

EXCESS MOLAR ENTHALPIES OF THE TERNARY SYSTEM *p*-XYLENE+DECANE+DIETHYL CARBONATE

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Excess molar enthalpies of the ternary system $\{x_1p\text{-xylene}+x_2\text{decane}+(1-x_1-x_2)\text{diethyl carbonate}\}$ and the involved binary mixtures $\{p\text{-xylene}+(1-x)\text{decane}\}$, $\{xp\text{-xylene}+(1-x)\text{diethyl carbonate}\}$ and $\{x\text{decane}+(1-x)\text{diethyl carbonate}\}$ have been determined at the temperature of 298.15 K and atmospheric pressure, over the whole composition range, using a Calvet microcalorimeter. The experimental excess molar enthalpies H_m^E are positive for all the binary systems studied over the whole composition range. Excess molar enthalpy for the ternary system is positive as well, showing maximum values at $x_1=0$, $x_2=0.4920$, $x_3=0.5080$, $H_{m,123}^E=1524\text{ J mol}^{-1}$.

Keywords: decane, diethyl carbonate, excess molar enthalpies, ternary mixture, *p*-xylene

Introduction

Continuing our previous studies on excess thermodynamic properties [1, 2], the present work reports experimental excess molar enthalpies of $\{x_1p\text{-xylene}+x_2\text{decane}+(1-x_1-x_2)\text{diethyl carbonate}\}$, $\{xp\text{-xylene}+(1-x)\text{decane}\}$, $\{xp\text{-xylene}+(1-x)\text{diethyl carbonate}\}$ and $\{x\text{decane}+(1-x)\text{diethyl carbonate}\}$ at the temperature of 298.15 K and atmospheric pressure. The measurement of excess molar enthalpies was carried out using a Calvet microcalorimeter. The results were fitted by means of different variable degree polynomials.

The thermophysical properties of binary mixtures of organic carbonates and *n*-alkanes have been studied by several workers. The excess molar enthalpies of $\{x\text{diethyl carbonate}+(1-x)\text{decane}\}$ and $\{x\text{diethyl carbonate}+(1-x)p\text{-xylene}\}$ at 298.15 K were measured by García *et al.* [3] and Lien *et al.* [4], respectively. Dominguez-Pérez *et al.* [13] have published data of excess molar enthalpy of $\{xx\text{ylene}+(1-x)\text{hexane}\}$ at 298.15 K.

We are not aware of any previous measurement of the ternary mixture to which this study is directed.

Experimental

Materials

The chemical substances employed were commercial products of the best quality grade (>099 mole fraction). Diethyl carbonate and *p*-xylene were supplied by Fluka, and decane was supplied by Aldrich. They

were subjected to no further purification other than drying with Union Carbide 0.4 nm molecular sieves to eliminate residual traces of water and degassed by ultrasound technique.

The handling and disposal of the chemicals used has been done according to the recommendation of the CRC Handbook of Chemistry and Physics [6].

Methods

The mixtures were prepared by mass using a Mettler H51 balance (precision $\pm 1 \cdot 10^{-5}$ g), ensuring a probable error in the mole fraction less than 10^{-4} . All molar quantities are based on the IUPAC relative atomic mass table [7].

The experimental excess molar enthalpies were measured using a Calvet microcalorimeter equipped with a device allowing operation in the absence of vapour phase, and having a calorimeter-cell volume of approximately 10 cm^3 . A Philips PM2535 multimeter and a data acquisition system were linked to the microcalorimeter. Calibration was performed electrically using a Setaram EJP30 stabilized current source. Further details about the experimental method of operation have been published [8, 9]. The apparatus and procedures were tested by determining excess enthalpies for the standard system hexane+cyclohexane at 298.15 K. The uncertainty in excess molar enthalpy measurements is estimated to be better than 1%.

Several experimental series of measurements were carried out for the ternary compositions resulting from adding diethyl carbonate to a binary mixture

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composed of $\{x'_1 p\text{-xylene} + x'_2 \text{decane}\}$. The ternary composition point is then a pseudobinary mixture composed by addition of diethyl carbonate to the mentioned binary mixture. Thus, the ternary excess molar enthalpy at the pseudobinary composition x_1 , x_2 , ($x_3 = 1 - x_1 - x_2$) can be expressed as

$$H_{m,123}^E = H_{m,\phi}^E + (x_1 + x_2)H_{m,12}^E \quad (1)$$

where $H_{m,\phi}^E$ is the measured excess molar enthalpy for the pseudobinary mixture and $H_{m,12}^E$ is the excess molar enthalpy of the initial binary $\{x'_1 p\text{-xylene} + x'_2 \text{decane}\}$ mixture. Values of $H_{m,12}^E$ at three mole fractions were interpolated by using a spline-fit method. Equation (1) does not involve any approximation.

Data correlation

Experimental values of H_m^E for the $\{xp\text{-xylene} + (1-x)\text{decane}\}$, $\{xp\text{-xylene} + (1-x)\text{diethyl carbonate}\}$ and $\{x\text{decane} + (1-x)\text{diethyl carbonate}\}$ are listed in Table 1. The experimental data of H_m^E were fitted to the variable-degree polynomials, suggested by Redlich–Kister [10], of the form

$$H_m^E (\text{J mol}^{-1}) = x(1-x) \sum_{i=1}^n A_i (2x-1)^{i-1} \quad (2)$$

The parameters A_i shown in Eq. (2) have been obtained by a fitting computer program which uses the least squares procedure and a Marquardt algorithm [11]. The number of parameters used was determined by applying the optimization F test [12]. These parameters and the standard deviations for H_m^E of the three binary mixtures involved in this ternary system are presented in Table 2.

Plots of the experimental values obtained together with the smoothing curves for H_m^E of the three involved binary systems are shown in Fig. 1. Literature data [3, 4] are also plotted.

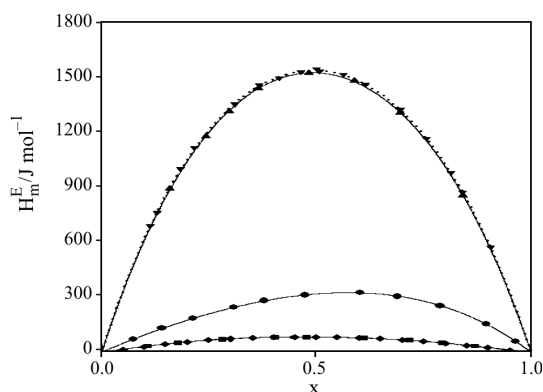


Fig. 1 Excess molar enthalpies $H_m^E/\text{J mol}^{-1}$ at 298.15 K of the three involved binary systems. Experimental values of: ● – $\{xp\text{-xylene} + (1-x)\text{decane}\}$; ■ – $\{xp\text{-xylene} + (1-x)\text{diethyl carbonate}\}$ and ▲ – $\{x\text{decane} + (1-x)\text{diethyl carbonate}\}$; — — fitted by Eq. (2); ▼ ··· — [3]; ◆ ····· — [4]

The measured values of ternary excess properties $H_{m,123}^E$, listed in Table 3, were correlated using the following equation:

$$H_{m,123}^E (\text{J mol}^{-1}) = H_{m,\text{bin}}^E + x_1 x_2 (1 - x_1 - x_2) \Delta_{123} \quad (4)$$

where

$$H_{m,\text{bin}}^E = H_{m,12}^E + H_{m,13}^E + H_{m,23}^E \quad (5)$$

is known as the binary contribution to the excess ternary properties and $H_{m,ij}^E$ are given by Eq. (2).

The last term stands for the ternary contribution to the magnitude, which was correlated using the expression suggested by Nagata and Tamura [13]

$$\Delta_{123} = (B_0 + B_1 x_1 + B_2 x_2 + B_3 x_1^2 + B_4 x_2^2) \quad (6)$$

The B_i parameters were calculated by an unweighted least-squares method using a non-linear optimization algorithm due to Marquardt [11]. These

Table 1 Excess molar enthalpies, H_m^E , of the binary systems at the temperature 298.15 K

x	$H_m^E/\text{J mol}^{-1}$	x	$H_m^E/\text{J mol}^{-1}$	x	$H_m^E/\text{J mol}^{-1}$
<i>xp</i> -xylene+(1- <i>x</i>)decane					
0.0740	71	0.3796	282	0.7883	
0.1406	132	0.4761	312	0.8958	254
0.2120	183	0.6016	325	0.9643	154
0.3076	244	0.6898	304		60
<i>xp</i> -xylene+(1- <i>x</i>)diethyl carbonate					
0.1080	35	0.4027	82	0.7169	66
0.1776	53	0.4766	83	0.7909	53
0.2819	72	0.6115	78	0.8692	35
<i>x</i> decane+(1- <i>x</i>)diethyl carbonate					
0.1597	891	0.3639	1438	0.6935	1307
0.2423	1179	0.4815	1521	0.8413	856
0.2965	1316	0.5882	1482		

parameters and the corresponding standard deviation are included in Table 4.

Figure 2 shows the pseudobinary representation of the measured experimental values, of $H_{m,123}^E$, together with the correlated curves, where Eq. (6) was applied to fit the ternary contribution.

The lines of constant ternary excess molar enthalpy, $H_{m,123}^E$ calculated using Eq. (4) are plotted in Fig. 3a. Figure 3b represents the ternary contribution $x_1x_2(1-x_1-x_2)\Delta_{123}$, to the excess molar enthalpy correlated with Eq. (6).

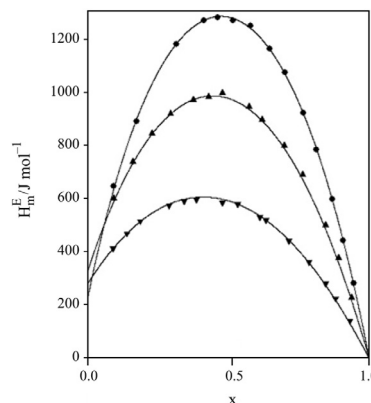


Fig. 2 Pseudobinary representation of ternary excess molar enthalpies $H_{m,123}^E/\text{J mol}^{-1}$ for $\{(1-x)(x'p\text{-xylene} + x_2'\text{decane}) + x\text{diethyl carbonate}\}$ at 298.15 K: \bullet – $x_1'=0.2558, x_2'=0.7442$; \blacktriangle – $x_1'=0.5038, x_2'=0.4920$, \blacktriangledown – $x_1'=0.7531, x_2'=0.2469$, — — correlated using Eq. (4)

Results and discussion

The experimental excess molar enthalpies H_m^E are positive for all the binary systems studied over the whole composition range. It suggests the predominance of breaking the previous interactions over the formation of new interactions during the mixing process.

García *et al.* [3] determined the H_m^E values for the system $\{x\text{decane} + (1-x)\text{diethyl carbonate}\}$ at 298.15 K obtaining $H_m^E(x=0.5)=1536 \text{ J mol}^{-1}$ somewhat upper than our $H_m^E(x=0.5)=1523 \text{ J mol}^{-1}$. The dotted curve shown in Fig. 1 was calculated from the smoothing equation reported by those authors. Not differences are showing between our results and those obtained by Lien *et al.* [4].

Table 2 Fitting parameters A_i for Eq. (2) and standard deviations, s

A_1	A_2	A_3	A_4	A_5	s
<i>xp</i> -xylene+(1- <i>x</i>)decane					
1273	370	120			1
<i>xp</i> -xylene+(1- <i>x</i>)diethyl carbonate					
332	-36	51	0	-94	0.3
<i>x</i> decane+(1- <i>x</i>)diethyl carbonate					
6096	-165	912			4

Table 3 Experimental excess molar enthalpies, $H_{m,123}^E$, at the temperature 298.15 K for the ternary mixture: $x_1p\text{-xylene} + x_2\text{decane} + (1-x_1-x_2)\text{diethyl carbonate}^a$

x_1	x_2	$H_{m,\phi}^E/\text{J mol}^{-1}$	$H_{m,123}^E/\text{J mol}^{-1}$	x_1	x_2	$H_{m,\phi}^E/\text{J mol}^{-1}$	$H_{m,123}^E/\text{J mol}^{-1}$
$x_1'=0.2558, H_{m,12}^E=213 \text{ J mol}^{-1}$							
0.2314	0.6732	454	647	0.0899	0.2615	1089	1164
0.2108	0.6133	715	891	0.0765	0.2226	1011	1075
0.1745	0.5077	1035	1181	0.0598	0.1740	873	923
0.1497	0.4355	1146	1271	0.0477	0.1388	746	786
0.1373	0.3994	1167	1282	0.0332	0.0967	571	598
0.1231	0.3583	1164	1267	0.0233	0.0679	424	444
0.1075	0.3127	1160	1250	0.0140	0.0408	270	282
$x_1'=0.5038, H_{m,12}^E=319 \text{ J mol}^{-1}$							
0.4554	0.4485	314	602	0.2145	0.2113	811	947
0.4215	0.4151	474	740	0.1909	0.1880	779	900
0.3881	0.3822	601	846	0.1517	0.1494	705	801
0.3543	0.3489	698	922	0.1191	0.1173	615	691
0.3138	0.3090	774	973	0.0777	0.0765	453	503
0.2863	0.2819	803	984	0.0550	0.0542	344	379
0.2617	0.2577	833	998	0.0311	0.0307	210	229
$x_1'=0.7531, H_{m,12}^E=277 \text{ J mol}^{-1}$							
0.6836	0.2241	161	412	0.2755	0.0903	420	521
0.6457	0.2117	232	470	0.2912	0.0955	424	531
0.6111	0.2003	291	516	0.2141	0.0702	365	443
0.5336	0.1749	377	573	0.1604	0.0526	303	362
0.4934	0.1617	410	591	0.1170	0.0383	239	282
0.4616	0.1513	427	597	0.0902	0.0296	192	225
0.3914	0.1283	442	586	0.0518	0.0170	121	140
0.3504	0.1149	451	580				

^aThree experimental series of measurements were carried out for the ternary compositions resulting from adding diethyl carbonate to a binary mixture composed of $\{x'p\text{-xylene} + x_2'\text{decane}\}$, where $x_2'=1-x_1'$.

Table 4 Fitting parameters, B_i , for Nagata and Tamura Eq. (6) and standard deviation, s

B_0	B_1	B_2	B_3	B_4	s
$x_1p\text{-xylene}+x_2\text{decane}+x_3\text{diethyl carbonate}$					
4060	0	-6931	0	8710	7

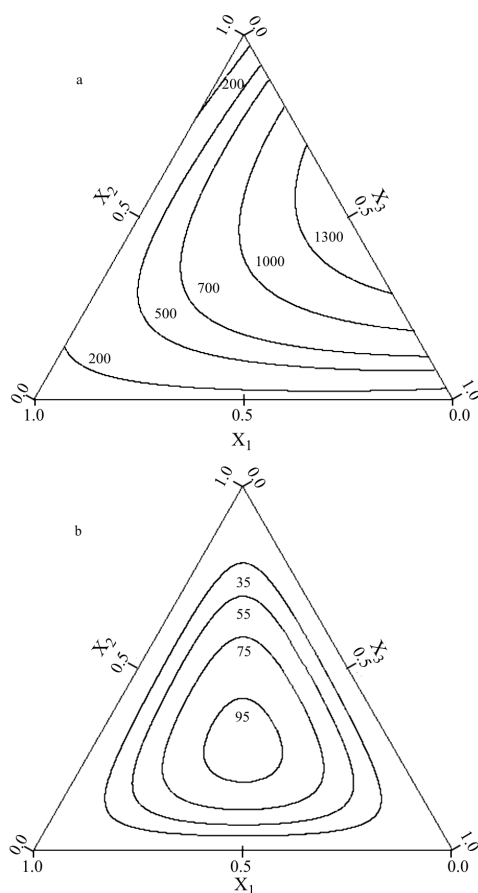


Fig. 3 Representation for $\{x_1p\text{-xylene}+x_2\text{decane}+(1-x_1-x_2)\text{ diethyl carbonate}\}$ at 298.15 K of: a – curves of constant ternary excess molar enthalpy, $H_{m,123}^E/\text{J mol}^{-1}$, b – curves of constant ternary contribution, $x_1x_2(1-x_1-x_2)\Delta_{123}$, to the excess molar enthalpy $H_{m,123}^E/\text{J mol}^{-1}$, calculated with Eq. (6)

Excess molar enthalpy for the ternary system is positive over the whole range of composition, showing maximum values at $x_1=0$, $x_2=0.4920$, $x_3=0.5080$, $H_{m,123}^E=1524 \text{ J mol}^{-1}$.

The ternary contribution is also positive, and the representation is symmetric. That means that, as can be seen in Fig. 3b, the position of the maximum coincides with the centre of the Gibbs triangle. There is a maximum value at $x_1=0.3571$, $x_2=0.2857$, $x_3=0.3572$, $H_{m,123}^E=102 \text{ J mol}^{-1}$. The value of maximum ternary contribution is about 7% of the value of the ternary enthalpy itself. Thus, excess molar enthalpy in the

ternary mixture can be probably ascribed to the effects that occur in the binary ones. Maximum value of the excess molar enthalpy is due to the contribution of the binary system $\{x\text{decane}+(1-x)\text{diethyl carbonate}\}$, where the predominant effect is the destruction of the dipolar order of the diethyl carbonate during mixing process.

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