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Binary Systems of 1,1,2,2-Tetrachloroethane with Benzene, Toluene, *p*-Xylene, Acetone, and Cyclohexane. 1. Excess Volumes, Ultrasonic Velocities, and Adiabatic Compressibilities at 298.15 and 308.15 K

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Measurements of excess volumes (V^E), ultrasonic velocities (u), and adiabatic compressibilities (k_s) at 298.15 and 308.15 K have been made for binary liquid mixtures of 1,1,2,2-tetrachloroethane ($CHCl_2CHCl_2$) with benzene, toluene, *p*-xylene, acetone, and cyclohexane. The values of V^E at both temperatures have been fitted by the method of least squares to the equation $V^E = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2]$ where x_1 refers to the mole fraction of $CHCl_2CHCl_2$, and A_0, A_1, and A_2 are constants characteristic of a system. The values of the quantity k_s^E, which refers to the deviations of the experimental values of the adiabatic compressibilities of the mixtures from the mole fraction mixture law values, have also been calculated and have been fitted by the method of least squares to the equation $k_s^E = x_1x_2[B_0 + B_1(x_1 - x_2) + B_2(x_1 - x_2)^2]$ where x_1 refers to the mole fraction of $CHCl_2CHCl_2$, and B_0, B_1, and B_2 are constants characteristic of a system. At both temperatures 298.15 and 308.15 K, values of V^E have been found to be negative for $CHCl_2CHCl_2$–benzene, $CHCl_2CHCl_2$–toluene, $CHCl_2CHCl_2$–*p*-xylene, and $CHCl_2CHCl_2$–acetone and positive for $CHCl_2CHCl_2$–cyclohexane. Further, the values of k_s^E at 298.15 and 308.15 K have been found to be negative for $CHCl_2CHCl_2$–benzene, $CHCl_2CHCl_2$–toluene, $CHCl_2CHCl_2$–acetone, and $CHCl_2CHCl_2$–cyclohexane and positive for $CHCl_2CHCl_2$–*p*-xylene. These results indicate the existence of specific interaction of $CHCl_2CHCl_2$ with the aromatic hydrocarbons and acetone.

Introduction

Table I. Values of Ultrasonic Velocities in, and Adiabatic Compressibilities for, Various Pure Liquids at 303.15 K

	u, m s^{-1}		10^6k_s, atm^{-1}	
liquid	this work	lit. value^a	this work	lit. value^a
benzene	1277	1278	71.6	71.5
toluene	1283	1284.5	71.8	71.8
acetone	1144	1146	99.3	99.1
chloroform	968	967.5	73.5	73.7
carbon tetrachloride	906	904	78.4	78.8

^{a} See ref *6*.

Binary systems of 1,1,2,2-tetrachloroethane ($CHCl_2CHCl_2$) with aromatic hydrocarbons, acetone, and cyclohexane are of considerable interest from the viewpoint of the existence of specific interaction between the components in the liquid state. The specific interaction of $CHCl_2CHCl_2$ with aromatics and acetone can be visualized to be due to the presence of four Cl atoms and two H atoms in $CHCl_2CHCl_2$ on account of which it can act as a σ acceptor toward, and be involved in hydrogen-bond formation with, the aromatics and acetone. The aromatics in their interaction with $CHCl_2CHCl_2$ will act as π donors, whereas acetone will act as an n donor. The system of cyclohexane with $CHCl_2CHCl_2$, in which case only the dispersion, dipolar, and induction forces are believed to be present, is of interest as it will act as a reference system. Extensive studies concerning the properties of these systems have not been made. In the present program, we have made measurements of ultrasonic velocities in, plus adiabatic compressibilities and excess volumes for, the binary liquid mixtures of $CHCl_2CHCl_2$ with benzene, toluene, *p*-xylene, acetone, and cyclohexane at 298.15 and 308.15 K, and the results obtained have been interpreted in this paper.

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Table II. Experimental Values of Excess Volumes for the Various Systems of 1,1,2,2-Tetrachloroethane at 298.15 and 308.15 K

temp = 298.15 K		temp = 308.15 K	
$x_1{}^a$	V^E, cm³ mol⁻¹	$x_1{}^a$	V^E, cm³ mol⁻¹
	$CHCl_2CHCl_2$-Benzene		
0.2261	−0.016	0.1888	−0.023
0.2945	−0.028	0.2007	−0.027
0.4366	−0.039	0.3045	−0.035
0.4576	−0.041	0.4059	−0.042
0.5190	−0.047	0.4576	−0.053
0.6645	−0.032	0.5336	−0.057
0.7321	−0.024	0.5502	−0.053
0.8018	−0.019	0.7757	−0.047
	$CHCl_2CHCl_2$-Toluene		
0.1828	−0.093	0.1090	−0.089
0.2382	−0.120	0.1750	−0.124
0.3255	−0.151	0.3397	−0.165
0.4178	−0.161	0.4265	−0.175
0.4972	−0.159	0.5283	−0.159
0.5795	−0.146	0.7339	−0.091
0.7222	−0.095		
	$CHCl_2CHCl_2$-*p*-Xylene		
0.1780	−0.130	0.2865	−0.176
0.3081	−0.165	0.3150	−0.177
0.4676	−0.147	0.3551	−0.178
0.4951	−0.144	0.4046	−0.170
0.5957	−0.118	0.5623	−0.134
0.7684	−0.062	0.5951	−0.121
0.8560	−0.042	0.6132	−0.118
		0.7487	−0.068
	$CHCl_2CHCl_2$-Acetone		
0.1015	−0.275	0.0973	−0.285
0.2020	−0.470	0.1334	−0.364
0.4797	−0.652	0.1456	−0.380
0.4922	−0.652	0.5174	−0.664
0.5092	−0.652	0.6365	−0.639
0.6390	−0.607	0.6846	−0.624
0.6548	−0.588	0.6960	−0.609
	$CHCl_2$-$CHCl_2$-Cyclohexane		
0.2994	0.449	0.2415	0.392
0.3125	0.450	0.2903	0.437
0.3330	0.465	0.3080	0.444
0.4498	0.471	0.4333	0.476
0.5198	0.462	0.6687	0.408
0.7554	0.323	0.7796	0.321
		0.8113	0.273

[a] x_1 refers to the mole fraction of $CHCl_2CHCl_2$.

Experimental Section

***Materials*.** Benzene and toluene, which were of AR or GR quality, were purified in a manner similar to that described by Rastogi, Nath, and Misra (*1*). *p*-Xylene (Pfizer) of reagent grade was subjected to treatments with concentrated sulfuric acid, with distilled water, with dilute sodium carbonate solution, and again with distilled water. It was further dried over anhydrous calcium chloride and then subjected to fractional crystallizations which were followed by fractional distillations. Spectral-grade cyclohexane (E. Merck, Darmstadt) was stored over anhydrous calcium chloride overnight and then distilled. Electronic-grade acetone was stored over anhydrous calcium chloride overnight and then fractionally distilled from phosphorus pentoxide. 1,1,2,2-Tetrachloroethane (BDH) was shaken with potassium carbonate solution. It was further dried over anhydrous potassium carbonate, followed by fractional distillation.

The densities of the purified samples of benzene, toluene, *p*-xylene, 1,1,2,2-tetrachloroethane, acetone, and cyclohexane at 303.15 K were found to be 0.868 42, 0.857 74, 0.852 30, 1.578 52, 0.779 23, and 0.769 21 g cm^{-3}, respectively, which are in good agreement with the literature values (*2*), 0.868 36, 0.857 70, 0.852 30, 1.578 60, 0.779 33, and 0.769 14 g cm^{-3}, respectively.

***Methods*. *Excess Volumes*.** The excess volumes, which are accurate to ±0.002 cm³ mol⁻¹, were measured by using a two-limbed dilatometer as described earlier (*1*). The working of the dilatometer was tested by measuring V^E for the system benzene–cyclohexane at 303.15 K. Our values of V^E for this system, which were found to be in reasonable agreement with the data of Powell and Swinton (*3*), have been fitted by least squares to the equation

$$V^E = x_1x_2[2.5535 - 0.0188(x_1 - x_2) + 0.0994(x_1 - x_2)^2] \quad (1)$$

with a standard deviation of ±0.003 cm³ mol⁻¹. In eq 1, V^E is in units of cm³ mol⁻¹, and x_1 is the mole fraction of benzene. For equimolal mixtures, our value of V^E = 0.638 cm³ mol⁻¹ compares favorably with the corresponding value 0.633 cm³ mol⁻¹ of Powell and Swinton (*3*).

***Ultrasonic Velocities and Adiabatic Compressibilities*.** The ultrasonic velocities, u, in pure liquids and their binary mixtures were measured with a single crystal interferometer (supplied by Mittal Enterprises, New Delhi) at a frequency of 2 MHz s⁻¹. The adiabatic compressibilities, k_s, were calculated from the relation (*4*, *5*)

$$k_s = u^{-2}\rho^{-1} \quad (2)$$

where ρ refers to the density. The densities used to calculate k_s for pure liquids at 298.15 and 308.15 K were obtained from the data reported by Timmermans (*2*), whereas the densities used to calculate k_s for mixtures were estimated from the densities of pure liquids and the excess volumes reported in this paper. The values of 10^6k_s are accurate to ±0.1 atm⁻¹.

The working of the interferometer was tested by making measurements for pure samples of benzene, toluene, acetone, chloroform, and carbon tetrachloride at 303.15 K. Table I shows that our values of u and k_s for these liquids are in good agreement with the data of Freyer, Hubbard, and Andrews (*6*).

Results and Discussion

Excess molar volumes of binary mixtures of $CHCl_2CHCl_2$ with benzene, toluene, *p*-xylene, acetone, and cyclohexane at 298.15 and 308.15 K are given in Table II, whereas those for u and k_s are given in Table III. The values of V^E have been fitted by least squares to the equation

$$V^E = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2] \quad (3)$$

where x_1 refers to the mole fraction of $CHCl_2CHCl_2$, and A_0, A_1, and A_2 are constants characteristic of a system. Values of the constants along with the standard deviations $\delta(V^E)$ are given in Table IV.

The values of the quantity $k_s{}^E$, which refers to the deviations of the experimental values of k_s for the various mixtures from the mole fraction mixture law values, are also given in Table III and have been fitted by least squares to the equation

$$k_s{}^E = x_1x_2[B_0 + B_1(x_1 - x_2) + B_2(x_1 - x_2)^2] \quad (4)$$

where x_1 refers to the mole fraction of $CHCl_2CHCl_2$, and B_0, B_1, and B_2 are constants characteristic of a system. The values of the constants for the various systems are given in Table V.

At both temperatures, the values of V^E have been found to be negative for the systems $CHCl_2CHCl_2$–benzene, $CHCl_2CHCl_2$–toluene, $CHCl_2CHCl_2$–*p*-xylene, and $CHCl_2CHCl_2$–acetone and positive for $CHCl_2CHCl_2$–cyclohexane. The negative values of V^E for the binary systems of $CHCl_2CHCl_2$ with aromatic hydrocarbons and acetone indicate the existence of

Table III. Experimental Values of Ultrasonic Velocities in, and Adiabatic Compressibilities for, the Various Systems of 1,1,2,2-Tetrachloroethane at 298.15 and 308.15 K

temp = 298.15 K				temp = 308.15 K			
x_1[a]	u, m s^{-1}	$10^6 k_s$, atm^{-1}	$10^6 k_s^E$, atm^{-1}	x_1[a]	u, m s^{-1}	$10^6 k_s$, atm^{-1}	$10^6 k_s^E$, atm^{-1}
$CHCl_2CHCl_2$-Benzene							
0.0000	1301	68.5		0.0000	1255	74.6	
0.0665	1276	67.0	−0.1	0.1003	1224	71.5	−0.8
0.1858	1243	64.0	−0.7	0.1944	1200	69.0	−1.1
0.1860	1243	63.9	−0.8	0.2000	1199	68.8	−1.1
0.2606	1227	62.1	−1.1	0.2859	1183	66.4	−1.5
0.4252	1201	58.2	−1.6	0.5407	1149	60.2	−1.8
0.5705	1181	55.5	−1.3	0.6835	1135	57.3	−1.4
0.6562	1172	53.9	−1.1	0.8539	1128	53.8	−0.9
0.7000	1168	53.1	−1.1	1.0000	1121	51.3	
0.8679	1160	50.0	−0.7				
0.9337	1158	48.9	−0.5				
1.0000	1153	48.0					
$CHCl_2CHCl_2$-Toluene							
0.0000	1306	68.9		0.0000	1265	74.2	
0.2623	1237	62.9	−0.5	0.0837	1243	71.8	−0.5
0.4200	1212	59.1	−1.0	0.1517	1230	69.6	−1.1
0.4364	1207	59.0	−0.8	0.1545	1230	69.5	−1.2
0.4586	1202	58.7	−0.6	0.1648	1227	69.3	−1.1
0.5325	1190	57.3	−0.5	0.3050	1198	65.9	−1.3
0.6841	1175	54.1	−0.5	0.4565	1170	62.7	−1.0
0.8942	1161	49.8	−0.4	0.6876	1141	57.8	−0.7
0.9001	1159	49.8	−0.3	0.7971	1133	55.4	−0.5
1.0000	1153	48.0		1.0000	1121	51.3	
$CHCl_2CHCl_2$-p-Xylene							
0.0000	1310	68.9		0.0000	1272	73.9	
0.0926	1282	67.1	0.2	0.0870	1248	72.1	0.2
0.2279	1253	64.2	0.1	0.0956	1245	72.0	0.3
0.2927	1239	62.9	0.1	0.3489	1192	66.3	0.3
0.4536	1209	59.7	0.3	0.4724	1171	63.6	0.4
0.4964	1202	58.8	0.3	0.7489	1136	57.4	0.4
0.5000	1201	58.8	0.3	0.9500	1124	52.5	0.1
0.5654	1193	57.3	0.2	0.9900	1122	51.5	0.0
0.6447	1181	55.8	0.4	1.0000	1121	51.3	
0.7785	1168	52.9	0.3				
1.0000	1153	48.0					
$CHCl_2CHCl_2$-Acetone							
0.0000	1164	95.3		0.0000	1120	104.4	
0.0604	1154	89.0	−3.4	0.0595	1109	97.9	−3.3
0.0713	1152	88.1	−3.8	0.1965	1098	85.3	−8.7
0.2374	1137	75.5	−8.6	0.2857	1093	79.3	−9.9
0.4579	1133	64.0	−9.6	0.4883	1099	67.6	−10.9
0.4964	1135	62.3	−9.5	0.4972	1100	67.1	−10.9
0.6507	1138	56.8	−7.7	0.6003	1104	62.7	−9.8
0.9267	1146	49.9	−1.6	0.7001	1106	59.4	−7.8
1.0000	1153	48.0		0.7712	1109	57.2	−6.2
				1.0000	1121	51.3	
$CHCl_2CHCl_2$-Cyclohexane							
0.0000	1254	83.3		0.0000	1210	90.5	
0.0537	1238	81.1	−0.3	0.2161	1154	81.7	−0.3
0.3000	1181	72.0	−0.7	0.4035	1125	74.2	−0.5
0.4164	1162	68.1	−0.5	0.4706	1119	71.4	−0.7
0.5000	1154	65.1	−0.6	0.7244	1108	61.6	−0.5
0.6904	1150	57.8	−1.1	0.8680	1113	56.1	−0.4
0.8832	1152	51.3	−0.8	0.9000	1115	54.9	−0.3
0.9139	1152	50.5	−0.5	1.0000	1121	51.3	
1.0000	1153	48.0					

[a] x_1 refers to the mole fraction of $CHCl_2CHCl_2$.

specific interaction between the two components of the various systems, leading to the formation of molecular complexes in the liquid state. The values of V^E, which are slightly negative for mixtures of $CHCl_2CHCl_2$ with aromatic hydrocarbons, show that the specific interaction of $CHCl_2CHCl_2$ with aromatic hydrocarbons is weak, as has also been pointed out by Gracia et al. (*7*). In comparison, the highly negative values of V^E for $CHCl_2CHCl_2$–acetone indicate the formation of a strong complex between $CHCl_2CHCl_2$ and acetone in the liquid state. The data show that the values of the temperature coefficient $(\partial V^E/\partial T)_P$ for all of the mixtures of $CHCl_2CHCl_2$ with benzene, toluene, *p*-xylene, and acetone are negative. This can be attributed to the self-association of $CHCl_2CHCl_2$ molecules through hydrogen bonding (*8*). Further, the data show that, at both temperatures, the values of k_s^E are slightly negative for $CHCl_2CHCl_2$–benzene, $CHCl_2CHCl_2$–toluene, and $CHCl_2CHCl_2$–cyclohexane and slightly

Table IV. Values of the Constants A_0, A_1, and A_2 of Eq 3 and the Standard Deviations $\delta(V^E)$ for the Various Systems at 298.15 and 308.15 K

system	temp, K	A_0, cm^3 mol^{-1}	A_1, cm^3 mol^{-1}	A_2, cm^3 mol^{-1}	$\delta(V^E)$, cm^3 mol^{-1}
$CHCl_2CHCl_2$-benzene	298.15	−0.1703	−0.0197	0.2063	0.003
	308.15	−0.2093	−0.1019	−0.0203	0.003
$CHCl_2CHCl_2$-toluene	298.15	−0.6425	0.2196	0.3730	0.002
	308.15	−0.6475	0.3597	0.0377	0.004
$CHCl_2CHCl_2$-*p*-xylene	298.15	−0.5681	0.4342	−0.1274	0.003
	308.15	−0.6069	0.5424	−0.1070	0.002
$CHCl_2CHCl_2$-acetone	298.15	−2.6177	0.1645	−0.4558	0.005
	308.15	−2.6411	−0.1869	−1.1536	0.005
$CHCl_2CHCl_2$-cyclohexane	298.15	1.8614	−0.4786	0.5052	0.004
	308.15	1.9149	−0.3190	0.2755	0.006

Table V. Values of the Constants B_0, B_1, and B_2 of Eq 4 for the Various Systems at 298.15 and 308.15 K

system	T, K	10^6B_0, atm^{-1}	10^6B_1, atm^{-1}	10^6B_2, atm^{-1}
$CHCl_2CHCl_2$-benzene	298.15	−5.660	−1.817	0.798
	308.15	−6.652	0.418	−1.795
$CHCl_2CHCl_2$-toluene	298.15	−2.695	0.182	−1.728
	308.15	−4.573	3.692	−1.203
$CHCl_2CHCl_2$-*p*-xylene	298.15	0.951	0.767	2.183
	308.15	1.733	−0.974	0.403
$CHCl_2CHCl_2$-acetone	298.15	−37.623	19.631	−4.605
	308.15	−43.202	15.759	−2.566
$CHCl_2CHCl_2$-cyclohexane	298.15	−2.829	−1.349	−5.184
	308.15	−2.435	−1.089	−0.061

positive for $CHCl_2CHCl_2$–*p*-xylene. For $CHCl_2CHCl_2$–acetone, the values of k_s^E are highly negative. This supports the above viewpoint concerning the existence of strong specific interaction due to hydrogen bonding between $CHCl_2CHCl_2$ and acetone.

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Registry No. 1,1,2,2-Tetrachloroethane, 79-34-5; benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3; acetone, 67-64-1; cyclohexane, 110-82-7.

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Volumetric Properties of Some Aqueous Nonelectrolyte Solutions

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Densities have been measured at 298.15 K with a flow densimeter for binary and ternary aqueous solutions of a large number of nonelectrolytes. There is a high degree of internal consistency and very good agreement with literature data where available.

Introduction

Recent (*1*, *2*) and forthcoming (*3*–*5*) publications from this laboratory contain data on the thermodynamic properties of aqueous solutions of nonelectrolytes. In accumulating heat of dilution, heat capacity, and freezing point data on the various systems, we have found it expedient to collect corresponding volumetric data. First, heat of dilution and heat capacity data have been obtained by using flow microcalorimetric techniques and in these instances it is necessary to convert volumetric flow rates to mass flow rates using density data. Second, the accumulation of volumetric data per se is warranted by the nature of the Savage–Wood group additivity principle under which the other thermodynamic data have been treated; the behavior observed for enthalpies (*6*, *7*) and free energies (*8*–*11*) can be tested against volumes. Finally, from a purely practical point of view the continued accumulation of volumetric data has been advantageous. Within the last 5 years, three researchers in this laboratory have performed a large number of density measurements, some being repetitions, in connection with other experimental techniques such as flow heat of dilution calorimetry and flow heat capacity calorimetry. In addition to their immediate experimental uses and their other common

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