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# Excess molar enthalpies for methanol + acetone and methanol + acetone + benzene mixtures at 298.15 K

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## Abstract

Excess molar enthalpies for the methanol + acetone and methanol + acetone + benzene systems were measured using a flow microcalorimeter. The measured values were correlated with polynomial equations and were compared with those calculated from a mole fraction association model having binary parameters alone.

LIST OF SYMBOLS

| | |
|---|---|
| $A_{n,ij}$ | coefficient of eqns. (1) or (2) |
| $a_{\mathrm{JI}}$ | binary interaction parameter for I–J pair |
| $C_{\mathrm{JI}}$, $D_{\mathrm{JI}}$ | coefficients of eqn. (17) |
| $C_n$ | constant of eqn. (4) |
| $G_{\mathrm{JI}}$ | coefficient as defined by $\exp(-\alpha_{\mathrm{JI}}\tau_{\mathrm{JI}})$ |
| $H^{\mathrm{E}}$ | excess molar enthalpy |
| $h_2$ | enthalpy of hydrogen bond formation of open dimer |
| $h$ | enthalpy of hydrogen bond formation in open *i*mer |
| $h_{\mathrm{AB}}$, $h_{\mathrm{AC}}$ | enthalpies of formation of chemical complexes $\mathrm{A}_i\mathrm{B}$ and $\mathrm{A}_i\mathrm{C}$ |
| $K_2$ | equilibrium constant of open dimer formation |
| $K_3$ | equilibrium constant of open-chain trimer formation |
| $K$ | equilibrium constant of open-chain *i*mer formation, $i > 3$ |
| $K_{\mathrm{cy}}$ | equilibrium constant for cyclization of open-chain *i*mer, $i > 4$ |
| $K_{\mathrm{AB}}$, $K_{\mathrm{AC}}$ | equilibrium constants of chemical complexes $\mathrm{A}_i\mathrm{B}$ and $\mathrm{A}_i\mathrm{C}$ |
| $R$ | universal gas constant |
| $S$ | stoichiometric sum |
| $T$ | absolute temperature |
| $x_{\mathrm{I}}$ | liquid phase mole fraction of component I |
| $z$ | coefficient as defined by $Kx_{\mathrm{A1}}$ |

*Greek letters*

| | |
|---|---|
| $\alpha_{\mathrm{JI}}$ | non-randomness parameter of NRTL equation for I–J pair |

| | |
|---|---|
| $\Delta$ | ternary contribution function as defined by eqn. (4) |
| $\theta$ | constant related to $K_{cy}$ |
| $\tau_{JI}$ | binary parameter as defined by $a_{JI}/T$ |

*Subscripts*

| | |
|---|---|
| A | methanol |
| $A_1$, $A_i$ | methanol monomer and open *i*mer |
| $A_iB$, $A_iC$ | complex formation between methanol open *i*mer and component B or C |
| chem | chemical |
| I, J, K | components |
| phys | physical |

*Superscripts*

| | |
|---|---|
| E | excess |
| * | pure methanol |

## INTRODUCTION

As part of a series of programs to measure excess molar enthalpies $H^E$ for alkanol + polar component + hydrocarbon mixtures, this paper presents experimental $H^E$ values for methanol + acetone and methanol + acetone + benzene mixtures. A flow microcalorimeter constructed in this laboratory was used to obtain $H^E$ data for these mixtures at 298.15 K. Experimental $H^E$ values will be reduced using polynomial equations and an association model. $H^E$ data for the two binaries constituting the ternary mixture at 298.15 K are available from the literature and are used in the data reduction for methanol + benzene [1] and acetone + benzene [2].

## EXPERIMENTAL

Methanol (first grade) was shaken with calcium oxide and fractionated in a glass column with McMahon packing. Acetone (Wako Pure Chemical Industries Ltd., guaranteed reagent grade) was dried over fresh potassium carbonate followed by fractional distillation in a vacuum. Benzene (first grade) was purified by recrystallization three times. The densities of the chemicals used for experimental work, measured with an Anton Paar densimeter (DMA40) at 298.15 K, agreed satisfactorily with literature values [3]. $H^E$ data were measured with the flow microcalorimeter described previously [4].

## RESULTS AND DATA ANALYSIS

Table 1 gives the experimental values of $H^E$ for methanol(1) + acetone(2) at 298.15 K together with the deviations $\delta H^E = (H^E - H^E_{ij})$ calculated from the equation

$$H^E_{ij} = x_i x_j \sum_{n=1}^{m} A_{n,ij}(x_i - x_j)^{n-1} \tag{1}$$

Figure 1 compares the present results with published values for methanol + acetone [5–11]. The $H^E$ data of methanol(1) + benzene(3) were correlated with the equation

$$H^E_{13} = \frac{10^4 x_1 x_3}{\sum_{n=1}^{m} A_{n,13}(x_1 - x_3)^{n-1}} \tag{2}$$

The data for acetone(2) + benzene(3) were fitted to eqn. (1). Table 2 shows the coefficients $A_{n,ij}$ of eqns. (1) and (2).

The experimental ternary values of $H^E$ for methanol(1) + acetone(2) + benzene(3) are listed in Table 3. Equation (3) was fitted to the ternary $H^E$ data

$$H^E = H^E_{12} + H^E_{13} + H^E_{23} + x_1 x_2 x_3 \Delta \tag{3}$$

where

$$\Delta/RT = C_0 - C_1 x_1 - C_2 x_2 - C_3 x_1^2 - C_4 x_2^2 - C_5 x_1 x_2 - C_6 x_1^3 \tag{4}$$

The coefficients of eqn. (4) were calculated by the method of unweighted least squares: $C_0 = 6.6654$, $C_1 = 21.5188$, $C_2 = 9.2843$, $C_3 = -22.2394$,

TABLE 1

Experimental excess molar enthalpies for methanol(1) + acetone(2) at 298.15 K

| $x_1$ | $H^E/(\mathrm{J\ mol^{-1}})$ | $\delta H^E/(\mathrm{J\ mol^{-1}})$ | $x_1$ | $H^E/(\mathrm{J\ mol^{-1}})$ | $\delta H^E/(\mathrm{J\ mol^{-1}})$ |
|---|---|---|---|---|---|
| 0.0500 | 171.3 | 1.4 | 0.5500 | 674.7 | 1.1 |
| 0.1000 | 307.0 | −2.9 | 0.6000 | 645.8 | 2.4 |
| 0.1500 | 423.1 | −0.4 | 0.6500 | 602.7 | 0.9 |
| 0.2000 | 513.5 | −0.5 | 0.7000 | 547.1 | −1.7 |
| 0.2500 | 584.4 | 0.4 | 0.7500 | 483.8 | −0.9 |
| 0.3000 | 634.6 | −1.2 | 0.8000 | 407.3 | −2.3 |
| 0.3500 | 671.4 | 0.3 | 0.8500 | 322.6 | −0.7 |
| 0.4000 | 692.2 | 0.6 | 0.9000 | 226.2 | 0.1 |
| 0.4500 | 699.8 | 1.6 | 0.9500 | 118.8 | 0.5 |
| 0.5000 | 693.6 | 1.6 | | | |

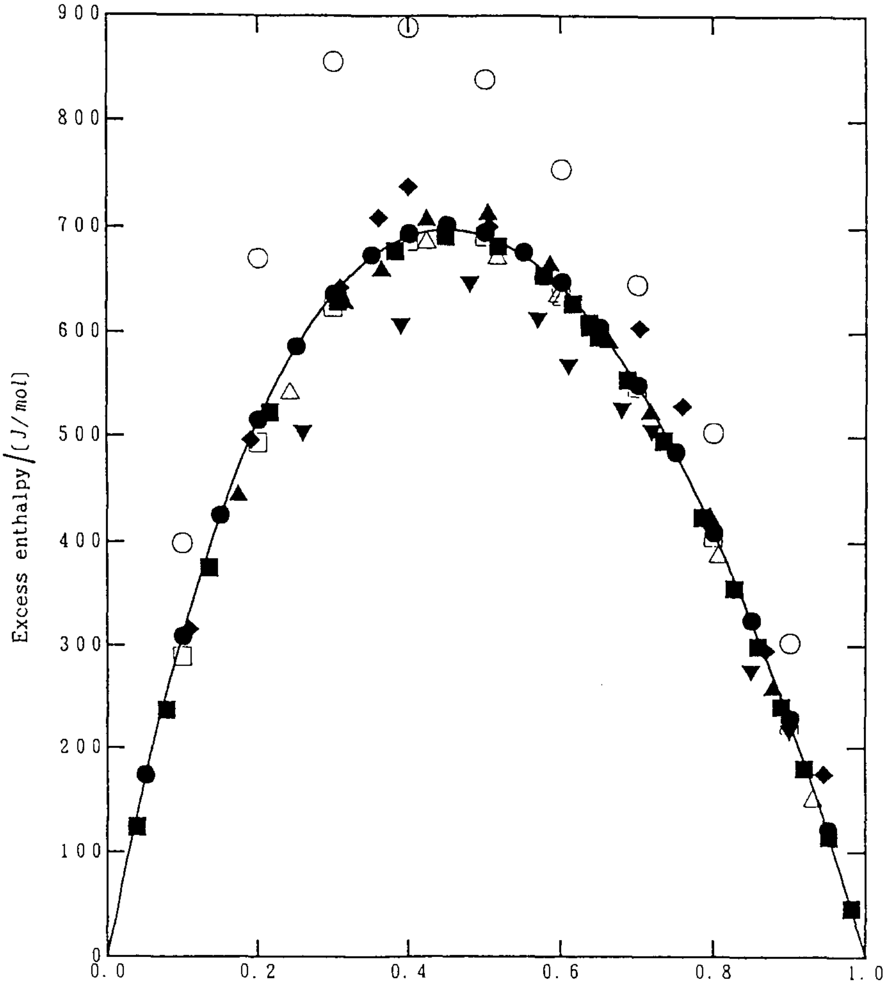

Fig. 1. Excess molar enthalpies for methanol(1) + acetone(2) at 298.15 K. Experimental: ●, this work; ■, ref. 5; ▲, ref. 6; ◆, ref. 7; ▼, ref. 8; ○, ref. 9; □, ref. 10; △, ref. 11; ——, calculated from eqn. (1).

TABLE 2

Binary coefficients of eqns. (1) and (2) and deviation

| System $(i+j)$ | $A_{1,ij}$ | $A_{2,ij}$ | $A_{3,ij}$ | $A_{4,ij}$ | $A_{5,ij}$ | $A_{6,ij}$ | $s$ |
|---|---|---|---|---|---|---|---|
| Methanol + acetone | 2768.15 | +496.28 | 327.64 | −1.33.33 | | | 1.5 |
| Methanol + benzene | 4.0083 | 2.4777 | −0.2986 | 0.4673 | 0.0729 | 0.0560 | |
| Acetone + benzene | 554.95 | −46.97 | 171.91 | 23.93 | 23.23 | −172.88 | 0.9 |

$C_4 = -4.9667$, $C_5 = -16.0702$ and $C_6 = 7.2229$; and the absolute mean deviation of the experimental values from the calculated results is 5.4 J mol$^{-1}$ and the standard deviation $s$ is 8.4. Figure 2 plots lines of constant values of the ternary $H^E$ calculated from eqns. (3) and (4).

TABLE 3

Experimental ternary excess molar enthalpies for methanol(1) + acetone(2) + benzene(3) mixtures at 298.15 K

| $x_1$ | $x_2$ | $H^E/(\mathrm{J\ mol^{-1}})$ | $x_1$ | $x_2$ | $H^E/(\mathrm{J\ mol^{-1}})$ | $x_1$ | $x_2$ | $H^E/(\mathrm{J\ mol^{-1}})$ |
|---|---|---|---|---|---|---|---|---|
| $x'_2 = 0.2499$ [a] | | | $x'_2 = 0.4989$ [a] | | | $x'_2 = 0.7502$ [a] | | |
| 0.0500 | 0.2375 | 411.2 | 0.0500 | 0.4740 | 371.1 | 0.0500 | 0.7127 | 296.2 |
| 0.1000 | 0.2250 | 549.3 | 0.1000 | 0.4490 | 502.5 | 0.1000 | 0.6752 | 427.5 |
| 0.1500 | 0.2125 | 641.6 | 0.1500 | 0.4241 | 600.7 | 0.1500 | 0.6377 | 534.6 |
| 0.2000 | 0.2000 | 698.3 | 0.2000 | 0.3991 | 671.1 | 0.2000 | 0.6002 | 616.3 |
| 0.2500 | 0.1875 | 724.9 | 0.2500 | 0.3742 | 716.0 | 0.2500 | 0.5627 | 675.7 |
| 0.3000 | 0.1750 | 739.7 | 0.3000 | 0.3492 | 735.5 | 0.3000 | 0.5251 | 713.7 |
| 0.3500 | 0.1625 | 736.3 | 0.3500 | 0.3243 | 744.8 | 0.3500 | 0.4876 | 735.1 |
| 0.4000 | 0.1500 | 721.8 | 0.4000 | 0.2993 | 739.5 | 0.4000 | 0.4501 | 738.7 |
| 0.4500 | 0.1375 | 693.6 | 0.4500 | 0.2744 | 717.7 | 0.4500 | 0.4126 | 730.2 |
| 0.5000 | 0.1250 | 657.3 | 0.5000 | 0.2495 | 690.7 | 0.5000 | 0.3751 | 708.2 |
| 0.5500 | 0.1125 | 614.0 | 0.5500 | 0.2245 | 652.8 | 0.5500 | 0.3376 | 682.7 |
| 0.6000 | 0.1000 | 569.2 | 0.6000 | 0.1996 | 606.0 | 0.6000 | 0.3001 | 641.6 |
| 0.6500 | 0.0875 | 515.1 | 0.6500 | 0.1745 | 554.5 | 0.6500 | 0.2626 | 588.8 |
| 0.7000 | 0.0750 | 456.0 | 0.7000 | 0.1497 | 494.2 | 0.7000 | 0.2251 | 531.0 |
| 0.7500 | 0.0625 | 387.9 | 0.7500 | 0.1247 | 426.8 | 0.7500 | 0.1876 | 460.6 |
| 0.8000 | 0.0500 | 319.9 | 0.8000 | 0.0998 | 353.1 | 0.8000 | 0.1500 | 384.9 |
| 0.8500 | 0.0375 | 245.4 | 0.8500 | 0.0748 | 274.0 | 0.8500 | 0.1125 | 299.9 |
| 0.9000 | 0.0250 | 168.4 | 0.9000 | 0.0499 | 188.1 | 0.9000 | 0.0750 | 207.1 |
| 0.9500 | 0.0125 | 85.2 | 0.9500 | 0.0250 | 97.6 | 0.9500 | 0.0375 | 106.8 |

[a] Ternary mixtures were obtained by mixing pure methanol with [$x'_2$ acetone + (1 − $x'_2$) benzene].

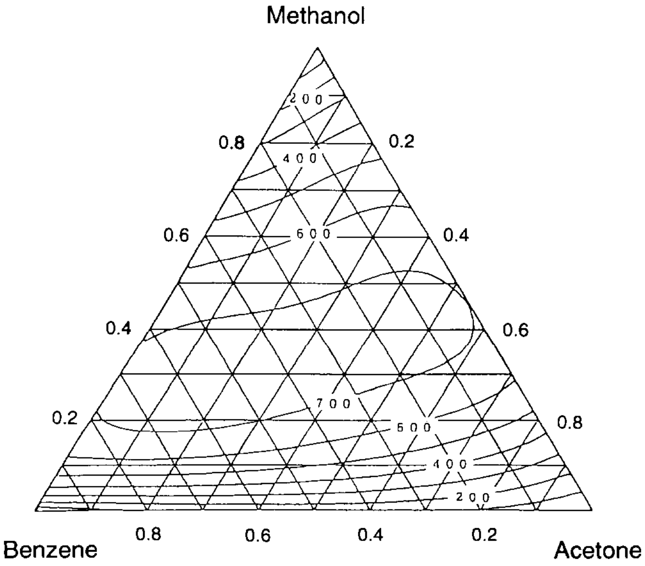

Fig. 2. Curves of constant excess molar enthalpies for methanol(1) + acetone(2) + benzene(3) at 298.15 K; ——, calculated from eqn. (3).

The ternary experimental $H^{E}$ results were compared with the predictions of an association model based on mole-fraction statistics [12]. According to this model the association constants and the enthalpies of hydrogen bond formation for alcohol open chains are: $K_2$ and $h_2$, for $A_1 + A_1 = A_2$; $K_3$ and $(2h - h_2)$, for $A_2 + A_1 = A_3$; $K$ and $h$, for $A_i + A_1 = A_{i+1}$, $(i \geqslant 3)$; cyclic chains are formed from open chains, $K_{cy} = \theta/i$ and $h$, for $A_i(\text{open}) = A_i(\text{cyclic})$ $(i > 4)$, $\theta$ being independent of $i$. The solvation constants and the enthalpies of complex formation between open chains ($A_i$) and one molecule of acetone (B) or benzene (C) are $K_{AB}$ and $h_{AB}$ for $A_i(\text{open}) + B_1 = A_iB$ $(i \geqslant 1)$; and $K_{AC}$ and $h_{AC}$ for $A_i(\text{open}) + C_1 = A_iC$ $(i \geqslant 1)$ . The equilibrium constants are defined in terms of the mole fractions of chemical species. The ternary expression of $H^{E}$ are given as the sum of two contribution terms: chemical and physical.

$$H^{E} = H^{E}_{\text{chem}} + H^{E}_{\text{phys}} \tag{5}$$

$$\begin{aligned} H^{E}_{\text{chem}} = {} & \{(1 + K_{AB}x_{B1} + K_{AC}x_{C1})[h_2K_2x^2_{A1} + hK_2K_3x^3_{A1}(2 - z)/(1 - z)^2] \\ & + hK_2K_3K^2\theta x^5_{A1}/(1 - z) \\ & + (h_{AB}K_{AB}x_{B1} + h_{AC}K_{AC}x_{C1})[x_{A1} + K_2x^2_{A1} + K_2K_3x^3_{A1}/(1 - z)]\}/S \\ & - x_A[h_2K_2x^{*2}_{A1} + hK_2K_3x^{*3}_{A1}(2 - z^*)/(1 - z^*)^2 \\ & + hK_2K_3K^2\theta x^{*5}_{A1}/(1 - z^*)]/S^* \end{aligned} \tag{6}$$

where $z = Kx_{A1}$ and $S$ is the stoichiometric sum given by

$$\begin{aligned} S = {} & (1 + K_{AB}x_{B1} + K_{AC}x_{C1})[x_{A1} + 2K_2x^2_{A1} + K_2K_3x^3_{A1}(3 - 2z)/(1 - z)^2] \\ & + K_2K_3K^2\theta x^5_{A1}/(1 - z) + (K_{AB}x_{B1} + K_{AC}x_{C1})[x_{A1} + K_2x^2_{A1} \\ & + K_2K_3x^3_{A1}/(1 - z)] + x_{B1} + x_{C1} \end{aligned} \tag{7}$$

The sum of the mole fractions of all chemical species is equal to unity

$$\begin{aligned} & (1 + K_{AB}x_{B1} + K_{AC}x_{C1})[x_{A1} + K_2x^2_{A1} + K_2K_3x^3_{A1}/(1 - z)] \\ & - (K_2K_3\theta/K^3)[\ln(1 - z) + z + z^2/2 + z^3/3 + z^4/4] + x_{B1} + x_{C1} = 1 \end{aligned} \tag{8}$$

The nominal mole fractions of the components, $x_A$, $x_B$ and $x_C$, are related to the monomeric mole fractions of the components, $x_{A1}$, $x_{B1}$ and $x_{C1}$, and the equilibrium constants

$$\begin{aligned} x_A = {} & \{(1 + K_{AB}x_{B1} + K_{AC}x_{C1})[x_{A1} + 2K_2x^2_{A1} + K_2K_3x^3_{A1}(3 - 2z)/(1 - z)^2] \\ & + K_2K_3K^2\theta x^5_{A1}/(1 - z)\}/S \end{aligned} \tag{9}$$

$$x_B = \{x_{B1} + K_{AB}x_{B1}[x_{A1} + K_2x^2_{A1} + K_2K_3x^3_{A1}/(1 - z)]\}/S \tag{10}$$

$$x_C = \{x_{C1} + K_{AC}x_{C1}[x_{A1} + K_2x^2_{A1} + K_2K_3x^3_{A1}/(1 - z)]\}/S \tag{11}$$

Equations (7)–(11) are solved simultaneously to obtain $x_{A1}$, $x_{B1}$ and $x_{C1}$.

At pure alcohol state, $z^* = Kx^*_{\mathrm{A1}}$, $x^*_{\mathrm{A1}}$ and $S^*$ are derived from the equations

$$x^*_{\mathrm{A1}} + K_2 x^{*2}_{\mathrm{A1}} + K_2 K_3 x^{*3}_{\mathrm{A1}}/(1 - z^*) - (K_2 K_3 \theta / K^3)[\ln(1 - z^*) + z^* + z^{*2}/2 + z^{*3}/3 + z^{*4}/4] = 1 \tag{12}$$

$$S^* = x^*_{\mathrm{A1}} + 2K_2 x^{*2}_{\mathrm{A1}} + K_2 K_3 x^{*3}_{\mathrm{A1}}(3 - 2z^*)/(1 - z^*)^2 + K_2 K_3 K^2 \theta x^{*5}_{\mathrm{A1}}/(1 - z^*) \tag{13}$$

The physical contribution term is given by applications of the Gibbs–Helmholtz equation to the NRTL equation for the excess Gibbs free energy [13]

$$H^{\mathrm{E}}_{\mathrm{phys}} = R \sum_{\mathrm{I}} x_{\mathrm{I}} \left( \frac{\sum\limits_{\mathrm{J}} x_{\mathrm{J}} \dfrac{\partial(\tau_{\mathrm{JI}} G_{\mathrm{JI}})}{\partial(1/T)}}{\sum\limits_{\mathrm{K}} G_{\mathrm{KI}} x_{\mathrm{K}}} - \frac{\sum\limits_{\mathrm{J}} \tau_{\mathrm{JI}} G_{\mathrm{JI}} x_{\mathrm{J}} \sum\limits_{\mathrm{K}} x_{\mathrm{K}} \dfrac{\partial G_{\mathrm{KI}}}{\partial(1/T)}}{(\sum\limits_{\mathrm{K}} G_{\mathrm{KI}} x_{\mathrm{K}})^2} \right) \tag{14}$$

where $\tau_{\mathrm{JI}}$ and $G_{\mathrm{JI}}$ are defined by

$$\tau_{\mathrm{JI}} = a_{\mathrm{JI}}/T \tag{15}$$

$$G_{\mathrm{JI}} = \exp(-\alpha_{\mathrm{JI}} \tau_{\mathrm{JI}}) \tag{16}$$

and the non-randomness parameter $\alpha_{\mathrm{JI}}$ is set as 0.3 for each binary mixture. The energy parameters $a_{\mathrm{JI}}$ are assumed to be linearly temperature-dependent

$$a_{\mathrm{JI}} = C_{\mathrm{JI}} + D_{\mathrm{JI}}(T - 273.15) \tag{17}$$

A simplex method [14] was used to obtain the coefficients $C_{\mathrm{JI}}$ and $D_{\mathrm{JI}}$.

The association parameters are $K_2 = 70$, $K_3 = 120$, $K = 100$ and $\theta = 90$ at 298.15 K, and $h_2 = -21.2$ and $h = -23.5$ kJ mol$^{-1}$. The solvation parameters are $K_{\mathrm{AB}} = 15$ at 323.15 K, $h_{\mathrm{AB}} = -21.0$ kJ mol$^{-1}$, $K_{\mathrm{AC}} = 3$ at 328.15 K and $h_{\mathrm{AC}} = -8.2$ kJ mol$^{-1}$ [12]. The temperature dependence of the equilibrium constants is fixed via the Van't Hoff equation. Table 4 gives the binary calculated results based on the association model. The ternary $H^{\mathrm{E}}$ predictions were performed using only binary information: the absolute arithmetic mean deviation between the experimental and calculated values for 57 data points is 9.3 J mol$^{-1}$ and the root-mean-squared deviation is 10.4 J mol$^{-1}$, indicating that agreement is good.

TABLE 4

Binary calculated results based on the association model

| Mixture (A + B) | $C_{\mathrm{BA}}$/(K) | $C_{\mathrm{AB}}$/(K) | $D_{\mathrm{BA}}$ | $D_{\mathrm{AB}}$ | Abs. arith. mean dev./(J mol$^{-1}$) |
|---|---|---|---|---|---|
| Methanol + acetone | 1070.58 | 338.58 | −3.8742 | 0.5540 | 5.8 |
| Methanol + benzene | −1084.29 | 843.71 | −3.8301 | 3.5643 | 4.4 |
| Acetone + benzene | 553.16 | 513.11 | 1.714 | 1.6470 | 1.0 |

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