, as shown in Table 1, are less than 0.9 g·cm$^{-3}$ at 20 °C. Their boiling points are between (125 and 151) °C.[8] Upon mixing with ketone molecules, some of the hydrogen-bonding structures of benzyl alcohol are broken and are replaced with those between unlike molecules. The positive enthalpies demonstrated in this study indicate the hydrogen-bonding interaction is weaker in the latter case. The systematic leaning to the ketone-rich region, at a mole fraction of benzyl alcohol between 0.3 and 0.4, of the enthalpy cones also supports the explanation.

The maxima of the excess enthalpies obtained in this study (between 300 J·mol$^{-1}$ and 500 J·mol$^{-1}$) are greater than those of the binary mixtures of benzyl alcohol with 2-butanone (154 J·mol$^{-1}$ at 313.15 K).[1] Probably the latter system can form stronger H-bonds between unlike molecules because of the shorter chain length of the ketone and thus is a less steric obstacle to the H-bond formation.

Increasing temperature decreased the excess enthalpies of the binary mixtures. This is probably due to the weakening of the hydrogen-bonding interactions between alcohol molecules prior to mixing.

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