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DETERMINATION OF EXCESS MOLAR ENTHALPIES FOR THE TERNARY SYSTEM *p*-XYLENE+OCTANE+DIETHYL CARBONATE

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Excess molar enthalpies, H^E, for the binary mixtures {*p*-xylene+(1–*x*) octane}, {*x p*-xylene+(1–*x*) diethyl carbonate}, {*x* octane+(1–*x*) diethyl carbonate} and the corresponding ternary system {x_1 *p*-xylene+x_2 octane+(1–x_1–x_2) diethyl carbonate} have been measured by using a Calvet microcalorimeter at 298.15 K under atmospheric pressure. The experimental H^E values are all positive for the binary and ternary mixtures over the entire composition range.

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

Introduction

Enthalpy calculation is essentially needed in process simulation and design of heat-transfer equipment. Excess molar enthalpy data are useful for determination or verification of model parameters with which the enthalpy values can be calculated with confidence. Experimental H^E results also provide information on the molecular interactions between constituent components.

Diethyl carbonate is a solvent used in a variety of liquid extraction processes, especially in the synthesis of pharmaceuticals and agricultural chemicals. This compound is also a good gasoline additive [1] to prevent the crack of abnormal burning and promote the blending octane values.

The present study is undertaken to measure excess enthalpies of {x_1 *p*-xylene+x_2 octane+(1–x_1–x_2) diethyl carbonate}, {*x p*-xylene+(1–*x*) octane}, {*x p*-xylene+(1–*x*) diethyl carbonate} and {*x* octane+(1–*x*) diethyl carbonate} at 298.15 K. Measurements were carried out using a Calvet microcalorimeter.

Excess molar enthalpies of {*x* diethyl carbonate+(1–*x*) octane} and {*x* diethyl carbonate+(1–*x*) *p*-xylene} at 298.15 K were measured by García *et al*. [2] and Pei-Jung Lien e*t al*. [3] respectively.

We are not aware of any previous measurement of $H^E_{m,123}$ of the ternary mixture to which this study is directed.

Experimental

Chemicals

Diethyl carbonate (Fluka, purity >99%), *p*-xylene (Fluka, purity >99%) and octane (Fluka, purity ≥99.5%) 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. Densities (Table 1) were measured with an Anton-Paar DMA 4500 densimeter (accuracy $\pm 5 \cdot 10^{-5}$ g cm^{-3}) at 298.15 K.

Table 1 Densities of pure components at 298.15 K

Compound	Density/g cm^{-3}	
	This work	Literature
p-xylene	0.8567	0.8567 [3]
Octane	0.6986	0.6986 [4]
Diethyl carbonate	0.9691	0.9692 [3]

Apparatus and procedure

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}.

The experimental excess molar enthalpies were measured using a Calvet microcalorimeter. 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. The apparatus and proce-

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dures 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 composed of $\{x_1'$ *p*-xylene+x_2' octane$\}$. 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

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

where $H^{E}_{m,\phi}$ is the measured excess molar enthalpy for the pseudobinary mixture and $H^{E}_{m,12}$ is the excess molar enthalpy of the initial binary $\{x_1'$ *p*-xylene+x_2' octane$\}$ mixture. Values of $H^{E}_{m,12}$ at three mole fractions were interpolated by using a spline-fit method. Equation (1) does not involve any approximation.

Data correlation

The experimental H^{E}_{m} data for the binaries $\{x$ *p*-xylene+(1–x) octane$\}$, $\{x$ *p*-xylene+(1–x) diethyl carbonate$\}$ and $\{x$ octane+(1–x) diethyl carbonate$\}$, listed in Table 2, are correlated with the empirical Redlich- Kister equation [5]:

$$H^{E}_{m}/\text{J mol}^{-1} = x(1-x)\sum_{i=1}^{n} A_i\,(2x-1)^{i-1} \qquad (2)$$

where the coefficients A_i were obtained by least-squares regression.

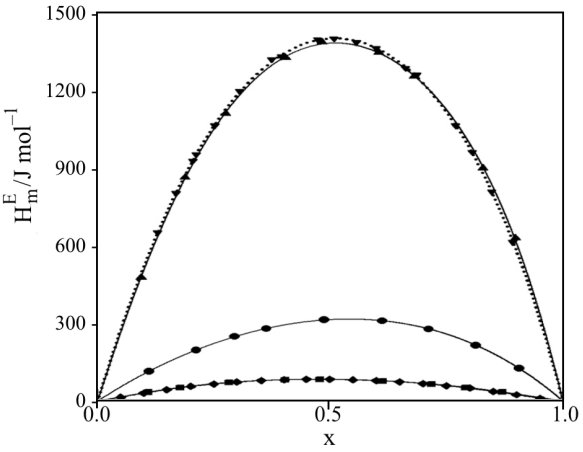

Fig. 1 Excess molar enthalpies H^{E}_{m}/J mol^{-1} at 298.15 K of the three involved binary systems. Experimental values of: • – $\{x$ *p*-xylene+(1–x) octane$\}$; ■ – $\{x$ *p*-xylene+(1–x) diethyl carbonate$\}$ and ▲ – $\{x$ octane+(1–x) diethyl carbonate$\}$; — – fitted by Eq. (2) ; ▼ ··· – Ref. [2]; ◆ – ·–· – Ref. [3]

Plots of the experimental values obtained together with the smoothing curves for H^{E}_{m} of the three involved binary systems are shown in Fig. 1. Literature data [2, 3] are also plotted.

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

$$H^{E}_{m,123}/\text{J mol}^{-1} = H^{E}_{m,12} + H^{E}_{m,13} + H^{E}_{m,23} + \\ + x_1x_2(1-x_1-x_2)\Delta_{123} \qquad (3)$$

where $H^{E}_{m,ij}$ is the binary contribution for each *ij* binary mixture, calculated with Eq. (2), $x_1x_2(1–x_1–x_2)\Delta_{123}$ is the ternary contribution which

Table 2 Excess molar enthalpies, H^{E}_{m}, of the binary systems at the temperature 298.15 K

x	H^{E}_{m}/J mol^{-1}	x	H^{E}_{m}/J mol^{-1}	x	H^{E}_{m}/J mol^{-1}
			x *p*-xylene+(1–x) octane		
0.1101	115	0.3621	280	0.7111	278
0.2115	196	0.4861	313	0.8129	215
0.2944	249	0.6115	309	0.9062	127
			x *p*-xylene+(1–x) 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
			x octane+(1–x) diethyl carbonate		
0.0931	476	0.4040	1325	0.6804	1252
0.1875	863	0.4816	1385	0.8278	899
0.2751	1110	0.6038	1345	0.8978	629

Table 3 Experimental excess molar enthalpies, $H^E_{m,123}$, at the temperature 298.15 K for the ternary mixture: x_1 *p*-xylene+x_2 octane+(1–x_1– x_2) diethyl carbonate[a]

x_1	x_2	$H^E_{m,\phi}$/J mol^{-1}	$H^E_{m,123}$/J mol^{-1}	x_1	x_2	$H^E_{m,\phi}$/J mol^{-1}	$H^E_{m,123}$/J mol^{-1}
			x'_1=0.2468, $H^E_{m,12}$=221 J mol^{-1}				
0.2267	0.6916	381	584	0.1061	0.3238	1014	1108
0.2079	0.6343	624	810	0.0924	0.2818	968	1050
0.1897	0.5787	800	970	0.0843	0.2571	931	1006
0.1735	0.5293	911	1067	0.0644	0.1966	804	861
0.1544	0.4711	1002	1141	0.0484	0.1477	665	708
0.1388	0.4234	1039	1163	0.0291	0.0888	439	465
0.1289	0.3934	1048	1163				
			x'_1=0.4974, $H^E_{m,12}$=314 J mol^{-1}				
0.4609	0.4657	219	509	0.2494	0.2520	719	876
0.4258	0.4303	390	658	0.2145	0.2168	698	833
0.3822	0.3862	537	778	0.2098	0.2120	689	821
0.3582	0.3620	604	830	0.1438	0.1454	588	677
0.3329	0.3364	656	866	0.0825	0.0834	394	446
0.2931	0.2962	696	881	0.0618	0.0625	288	327
			x'_1=0.7479, $H^E_{m,12}$=260 J mol^{-1}				
0.6885	0.2321	126	365	0.3678	0.1240	383	510
0.6515	0.2196	197	423	0.3040	0.1024	371	477
0.5979	0.2015	269	477	0.2996	0.1010	358	462
0.5375	0.1812	327	514	0.2095	0.0706	309	382
0.4309	0.1452	385	535	0.1758	0.0593	263	324
0.4151	0.1399	377	521	0.0924	0.0311	167	199

[a]Three experimental series of measurements were carried out for the ternary compositions resulting from adding diethyl carbonate to a binary mixture composed of {x'_1 *p*-xylene+x'_2 octane}, where x'_2 =1–x'_1

was correlated using the expression suggested by Cibulka [6]

$$\Delta_{123} = (B_0 + B_1x_1 + B_2x_2) \quad (4)$$

The parameters A_i and B_i of Eqs (2) and (4) are given in Table 4, in which the standard deviations *s* is defined as:

$$s(h^E) = \sqrt{\frac{\sum_{i=1}^{N}(h^E_{i,exp} - h^E_{i,cal})^2}{N-n}} \quad (5)$$

where *N* and *n* are the number of data points and the number of coefficients, respectively.

Table 4 Fitting parameters A_i, B_i for Eqs (2) and (4) and standard deviations, *s*

A_1	A_2	A_3	A_4	A_5	*s*
		x p-xylene+(1–*x*) octane			
1256	190	106			1
		x *p*-xylene+(1–*x*) diethyl carbonate			
332	–36	51	0	–94	0.3
		x octane+(1–*x*) diethyl carbonate			
5523	185	1092	827	0	6
B_0		B_1	B_2		*s*
		x_1 *p*-xylene+x_2 octane+x_3 diethyl carbonate			
1127		1117	1259		6

Results and discussion

The experimental excess molar enthalpies H^E_m 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.

In Fig. 1 experimental values of {*x* octane+(1–*x*) diethyl carbonate} and {*x* octane+(1–*x*) diethyl carbonate} were compared with literature. Not significant differences are showing between our results and those obtained by García *et al*. [2] and Pei-Jung Lien *et al*. [3].

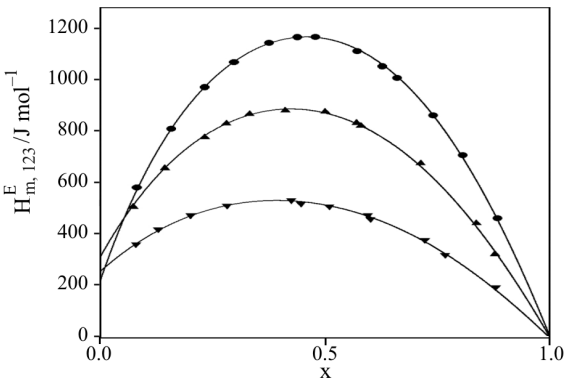

Fig. 2 Pseudobinary representation of ternary excess molar enthalpies $H^E_{m,123}$/J mol^{-1} for {(1–x) (x_1' *p*-xylene+x_2' octane)+x diethyl carbonate} at 298.15 K: • – x_1'=0.2468, x_2'=0.75321; ▲ – x_1'=0.5038, x_2'=0.4920, ▼– x_1'=0.7479, x_2'=0.2521, — – correlated using Eq. (3)

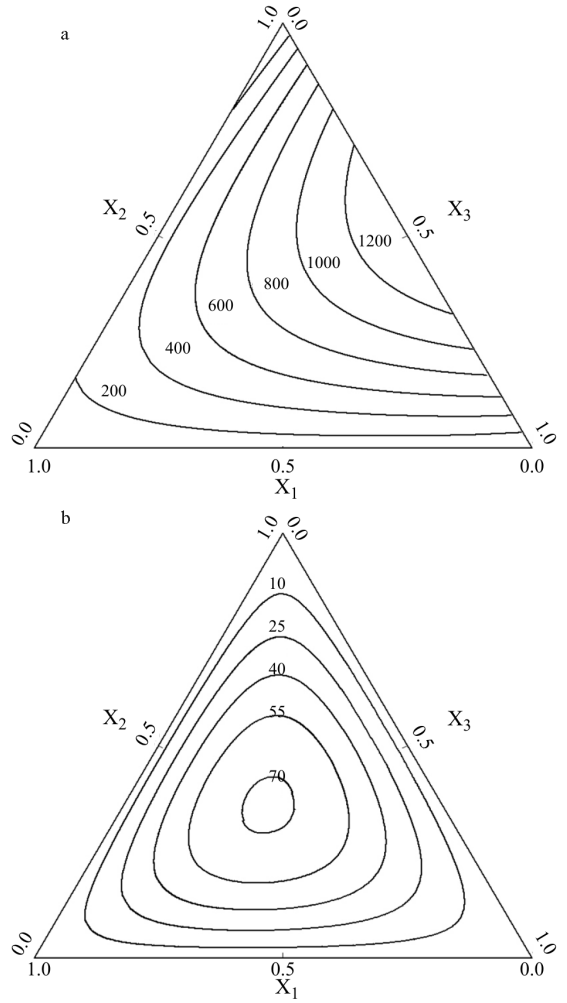

Fig. 3 Representation for {x_1 *p*-xylene+x_2 octane+(1–x_1–x_2) diethyl carbonate} at 298.15 K of: a – Curves of constant ternary excess molar enthalpy, $H^E_{m,123}$/J mol^{-1}, b – Curves of constant ternary contribution, $x_1x_2(1–x_1–x_2)\Delta_{123}$, to the excess molar enthalpy $H^E_{m,123}$/J mol^{-1}, calculated with Eq. (4)

Figure 2 shows the pseudobinary representation of the measured experimental values, of $H^E_{m,123}$, together with the correlated curves. The lines of constant ternary excess molar enthalpy, $H^E_{m,123}$, calculated using Eq. (3), 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. (4).

Excess molar enthalpy for the ternary system is positive over the whole range of composition. The ternary contribution is also positive, being always less than 6%, so the three-body effects in mixture are not relevant. Thus, the excess molar enthalpy in the ternary mixture can be probably ascribed to the effects that occur in the binary ones. The maximum value of the excess molar enthalpy is due to the contribution of the binary system {x octane+(1–x) diethyl carbonate}, where the predominant effect is the destruction of the dipolar order of the diethyl during mixing.

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