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# Excess molar enthalpies of mixtures of a cycloalkane and an alkanol

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**Abstract**

The excess molar enthalpies, $H_m^E$, for the sixteen mixtures, (cyclo-$C_5H_{10}$ + $CH_3OH$) and (cyclo-$C_kH_{2k}$ + $C_lH_{2l+1}OH$) with $k = 5$, 6, 7, 8 and 10 and $l = 2$ and 3, were measured at 298.15 K. The $H_m^E$ results are discussed in terms of the size of the cycloalkane ring and the length of the alkanol chain.

## INTRODUCTION

In the present work, we investigated the excess molar enthalpy ($H_m^E$) values obtained on mixing a cycloalkane with an alkanol. Our results show the effect on $H_m^E$ of increasing the ring size of the cycloalkane and also the effect of increasing the chain length of the alkanol. We studied the systems ($x$c-$C_5H_{10}$ + $(1-x)CH_3OH$) and ($x$c-$C_kH_{2k}$ + $(1-x)C_lH_{2l+1}OH$) for $k$ = 5, 6, 7, 8 and 10, and $l = 2$ and 3. These mixtures are miscible over the whole concentration range.

The $H_m^E$ values for five of these sixteen systems have been published [1–9] and are compared with our results.

## EXPERIMENTAL

The purification procedures used [10–12] and the flow calorimeter (LKB 2107) method for determining $H_m^E$ have been previously described [13].

## RESULTS

The $H_m^E$ results for each of the sixteen systems are given in Table 1 together with the deviations, $\Delta$, calculated from the smoothing equation

$$\Delta(\mathrm{J\ mol^{-1}}) = H_m^E(\mathrm{J\ mol^{-1}}) - x(1-x)\sum_{r=0}^{r} A_r(1-2x)^r \qquad (1)$$

where $x$ denotes the mole fraction. The coefficients, $A_r$, are given in Table 2.

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TABLE 1

Molar excess enthalpies, $H_m^E$ for $(xC_kH_{2k}+(1-x)C_lH_{2l+1}OH)$ at 298.15 K and the deviations, Δ, from eqn. (1) and the coefficients of Table 2

| $x$ | $H_m^E$ (J mol$^{-1}$) | Δ (J mol$^{-1}$) | $x$ | $H_m^E$ (J mol$^{-1}$) | Δ (J mol$^{-1}$) | $x$ | $H_m^E$ (J mol$^{-1}$) | Δ (J mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| $xc\text{-}C_5H_{10}+(1-x)CH_3OH$ | | | | | | | | |
| 0.0747 | 249.8 | −4.9 | 0.3754 | 556.1 | −0.2 | 0.6735 | 513.6 | −0.7 |
| 0.1332 | 375.9 | 4.0 | 0.4072 | 562.0 | −0.7 | 0.7964 | 438.1 | 0.7 |
| 0.1953 | 452.5 | 1.3 | 0.4817 | 566.3 | −0.6 | 0.8523 | 375.4 | −3.7 |
| 0.2410 | 491.4 | 0.2 | 0.5762 | 553.7 | 2.7 | 0.9188 | 269.5 | 3.3 |
| 0.3009 | 526.0 | −2.1 | | | | | | |
| $xc\text{-}C_5H_{10}+(1-x)C_2H_5OH$ | | | | | | | | |
| 0.0639 | 119.1 | −4.7 | 0.4114 | 482.8 | −4.3 | 0.6659 | 537.2 | 3.2 |
| 0.1251 | 210.3 | −1.2 | 0.4836 | 519.4 | −0.1 | 0.7752 | 497.7 | −9.4 |
| 0.1911 | 297.0 | 5.9 | 0.5732 | 538.7 | 2.2 | 0.8863 | 404.5 | 3.6 |
| 0.2398 | 346.8 | 2.7 | 0.6205 | 541.0 | 3.7 | 0.9493 | 240.7 | 1.8 |
| 0.3365 | 430.9 | −3.9 | | | | | | |
| $xc\text{-}C_5H_{10}+(1-x)C_3H_7OH$ | | | | | | | | |
| 0.1005 | 127.2 | −2.2 | 0.4839 | 455.0 | −5.0 | 0.7215 | 528.4 | 2.0 |
| 0.1833 | 200.4 | 1.0 | 0.5220 | 478.2 | −1.9 | 0.7965 | 512.3 | −5.2 |
| 0.3001 | 311.7 | 3.8 | 0.5610 | 500.7 | 4.6 | 0.8512 | 480.7 | −3.3 |
| 0.4070 | 405.1 | −0.7 | 0.6198 | 520.3 | 7.4 | 0.9183 | 376.4 | 6.6 |
| 0.4536 | 437.5 | 3.3 | 0.6833 | 521.0 | −2.5 | 0.9581 | 232.8 | −0.3 |
| $xc\text{-}C_5H_{10}+(1-x)CH_3CH(OH)CH_3$ | | | | | | | | |
| 0.1025 | 192.7 | −3.5 | 0.4137 | 604.8 | −4.2 | 0.7757 | 662.8 | −6.7 |
| 0.1745 | 304.3 | −0.1 | 0.5225 | 685.9 | −0.9 | 0.8427 | 595.6 | 0.2 |
| 0.1806 | 317.0 | 3.7 | 0.6040 | 715.3 | 3.7 | 0.9183 | 419.4 | 2.4 |
| 0.2971 | 477.8 | 2.5 | 0.6302 | 715.8 | 2.0 | 0.9503 | 291.2 | 0.8 |
| 0.3497 | 539.6 | −1.2 | 0.7251 | 699.6 | 1.8 | | | |
| $xc\text{-}C_6H_{12}+(1-x)C_2H_5OH$ | | | | | | | | |
| 0.0983 | 241.1 | 0.7 | 0.4884 | 632.0 | −2.4 | 0.7150 | 602.5 | 2.8 |
| 0.1736 | 361.5 | −1.9 | 0.5317 | 637.7 | −2.1 | 0.8009 | 540.5 | −8.7 |
| 0.2558 | 473.5 | 4.2 | 0.5844 | 639.4 | 2.3 | 0.8619 | 475.0 | −5.6 |
| 0.3586 | 570.1 | 0.2 | 0.6533 | 627.5 | 5.6 | 0.8967 | 426.2 | 9.9 |
| 0.4530 | 621.5 | −2.7 | | | | | | |
| $xc\text{-}C_6H_{12}+(1-x)C_3H_7OH$ | | | | | | | | |
| 0.1436 | 230.7 | −1.7 | 0.5543 | 604.5 | −3.8 | 0.7483 | 592.3 | −5.0 |
| 0.2511 | 356.7 | 3.2 | 0.6018 | 619.5 | 2.8 | 0.8198 | 554.2 | −1.5 |
| 0.3642 | 479.4 | −0.9 | 0.6415 | 621.3 | 3.6 | 0.8936 | 451.6 | 1.1 |
| 0.4157 | 528.0 | −1.4 | 0.6935 | 614.8 | 2.7 | 0.9344 | 338.2 | 1.4 |
| $xc\text{-}C_6H_{12}+(1-x)CH_3CH(OH)CH_3$ | | | | | | | | |
| 0.1347 | 313.6 | −4.2 | 0.5536 | 826.1 | −0.9 | 0.7455 | 766.2 | −6.1 |
| 0.2619 | 542.1 | 10.2 | 0.5942 | 836.7 | 4.6 | 0.8362 | 651.4 | −7.6 |
| 0.3557 | 663.0 | −5.5 | 0.6251 | 835.3 | 5.4 | 0.8991 | 517.6 | 8.4 |
| 0.4471 | 762.3 | −6.1 | 0.6895 | 812.0 | 2.8 | | | |

TABLE 1 (continued)

| $x$ | $H_m^E$ (J mol$^{-1}$) | Δ (J mol$^{-1}$ | $x$ | $H_m^E$ (J mol$^{-1}$) | Δ (J mol$^{-1}$) | $x$ | $H_m^E$ (J mol$^{-1}$) | Δ (J mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| $xc\text{-}C_7H_{14} + (1-x)C_2H_5OH$ | | | | | | | | |
| 0.0889 | 243.6 | −2.2 | 0.5299 | 660.9 | −3.6 | 0.7526 | 592.1 | −6.0 |
| 0.1641 | 383.4 | 0.1 | 0.6003 | 657.6 | 3.2 | 0.8369 | 530.3 | −1.7 |
| 0.2447 | 499.7 | 4.0 | 0.6646 | 639.8 | 4.3 | 0.8891 | 449.3 | −0.7 |
| 0.3431 | 594.8 | −1.2 | 0.6856 | 630.6 | 2.7 | 0.9521 | 265.0 | 5.2 |
| 0.4076 | 635.9 | 2.1 | | | | | | |
| $xc\text{-}C_7H_{14} + (1-x)C_3H_7OH$ | | | | | | | | |
| 0.0913 | 171.6 | −5.2 | 0.4174 | 557.7 | −2.6 | 0.6589 | 636.0 | 1.8 |
| 0.1685 | 296.5 | 4.6 | 0.5438 | 619.2 | −2.1 | 0.7026 | 626.7 | −2.4 |
| 0.2519 | 402.8 | 3.1 | 0.5850 | 633.6 | 3.4 | 0.8655 | 495.7 | −9.8 |
| 0.3516 | 503.0 | −3.6 | 0.6073 | 636.2 | 3.2 | 0.9132 | 407.2 | 10.1 |
| $xc\text{-}C_7H_{14} + (1-x)CH_3CH(OH)CH_3$ | | | | | | | | |
| 0.0969 | 259.8 | 0.9 | 0.5051 | 837.1 | 2.7 | 0.6320 | 865.2 | −7.0 |
| 0.1776 | 440.6 | 0.4 | 0.5462 | 860.1 | 3.3 | 0.7298 | 815.2 | 6.3 |
| 0.3191 | 656.4 | −5.5 | 0.5732 | 865.0 | −1.9 | 0.7998 | 690.6 | 1.9 |
| 0.4205 | 774.6 | 5.9 | 0.6003 | 867.9 | −4.6 | 0.9008 | 388.0 | −3.0 |
| $xc\text{-}C_8H_{16} + (1-x)C_2H_5OH$ | | | | | | | | |
| 0.0793 | 237.1 | −1.6 | 0.4362 | 615.0 | −3.6 | 0.7244 | 575.8 | 2.2 |
| 0.1473 | 369.4 | −1.7 | 0.4718 | 623.2 | −1.4 | 0.8065 | 517.3 | −6.1 |
| 0.2182 | 472.6 | 3.1 | 0.5023 | 624.6 | −1.6 | 0.8695 | 442.8 | −5.9 |
| 0.3047 | 557.2 | 3.9 | 0.5632 | 623.4 | 1.9 | 0.9219 | 345.1 | 9.7 |
| 0.3791 | 596.3 | −2.7 | 0.6237 | 614.0 | 5.5 | | | |
| $xc\text{-}C_8H_{16} + (1-x)C_3H_7OH$ | | | | | | | | |
| 0.0430 | 95.5 | −2.0 | 0.5220 | 617.6 | 3.6 | 0.8202 | 563.4 | −1.8 |
| 0.1531 | 284.5 | −0.5 | 0.5663 | 632.2 | 1.1 | 0.8772 | 476.6 | −6.3 |
| 0.2314 | 394.2 | 2.8 | 0.6095 | 638.7 | 3.3 | 0.9151 | 395.2 | 3.9 |
| 0.3902 | 552.7 | −6.0 | 0.6433 | 637.9 | 2.4 | 0.9542 | 255.3 | 5.0 |
| 0.4402 | 584.6 | −1.8 | 0.7015 | 628.2 | −0.2 | | | |
| $xc\text{-}C_8H_{16} + (1-x)CH_3CH(OH)CH_3$ | | | | | | | | |
| 0.0631 | 192.9 | −5.2 | 0.5287 | 788.6 | 0.2 | 0.7033 | 767.4 | −4.6 |
| 0.1371 | 377.2 | 2.4 | 0.5852 | 796.1 | 2.1 | 0.7828 | 712.9 | −7.2 |
| 0.2371 | 558.2 | 5.4 | 0.6093 | 796.8 | 3.5 | 0.8512 | 630.3 | 5.5 |
| 0.3402 | 675.3 | −5.6 | 0.6459 | 793.1 | 4.4 | 0.9217 | 430.1 | 0.3 |
| 0.4458 | 757.1 | −2.6 | | | | | | |
| $xc\text{-}C_{10}H_{20} + (1-x)C_2H_5OH$ | | | | | | | | |
| 0.1168 | 450.2 | 0.7 | 0.4037 | 489.6 | 1.1 | 0.6513 | 450.4 | 1.5 |
| 0.2081 | 367.4 | −1.3 | 0.4818 | 496.5 | −1.3 | 0.7512 | 370.9 | −1.4 |
| 0.3034 | 445.6 | −0.5 | 0.5362 | 490.1 | 2.4 | 0.8921 | 211.0 | 0.7 |
| 0.3523 | 473.0 | 1.7 | 0.6034 | 474.3 | 1.7 | 0.9317 | 117.4 | −0.5 |

TABLE 1 (continued)

| $x$ | $H_m^E$ (J mol$^{-1}$) | Δ (J mol$^{-1}$ | $x$ | $H_m^E$ (J mol$^{-1}$) | Δ (J mol$^{-1}$) | $x$ | $H_m^E$ (J mol$^{-1}$) | Δ (J mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| $x$c-$C_{10}H_{20}$ + (1 − $x$)$C_3H_7OH$ | | | | | | | | |
| 0.1394 | 246.2 | −2.4 | 0.5350 | 489.4 | −1.6 | 0.7236 | 460.2 | 1.5 |
| 0.2453 | 353.7 | 4.1 | 0.5736 | 494.2 | 0.9 | 0.7850 | 419.9 | −0.7 |
| 0.3465 | 420.8 | 0.1 | 0.6019 | 494.0 | 1.8 | 0.8693 | 320.1 | −10.0 |
| 0.4502 | 466.6 | −4.2 | 0.6575 | 485.6 | 2.8 | 0.9321 | 223.1 | 10.3 |
| $x$c-$C_{10}H_{20}$ + (1 − $x$)$CH_3CH(OH)CH_3$ | | | | | | | | |
| 0.0729 | 233.1 | 6.1 | 0.5037 | 662.2 | −4.1 | 0.6512 | 658.2 | 1.7 |
| 0.1467 | 353.2 | −6.7 | 0.5448 | 668.2 | −4.7 | 0.7126 | 636.2 | 9.9 |
| 0.2172 | 448.0 | −1.1 | 0.5819 | 670.0 | −2.5 | 0.8382 | 493.3 | −11.9 |
| 0.3560 | 593.3 | 8.7 | 0.6156 | 668.9 | 1.7 | 0.9301 | 312.6 | 7.3 |
| 0.4362 | 638.2 | −1.1 | | | | | | |

TABLE 2

Smoothing coefficients, $A_r$, for $x$c-$C_kH_{2k}$ + (1 − $x$)$C_lH_{2l+1}OH$

| $k$ | Alkanol | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ |
|---|---|---|---|---|---|---|
| 5 | $CH_3OH$ | 2262.1 | 194.0 | 958.3 | −226.7 | 1345.0 |
| 5 | $C_2H_5OH$ | 2097.1 | −542.5 | 507.3 | −1288.6 | 1582.6 |
| 5 | $C_3H_7OH$ | 1876.2 | −1068.9 | 300.3 | −1407.0 | 2295.6 |
| 5 | $CH_3CH(OH)CH_3$ | 2699.9 | −1149.8 | 493.0 | −1254.6 | 1666.8 |
| 6 | $C_2H_5OH$ | 2546.4 | −324.6 | 495.3 | −1270.7 | 1876.9 |
| 6 | $C_3H_7OH$ | 2350.1 | −1005.1 | 104.3 | −1197.5 | 2467.1 |
| 6 | $CH_3CH(OH)CH_3$ | 3223.4 | −1104.3 | 280.7 | −1034.4 | 1978.1 |
| 7 | $C_2H_5OH$ | 2655.7 | −153.3 | 643.9 | −1463.8 | 1935.0 |
| 7 | $C_3H_7OH$ | 2425.1 | −828.2 | 762.7 | −1331.1 | 1346.1 |
| 7 | $CH_3CH(OH)CH_3$ | 3324.0 | −1307.3 | 1437.0 | 661.1 | −1402.0 |
| 8 | $C_2H_5OH$ | 2505.1 | −24.3 | 961.5 | −1114.6 | 1533.1 |
| 8 | $C_3H_7OH$ | 2456.4 | −719.4 | 793.3 | −1372.3 | 1369.4 |
| 8 | $CH_3CH(OH)CH_3$ | 3125.7 | −590.4 | 1262.9 | −1378.6 | 1197.5 |
| 10 | $C_2H_5OH$ | 1988.6 | 133.5 | 360.3 | 198.4 | 76.0 |
| 10 | $C_3H_7OH$ | 1940.8 | −434.6 | 507.8 | −205.4 | 956.1 |
| 10 | $CH_3CH(OH)CH_3$ | 2661.3 | −538.8 | 452.4 | −301.8 | 1905.9 |

## DISCUSSION

The $H_m^E$ values for five of the sixteen systems investigated here have been published previously. The results of Stokes and Burfitt [1] for cyclopentane plus ethanol and cycloheptane plus ethanol are within 5 J mol$^{-1}$ of the smoothing curves fitted to our results, except at very low alcohol concentrations. For cyclohexane plus ethanol, our results are within 10 J mol$^{-1}$, in the worst case, of the results given by Nagata and Kazuma [2] and also by

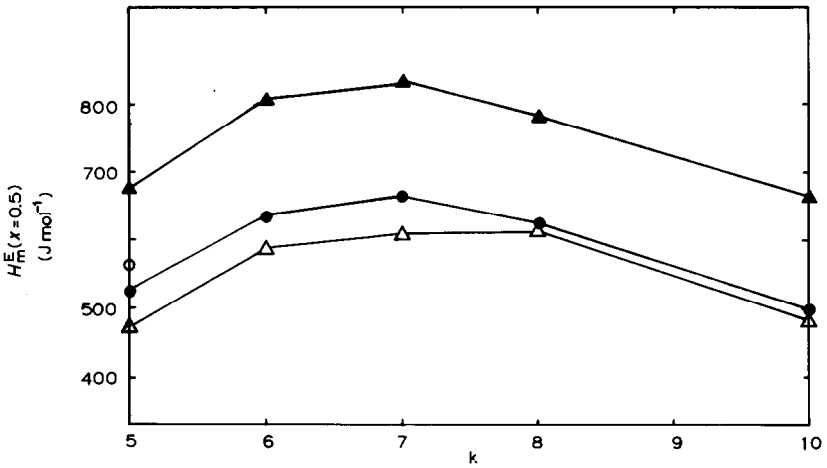


Fig. 1. Interpolated excess molar enthalpy data, $H_m^E(x = 0.5)$, for $(xc\text{-}C_kH_{2k} + (1 - x)C_lC_{2l+1}OH)$ as a function of $k$: ○, $CH_3OH$; ●, $C_2H_5OH$; △, $C_3H_7OH$; and ▲, $CH_3CH(OH)CH_3$.

Stokes and Adamson [3]. Our results for cyclohexane plus 2-propanol are within 10 J mol$^{-1}$ of the smoothing curves based on the data of Veselý et al. [4] and Nagata et al. [5].

There are four sets of data in the literature for the $H_m^E$ value for $(xC_6H_{12} + (1 - x)C_3H_7OH)$ [6–9]. Our results are within 5 J mol$^{-1}$, in the worst case, of the smoothing curve for the data given by Nagata and Kazuma [6] but almost 30 J mol$^{-1}$ higher than the published data of Veselý and Pick [7,8] and 80 J mol$^{-1}$ lower than the published data of Belousov et al. [9].

The $H_m^E$ values for all the sixteen systems discussed here are positive, with $H_m^E$(maximum) ranging from 490 to 866 J mol$^{-1}$. This reflects the breakdown of the hydrogen bonding between the alkanol molecules on mixing with a cyclo compound.

For each particular alkanol, the value of $H_m^E$(maximum) or $H_m^E(x = 0.5)$ increases with increasing cycloalkane carbon number from $k = 5$ to $k = 7$ and decreases from $k = 7$ to $k = 10$. This can be seen in Fig. 1 where $H_m^E(x = 0.5)$ has been plotted against $k$. The concentration of the cycloalkane at which $H_m^E$(maximum) occurs for a particular alkanol, decreases with increasing cycloalkane carbon number. For example for ethanol systems, $H_m^E$(maximum) occurs at $x = 0.61$ for $k = 5$, $x = 0.56$ for $k = 6$, $x = 0.54$ for $k = 7$, $x = 0.51$ for $k = 8$ and $x = 0.45$ for $k = 10$.

For cyclopentane systems, $H_m^E(x = 0.5)$ decreases with increasing chain length of the l-alkanols from $l = 1$ to $l = 3$. The same is true for each of the other cycloalkanes for $l = 2$ and 3. This can be attributed to the decreasing hydrogen bonding between alcohol molecules as $l$ increases from 1 to 3.

The $H_m^E(x = 0.5)$ value for $(xc\text{-}C_kH_{2k} + (1 - x)CH_3CH(OH)CH_3)$ is larger than $H_m^E(x = 0.5)$ for $(xc\text{-}C_kH_{2k} + (1 - x)C_2H_5OH)$ or $(xc\text{-}C_kH_{2k} + (1 - x)C_3H_7OH)$ for $k$ between 5 and 10. This implies a stronger hydrogen bonding between 2-propanol molecules than between ethanol molecules or between 1-propanol molecules. This could be due to the inductive effect of the methyl groups of 2-propanol.

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