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Excess molar volumes and enthalpies for the binary systems propyl propanoate + *o*-xylene, *m*-xylene, and *p*-xylene at 298.15 K

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Abstract

This paper reports excess molar enthalpies, H_m^E, and excess molar volumes, V_m^E, of the binary systems {propyl propanoate + *o*-xylene}, {propyl propanoate + *m*-xylene} and {propyl propanoate + *p*-xylene} at the temperature 298.15 K and atmospheric pressure, over the whole composition range. V_m^E was calculated from the experimental measurement of the corresponding densities, while H_m^E was measured directly. The excess magnitudes were correlated to a Redlich-Kister type equation. Finally, we will discuss the results of the three mixtures studied here and by comparison with other binary systems containing propyl propanoate and a benzene-based compound previously published.

Keywords: Excess volume; Excess enthalpy; Propyl propanoate; Xylene; Benzene-based compounds

1. Introduction

This work continues our studies about the excess thermodynamic properties for binary mixtures containing propyl propanoate and an aromatic hydrocarbon as components [1,2]. We present here the excess molar volumes and enthalpies for the binary systems propyl propanoate + *o*-xylene, + *m*-xylene, and + *p*-xylene at the temperature 298.15 K and atmospheric pressure, over the whole composition range. The mixtures presented are specially important because they are widely used as solvents for dyes and colouring. Also, xylenes are used as raw material in plastic industry to make synthetic fibres and soft plastic for aircrafts and vehicles.

2. Experimental

2.1. Materials

The chemicals employed were supplied by Fluka and Sigma-Aldrich. Their mass purities were propyl propanoate (Sigma-Aldrich >99%), *o*-xylene (Fluka ≥99%), *m*-xylene (Fluka ≥99%) and *p*-xylene (Fluka ≥99%). The substances were degassed by ultrasound and dried over molecular sieves (Sigma type 0.4 nm), otherwise used as supplied.

2.2. Apparatus and procedure

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 $\pm 1 \times 10^{-4}$. Densities of pure liquids and their corresponding mixtures were measured using an Anton Paar digital densimeter (model 60/602) thermostated with a Schott-Gërate CT 1450 circulating-water bath, with a precision in the temperature control of 0.01 K. The accuracy of the densities is $\pm 1 \times 10^{-5}\,\mathrm{g\,cm^{-3}}$. Calibration is performed daily with Milli-Q water and heptane (Sigma >99%). From the density data we determine the excess molar volumes. 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 1%. Calibration was performed electrically using a Setaram EJP 30 stabilised current source and tested further with an hexane and cyclohexane (both Fluka ≥99.5%) mixture [3]. Details of the experimental procedure to measure H_m^E were described by Paz Andrade et al. [4,5].

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Table 1
Densities of the pure components at 298.15 K

Component	ρ (g cm^{-3})	
	Experimental	Literature
Propyl propanoate	0.87553	0.87549 [6]
o-Xylene	0.87489	0.87505 [7]
m-Xylene	0.85978	0.85976 [8]
p-Xylene	0.85650	0.85661 [9]

3. Results

The measured densities of the four pure liquids used at $T = 298.15$ K are listed in Table 1 with literature values. The agreement, within the experimental uncertainties, between both sets of data indicates that our experimental equipment has good accuracy.

Measured densities, ρ, of the three binary mixtures are shown in Table 2 for the whole composition range. In Table 3 we include the measured excess molar enthalpies for the whole composition range.

Table 2
Densities, ρ, and excess molar volumes, V_m^E, for binary mixtures at 298.15 K

x_1	ρ (g cm^{-3})	V_m^E (cm^3 mol^{-1})	x_1	ρ (g cm^{-3})	V_m^E (cm^3 mol^{-1})
Propyl propanoate + *o*-xylene					
0.0407	0.87508	−0.0244	0.5390	0.87616	−0.1411
0.1159	0.87539	−0.0619	0.5894	0.87617	−0.1381
0.1657	0.87558	−0.0844	0.6315	0.87614	−0.1310
0.2118	0.87572	−0.1011	0.6850	0.87610	−0.1215
0.2590	0.87585	−0.1163	0.7405	0.87602	−0.1066
0.3323	0.87599	−0.1307	0.7845	0.87592	−0.0882
0.3830	0.87610	−0.1430	0.8381	0.87582	−0.0701
0.4323	0.87613	−0.1441	0.8899	0.87570	−0.0490
0.4875	0.87617	−0.1467	0.9423	0.87556	−0.0243
Propyl propanoate + *m*-xylene					
0.0482	0.86064	−0.0166	0.5421	0.86900	−0.0647
0.1236	0.86205	−0.0376	0.5887	0.86969	−0.0600
0.1711	0.86290	−0.0475	0.6358	0.87040	−0.0544
0.2186	0.86374	−0.0558	0.6907	0.87119	−0.0488
0.2693	0.86461	−0.0606	0.7418	0.87192	−0.0413
0.3156	0.86539	−0.0648	0.7921	0.87265	−0.0342
0.3903	0.86662	−0.0680	0.8367	0.87329	−0.0275
0.4436	0.86747	−0.0683	0.9041	0.87420	−0.0159
0.4925	0.86823	−0.0676	0.9438	0.87475	−0.0089
Propyl propanoate + *p*-xylene					
0.1243	0.85942	−0.0608	0.5874	0.86882	−0.1278
0.1722	0.86054	−0.0844	0.6426	0.86980	−0.1216
0.2192	0.86156	−0.0989	0.6892	0.87060	−0.1113
0.2642	0.86252	−0.1103	0.7414	0.87147	−0.0989
0.3148	0.86359	−0.1222	0.7934	0.87231	−0.0820
0.3688	0.86469	−0.1305	0.8381	0.87303	−0.0683
0.4374	0.86606	−0.1383	0.8925	0.87388	−0.0494
0.4931	0.86710	−0.1356	0.9487	0.87473	−0.0260
0.5394	0.86795	−0.1326			

Table 3
Excess molar enthalpies, H_m^E, for the binary mixtures at 298.15 K

x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
Propyl propanoate + *o*-xylene					
0.0305	−9.7	0.3582	−68.7	0.6217	−65.2
0.1012	−26.4	0.4001	−71.3	0.6618	−59.9
0.1586	−39.8	0.4255	−71.7	0.7648	−45.4
0.2023	−47.1	0.5266	−71.8	0.8245	−34.7
0.2316	−53.6	0.5473	−71.3	0.9192	−17.5
0.2689	−60.8	0.5990	−68.0	0.9694	−6.6
0.3170	−65.1				
Propyl propanoate + *m*-xylene					
0.0773	−18.7	0.5498	−58.3	0.8160	−26.9
0.0975	−24.1	0.5863	−56.1	0.8561	−20.0
0.1378	−31.3	0.6238	−51.6	0.8668	−18.4
0.1696	−37.3	0.6587	−48.1	0.9040	−14.7
0.2505	−48.4	0.6872	−45.0	0.9191	−12.2
0.3158	−54.6	0.7099	−41.1	0.9408	−8.7
0.4081	−59.3	0.7679	−32.3	0.9571	−6.7
0.4828	−59.5				
Propyl propanoate + *p*-xylene					
0.0767	−32.9	0.3794	−99.8	0.7219	−68.4
0.0926	−39.9	0.4634	−100.3	0.8067	−50.2
0.1741	−63.7	0.5355	−97.3	0.8315	−45.9
0.1922	−70.3	0.6039	−90.6	0.9048	−24.7
0.2456	−82.5	0.6797	−77.4	0.9574	−14.1
0.3125	−92.0	0.6979	−74.7		

From the measured densities we extract the excess molar volumes using the usual expression:

$$V_m^E = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}) \qquad (1)$$

In this equation ρ is the density in the mixture. The ρ_i is the density of the pure components, and N the number of the components in the mixture (so $N = 2$ in our case). The V_m^E calculated and the H_m^E measured of the binary systems can be represented by a Redlich-Kister type equation [10]

$$Q_{ij}^E = x_i x_j \sum_{K=0}^{m} A_K (2x_i - 1)^K \qquad (2)$$

where Q_{ij}^E represents V_m^E or H_m^E; 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 [11]. The coefficients A_K for Eq. (2) and the standard deviation, s, defined by Eq. (3), are given in Table 4:

$$s = \sqrt{\frac{\sum_{i=1}^{N} (Y_{\text{cal}} - Y_{\text{exp}})^2}{N - 1}} \qquad (3)$$

where N the number of data points, Y_{cal} the calculated value and Y_{exp} the experimental value.

In Fig. 1 we plot the measured H_m^E for the three mixtures measured. The excess molar enthalpy for all mixtures is negative and the minimum is slightly displaced toward

Table 4
Coefficients A_K and standard deviations, s

	A_0	A_1	A_2	A_3	A_4	s
Propyl propanoate + *o*-xylene						
V_m^E (cm^3 mol^{-1})	−0.5833	0.0647	0.0466			0.0016
H_m^E (J mol^{-1})	−290.5	43.7	46.2			0.8
Propyl propanoate + *m*-xylene						
V_m^E (cm^3 mol^{-1})	−0.2659	0.1010				0.0006
H_m^E (J mol^{-1})	−240.5	65.5	84.0		−68.3	0.7
Propyl propanoate + *p*-xylene						
V_m^E (cm^3 mol^{-1})	−0.5433	0.0770		−0.0597		0.0013
H_m^E (J mol^{-1})	−397.2	101.5	24.2			1.1

mixtures richer in xylene (at about $x = 0.45$). The value of H_m^E is lower for the mixture with *p*-xylene than that with *o*-xylene and both lower than the *m*-xylene one.

In Fig. 2 we present the excess molar volume for the three mixtures studied versus the molar fraction of the propyl propanoate. As observed V_m^E is negative, which means a better packing of the molecules in the mixture than in the pure compound. The V_m^E data for the mixtures with *o*-xylene and *p*-xylene are very similar and the minimum is around the equimolar composition. In contrast V_m^E for the mixture with *m*-xylene is about half than the other two and their minimum is driven toward a mixture richer in *m*-xylene (at about $x = 0.4$).

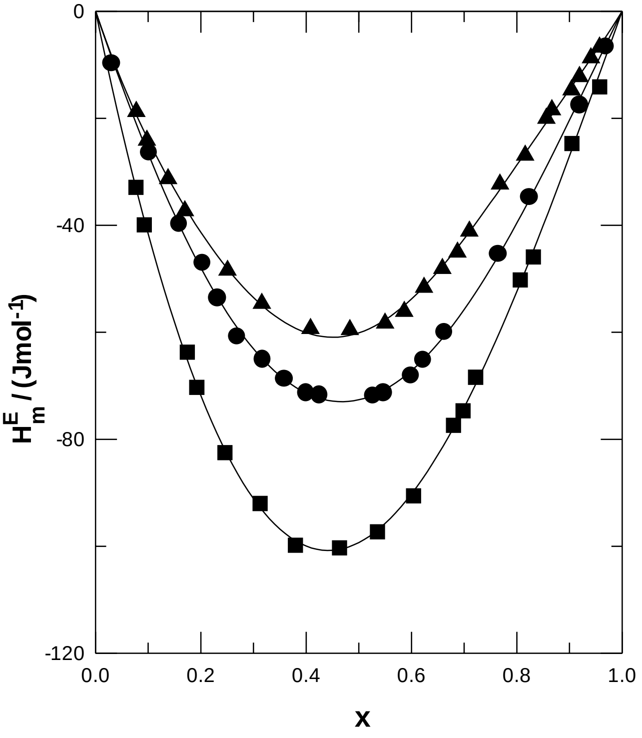

Fig. 1. Excess molar enthalpies of: (●) {propyl propanoate + *o*-xylene}; (▲) {propyl propanoate + *m*-xylene}; (■) {propyl propanoate + *p*-xylene} at 298.15 K.

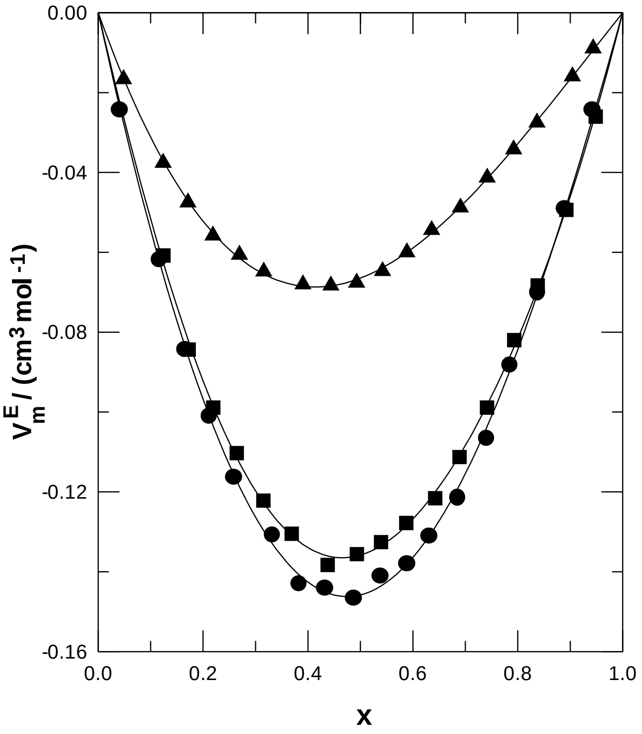

Fig. 2. Excess molar volumes of: (●) {propyl propanoate + *o*-xylene}; (▲) {propyl propanoate + *m*-xylene}; (■) {propyl propanoate + *p*-xylene} at 298.15 K.

4. Discussion

In this section we will compare the results measured here with other data from the literature for similar systems (i.e. propyl propanoate + benzene-based compounds). For that, in Fig. 3 we present the excess molar enthalpy measured by us and that obtained from literature for propyl propanoate + toluene [12] and propyl propanoate + benzene [1]. We have not found any published measurement of the same mixtures we present here. As observed in Fig. 3, H_m^E is negative for all mixtures which means that the interactions between the molecules of the mixture are stronger than those between the molecules of the pure compounds. The novel

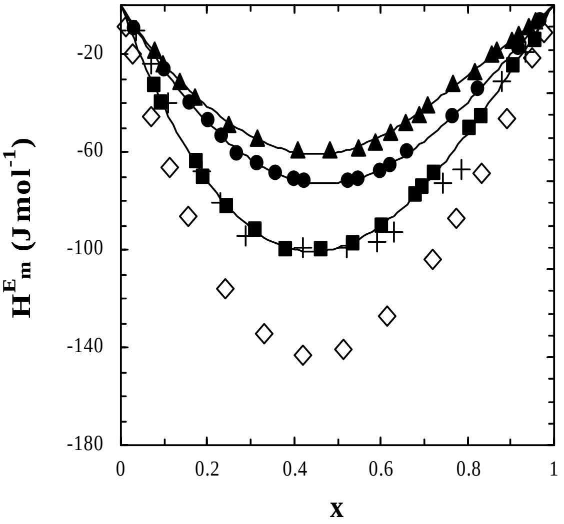

Fig. 3. Excess molar enthalpies of: (●) {propyl propanoate + *o*-xylene}; (▲) {propyl propanoate + *m*-xylene}; (■) {propyl propanoate + *p*-xylene}; (◇) {propyl propanoate + toluene} [12]; (+) {propyl propanoate + benzene} [1].

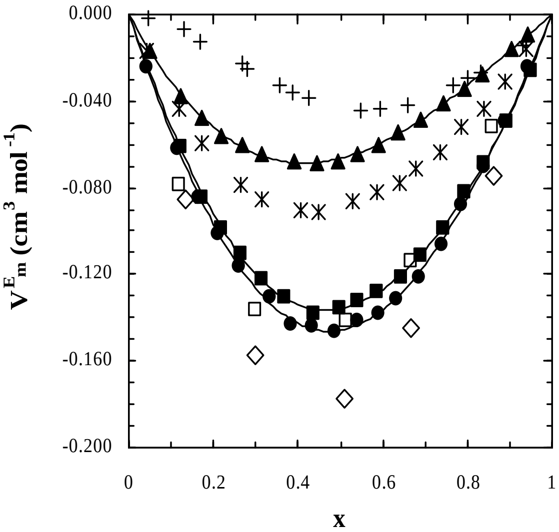

Fig. 4. Excess molar volumes of: (●) {propyl propanoate + *o*-xylene}; (▲) {propyl propanoate + *m*-xylene}; (■) {propyl propanoate + *p*-xylene}; (△) {propyl propanoate + *p*-xylene} [14]; (◇) {propyl propanoate + toluene} [14]; (✳) {propyl propanoate + ethylbenzene} [16]; (+) {propyl propanoate + benzene} [15].

interactions in the mixture must happen between the aromatic ring and the carboxyl group of the propyl propanoate. The absolute value of H^E_m will indicate the strength (and the number) of those new created interactions, less the strength (and the number) of the broken interactions between the molecules of the pure compounds. Higher absolute value indicates more (or stronger) novel interactions. Thus, the propyl propanoate + toluene is the mixture with stronger interactions, the benzene and the *p*-xylene show the same value of H^E_m, the *o*-xylene has smaller and the smallest value of H^E_m corresponds to the *m*-xylene. An explanation to the results shown in Fig. 3 could be that the introduction of a methyl group in benzene (as in toluene or xylene) would render the π-electron cloud of the aromatic ring more labile [13]. Accordingly, compared with benzene, toluene interacts stronger with propyl propanoate, as observed in Fig. 3. In the case of xylenes, that effect is minimised due to the lower free space to react in the aromatic ring, and thus the H^E_m will be governed meanly by the geometry of the xylene molecule. The free space to perform novel interactions would be higher in *p*-xylene, lower in *o*-xylene and even smaller for *m*-xylene, in a proportion of, respectively, 4–3–2.5 (given by the corresponding H^E_m values).

In Fig. 4 we show the excess molar volumes, V^E_m, for the three mixtures measured here and those formed by propyl propanoate + toluene [14], + benzene [15], + ethyl benzene [16] and previous published data for propyl propanoate + *p*-xylene [14]. As noted, the data measured here for the mixture with *p*-xylene and that published previously are quite similar in absolute value and shape. With respect to the physical meaning of V^E_m, the data measured comes from two different and independent physical mechanisms. First, the variation in the molecular packing as a consequence of different sizes and shapes of the molecular components. Second, the variation of intermolecular forces when the two components of the sample come in contact [17]. This last effect is governed by the excess molar enthalpies presented in Fig. 3. If the first effect were not relevant, the absolute value of V^E_m must be proportional to the absolute value of H^E_m, which seems to be the case for the mixtures containing toluene and *m*-xylene (about triple the first respecting the second for both excess magnitudes). The mixtures with benzene, *o*-xylene and *p*-xylene do not follow that rule, which seems to indicate that the molecular packing has varied in a different manner than for the two first mentioned mixtures. Thus, the V^E_m and H^E_m data suggest that in the mixture with benzene the packing of the molecules is worse after the mixture than for the pure compounds, it is better for the mixture with *p*-xylene and much better for that with *o*-xylene. This qualitative explanation agrees with the shape of the aromatic molecules analysed here. Finally, the mixture of propyl propanoate + ethyl benzene is included for comparison, but due to the lack of data on its H^E_m the explanation of the V^E_m data presented is difficult to perform.

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