Table I. Experimental Data for the Solubility of Carbon Dioxide in Molten Salts

salt	temp, °C	density, g/cm³	solubility,[a] mol/cm³	std dev
$ZnCl_2$	300	2.534	1.76×10^{-6}	0.08×10^{-6}
	325	2.521	1.80×10^{-6}	
	350	2.504	1.71×10^{-6}	0.11×10^{-6}
	375	2.494	1.65×10^{-6}	
	400	2.481	1.47×10^{-6}	0.10×10^{-6}
	450	2.459	1.38×10^{-6}	0.02×10^{-6}
$ZnBr_2$	400	3.467	2.19×10^{-6}	0.17×10^{-6}
	450	3.420	1.80×10^{-6}	
	475	3.396	1.78×10^{-6}	
$SnCl_2$	270	3.336	3.86×10^{-7}	
	300	3.328	4.01×10^{-7}	
	350	3.268	3.96×10^{-7}	0.37×10^{-7}
	400	3.208	3.75×10^{-7}	0.25×10^{-7}
$NaNO_3$	310	1.916	1.07×10^{-6}	0.01×10^{-6}
	330	1.902	1.03×10^{-6}	0.08×10^{-6}
	350	1.888	1.08×10^{-6}	0.10×10^{-6}

[a] mol/cm³ of CO_2 in molten salt at 1 atm.

are plotted against $1/T$ on semilogarithmic coordinates. The solubilities slightly decrease with increasing temperature in this temperature range. The slopes are steeper in $ZnCl_2$ and $ZnBr_2$ than in the others. It is said that these two salts are to some extent associated liquids at temperatures above the melting point and that the degree of association diminishes with temperature (*9*). This might be responsible for the steep slopes and the relatively high solubilities in these salts. The value of the solubility of carbon dioxide in molten $ZnCl_2$ measured by Borodzinski et al. (*2*) is shown in Figure 3. The result obtained in this work agrees well with their result.

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Heat Capacities of Binary C_8 Alkylbenzene Mixtures

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A Picker flow microcalorimeter was used to determine volumetric heat capacities at 298.15 K for the six binary systems formed from the C_8 alkylbenzenes: ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene. Excess heat capacities obtained from the results are compared with the meager information available in the literature for the temperature variation of the excess enthalpies of these mixtures.

Previously we described determinations of excess heat capacities of binary systems formed by mixing the C_8 alkylbenzenes (ethylbenzene and the three isomeric xylenes) with benzene and with toluene (*3*). As an extension of that investigation we have carried out similar measurements for binary mixtures comprised of the C_8 aromatics alone.

We are not aware of previous measurements of the excess heat capacities of binary C_8 alkylbenzene mixtures. However, excess enthalpies at two different temperatures have been reported for some of them (*5*).

Experimental Section

The samples of the component liquids were the same as used in our earlier work (*3*) where characteristic densities and refractive indices are reported. The use of the Picker flow microcalorimeter for measuring differences of volumetric heat capacity following a stepwise procedure has been described previously (*1*, *3*, *4*). The initial reference liquids adopted in order of precedence were ethylbenzene, *o*-xylene, and *m*-xylene; values of their heat capacities determined relative to benzene were taken from ref 3. A temperature interval of about 1.4 K centered on 298.15 K was used for all measurements. The precision of the excess heat capacities is believed to be about ±0.02 J K^{-1} mol^{-1}.

Results and Discussion

A summary of the experimental measurements is given in Table I. At any mole fraction, $\Delta(C_p/V)$ is the amount by which the volumetric heat capacity of the mixture exceeds that of the preceding mixture. Each entry for $\Delta(C_p/V)$ is an average of two measurements in which the roles of the two mixtures, as test and reference, were reversed (*1*). Molar heat capacities were obtained from the volumetric heat capacities using molar volumes calculated from the densities of the component liquids (*3*) and the excess volumes of the mixtures (*6*, *10*).

In all cases the heat capacities of the pure xylenes obtained from measurements with respect to different reference liquids agree within less than 0.1%. Close agreement is also evident between these results and the values obtained in our previous studies in which the xylenes were measured against toluene (*1*) and tetrachloromethane (*2*).

The values of the excess heat capacity in Table I were calculated from the equation

$$C_p^{\mathrm{E}} = C_p - x_1 C_{p1} - x_2 C_{p2} \qquad (1)$$

where C_p and C_{pi} are the molar heat capacities of the mixture and of pure component *i*, respectively. In each case the value of C_{p2} measured for the particular system was used to ensure

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Table I. Experimental Results for the Change of Volumetric Heat Capacity $\Delta(C_p/V)$, Molar Heat Capacity C_p, and Molar Excess Heat Capacity C_p^E at 298.15 K

x_1	$\Delta(C_p/V)$, J K^{-1} cm^{-3}	C_p, J K^{-1} mol^{-1}	C_p^E, J K^{-1} mol^{-1}	x_1	$\Delta(C_p/V)$, J K^{-1} cm^{-3}	C_p, J K^{-1} mol^{-1}	C_p^E, J K^{-1} mol^{-1}
	Ethylbenzene (1)-*o*-Xylene (2)				*o*-Xylene (1)-*m*-Xylene (2)		
1	0	185.572[a]	0	1	0	187.653[a]	0
0.895 68	0.003 553	185.736	−0.046	0.901 46	−0.007 975	187.027	−0.033
0.800 63	0.003 221	185.878	−0.094	0.807 05	−0.007 574	186.431	−0.061
0.695 02	0.003 756	186.052	−0.132	0.691 27	−0.009 153	185.713	−0.083
0.595 37	0.003 714	186.231	−0.153	0.607 55	−0.006 496	185.206	−0.086
0.495 02	0.003 807	186.415	−0.171	0.508 88	−0.007 599	184.612	−0.086
0.394 58	0.003 927	186.608	−0.180	0.396 09	−0.008 642	183.936	−0.084
0.309 44	0.003 478	186.785	−0.174	0.305 50	−0.006 864	183.399	−0.076
0.200 34	0.004 787	187.045	−0.133	0.205 94	−0.007 425	182.820	−0.055
0.104 05	0.004 426	187.291	−0.079	0.099 90	−0.007 838	182.209	−0.029
0	0.005 034	187.580	0	0	−0.007 324	181.637	0
	Ethylbenzene (1)-*m*-Xylene (2)				*o*-Xylene (1)-*p*-Xylene (2)		
1	0	185.572[a]	0	1	0	187.653[a]	0
0.897 13	−0.004 267	185.140	−0.004	0.898 81	−0.008 801	187.005	−0.058
0.801 05	−0.003 934	184.736	−0.009	0.802 72	−0.008 222	186.402	−0.101
0.692 82	−0.004 372	184.280	−0.016	0.714 64	−0.007 454	185.856	−0.134
0.601 51	−0.003 610	183.898	−0.018	0.598 29	−0.009 636	185.157	−0.155
0.500 34	−0.003 960	183.474	−0.022	0.507 02	−0.007 397	184.625	−0.155
0.398 91	−0.003 918	183.048	−0.026	0.396 37	−0.008 874	183.988	−0.148
0.301 43	−0.003 644	182.647	−0.022	0.303 39	−0.007 344	183.464	−0.130
0.199 95	−0.003 756	182.227	−0.021	0.205 49	−0.007 582	182.927	−0.096
0.104 70	−0.003 412	181.839	−0.013	0.106 17	−0.007 610	182.389	−0.056
0	−0.003 648	181.417	0	0	−0.007 997	181.826	0
	Ethylbenzene (1)-*p*-Xylene (2)				*m*-Xylene (1)-*p*-Xylene (2)		
1	0	185.572[a]	0	1	0	181.550[a]	0
0.899 06	−0.003 479	185.272	0.084	0.889 35	−0.000 183	181.595	0.008
0.796 15	−0.003 659	184.952	0.155	0.797 80	−0.000 201	181.626	0.008
0.704 39	−0.003 437	184.645	0.197	0.694 18	−0.000 231	181.661	0.009
0.600 26	−0.004 010	184.283	0.230	0.607 29	−0.000 194	181.691	0.010
0.494 46	−0.004 284	183.888	0.237	0.499 93	−0.000 220	181.733	0.016
0.398 45	−0.004 087	183.505	0.219	0.393 89	−0.000 277	181.769	0.016
0.309 10	−0.003 884	183.137	0.191	0.304 70	−0.000 234	181.800	0.018
0.194 64	−0.005 121	182.648	0.137	0.205 09	−0.000 279	181.834	0.019
0.097 89	−0.004 469	182.217	0.074	0.103 84	−0.000 316	181.865	0.016
0	−0.004 593	181.771	0	0	−0.000 431	181.883	0

[a] C_p from measurements relative to benzene in ref 3.

Table II. Coefficients a_j and Standard Deviations σ for Representations of C_p^E for Binary C_8 Alkylbenzene Mixtures at 298.15 *K* by Equation 2

component		a_j, J K^{-1} mol^{-1}			
1	2	a_1	a_2	a_3	σ
ethylbenzene	*o*-xylene	−0.699	−0.229		0.004
	m-xylene	−0.091	−0.057		0.001
	p-xylene	0.941	−0.068	−0.090	0.002
o-xylene	*m*-xylene	−0.359	0.038		0.002
	p-xylene	−0.627	0.044		0.002
m-xylene	*p*-xylene	0.067	0.056		0.004

consistent values of C_p^E. The results were fitted with the equation

$$C_p^E = x_1 x_2 \sum_{j=1}^{n} a_j (1 - 2x_1)^{j-1} \tag{2}$$

using the method of least-squares and assigning equal weights to all points. Values of the coefficients a_j obtained from the analysis are listed in Table II along with the standard deviation σ for the representation.

The experimental excess heat capacities for the mixtures of ethylbenzene with the xylenes are plotted in Figure 1, and those for the binary xylene mixtures in Figure 2. The smooth representations by eq 2 are shown as solid curves in these figures. The excess heat capacities of all the binary C_8 alkylbenzene mixtures are negative at 298.15 K with the exception of ethylbenzene-*p*-xylene and *m*-xylene-*p*-xylene. The values of C_p^E for ethylbenzene-*p*-xylene are about 4 times more positive than those we found previously for ethylbenzene–toluene

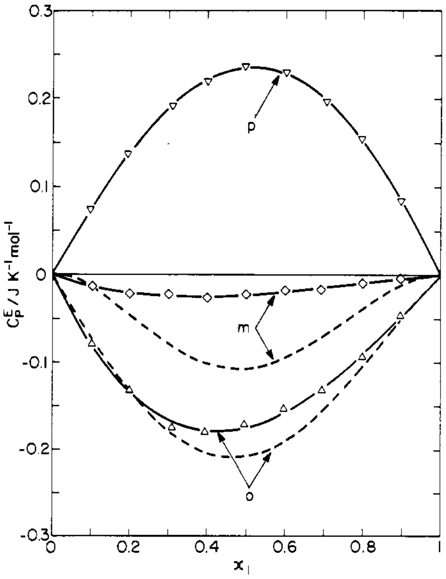

Figure 1. Molar excess heat capacities of ethylbenzene (1)-isomeric xylene (2) at 298.15 K. Labels indicate component 2: o, *o*-xylene; m, *m*-xylene; p, *p*-xylene. Points are experimental results. Solid curves are least-squares representations of results by eq 2. Broken curves are $(\partial H^E/\partial T)_p$ derived from ref 5.

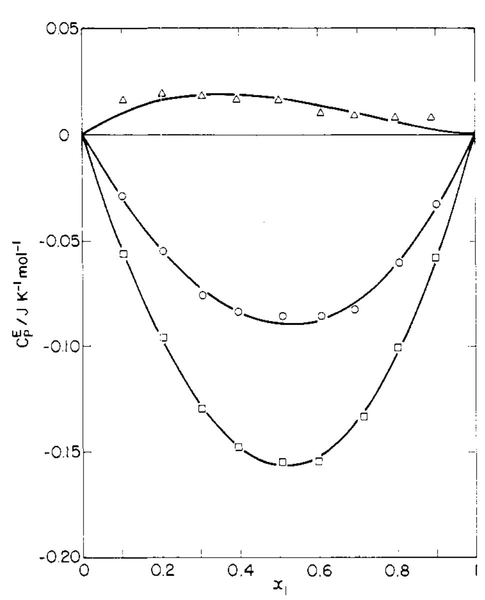

Figure 2. Molar excess heat capacities of binary mixtures of isomeric xylenes at 298.15 K. Points are experimental results: O, *o*-xylene (1)-*m*-xylene (2); □, *o*-xylene (1)-*p*-xylene (2); Δ, *m*-xylene (1)-*p*-xylene (2). Curves are least-squares representations of results by eq 2.

Table III. Smoothed Values of Molar Excess Heat Capacities, Enthalpies, and Volumes for Equimolar Mixtures of Aromatic Hydrocarbons at 298.15 K

mixture	$C_p{}^E(0.5)$, J K^{-1} mol^{-1}	$H^E(0.5)$, J mol^{-1}	$V^E(0.5)$, cm^3 mol^{-1}
benzene–toluene	-0.31^a	68.1^b	0.088^b
–ethylbenzene	-0.82^a	97.7^c	0.124^d
–*o*-xylene	-1.44^a	216.2^e	0.249^e
–*m*-xylene	-1.10^a	223.2^e	0.293^e
–*p*-xylene	-0.64^a	164.1^e	0.207^e
toluene–ethylbenzene	0.05^a	-9.2^c	-0.014^d
–*o*-xylene	-0.47^a	46.9^b	0.042^b
–*m*-xylene	-0.21^a	42.8^b	0.051^b
–*p*-xylene	-0.03^a	18.9^b	0.017^b
ethylbenzene–*o*-xylene	-0.17^f	39.5^c	0.036^d
–*m*-xylene	-0.02^f	35.2^c	0.057^d
–*p*-xylene	0.24^f	-9.9^c	-0.002^d
o-xylene–*m*-xylene	-0.09^f	11.3^g	-0.002^g
–*p*-xylene	-0.16^f	6.4^g	-0.008^g
m-xylene–*p*-xylene	0.02^f	-7.6^g	-0.011^g

[a] Reference 3. [b] Reference 7. [c] Reference 9. [d] Reference 10. [e] Reference 8. [f] Present work. [g] Reference 6.

(*3*). In the case of *m*-xylene–*p*-xylene, the values of $C_p{}^E$ are all positive but of the same magnitude as their estimated experimental uncertainty. This latter statement is also applicable to the small negative $C_p{}^E$ values found for ethylbenzene–*m*-xylene.

Holt and Smith (*5*) have reported excess enthalpies at 298.15 and 343.15 K for mixtures of ethylbenzene with *o*-xylene and with *m*-xylene. Values of $(\partial H^E/\partial T)_p$, calculated on the assumption that H^E varies linearly with temperature, are shown as broken curves in Figure 1. These agree fairly well with our observations bearing in mind the experimental uncertainty and the assumed temperature dependence of H^E.

Smoothed values of $C_p{}^E$, H^E, and V^E for equimolar mixtures of aromatic hydrocarbons, obtained from our present and previous (*3*, *6*–*10*) investigations, are summarized in Table III. In all cases, $C_p{}^E$ and H^E have opposite signs. The occurrence of negative values of H^E and positive values of $C_p{}^E$ sometimes indicates the formation of a mixed complex, but this seems unlikely in the present systems (toluene–ethylbenzene, ethylbenzene–*p*-xylene, and *m*-xylene–*p*-xylene). The correlations between $C_p{}^E$ and H^E and between $C_p{}^E$ and V^E are roughly linear (coefficients of correlation = −0.94 and −0.91, respectively). The values of $C_p{}^E$ for mixtures of the xylenes with benzene, with toluene, and with ethylbenzene decrease in the order benzene < toluene < ethylbenzene with ortho < meta < para in each set.

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Glossary

a_1, a_2, ..., a_j	coefficients in representation of molar excess heat capacity by eq 2
C_p	molar heat capacity, J K^{-1} mol^{-1}
$C_p{}^E$	molar excess heat capacity, J K^{-1} mol^{-1}
C_{pi}	molar heat capacity of component *i*, J K^{-1} mol^{-1}
H^E	molar excess enthalpy, J mol^{-1}
n	number of coefficients in eq 2
T	thermodynamic temperature, K
V	molar volume, cm^3 mol^{-1}
V^E	molar excess volume, cm^3 mol^{-1}
x_i	mole fraction of component *i*

Greek Letters

σ	standard deviation

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