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

Literature Cited

(1) Arm, H. Hügli, F., Signer, R., *Helv. Chim. Acta*, **40**, 1200 (1957).
(2) Cheesman, G. H., Ladner, W. R., *Proc. R. Soc., London, Ser. A*, **229**, 387 (1955).
(3) Flory, P. J., *J. Am. Chem. Soc.*, **87**, 1833 (1965).
(4) Fortier, J.-L., Benson, G. C., *J. Chem. Thermodyn.*, **8**, 411 (1976).
(5) Fortier, J.-L., Benson, G. C., *J. Chem. Thermodyn.*, **9**, 1181 (1977).
(6) Fortier, J.-L., Benson, G. C., Picker, P., *J. Chem. Thermodyn.*, **8**, 289 (1976).
(7) Kiyohara, O., Benson, G. C., *J. Chem. Thermodyn.*, **9**, 691 (1977).
(8) Lewis, G., Johnson, A. F., *J. Chem. Eng. Data*, **14**, 484 (1969).
(9) Mathieson, A. R., Thynne, J. C. J., *J. Chem. Soc.*, 3708 (1956).
(10) Murakami, S., Lam, V. T., Benson, G. C., *J. Chem. Thermodyn.*, **1**, 397 (1969).
(11) Rastogi, R. P. Nath, J., Misra, J., *J. Phys. Chem.*, **71**, 1277 (1967).
(12) Rastogi, R. P., Nath, J., Misra, J., *J. Phys. Chem.*, **71**, 2524 (1967).
(13) Selected Values of Properties of Hydrocarbons and Related Compounds, American Petroleum Institute Research Project 44, Thermochemical Research Center, Texas A&M University, College Station, Texas (loose leaf sheet dated Oct 31, 1950).
(14) Singh, J., Pflug, H. D., Benson, G. C., *J.* Phys. *Chem.*, **72**, 1939 (1968).
(15) Tager, A. A., Kargin, V. A., *Kolloidn. Zh.*, **14**, 367 (1952).
(16) Tanaka, R., Benson, G. C., *J. Chem. Thermodyn.*, **8**, 259 (1976).
(17) Tanaka, R., Kiyohara, O., D'Arcy, P. J., Benson, G. C., *Can. J. Chem.*, **53**, 2262 (1975).
(18) Wôycicki, W., *J. Chem. Thermodyn.*, **6**, 141 (1974).

Received for review May 17, 1978. Accepted August 31, 1978. Issued as NRCC No. 17120.

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

Reiji Tanaka[†] **and George C. Benson***

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

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

$$X^E = x_1x_2\sum_{j=1}^{n} c_j(x_2 - x_1)^{j-1} \qquad (1)$$

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

---

[†] NRCC Postdoctorate Fellow 1973–1975.

0021-9568/79/1724-0037$01.00/0

Table I. Experimental Values of the Molar Excess Enthalpies of Binary Mixtures of Some Chlorobenzenes at 298.15 K

x_1	H^E, J mol^{-1}	x_1	H^E, J mol^{-1}	x_1	H^E, J mol^{-1}	x_1	H^E, J mol^{-1}
Chlorobenzene (1)–*o*-Dichlorobenzene (2)							
0.0500	11.28	0.3000	52.12	0.5000	63.38	0.7500	49.75
0.1000	21.77	0.3500	57.06	0.5500	63.14	0.8000	42.54
0.1500	30.87	0.4000	59.89	0.6000	61.58	0.8500	33.92
0.2000	39.21	0.4500	62.14	0.6500	58.89	0.9000	24.68
0.2500	45.77	0.5000	63.48	0.7000	54.61	0.9500	12.39
Chlorobenzene (1)-*m*-Dichlorobenzene (2)							
0.0500	10.70	0.3000	52.05	0.5000	66.11	0.7500	53.49
0.1000	21.13	0.3500	57.37	0.5500	66.35	0.8000	46.15
0.1500	30.29	0.4000	61.72	0.6000	65.29	0.8500	37.26
0.2000	38.72	0.4500	64.45	0.6500	62.82	0.9000	27.01
0.2500	46.01	0.5000	66.01	0.7000	58.85	0.9500	14.68
o-Dichlorobenzene (1)-*m*-Dichlorobenzene (2)							
0.0500	2.04	0.3000	8.81	0.5000	9.12	0.7500	5.93
0.1000	4.06	0.3500	9.26	0.5500	8.85	0.8000	4.89
0.1500	5.74	0.4000	9.51	0.6000	8.24	0.8500	3.81
0.2000	7.02	0.4500	9.44	0.6500	7.57	0.9000	2.66
0.2500	8.09	0.5000	9.18	0.7000	6.81	0.9500	1.39

Table II. Experimental Values of the Molar Excess Volumes of Binary Mixtures of Some Chlorobenzenes at 298.15 K

x_1	V^E, cm^3 mol^{-1}	x_1	V^E, cm^3 mol^{-1}	x_1	V^E, cm^3 mol^{-1}	x_1	V^E, cm^3 mol^{-1}
Chlorobenzene (1)–*o*-Dichlorobenzene (2)							
0.063 11	0.004 18	0.361 90	0.016 80	0.541 74	0.018 19	0.808 39	0.010 23
0.123 11	0.008 16	0.418 45	0.017 55	0.581 67	0.017 98	0.855 22	0.007 35
0.176 81	0.010 87	0.463 81	0.017 75	0.627 74	0.016 77	0.901 01	0.005 17
0.228 46	0.012 91	0.479 82	0.018 25	0.682 50	0.015 46	0.945 86	0.002 84
0.292 87	0.015 09	0.507 24	0.018 21	0.746 18	0.013 48		
Chlorobenzene (1)-*m*-Dichlorobenzene (2)							
0.051 10	0.005 62	0.357 80	0.029 33	0.526 19	0.032 99	0.767 96	0.026 12
0.112 19	0.012 08	0.416 80	0.031 33	0.560 31	0.033 05	0.818 32	0.022 17
0.165 35	0.016 92	0.466 64	0.032 27	0.602 83	0.032 68	0.866 48	0.017 52
0.222 42	0.021 73	0.496 15	0.032 90	0.650 01	0.031 61	0.911 82	0.012 55
0.286 74	0.025 82	0.508 31	0.032 78	0.705 69	0.029 61	0.954 75	0.006 60
o-Dichlorobenzene (1)-*m*-Dichlorobenzene (2)							
0.061 07	−0.004 80	0.254 97	−0.015 84	0.478 47	−0.021 66	0.856 73	−0.010 21
0.126 88	−0.009 11	0.275 92	−0.016 64	0.513 62	−0.021 83	0.897 31	−0.007 42
0.140 68	−0.010 01	0.326 37	−0.018 80	0.544 07	−0.022 08	0.950 87	−0.003 65
0.171 15	−0.011 60	0.385 50	−0.020 50	0.679 53	−0.018 86		
0.197 61	−0.012 95	0.435 34	−0.021 79	0.746 58	−0.016 08		
0.224 00	−0.014 18	0.477 39	−0.022 12	0.802 17	−0.013 31		

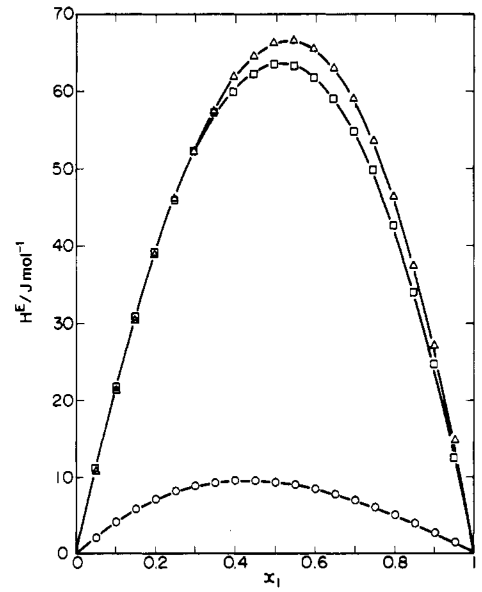

Figure 1. Molar excess enthalpies of binary mixtures of chlorobenzenes at 298.15 K: □, chlorobenzene (1)-*o*-dichlorobenzene (2); △, chlorobenzene (1)-*m*-dichlorobenzene (2); ○, *o*-dichlorobenzene (1)-*m*-dichlorobenzene (2). Solid curves are least-squares representations of results by eq 1.

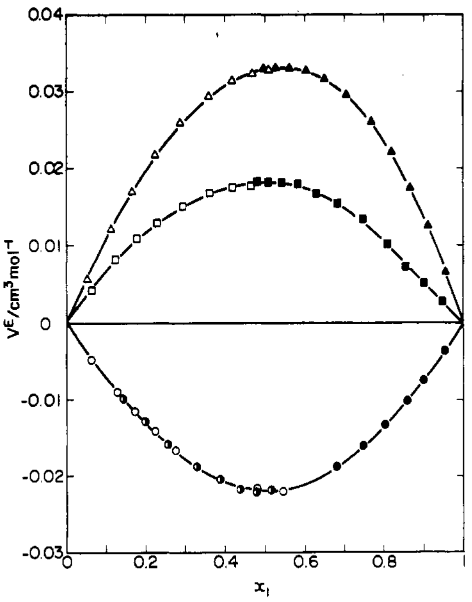

Figure 2. Molar excess volumes of binary mixtures of chlorobenzenes at 298.15 K: □ and ■, chlorobenzene (1)-*o*-dichlorobenzene (2) (two separate dilutions); △ and ▲, chlorobenzene (1)-*m*-dichlorobenzene (2) (two separate dilutions); ○, ◑, and ●, *o*-dichlorobenzene (1)-*m*-dichlorobenzene (2) (three separate dilutions.) Solid curves are least-squares representations of results by eq 1.

Table III. Coefficients and Standard Deviations for Representations of Excess Functions of Binary Mixtures of Some Chlorobenzenes at 298.15 K by Equation 1

component 1	component 2	function[a]	c_1	c_2	c_3	c_4	σ
chlorobenzene	*o*-dichlorobenzene	H^E	254.020	−17.452			0.29
		V^E	0.07303	−0.00138	−0.00909	0.01954	0.00023
chlorobenzene	*m*-dichlorobenzene	H^E	264.150	−39.818	3.102		0.15
		V^E	0.13177	−0.01997	0.01095		0.00018
o-dichlorobenzene	*m*-dichlorobenzene	H^E	37.016	11.202			0.10
		V^E	−0.08777	0.00142	0.01214		0.00021

[a] Units: H^E, J mol^{-1}; V^E, cm^3 mol^{-1}.

Table IV. Summary of Calculations Using the Flory Theory[a]

system	X_{12}, J cm^{-3}	$V^E(0.5)$, cm^3 mol^{-1} theory	$V^E(0.5)$, cm^3 mol^{-1} eq 1
chlorobenzene-*o*-dichlorobenzene	2.88	−0.0239	0.0183
-*m*-dichlorobenzene	2.91	0.0113	0.0329
o-chlorobenzene-*m*-dichlorobenzene	0.39	−0.0010	−0.0219
chlorobenzene-benzene[b]	0.27	−0.0143	0.0260
-toluene[b]	−5.07	−0.1219	−0.0900
-ethylbenzene[b]	−6.31	−0.1136	−0.1317
-*o*-xylene[b]	−4.47	−0.0577	−0.0239
-*m*-xylene[b]	−4.52	−0.0813	−0.0493
-*p*-xylene[b]	−4.83	−0.0991	−0.0739
o-dichlorobenzene-benzene[c]	8.95	−0.0595	0.1004
-toluene[c]	−0.76	−0.2228	−0.1047
-ethylbenzene[c]	−2.25	−0.1910	−0.1341
-*o*-xylene[c]	−3.90	−0.1557	−0.0860
-*m*-xylene[c]	−3.49	−0.2062	−0.1395
-*p*-xylene[c]	−3.52	−0.2416	−0.1596
m-dichlorobenzene-benzene[d]	9.17	0.0192	0.1843
-toluene[d]	−4.60	−0.2135	−0.1153
-ethylbenzene[d]	−4.37	−0.1671	−0.1105
-*o*-xylene[d]	−9.70	−0.1955	−0.1483
-*m*-xylene[d]	−10.24	−0.2504	−0.2140
-*p*-xylene[d]	−10.45	−0.2841	−0.2281

[a] Characteristic parameters used for chlorobenzene, *o*-dichlorobenzene, and *m*-dichlorobenzene are respectively: $p^* =$ 593.9, 630.4, and 608.5 J cm^{-3}; $V^* =$ 90.50, 92.87, and 93.70 cm^3 mol^{-1}; $T^* =$ 5287, 5719, and 5618 K. Values for aromatic hydrocarbons taken from ref 2 and 4. [b] H^E and V^E taken from ref 3. [c] H^E and V^E taken from ref 5. [d] H^E and V^E taken from ref 6.

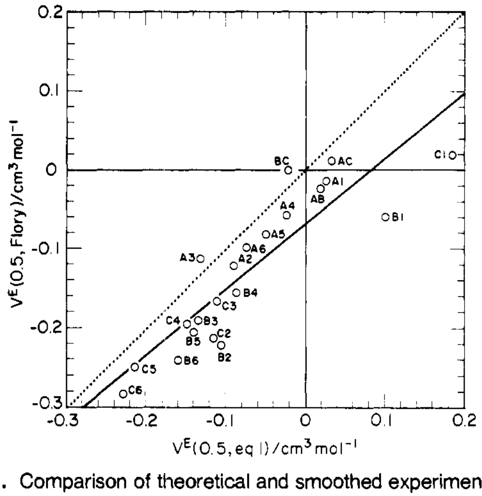

Figure 3. Comparison of theoretical and smoothed experimental values of V^E for equimolar mixtures at 298.15 K. Labels indicate the following components: A, chlorobenzene; B, *o*-dichlorobenzene; C, *m*-dichlorobenzene; 1, benzene; 2, toluene; 3, ethylbenzene; 4, *o*-xylene; 5, *m*-xylene; 6, *p*-xylene. Lines are as follows: —, least-squares line with $r = 0.88$; ···, perfect correlation with $r = 1$.

with values of V^E for equimolar mixtures calculated from the theory and from eq 1. For the aromatic hydrocarbons, values of the characteristic parameters (p^*, V^*, T^* in Flory's formulation) were taken from previous calculations involving those components (*2*, *4*). Characteristic parameters for the chlorobenzenes were estimated from the rather meager data available for their thermal expansivities, ultrasonic velocities, and heat capacities; the resulting values are given in the footnote to Table IV. Although there are sizable differences between the theoretical and smoothed experimental values of V^E, the comparison plot in Figure 3 shows a fairly high degree of correlation. The Flory theory predicts the correct sign of V^E for 18 of the 21 systems and the least-squares line corresponds to a coefficient of correlation equal to 0.88. However, in most cases the theoretical values are algebraically less than the experimental findings.

Acknowledgment

We thank Mr. P. J. D'Arcy and Mr. C. J. Halpin for technical assistance during this investigation.

Glossary

c_1, c_2, ..., 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
p^*	characteristic pressure, J cm^{-3}
r	coefficient of correlation
V^E	molar excess volume, cm^3 mol^{-1}
V^*	characteristic volume, cm^3 mol^{-1}
T^*	characteristic temperature, K
X^E	typical molar excess property
X_{12}	interaction parameter in Flory theory, J cm^{-3}
x_i	mole fraction of component *i*

Greek Letters

σ	standard deviation defined in eq 2

Literature Cited

(1) Flory, P. J., *J. Am. Chem. Soc.*, **87**, 1833 (1965).
(2) Murakami, S., Lam, V. T., Benson, G. C., *J. Chem. Thermodyn.*, **1**, 397 (1969).
(3) Tanaka, R., Benson, G. C., *J. Chem. Eng. Data*, **21**, 320 (1976).
(4) Tanaka, R., Benson, G. C., *J. Chem. Thermodyn.*, **8**, 259 (1976).
(5) Tanaka, R., Benson, G. C., *J. Chem. Eng. Data*, **22**, 291 (1977).
(6) Tanaka, R., Benson, G. C., *J. Chem. Eng. Data*, **23**, 75 (1978).
(7) Tanaka, R., D'Arcy, P. J., Benson, G. C., *Thermochim. Acta*, **11**, 163 (1975).
(8) Tanaka, R., Kiyohara, O., D'Arcy, P. J., Benson, G. C., *Can. J. Chem.*, **53**, 2262 (1975).

Received for review May 22, 1978. Accepted August 31, 1978. Issued as NRCC No. 17119.