The theory is only qualitatively correct in predicting the behavior of different electrolytes and it is suggested that for practical purposes an empirical constant ϕ characteristic of the electrolyte be used. Values of ϕ are given for various electrolytes and for seawater, which permit the rapid calculation of the effect of the electrolytes in salting-out or decreasing the aqueous solubility of organic solutes or increasing their Henry's law constants or organic–water partition coefficients. The data for the chlorobenzenes suggest that properties of halogenated hydrocarbons, which are of considerable environmental concern, may be calculated using existing data for hydrocarbons.

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Heat Capacities of Some Binary Aromatic Hydrocarbon Mixtures Containing Benzene or Toluene

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A Picker flow microcalorimeter was used to determine volumetric heat capacities at 298.15 K for mixtures of benzene with toluene and for the eight binary systems formed by mixing these components separately with ethylbenzene and the three isomeric xylenes. Excess heat capacities obtained from the results are compared with the temperature variation of excess enthalpies from the literature.

Previous studies in our laboratory have demonstrated the suitability of the Picker flow calorimeter for determining differences of the volumetric heat capacities of organic liquids and their mixtures (*4*, *6*). The present paper describes the results of applying this technique to obtain the excess heat capacities of binary systems formed by mixing benzene with toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene and by mixing toluene with ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene. Direct determinations of the excess heat capacities of these mixtures have not been reported previously, although there have been many investigations of their excess enthalpies (*1*, *2*, *8*–*12*, *14*–*16*, *18*).

Experimental Section

The component liquids were reagent grade solvents which were purified by GLC. Densities ρ and refractive indices n_D characterizing the samples used for the calorimetric studies are as follows: benzene 0.873 69 and 1.497 90, toluene 0.862 25 and 1.494 06, ethylbenzene 0.862 62 and 1.493 19, *o*-xylene 0.875 85 and 1.502 82, *m*-xylene 0.859 86 and 1.494 56, and *p*-xylene 0.856 74 and 1.493 11. In most cases these are averages of determinations for several different preparations during the course of the investigation. For individual samples, the variations of the results from these averages were less than ±0.000 05 g cm^{-3} and ±0.000 03 for the densities and refractive indices, respectively. The characteristics given above are very similar to those of the component liquids we have used in other recent studies (*5*, *7*, *17*) and are in reasonable agreement with the literature values (*13*).

Mixtures were prepared by mass as in our earlier work (*4*). The error of the mole fraction is estimated to be less than 5 × 10^{-5}. Differences of volumetric heat capacity $\Delta(C_p/V)$ were determined in a Picker flow calorimeter, following the operating techniques described previously (*4*, *6*). A temperature increment of 1.4 K centered on 298.15 K was used for all measurements. Each system was studied by a stepwise procedure with a mole fraction difference of about 0.1 between the test and reference liquids. Benzene and toluene were used as initial reference liquids for the two series of systems. A value of 135.760 J K^{-1} mol^{-1}, derived from our previous work (*6*), was adopted for the heat capacity of benzene at 298.15 K; the heat capacity of toluene was obtained from the present measurements on benzene–toluene mixtures. Corrections were applied for power losses, and in order to cancel mixing effects (*6*), all measurements were repeated with the test and reference liquids interchanged. The precision of the excess heat capacities is believed to be about ±0.02 J K^{-1} mol^{-1}.

Results and Discussion

The experimental measurements are summarized 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. As indicated above, each entry for $\Delta(C_p/V)$ is an average of measurements taken with the roles of the two mixtures reversed (i.e., as test and reference). Molar heat capacities were obtained from the volumetric heat capacities using molar volumes calculated from the densities of the component liquids and the excess volumes of the mixtures (*10*, *14*, *17*).

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Table I. Experimental Results for the Change of Volumetric Heat Capacity $\Delta(C_p/V)$, Heat Capacity C_p, and 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}
	Benzene (1)–Toluene (2)						
1	0	135.760^a	0				
0.892 97	−0.007 857	137.937	−0.102				
0.796 79	−0.006 684	139.888	−0.200				
0.703 08	−0.005 839	141.819	−0.265				
0.594 59	−0.005 988	144.092	−0.302				
0.500 62	−0.004 699	146.081	−0.315				
0.407 01	−0.004 172	148.090	−0.300				
0.293 74	−0.004 464	150.551	−0.251				
0.205 54	−0.003 185	152.477	−0.203				
0.112 69	−0.002 808	154.542	−0.116				
0	−0.003 085	157.057	0				
	Benzene (1)–Ethylbenzene (2)				Toluene (1)–Ethylbenzene (2)		
1	0	135.760^a	0	1	0	157.057^b	0
0.896 84	−0.006 287	140.535	−0.364	0.900 17	0.004 657	159.935	0.021
0.794 33	−0.004 367	145.390	−0.615	0.811 73	0.003 937	162.477	0.032
0.695 71	−0.002 704	150.161	−0.757	0.692 37	0.005 092	165.903	0.042
0.599 57	−0.001 562	154.887	−0.819	0.601 96	0.003 749	168.501	0.052
0.508 66	−0.000 699	159.416	−0.818	0.490 79	0.004 381	171.686	0.056
0.407 11	−0.000 037	164.538	−0.755	0.403 81	0.003 229	174 168	0.048
0.305 91	0.000 605	169.702	−0.632	0.303 09	0.003 658	177.045	0.042
0.206 81	0.001 081	174.807	−0.463	0.204 75	0.003 390	179.846	0.029
0.096 16	0.001 557	180.546	−0.236	0.093 19	0.003 754	183.026	0.016
0	0.001 659	185.572	0	0	0.002 997	185.677	0
	Benzene (1)–*o*-Xylene (2)				Toluene (1)–*o*-Xylene (2)		
1	0	135.760^a	0	1	0	157.057^b	0
0.893 08	−0.003 710	140.748	−0.560	0.889 14	0.007 868	160.284	−0.176
0.791 75	−0.001 661	145.588	−0.979	0.795 87	0.006 680	163.019	−0.304
0.695 19	0.000 173	150.328	−1.250	0.682 01	0.008 431	166.406	−0.411
0.600 44	0.001 598	155.094	−1.400	0.601 21	0.006 178	168.845	−0.452
0.497 94	0.003 117	160.377	−1.437	0.496 59	0.008 243	172.046	−0.462
0.406 90	0.003 945	165.186	−1.351	0.406 84	0.007 179	174.821	−0.442
0.308 87	0.004 917	170.440	−1.185	0.297 95	0.008 949	178.234	−0.371
0.208 32	0.005 589	175.897	−0.946	0.208 29	0.007 404	181.066	−0.292
0.100 64	0.007 437	181.924	−0.506	0.109 61	0.008 354	184.224	−0.162
0	0.007 564	187.653	0	0	0.009 234	187.750	0
	Benzene (1)–*m*-Xylene (2)				Toluene (1)–*m*-Xylene (2)		
1	0	135.760^a	0	1	0	157.057^b	0
0.886 62	−0.015 020	140.426	−0.525	0.896 28	−0.000 982	159.513	−0.081
0.785 14	−0.010 163	144.764	−0.835	0.809 16	−0.000 658	161.586	−0.139
0.704 52	−0.006 348	148.296	−0.994	0.704 85	−0.000 467	164.093	−0.183
0.606 41	−0.005 938	152.694	−1.089	0.600 70	−0.000 205	166.618	−0.206
0.499 21	−0.004 892	157.582	−1.109	0.496 40	0.000 016	169.165	−0.210
0.407 51	−0.002 811	161.854	−1.036	0.392 14	0.000 226	171.729	−0.197
0.300 73	−0.002 217	166.895	−0.885	0.303 79	0.000 319	173.912	−0.174
0.198 48	−0.001 039	171.805	−0.657	0.196 75	0.000 585	176.577	−0.127
0.104 49	−0.000 228	176.378	−0.388	0.094 91	0.000 704	179.127	−0.069
0	0.000 643	181.550	0	0	0.000 797	181.517	0
	Benzene (1)–*p*-Xylene (2)				Toluene (1)–*p*-Xylene (2)		
1	0	135.760^a	0	1	0	157.057^b	0
0.877 21	−0.013 338	141.097	−0.333	0.882 87	−0.000 648	159.936	−0.020
0.789 69	−0.007 721	144.970	−0.502	0.791 31	−0.000 395	162.194	−0.029
0.687 84	−0.007 224	149.563	−0.612	0.685 54	−0.000 370	164.808	−0.034
0.587 91	−0.005 586	154.146	−0.644	0.584 15	−0.000 162	167.331	−0.020
0.497 51	−0.004 104	158.337	−0.626	0.500 36	−0.000 187	169.409	−0.017
0.404 60	−0.003 507	162.677	−0.577	0.414 52	−0.000 314	171.521	−0.029
0.295 75	−0.003 224	167.811	−0.470	0.298 27	−0.000 131	174.414	−0.015
0.209 07	−0.001 998	171.931	−0.352	0.200 04	−0.000 162	176.849	−0.011
0.100 78	−0.001 899	177.115	−0.169	0.115 87	−0.000 045	178.946	0.002
0	−0.001 531	181.937	0	0	−0.000 182	181.812	0

[a] C_p from ref 1. [b] C_p from benzene (1)–toluene (2) results.

The two values of the heat capacity of ethylbenzene and of the xylenes, obtained from the measurements on mixtures with benzene and with toluene, agree within less than 0.1% in all cases and attest to the self-consistent character of the flow calorimetric technique. Further evidence of this is to be found in the agreement between the present results and values obtained in our previous studies in which some of the same components were measured against *n*-heptane (*4*) and tetrachloromethane (*5*). Summaries of heat capacity data derived from other calorimetric techniques can also be found in those references.

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

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

where C_p and C_{pi} are the molar heat capacities of the mixture

Table II. Coefficients and Standard Deviations for Representations of C_p^E for Some Binary Aromatic Hydrocarbon Mixtures at 298.15 K by Equation 2

component 1	component 2	a_1 (J K^{-1} mol^{-1})	a_2 (J K^{-1} mol^{-1})	a_3 (J K^{-1} mol^{-1})	σ (J K^{-1} mol^{-1})
benzene	toluene	−1.239			0.007
	ethylbenzene	−3.260	0.777	−0.102	0.002
	o-xylene	−5.743	0.292		0.016
	m-xylene	−4.414	0.700	−0.426	0.004
	p-xylene	−2.542	0.765		0.006
toluene	ethylbenzene	0.206			0.003
	o-xylene	−1.862	0.108	0.177	0.004
	m-xylene	−0.846	0.068		0.002
	p-xylene	−0.102	0.095		0.006

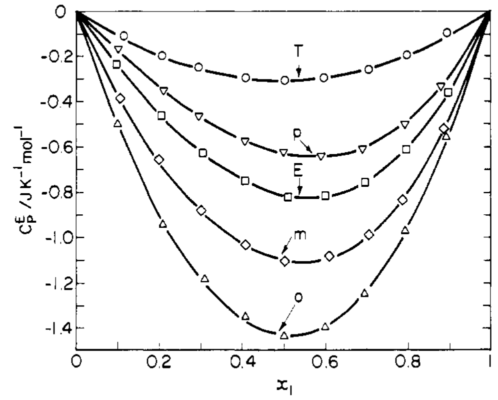

Figure 1. Molar excess heat capacities of benzene (1)-aromatic hydrocarbon (2) at 298.15 K. Labels indicate component 2: T, toluene; E, ethylbenzene; o, *o*-xylene; m, *m*-xylene; p, *p*-xylene. Points are experimental results. Solid curves are least-squares representations of these results by eq 2.

and of pure component *i*, respectively. In each case, the value of C_{p2} measured for the system under investigation was used in order to obtain consistent values of C_p^E. The equation

$$C_p^E = x_1x_2\sum_{j=1}^{n} a_j(1 - 2x_1)^{j-1} \qquad (2)$$

was fitted to each set of results by the method of least squares with all points weighted equally. Values of the coefficients a_j obtained from the analysis are listed in Table II, along with the standard deviation

$$\sigma = [\sum_{1}^{m}\{C_p^E(\text{obsd}) - C_p^E(\text{eq 2})\}^2/(m - n)]^{1/2} \qquad (3)$$

for the representation.

The experimental excess heat capacities for the series of benzene and of toluene mixtures are plotted in Figures 1 and 2, respectively. The smoothed representations by eq 2 are shown as solid curves in the figures. For the most part, these curves are typical of the behavior of binary mixtures of nonpolar or weakly polar liquids. Thus, with the exception of toluene-ethylbenzene, the excess heat capacities for all of the present systems are negative at 298.15 K. In the case of toluene-*p*-xylene, C_p^E is of the same magnitude as the experimental precision, but its values are predominantly negative. The curves for mixtures of the xylenes with benzene become increasingly negative in the order para, meta, and ortho. The same order is observed for the toluene mixtures, but the magnitudes of C_p^E are much smaller. Previous studies (*10*, *14*) show that the excess enthalpies and volumes for the toluene mixtures are also much smaller than those for the corresponding benzene mixtures but the order of the curves is different.

Although there have been many investigations of the excess enthalpies of the present systems (*1*, *2*, *8–12*, *14–16*, *18*), it is difficult to obtain reliable estimates of C_p^E from these. Studies of the temperature variation of the excess enthalpies of equimolar mixtures by Cheesman and Ladner (*2*) lead to values of −0.43, −0.81, and 0.15 J K^{-1} mol^{-1} for benzene-toluene, benzene-*p*-xylene, and toluene-*p*-xylene, respectively. These agree approximately with our results. The single value of −0.8 J K^{-1} mol^{-1} estimated for an equimolar mixture of toluene with ethylbenzene by Wóycicki (*18*) differs in sign and magnitude from our result. Equations representing the excess enthalpies of binary mixtures of benzene with toluene and the three xylenes as functions of temperature and mole fraction have been reported by Rastogi et al. (*11*, *12*). Values of $(\partial H^E/\partial T)_p$ calculated from these roughly support our results in the central range of mole fractions. However, the overall shapes of the curves are very different from ours since they have two or three extrema.

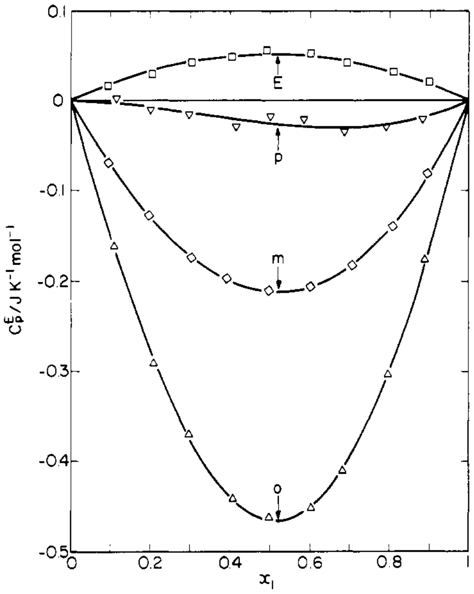

Figure 2. Molar excess heat capacities of toluene (1)-aromatic hydrocarbon (2) at 298.15 K. Labels indicate component 2: E, ethylbenzene; o, *o*-xylene; m, *m*-xylene; p, *p*-xylene. Points are experimental results. Solid curves are least-squares representations of these results by eq 2.

Theoretical treatments of mixtures have not yet developed to the point where a quantitative interpretation of the present results is possible. Previously we have used the Flory theory (*3*) to correlate the excess enthalpies and volumes of the present binary mixtures of aromatic hydrocarbons (*10*, *14*, *16*). Assuming that the interaction parameter X_{12} for the mixture and the characteristic values of the pressure, volume, and temperature for the pure components (p_i^*, V_i^*, and T_i^* in Flory's formulation) are all independent of temperature, the Flory theory leads to values of C_p^E which are negative for most of the mixtures but are considerably smaller than the experimental results. Indeed in some cases the calculated values are so small and the parameters are of such doubtful accuracy that even the sign of the estimated C_p^E is unreliable.

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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}
m	number of experimental points in a set of results

n	number of coefficients in eq 2
n_D	refractive index for sodium light
T	thermodynamic temperature, K
V	molar volume, cm^3 mol^{-1}
x_i	mole fraction of component i

Greek Letters

ρ	density, g cm^{-3}
σ	standard deviation defined in eq 3

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Excess Enthalpies and Volumes for Binary Mixtures of Some Chlorobenzenes at 298.15 K

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Determinations of excess enthalpies in a flow microcalorimeter and of excess volumes in a successive dilution dilatometer were carried out at 298.15 K for binary mixtures formed from the components chlorobenzene, *o*-dichlorobenzene, and *m*-dichlorobenzene.

Previous publications from our laboratory have described measurements of excess enthalpies and volumes for binary mixtures of chlorobenzene (*3*), *o*-dichlorobenzene (*5*), and *m*-dichlorobenzene (*6*) with a number of aromatic hydrocarbons. The present paper reports the results of similar measurements for the three binary mixtures formed from the chlorobenzenes alone (i.e., chlorobenzene–*o*-dichlorobenzene, chlorobenzene–*m*-dichlorobenzene, and *o*-dichlorobenzene–*m*-dichlorobenzene). We are not aware of any previous investigations of the excess enthalpies and volumes of these systems.

Experimental Section

Measurements of excess enthalpy H^E were carried out in an LKB flow microcalorimeter. This equipment and its operating procedure have been described previously (*7*). The error in the determination of H^E is estimated to be less than $(0.1 + 0.005 |H^E|)$ J mol^{-1}.

Excess volumes V^E were measured at constant pressure in a micrometer syringe dilatometer, using a successive dilution technique (*8*). For the present systems, the error in the determination of V^E is estimated to be less than $(0.0003 + 0.003|V^E|)$ cm^3 mol^{-1}.

The samples of the chlorobenzenes were the same as used in our earlier investigations (*3*, *5*, *6*). Densities and refractive indices characterizing them are given in those references.

Results and Discussion

The experimental results for H^E and V^E are listed in Tables I and II, respectively. Graphical presentations are provided in Figures 1 and 2. For each system, the values of V^E were obtained from two or three separate dilution runs, as indicated by the different symbols in Figure 2.

The smoothing function

$$X^E = x_1 x_2 \sum_{j=1}^{n} c_j (x_2 - x_1)^{j-1} \qquad (1)$$

where X^E is either H^E or V^E, was fitted to each set of results by the method of least squares with all points weighted equally. Choice of the appropriate number n of coefficients c_j was based on the variation of the standard deviation

$$\sigma = [\sum_{1}^{m} \{X^E(\text{obsd}) - X^E(\text{eq 1})\}^2/(m - n)]^{1/2} \qquad (2)$$

where the sum is taken over the m results in a set. The values of c_j and of σ obtained from this analysis are given in Table III. The solid curves in Figures 1 and 2 were calculated from eq 1 using these values of the coefficients.

The excess enthalpies for all three of the systems are positive. The excess volumes for the two systems containing chlorobenzene are also positive; however, V^E is negative for *o*-dichlorobenzene–*m*-dichlorobenzene. It is difficult to rationalize this behavior in terms of the differences of the molar volumes of the components and of their dipole moments.

We investigated the use of the Flory theory (*1*) to correlate the excess enthalpies and volumes obtained in our present and previous studies (*3*, *5*, *6*). The interaction parameter X_{12} was determined for each mixture by fitting the Flory formula for H^E to the smoothed representation of the experimental results by eq 1. The results for X_{12} are summarized in Table IV along

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