

Excess Enthalpies and Volumes for Mixtures of *m*-Dichlorobenzene with Some Aromatic Hydrocarbons 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 of *m*-dichlorobenzene with benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene.

This paper describes measurements of excess enthalpies and excess volumes at 298.15 K for binary mixtures of *m*-dichlorobenzene with benzene, toluene, ethylbenzene, and the three isomeric xylenes. The measurements were undertaken as part of an investigation of the interactions between halobenzenes and aromatic hydrocarbons. Previous publications from our laboratory have reported the results of similar measurements for mixtures of chlorobenzene (2) and of *o*-dichlorobenzene (3) with the same set of aromatic components.

Experimental Section

Excess enthalpies, H^E , and volumes, V^E , were determined in the same flow microcalorimeter (4) and successive dilution dilatometer (5) as used in our earlier work (2, 3). Details of the equipment and operating procedures can be found in these publications. The magnitudes of the errors in determinations of H^E and V^E for the present systems are estimated to be less than $(0.1 + 0.005|H^E|)$ J mol⁻¹ and $(0.0003 + 0.003|V^E|)$ cm³ mol⁻¹, respectively.

The samples of the aromatic hydrocarbons were the same as used in our previous studies (2, 3). The *m*-dichlorobenzene was purified chromatographically. At 298.15 K its density, 1.282 76 g cm⁻³, and refractive index (n_D), 1.543 80, were in reasonable agreement with values from the literature (7) (1.282 80 g cm⁻³ and 1.543 37).

Results and Discussion

The experimental results from measurements of H^E and V^E at 298.15 K are listed in Tables I and II. In all cases, x_1 is the mole fraction of *m*-dichlorobenzene. Graphical presentations of the results are given in Figures 1–4. The open and solid symbols used in Figures 3 and 4 indicate the values of V^E obtained in two separate dilution runs for each system.

Each set of results was fitted with the smoothing function

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

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

$$\sigma = \left[\sum_1^m \{X^E(\text{obsd}) - X^E(\text{eq 1})\}^2 / (m - n) \right]^{1/2} \quad (2)$$

where the sum extends over the m results in a set. Table III summarizes the values of c_j and σ obtained from this analysis.

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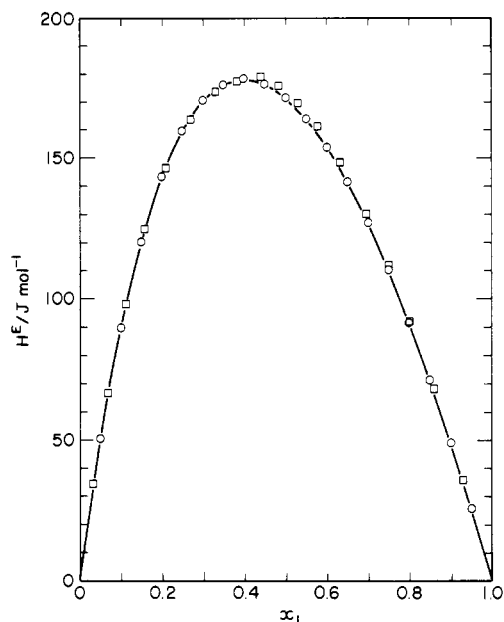


Figure 1. Molar excess enthalpy of *m*-dichlorobenzene (1)–benzene (2) at 298.15 K: O, present work; □, Tanaka et al. (6). Solid curve is least-squares representation of our results by eq 1.

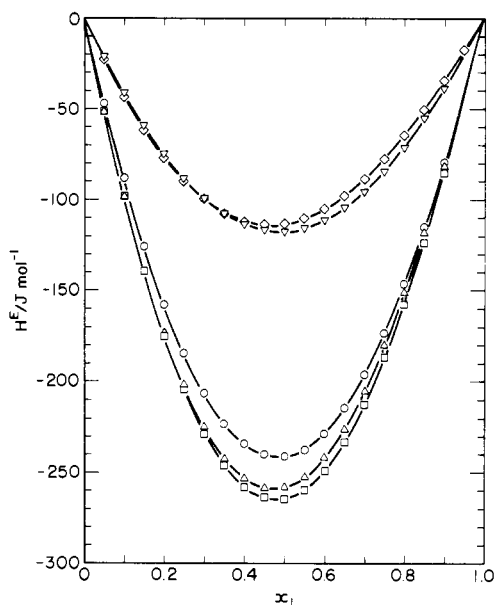


Figure 2. Molar excess enthalpies of *m*-dichlorobenzene (1)–aromatic hydrocarbon (2) at 298.15 K. Component 2: ∇, toluene; ◇, ethylbenzene; O, *o*-xylene; Δ, *m*-xylene; □, *p*-xylene. Solid curves are least-squares representations of our results by eq 1.

The smoothed representations of the results by eq 1 are shown as solid curves in Figures 1–4.

Values of H^E for *m*-dichlorobenzene–benzene at 298.15 K have also been determined by Tanaka et al. (6) using an iso-

Table I. Experimental Values of the Molar Excess Enthalpies of *m*-Dichlorobenzene (1)-Aromatic Hydrocarbon (2) Mixtures at 298.15 K

x_1	$H^E, \text{J mol}^{-1}$ Component 2					
	C_6H_6	$\text{C}_6\text{H}_5\text{CH}_3$	$\text{C}_6\text{H}_5\text{C}_2\text{H}_5$	$\alpha\text{-C}_6\text{H}_4(\text{CH}_3)_2$	$m\text{-C}_6\text{H}_4(\text{CH}_3)_2$	$p\text{-C}_6\text{H}_4(\text{CH}_3)_2$
0.0500	50.30	-21.89	-23.42	-47.56	-52.24	-52.30
0.1000	89.72	-41.67	-44.07	-88.85	-98.84	-99.12
0.1500	120.12	-59.78	-62.37	-126.48	-140.32	-139.98
0.2000	143.26	-75.43	-77.77	-158.46	-173.65	-175.46
0.2500	159.53	-89.08	-90.45	-185.34	-202.51	-204.91
0.3000	170.35	-99.88	-100.58	-207.14	-225.21	-229.27
0.3500	176.09	-108.53	-107.79	-223.54	-243.02	-246.57
0.4000	178.25	-114.20	-112.33	-234.62	-253.71	-258.64
0.4500	176.31	-117.19	-114.28	-240.35	-259.31	-264.18
0.5000	171.15	-118.26	-113.67	-241.39	-258.72	-265.23
0.5000	171.44	-118.08	-113.91	-241.58	-258.35	-264.85
0.5500	163.72	-116.35	-110.71	-237.63	-252.93	-260.14
0.6000	153.64	-111.65	-105.72	-228.95	-241.94	-249.51
0.6500	141.46	-104.89	-98.52	-214.79	-226.60	-233.67
0.7000	126.96	-95.99	-89.23	-196.60	-206.03	-212.93
0.7500	110.31	-84.97	-78.17	-173.96	-180.92	-187.44
0.8000	91.56	-71.70	-65.15	-146.76	-151.78	-158.22
0.8500	71.20	-55.73	-50.91	-115.47	-119.18	-124.24
0.9000	49.11	-38.95	-34.71	-80.57	-82.68	-85.88
0.9500	25.52		-17.75			

Table II. Experimental Values of the Molar Excess Volumes of *m*-Dichlorobenzene (1)-Aromatic Hydrocarbon (2) Mixtures at 298.15 K

x_1	$V^E, \text{cm}^3 \text{mol}^{-1}$	x_1	$V^E, \text{cm}^3 \text{mol}^{-1}$	x_1	$V^E, \text{cm}^3 \text{mol}^{-1}$	x_1	$V^E, \text{cm}^3 \text{mol}^{-1}$
<i>m</i> -Dichlorobenzene (1)-Benzene (2)							
0.0423	0.0481	0.2776	0.1802	0.5064	0.1843	0.8148	0.0922
0.0882	0.0902	0.3304	0.1883	0.5552	0.1757	0.8673	0.0682
0.1264	0.1179	0.3748	0.1912	0.6162	0.1612	0.9345	0.0348
0.1713	0.1435	0.4149	0.1910	0.6912	0.1390		
0.2185	0.1635	0.4502	0.1889	0.7504	0.1183		
<i>m</i> -Dichlorobenzene (1)-Toluene (2)							
0.0527	-0.0231	0.4150	-0.1134	0.5219	-0.1150	0.8322	-0.0586
0.1057	-0.0455	0.4394	-0.1149	0.5475	-0.1130	0.8825	-0.0429
0.1649	-0.0647	0.4560	-0.1154	0.5950	-0.1088	0.9450	-0.0211
0.2467	-0.0880	0.4695	-0.1153	0.6535	-0.1009		
0.3114	-0.1011	0.4919	-0.1156	0.7188	-0.0882		
0.3672	-0.1090	0.5053	-0.1152	0.7764	-0.0743		
<i>m</i> -Dichlorobenzene (1)-Ethylbenzene (2)							
0.0622	-0.0280	0.3498	-0.1041	0.5790	-0.1059	0.8547	-0.0480
0.1184	-0.0494	0.4077	-0.1089	0.6251	-0.0999	0.8980	-0.0336
0.1741	-0.0678	0.4563	-0.1108	0.6784	-0.0909	0.9422	-0.0196
0.2236	-0.0812	0.4978	-0.1103	0.7402	-0.0776		
0.2824	-0.0938	0.5329	-0.1089	0.8070	-0.0613		
<i>m</i> -Dichlorobenzene (1)- <i>o</i> -Xylene (2)							
0.0552	-0.0327	0.3345	-0.1367	0.5422	-0.1456	0.8039	-0.0854
0.1145	-0.0639	0.3931	-0.1453	0.5838	-0.1407	0.8568	-0.0648
0.1774	-0.0918	0.4426	-0.1488	0.6332	-0.1325	0.8975	-0.0479
0.2179	-0.1064	0.4720	-0.1488	0.6924	-0.1193	0.9534	-0.0224
0.2743	-0.1234	0.5047	-0.1480	0.7537	-0.1022		
<i>m</i> -Dichlorobenzene (1)- <i>m</i> -Xylene (2)							
0.0544	-0.0479	0.3372	-0.1996	0.5463	-0.2093	0.7676	-0.1404
0.1086	-0.0897	0.3954	-0.2096	0.5561	-0.2088	0.8132	-0.1170
0.1575	-0.1223	0.4444	-0.2135	0.5985	-0.2006	0.8592	-0.0918
0.2152	-0.1544	0.4869	-0.2139	0.6479	-0.1875	0.9043	-0.0639
0.2703	-0.1783	0.5231	-0.2115	0.7066	-0.1671	0.9507	-0.0341
<i>m</i> -Dichlorobenzene (1)- <i>p</i> -Xylene (2)							
0.0499	-0.0447	0.3200	-0.2032	0.5155	-0.2272	0.7450	-0.1637
0.1020	-0.0870	0.3817	-0.2188	0.5459	-0.2247	0.8042	-0.1330
0.1527	-0.1232	0.4336	-0.2262	0.5866	-0.2177	0.8479	-0.1081
0.2044	-0.1535	0.4779	-0.2285	0.6336	-0.2060	0.8979	-0.0753
0.2555	-0.1791	0.5110	-0.2283	0.6803	-0.1907	0.9521	-0.0370

Table III. Coefficients and Standard Deviations for Representations of Excess Functions of *m*-Dichlorobenzene (1)–Aromatic Hydrocarbon (2) Mixtures at 298.15 K by Equation 1

Component 2	Function ^a	c_1	c_2	c_3	c_4	σ
Benzene	H^E	685.716	251.056	134.351	47.946	0.15
	V^E	0.73719	0.26933	0.16444	0.09067	0.00037
Toluene	H^E	-472.399	-24.702	36.959	8.291	0.19
	V^E	-0.46112	-0.04038	0.03229		0.00031
Ethylbenzene	H^E	-455.302	-66.092	24.249		0.16
	V^E	-0.44188	-0.05744	0.02859	-0.01337	0.00029
<i>o</i> -Xylene	H^E	-966.469	-61.238	35.250		0.22
	V^E	-0.59323	-0.07553	0.02765	0.01088	0.00022
<i>m</i> -Xylene	H^E	-1034.53	-115.966	42.551		0.39
	V^E	-0.85593	-0.11448	0.02848		0.00053
<i>p</i> -Xylene	H^E	-1060.14	-92.160	50.037		0.29
	V^E	-0.91238	-0.08020	0.04306		0.00035

^a Units: H^E , J mol⁻¹; V^E , cm³ mol⁻¹.

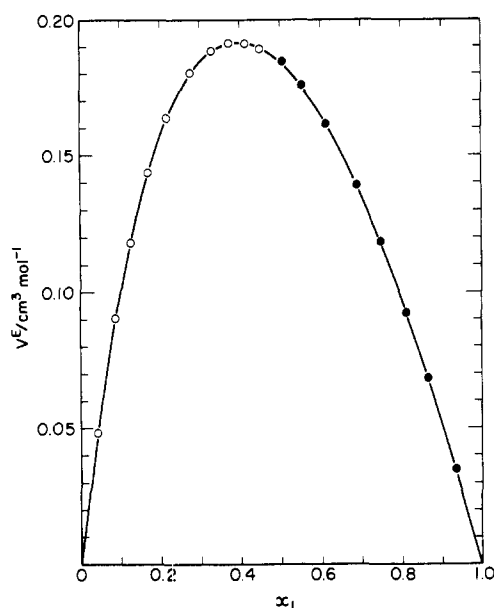


Figure 3. Molar excess volume of *m*-dichlorobenzene (1)–benzene (2) at 298.15 K: O and ●, present work (two separate dilutions). Solid curve is least-squares representation of our results by eq. 1.

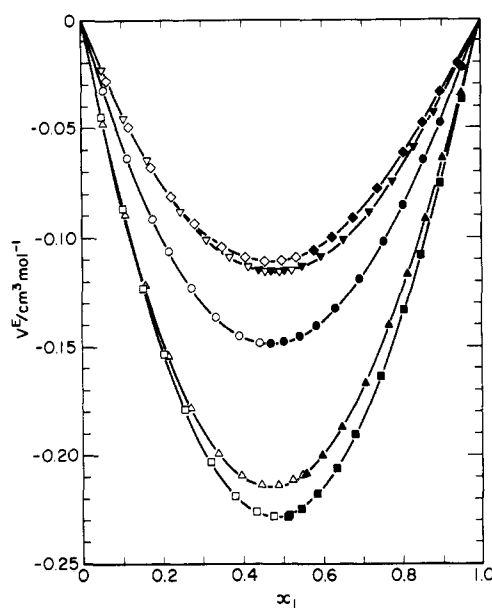


Figure 4. Molar excess volumes of *m*-dichlorobenzene (1)–aromatic hydrocarbon (2) at 298.15 K. Component 2: ▽ and ▼, toluene; ◇ and ♦, ethylbenzene; ○ and ●, *o*-xylene; △ and ▲, *m*-xylene; □ and ■, *p*-xylene. Open and solid symbols are results of separate dilutions. Solid curves are least-squares representations of our results by eq. 1.

thermal displacement calorimeter. These are plotted in Figure 1 for comparison. For $x_1 > 0.4$ they fall systematically above the present results; at $x_1 = 0.5$ the difference is about 2 J mol⁻¹. These differences are probably attributable to an error in one of the dilution runs in ref 6.

It is interesting to compare the present results for *m*-dichlorobenzene mixtures with our previous results for chlorobenzene (2) and *o*-dichlorobenzene (3) mixtures. Both H^E and V^E for mixtures with benzene are positive or only slightly negative (in the case of H^E for chlorobenzene–benzene). However, they are negative for mixtures with all of the alkylbenzenes. For the present *m*-dichlorobenzene mixtures, there are again very noticeable decreases of H^E and V^E when benzene is replaced by the various alkylbenzenes. In general, these decreases are in the order *m*-dichlorobenzene > *o*-dichlorobenzene > chlorobenzene.

In conclusion, it should be noted that the pair of components with the smallest net dipole moment, *m*-dichlorobenzene–*p*-xylene, leads to the largest negative values of H^E and V^E . Thus it appears that dipole–dipole interaction is not a dominant factor in stabilizing mixtures of this type.

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Glossary

c_1, c_2, \dots, c_j	coefficients in representations of excess properties by eq 1
H^E	molar excess enthalpy, J mol ⁻¹
m	number of experimental points in a set of results
n	number of coefficients in eq 1
n_D	refractive index for sodium light
V^E	molar excess volume, cm ³ mol ⁻¹
X^E	typical molar excess property
x_i	mole fraction of component i

Greek letters σ standard deviation defined in eq 2**Subscripts**

- 1 *m*-dichlorobenzene
2 aromatic hydrocarbon

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Vapor-Liquid Equilibria in the System Hydrogen Sulfide-Methanethiol

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The compositions of the coexisting phases in the H₂S-CH₃SH system have been measured at a pressure of 2413 kPa (350 psia).

The purpose of the present work is to provide data useful for the design of a process for the purification of hydrogen sulfide containing small amounts of methanethiol. No data for this system are extant in the literature.

Experimental Section

Matheson C.P. grade hydrogen sulfide and methanethiol were used without further purification. The equilibrium cell consisted of a Jerguson liquid level gauge (Model 19-T-20) with a 250-cm³ tubular reservoir mounted at the top and is shown in Figure 1. A magnetic pump (5) was used to circulate the gas phase from the reservoir to the bottom of the Jerguson gauge. The cell and pump were housed in an air bath controlled within ± 0.1 °C. The pressure of the experiments was kept at 2413 kPa by adjustment of the bath temperature. The temperature was measured by a calibrated mercury thermometer and the pressure in the cell was measured by a calibrated Heise bourdon tube gauge. The vapor sample was taken from the recirculation line and passed directly to the chromatograph for analysis. This equipment was used previously for measurements of the solubility of H₂S in DEA solutions (3).

A sample of the liquid was taken from the bottom of the cell and expanded into a 750-cm³ stainless steel vessel maintained at 100 °C so that the liquid sample was completely vaporized. The pressure in the vessel after sampling did not exceed 800 kPa. A sample from this vessel was then passed to the chromatograph for analysis. The chromatograph used a 6 ft long \times 1/8 in. o.d. Porapak column operated isothermally at 130 °C. A thermal conductivity detector was used and response factors for the calculation of the composition were obtained from Dietz (2).

Results and Discussion

The experimental data are presented in Table I. Most of the data were obtained at a pressure of 2413 kPa at concentrations of hydrogen sulfide in the liquid phase greater than 80 mol %. Figure 2 shows the data for 2413 kPa on a temperature-composition diagram and smoothed data for this pressure are given in Table II.

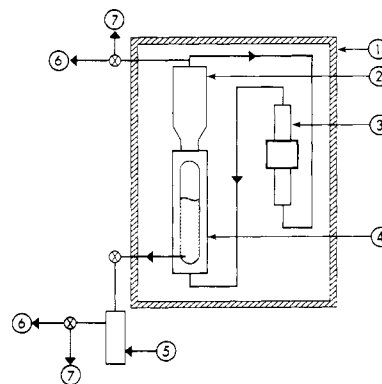


Figure 1. Schematic diagram of experimental apparatus: 1, insulated air bath; 2, vapor reservoir; 3, magnetic pump; 4, high-pressure liquid level gauge; 5, liquid sample vessel; 6, to gas chromatograph; 7, vent line.

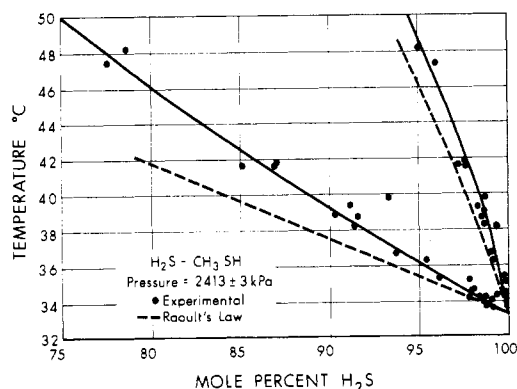


Figure 2. Vapor-liquid equilibria for H₂S-CH₃SH at 2413 kPa.

Also shown on Figure 2 are dashed lines obtained by the use of Raoult's law for the calculation of the equilibria. Values of the vapor pressures for the pure compounds were obtained from the Matheson data book (1), and at the pressure of 2413 kPa, the corresponding temperatures for pure H₂S and pure CH₃SH are 33.3 and 126.1 °C, respectively. The results indicate a small negative deviation from Raoult's law for CH₃SH concentrations less than about 15 mol %. A *y-x* diagram for this system was