

Excess Enthalpies and Volumes for Mixtures of *o*-Dichlorobenzene with Some Aromatic Hydrocarbons at 298.15 K

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Measurements 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 *o*-dichlorobenzene with benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene.

A recent paper (3) from our laboratory reported excess enthalpies and volumes for binary mixtures of chlorobenzene with benzene, toluene, ethylbenzene, and the three isomeric xylenes. As an extension of that work we have made similar measurements for mixtures of *o*-dichlorobenzene with the same set of aromatic components. The purpose of these investigations is to provide information about the thermodynamic properties of halobenzene–aromatic hydrocarbon mixtures with a view to understanding the interactions between unlike molecules in such mixtures.

Experimental Section

Measurements of excess enthalpy were made in an LKB flow microcalorimeter (Model 10700-1) using the auxiliary equipment and operating procedure described previously (4). The magnitude of the total error in the determination of H^E is estimated to be less than $(0.1 + 0.005|H^E|)$ J mol⁻¹.

Excess volumes were measured at constant pressure by a successive dilution technique in a micrometer syringe dilatometer (5). Two dilution runs starting from opposite ends of the mole fraction range were carried out for each system. The overlap of the results in the central part of the range provided a good check on the consistency of the technique. The error in the determination of V^E is estimated to be less than $(0.0003 + 0.003|V^E|)$ cm³ mol⁻¹ for the present systems.

The samples of the aromatic hydrocarbons were the same as used in our previous work (3). The *o*-dichlorobenzene was

purified chromatographically. At 298.15 K its density, 1.300 14 g cm⁻³, and refractive index, (n_D) 1.549 13, agreed reasonably with values from the literature (2) (1.300 33 g cm⁻³ and 1.549 11, respectively).

Results and Discussion

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

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 , 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 error of estimate

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

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

There have been very few previous studies of the present systems. Values of H^E for *o*-dichlorobenzene–benzene at 298.15 K, taken from the work of Tanaka et al. (6), are plotted in Figure 1 for comparison. These results agree with ours within 0.5% over most of the mole fraction range. Smoothing functions for excess volumes measured at 303.15 and 308.15 K have been reported by Dhillon (7) for all of the present systems except for that containing ethylbenzene. The dotted curves in Figures 3 and

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

x_1	Component 2 (H^E , J mol ⁻¹)					
	C ₆ H ₆	C ₆ H ₅ CH ₃	C ₆ H ₅ C ₂ H ₅	<i>o</i> -C ₆ H ₄ (CH ₃) ₂	<i>m</i> -C ₆ H ₄ (CH ₃) ₂	<i>p</i> -C ₆ H ₄ (CH ₃) ₂
0.0500	41.12	-4.43	-12.13	-18.76	-18.07	-17.12
0.1000	74.20	-9.42	-23.70	-36.12	-34.72	-33.17
0.1500	100.86	-14.46	-34.46	-51.77	-49.85	-48.32
0.2000	121.77	-19.04	-43.88	-65.94		-61.68
0.2500	137.92	-23.30	-51.91	-77.01	-74.48	-73.39
0.3000	150.33	-26.45	-57.64	-86.48	-83.02	-82.54
0.3500	158.63	-28.81	-61.80	-93.09	-89.14	-89.24
0.4000	163.47	-30.25	-64.43	-97.85	-93.03	-93.72
0.4500	164.74	-30.86	-65.22	-99.87	-94.61	-95.89
0.5000	163.05	-30.57	-64.43	-100.09	-93.86	-95.66
0.5000	163.53	-30.61	-64.59	-100.19	-93.97	-95.66
0.5500	158.80	-29.59	-62.42	-97.97	-91.09	-93.34
0.6000	151.30	-27.75	-58.61	-93.77	-86.16	-89.00
0.6500	141.51	-25.31	-53.65	-87.39	-79.49	-82.45
0.7000	128.46	-22.33	-47.58	-79.29	-71.01	-74.34
0.7500	113.13	-18.96	-40.47	-69.32	-61.20	-64.57
0.8000	95.07	-15.24	-32.76	-57.31	-50.15	-53.64
0.8500	75.02	-11.85	-24.73	-44.70	-38.36	-41.10
0.9000	52.50	-7.76	-16.68	-31.20	-26.15	-27.92
0.9500	27.57	-3.61	-8.06	-15.87	-13.09	-14.02

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Table II. Experimental Values of the Molar Excess Volumes of *o*-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>o</i> -Dichlorobenzene (1)–Benzene (2)							
0.0395	0.0181	0.2838	0.0860	0.4456	0.1002	0.6951	0.0840
0.0876	0.0374	0.3343	0.0925	0.4811	0.1005	0.7648	0.0711
0.1232	0.0494	0.3779	0.0963	0.5220	0.1000	0.8221	0.0576
0.1658	0.0618	0.4157	0.0987	0.5704	0.0979	0.8694	0.0450
0.2268	0.0760	0.4163	0.0990	0.6268	0.0930	0.9340	0.0241
<i>o</i> -Dichlorobenzene (1)–Toluene (2)							
0.0521	-0.0254	0.3805	-0.1050	0.5120	-0.1042	0.7825	-0.0594
0.1052	-0.0479	0.4260	-0.1063	0.5311	-0.1025	0.8360	-0.0458
0.1494	-0.0629	0.4476	-0.1073	0.5506	-0.1005	0.8813	-0.0340
0.1992	-0.0776	0.4672	-0.1058	0.5990	-0.0948	0.9467	-0.0156
0.2598	-0.0905	0.4774	-0.1062	0.6540	-0.0860		
0.3270	-0.1006	0.5011	-0.1046	0.7224	-0.0728		
<i>o</i> -Dichlorobenzene (1)–Ethylbenzene (2)							
0.0452	-0.0277	0.4082	-0.1352	0.5470	0.1296	0.8563	-0.0524
0.1196	-0.0658	0.4569	-0.1360	0.5882	-0.1236	0.9022	-0.0358
0.1660	-0.0851	0.4826	-0.1353	0.6364	-0.1148	0.9571	-0.0156
0.2219	-0.1046	0.4979	-0.1344	0.6929	-0.1020		
0.2798	-0.1196	0.5112	-0.1331	0.7602	-0.0836		
0.3498	-0.1305	0.5327	-0.1316	0.8082	-0.0684		
<i>o</i> -Dichlorobenzene (1)– <i>o</i> -Xylene (2)							
0.0452	-0.0170	0.3295	-0.0816	0.5466	-0.0842	0.8101	-0.0441
0.0990	-0.0350	0.3885	-0.0858	0.5864	-0.0805	0.8562	-0.0338
0.1478	-0.0497	0.4365	-0.0868	0.6330	-0.0747	0.8981	-0.0246
0.1989	-0.0612	0.4775	-0.0863	0.6906	-0.0661	0.9482	-0.0129
0.2628	-0.0729	0.5132	-0.0851	0.7500	-0.0558		
<i>o</i> -Dichlorobenzene (1)– <i>m</i> -Xylene (2)							
0.0566	-0.0353	0.3394	-0.1341	0.5967	-0.1286	0.8616	-0.0534
0.1145	-0.0656	0.3966	-0.1397	0.6430	-0.1193	0.9059	-0.0372
0.1597	-0.0856	0.4472	-0.1410	0.6968	-0.1062	0.9627	-0.0145
0.2133	-0.1052	0.4883	-0.1399	0.7607	-0.0875		
0.2720	-0.1210	0.5247	-0.1374	0.8128	-0.0704		
<i>o</i> -Dichlorobenzene (1)– <i>p</i> -Xylene (2)							
0.0506	-0.0343	0.3455	-0.1517	0.5318	-0.1574	0.7478	-0.1084
0.1182	-0.0739	0.4035	-0.1585	0.5438	-0.1557	0.8060	-0.0870
0.1654	-0.0966	0.4534	-0.1607	0.5843	-0.1499	0.8545	-0.0677
0.2222	-0.1200	0.4957	-0.1601	0.6300	-0.1411	0.8948	-0.0500
0.2727	-0.1357	0.5098	-0.1592	0.6836	-0.1280	0.9555	-0.0218

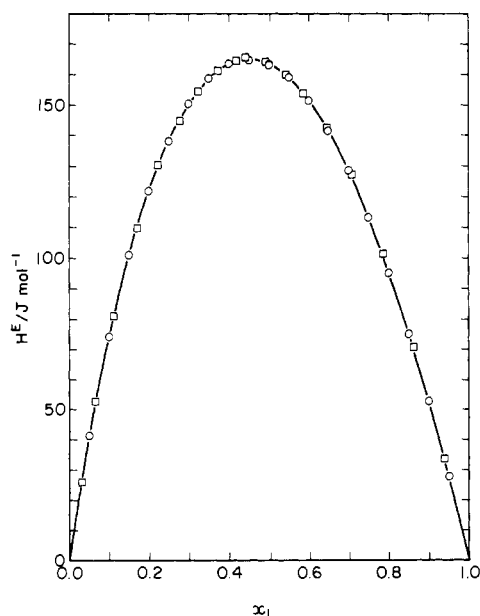


Figure 1. Molar excess enthalpy of *o*-dichlorobenzene (1)–benzene (2) at 298.15 K: O, present work; □, Tanaka et al. (6). Solid curve is least-squares representation of our results by eq 1.

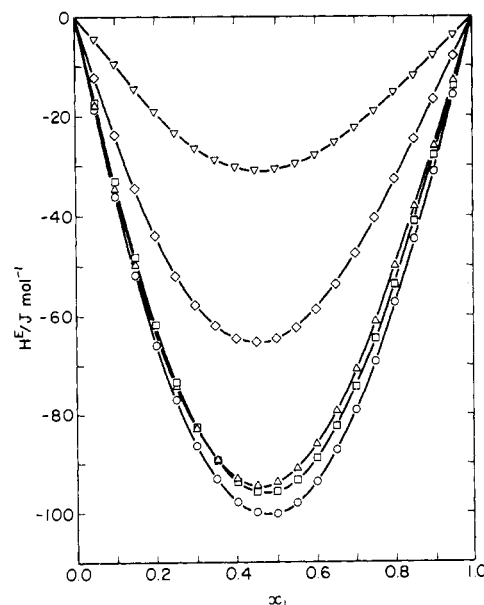


Figure 2. Molar excess enthalpies of *o*-dichlorobenzene (1)–aromatic hydrocarbon (2) at 298.15 K. Component 2: ∇, toluene; ◇, ethylbenzene; ○, *o*-xylene; Δ, *m*-xylene; □, *p*-xylene. Solid curves are least-squares representations of our results by eq 1.

Table III. Coefficients and Standard Errors for Representations of Excess Functions of *o*-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	C_5	σ
Benzene	H^E	653.388	122.330	57.293	44.850	33.689	0.16
	V^E	0.401 69	0.024 86	0.041 86	0.030 42		0.000 15
Toluene	H^E	-122.599	-28.381	41.700	25.436		0.12
	V^E	-0.418 73	-0.117 79	0.010 97			0.000 30
Ethylbenzene	H^E	-258.181	-63.378	46.358	18.831	12.014	0.16
	V^E	-0.536 35	-0.137 73	0.027 17			0.000 22
<i>o</i> -Xylene	H^E	-400.663	-44.626	42.981	11.204		0.22
	V^E	-0.344 14	-0.079 62	0.021 27			0.000 36
<i>m</i> -Xylene	H^E	-375.840	-74.340	59.239	20.357		0.13
	V^E	-0.557 87	-0.128 31	0.024 61	-0.012 63		0.000 27
<i>p</i> -Xylene	H^E	-382.789	-51.586	56.271	22.593	16.971	0.11
	V^E	-0.638 35	-0.114 36	0.029 63			0.000 21

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

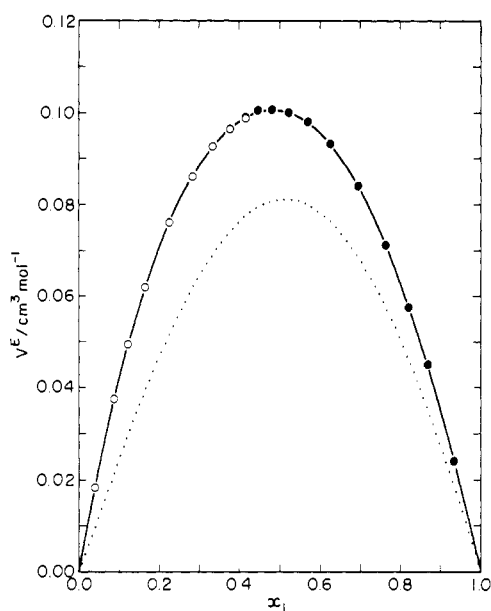


Figure 3. Molar excess volume of *o*-dichlorobenzene (1)–benzene (2) at 298.15 K: O and ●, present work (two separate dilutions). Solid curve is least-squares representation of our results by eq 1. Dotted curve is extrapolated from smoothing functions given by Dhillon (7).

4 were calculated by extrapolating Dhillon's functions linearly to 298.15 K. Although the order of the curves is the same as we find, the magnitudes of V^E are less and the asymmetries are different.

It is interesting to compare the present results for *o*-dichlorobenzene mixtures with our previous results for chlorobenzene mixtures (3). In the latter case, we found that the H^E and V^E curves fell in the same relative order. However, there is no direct correlation between H^E and V^E for the series of *o*-dichlorobenzene mixtures. H^E is positive for *o*-dichlorobenzene–benzene but has small negative values for chlorobenzene–benzene. Apart from this, the magnitudes of H^E for mixtures of the other aromatics with *o*-dichlorobenzene are smaller than for the corresponding mixtures with chlorobenzene, and the magnitudes of V^E for the *o*-dichlorobenzene mixtures are larger than for the chlorobenzene mixtures.

A notable characteristic of the results for mixtures of aromatic hydrocarbons with both chlorobenzene and *o*-dichlorobenzene is the significant decrease of H^E and V^E which occurs when benzene is replaced by an alkylbenzene. The relatively large positive values of H^E and V^E for *o*-dichlorobenzene–benzene mixtures compared to chlorobenzene–benzene mixtures are probably attributable to a greater stabilization of *o*-dichloro-

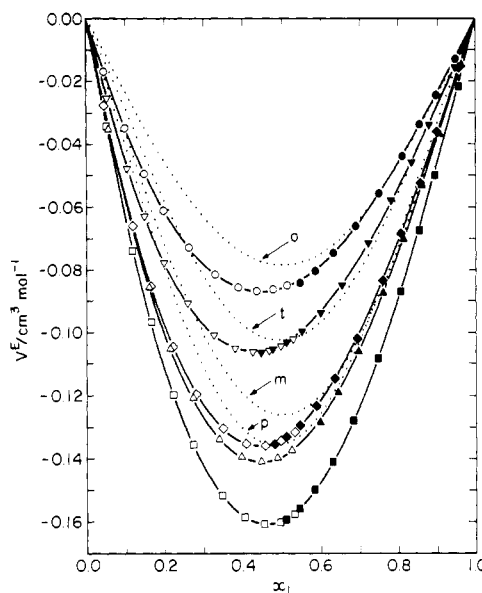


Figure 4. Molar excess volumes of *o*-dichlorobenzene (1)–aromatic hydrocarbon (2) at 298.15 K. Component 2: ▽ and ▼, toluene; ◇ and ◆, ethylbenzene; ○ and ●, *o*-xylene; △ and ▲, *m*-xylene; □ and ■, *p*-xylene. Open and solid symbols are results of separate dilutions. Solid curves are least-squares representations of our results by eq 1. Dotted curves are extrapolated from smoothing functions given by Dhillon (7) and labeled with first letter of name of component 2.

benzene in the pure component state by dispersive and electrostatic interactions.

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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 error defined in eq 2
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Subscripts

- 1 o-dichlorobenzene
2 aromatic hydrocarbon

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Vapor-Liquid Equilibria of the Ternary System Methyl Borate-Methyl Alcohol-Carbon Tetrachloride

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Vapor-liquid equilibrium measurements at 760 Torr are reported for the methyl borate-methyl alcohol-carbon tetrachloride system. Analysis of the results shows that the ternary system can be adequately represented from binary data by means of the van Laar correlations (average error 2.2%) and well represented by the Wilson equation (average error 0.9%).

The vapor-liquid equilibria have been measured for the ternary system methyl borate-methyl alcohol-carbon tetrachloride at a pressure of 760 ± 1 Torr. An Altsheuler (circulation type) still was used and is described in detail by Hala et al. (3). The methyl borate used was purchased from Apache Chemicals, Inc., at a nominal 98% purity and was further purified by successive fractional distillation to 99.9+%. Analysis of the borate was by the standard mannitol-sodium hydroxide titration (6). Methyl alcohol ("absolute") and carbon tetrachloride were used as purchased. Properties of these compounds compared with literature values are shown in Table I.

Mixture analyses were made by a combination of chemical analysis and physical property measurements. Measurements necessary were the weight fraction of methyl borate, which was again determined by the mannitol-sodium hydroxide titration, refractive indices, and densities of both the pure components and the mixtures. Once the weight fraction of methyl borate was known, the Lorentz-Lorenz equation (8)

$$\frac{(\eta^2 - 1)}{(\eta^2 + 2)\rho} = \sum_1^3 (\omega_i) \frac{(\eta_i^2 - 1)}{(\eta_i^2 + 2)\rho_i} \quad (1)$$

and

$$\sum_1^3 \omega_i = 1 \quad (2)$$

were used to obtain the weight fraction of the other two components. To verify this procedure, several mixtures of known composition were assayed and the results were to within $\pm 0.1\%$ of the known values. Experimental evidence showed no necessity of including a liquid volume correction term to eq 1. Refractive indices were measured with a Bausch and Lomb Model 33-45-03 refractometer capable of precision to ± 0.00003 RI units. The sodium D line at 25.0 ± 0.1 °C was used. Densities were determined by means of a pycnometer, with a nominal volume of 10 mL, at 25.0 ± 0.05 °C. The pycnometer was calibrated with deionized water, specific resistance approximately 450000Ω , and weighed to ± 0.0001 g.

Experimental data are tabulated in Table II and the tie lines are also shown in Figure 1. Three-dimensional models representing the temperature-vapor and temperature-liquid compositions were constructed from these data. Estimated isotherms on these surfaces have been projected as shown in Figures 2 and 3.

For the liquid surface, a sharp temperature drop occurs from the methyl borate-carbon tetrachloride binary as a small amount of methyl alcohol is added. The decline is less severe at high methyl borate concentrations. A nearly flat interior is seen at all points reasonably removed from the pure components. The flat interior rises quickly to a point as pure methyl alcohol is approached. The vapor surface shows a trough connecting the two binary azeotropes (methyl borate-methyl alcohol and methyl alcohol-carbon tetrachloride) which is nearly linear. The surfaces rising from the trough to pure methyl alcohol and also to the methyl borate-carbon tetrachloride binary show slight upward curvature. There is no evidence of a ternary azeotrope.

Activity coefficients of the components were calculated from the equation

$$\gamma_i = \frac{y_i P}{x_i P_i^0} \quad (3)$$

Table I

Compound	Bp, °C		Refractive index, 25 °C sodium D line		Density 25 °C, g mL ⁻¹	
	This work	Lit.	This work	Lit.	This work	Lit.
Methyl borate	68.6 ± 0.1	68.7 (7)	1.35504	—	0.9273	0.9273 (2)
Methyl alcohol	64.6 ± 0.1	64.51 (1)	1.3268	1.326 (4)	0.7867	0.7867 (7)
Carbon tetrachloride	76.7 ± 0.1	76.54 (4)	1.4575	1.459 (4)	1.5843	1.5867 (7)