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# EXCESS THERMODYNAMICS PROPERTIES OF PROPYL PROPANOATE+HEXANE+CYCLOHEXANE AT 298.15 K

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In this paper we present excess molar volumes and excess molar enthalpies of binary and ternary mixtures containing propyl propanoate, hexane and cyclohexane as components at 298.15 K. Excess molar volumes were calculated from the density of the pure liquids and mixtures. The density was measured using an Anton Paar DMA 60/602 vibrating-tube densimeter. Excess molar enthalpies were obtained using a Calvet microcalorimeter.

***Keywords:*** *cyclohexane, excess molar enthalpies, excess molar volumes, hexane, propyl propanoate*

## Introduction

This work continues our studies about excess thermodynamic properties of ternary mixtures containing propyl propanoate and hydrocarbon as components [1–4]. We report here the excess molar volumes and enthalpies for the ternary mixture propyl propanoate+hexane+cyclohexane, as well as the excess molar volumes and enthalpies of hexane+cyclohexane, at the temperature of 298.15 K and normal atmospheric pressure, over the whole composition range. Some of the binary mixtures were studied by us previously [1–4].

The substances studied are widely employed in different industrial process. Thus, propyl propanoate and hexane are used as solvents as well as components in the manufacture of colourings. Cyclohexane is used as raw material in plastic industry to make synthetic fibres and soft plastic for vehicles and sport equipment.

## Experimental

The chemical substances employed were supplied by Fluka and Sigma-Aldrich. Their mass purities were propyl propanoate (Sigma-Aldrich >99%), hexane (Fluka >99.5%) and cyclohexane (Fluka >99.5%). All substances were degassed by ultrasound and dried over molecular sieves (Sigma type 0.4 nm) and otherwise used as supplied. The density of pure liquids presents a good agreement with literature values as shown in Table 1.

All the mixtures were prepared by mass using a Mettler AT 201 balance. The precision of the mole fraction is estimated to be better than $\pm 1 \cdot 10^{-4}$. Densities of pure liquids and their corresponding mixtures were measured using an Anton Paar vibrating tube densimeter (model DMA 60/602) thermostated with a Schott–Geräte CT1450 circulating-water bath, with a precision in the temperature control of 0.01 K. The accuracy of the densities is $\pm 1 \cdot 10^{-5}$ g cm$^{-3}$. Calibration is performed daily with Milli-Q water and heptane (Sigma >99%).

**Table 1** Densities of the pure liquids at 298.15 K

| Compound | $\rho$/g cm$^{-3}$ | |
|---|---|---|
| | exp. | lit. |
| propyl propanoate | 0.87574 | 0.87569[a] |
| hexane | 0.65468 | 0.65471[b] |
| cyclohexane | 0.77367 | 0.77387[b] |

[a]Lorenzana *et al*. [12], [b]TRC [13]

Excess molar enthalpies were measured using a Calvet microcalorimeter connected to a Philips PM 2535 voltmeter. The inaccuracy of the excess enthalpy measurements was estimated to be better than 1%. Calibration was performed electrically using a Setaram EJP 30 stabilised current source and tested further with hexane and cyclohexane mixture [5]. Details of procedure were described by Paz Andrade *et al*. [6, 7]. Six experimental runs were carried out for the ternary mixture formed by adding cyclohexane to a binary mixture of propyl propanoate($x_1'$)+hexane($x_2'$), where $x_2' = 1 - x_1'$. A ternary mixture may be considered as a pseudobinary mixture composed of that binary mixture ($x_1$) and cyclohexane ($x_2$).

The ternary excess molar enthalpies at composition $x_1$, $x_2$ and $x_3$ can be expressed as:

$$H^{\mathrm{E}}_{\mathrm{m},123} = H^{\mathrm{E}}_{\mathrm{m},\varphi} + (x_1 + x_2) H^{\mathrm{E}}_{\mathrm{m},12} \qquad (1)$$

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**Table 2** Densities, ρ, for binary mixture at 298.15 K

| $x_1$ | ρ/g cm$^{-3}$ | $x_1$ | ρ/g cm$^{-3}$ | $x_1$ | ρ/g cm$^{-3}$ |
|---|---|---|---|---|---|
| | | $x$ hexane+(1–$x$) cyclohexane | | | |
| 0.0511 | 0.76602 | 0.3747 | 0.72280 | 0.6838 | 0.68715 |
| 0.0926 | 0.76002 | 0.4297 | 0.71611 | 0.7395 | 0.68117 |
| 0.1450 | 0.75268 | 0.4779 | 0.71037 | 0.7910 | 0.67575 |
| 0.2131 | 0.74342 | 0.5011 | 0.70766 | 0.8484 | 0.66982 |
| 0.2576 | 0.73758 | 0.5774 | 0.69892 | 0.9336 | 0.66123 |
| 0.3014 | 0.73196 | 0.6335 | 0.69267 | | |

where $H^{E}_{m,\varphi}$ is the measured excess molar enthalpy and $H^{E}_{m,12}$ is the excess molar enthalpy of the initial binary mixture propyl propanoate+hexane. Values of $H^{E}_{m,12}$ at different mole fractions were interpolated by using a spline-fit method.

## Results

Measured densities, ρ, of the binary mixture hexane +cyclohexane are shown in Table 2 for the whole composition range. The excess molar volumes, $V^{E}_{m}$, were calculated from the densities as follow:

$$V^{E}_{m,ij} = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (2)$$

In this equation, ρ is the density in the mixture, $\rho_i$ is the density of the pure components, and $N$ is the number of the components in the mixture.

Excess molar volumes and excess molar enthalpies, $H^{E}_{m}$, of the binary mixtures at 298.15 K were fitted to a variable-degree Redlich–Kister polynomial equation [8] using a least-squares method:

$$Q^{E} = x_i x_j \sum_{K=0}^{n} A_K (x_i - x_j)^K \quad (3)$$

where $Q^{E}$ represents $V^{E}_{m}$ (cm$^3$ mol$^{-1}$) or $H^{E}_{m}$ (J mol$^{-1}$); $x_i$ and $x_j$ are the mole fractions of components $i$ and $j$, respectively; and $A_K$ denotes the polynomial coefficients. The degree of the polynomial Redlich–Kister equation was optimised by applying the $F$-test [9]. Excess properties for the binary mixtures studied here are shown in Figs 1 and 2.

Values of excess molar volumes, $V^{E}_{m,123}$, and excess molar enthalpies, $H^{E}_{m,123}$, for the ternary mixture were adequately correlated by Cibulka equation [10]:

$$Q^{E}_{m,123} = Q^{E}_{m,12} + Q^{E}_{m,13} + Q^{E}_{m,23} + \\ + x_1 x_2 (1 - x_1 - x_2) \Delta_{123} \quad (4)$$

where

$$\Delta_{123} = B_0 + B_1 x_1 + B_2 x_2 \quad (5)$$

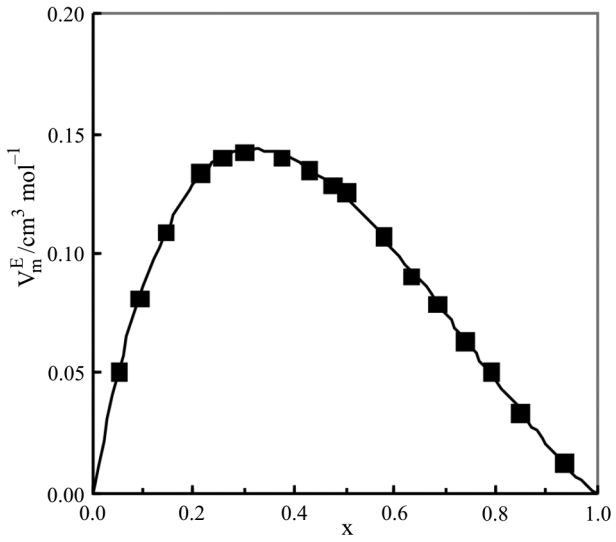


**Fig. 1** Excess molar volumes for the binary mixture at 298.15 K: ■ – $x$ hexane+(1–$x$)cyclohexane

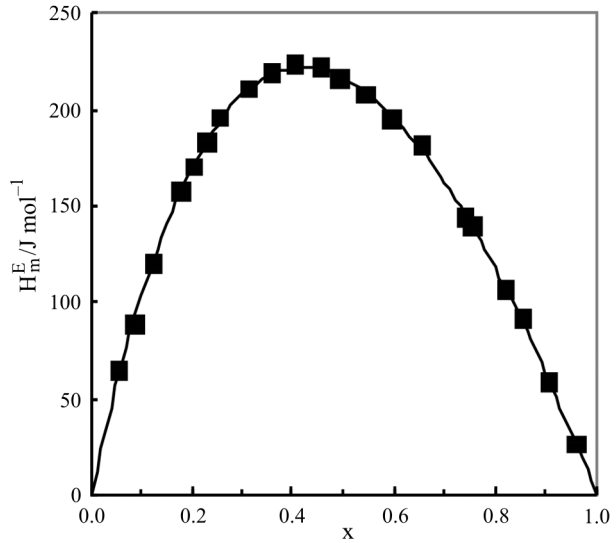


**Fig. 2** Excess molar enthalpies for the binary mixture at 298.15 K: ■ – $x$ hexane+(1–$x$)cyclohexane

**Table 3** Coefficients $A_k$, $B_i$ and standard deviations, $s$

| | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $A_4$ | $s$ |
|---|---|---|---|---|---|---|
| | | | $x$ propyl propanoate+(1–$x$)hexane | | | |
| $V^E_m$/cm$^3$ mol$^{-1}$[a] | 1.366 | –0.652 | 0.300 | | | 0.005 |
| $H^E_m$/J mol$^{-1}$[b] | 3353 | –214 | 0 | –1013 | 1085 | 7 |
| | | | $x$ propyl propanoate+(1–$x$)cyclohexane | | | |
| $V^E_m$/cm$^3$ mol$^{-1}$[a] | 3.028 | –0.879 | 0.388 | –0.349 | 0.184 | 0.0013 |
| $H^E_m$/J mol$^{-1}$[b] | 3736 | –843.8 | –662.3 | –430.7 | 1441 | 6 |
| | | | $x$ hexane+(1–$x$)cycyclohexane | | | |
| $V^E_m$/cm$^3$ mol$^{-1}$[a] | 0.494 | –0.389 | 0.156 | –0.104 | | 0.0013 |
| $H^E_m$/J mol$^{-1}$[b] | 866.4 | –272.7 | 96.8 | | | 1.5 |
| | $B_1$ | $B_2$ | $B_3$ | | | $s$ |
| | | | $x_1$ propyl propanoate+$x_2$ hexane+(1–$x_1$–$x_2$)cyclohexane | | | |
| $V^E_m$/cm$^3$ mol$^{-1}$[a] | 0.446 | 1.127 | 0.195 | | | 0.008 |
| $H^E_{m,123}$/J mol$^{-1}$[b] | 2078.9 | –2395.3 | 75.2 | | | 14 |

[a][2], [b][1]

and $Q^E_{m,123}$ is $V^E_{m,123}$ (cm$^3$ mol$^{-1}$) or $H^E_{m,123}$ (J mol$^{-1}$) in each case. The $B_i$ parameters were calculated by the unweighted least-squares method using a non-linear optimisation algorithm due to Marquardt [11]. Results for excess molar volumes and enthalpies of the ternary mixtures are shown in Figs 3 and 4, respectively.

Table 3 shows the values of the mentioned parameters $A_K$ and $B_i$, and the corresponding standard deviations, $s$. The $A_K$ parameters for the binary mixtures propyl propanoate+hexane and propyl propanoate+cyclohexane were taken from [1–4].

The results obtained for $V^E_{m,123}$ and $H^E_{m,123}$ in this work are significantly different from those published previously by us [1, 2] with benzene as third component of the ternary mixture. The behaviour of cyclohexane as destructor of structure is reflected in a greater size of the excess ternary properties in comparison with those obtained for the mixture with benzene as component. The electron from the π ring of the aromatic molecule can be transferred generating new interactions with the carboxyl group of the ester, resulting in negative values of $V^E_{m,123}$ and $H^E_{m,123}$.

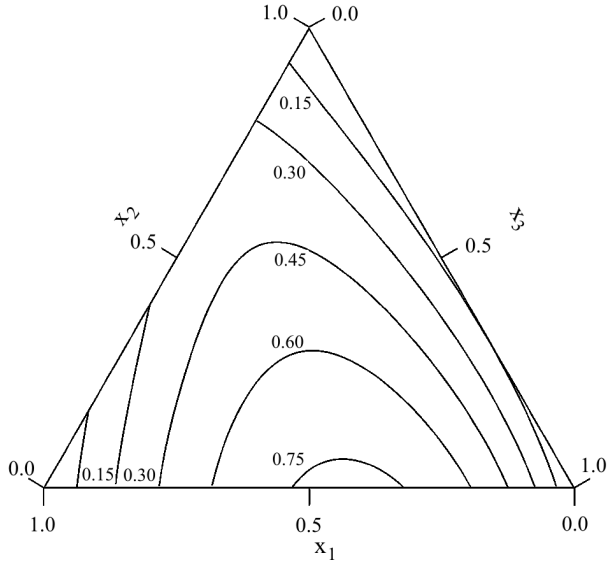


**Fig. 3** Curves of constant excess molar volumes at 298.15 K in cm$^3$ mol$^{-1}$ of $x_1$ propyl propanoate+$x_2$ hexane+$x_3$ cyclohexane

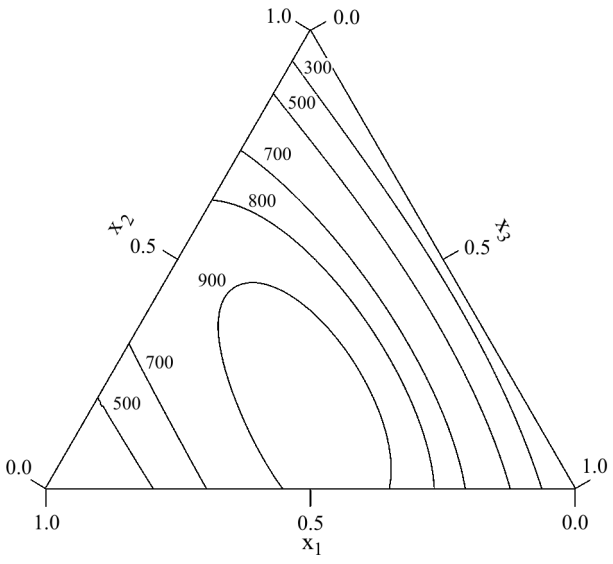


**Fig. 4** Curves of constant excess molar enthalpies at 298.15 K in J mol$^{-1}$ of $x_1$ propyl propanoate+$x_2$ hexane+$x_3$ cyclohexane

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