Ultrasonic Velocities in, and Adiabatic Compressibilities and Excess Volumes for, Binary Liquid Mixtures of Acetone with Tetrachloroethylene, Trichloroethylene, Methylene Chloride, 1,2-Dichloroethane, and Cyclohexane

Jagan Nath* and Atma Prakash Dixit

Chemistry Department, Gorakhpur University, Gorakhpur 273001, India

Excess volumes (V^E) have been measured for binary mixtures of acetone with tetrachloroethylene (CCl_2CCl_2), trichloroethylene ($CHClCCl_2$), and 1,2-dichloroethane (CH_2ClCH_2Cl) at 298.15 and 308.15 K, for mixtures of acetone with methylene chloride (CH_2Cl_2) at 293.15 and 303.15 K, and for mixtures of acetone with cyclohexane at 308.15 K. Ultrasonic velocities (u) in, and adiabatic compressibilities (k_s) for, binary mixtures of acetone with CCl_2CCl_2, $CHClCCl_2$, CH_2ClCH_2Cl, CH_2Cl_2, and c-C_6H_{12} have also been measured at 298.15 and 308.15 K. The values of V^E have been fitted by least squares to the equation $V^E = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2]$, where x_1 refers to the mole fraction of acetone, and A_0, A_1, and A_2 are constants characteristic of a system at a given temperature. The values of the quantity k_s^E, which refers to the deviations of the experimental values of k_s for mixtures from the mole fraction mixture law values, have been fitted by least squares to the equation $k_s^E = x_1x_2[B_0 + B_1(x_1 - x_2) + B_2(x_1 - x_2)^2]$, where x_1 refers to the mole fraction of acetone, and B_0, B_1, and B_2 are constants characteristic of a system at a given temperature. The results of measurements of V^E and k_s^E for the various systems indicate the existence of specific interaction of acetone with CCl_2CCl_2, $CHClCCl_2$, CH_2ClCH_2Cl, and CH_2Cl_2.

Introduction

Binary systems of acetone with tetrachloroethylene (CCl_2CCl_2), trichloroethylene ($CHClCCl_2$), methylene chloride (CH_2Cl_2), 1,2-dichloroethane (CH_2ClCH_2Cl), and cyclohexane (c-C_6H_{12}) are of considerable interest from the viewpoint of the existence of specific interaction leading to the formation of adducts between the components in the liquid state. The specific interaction of acetone with these chloro compounds can be visualized to be due to the presence of two lone pairs of electrons on the oxygen atom of acetone on account of which it can act as a lone-pair (n) donor toward these chloro compounds. Both CCl_2CCl_2 and $CHClCCl_2$, in their interaction with acetone, can act as both σ- and π-type acceptors (*1*, *2*), whereas CH_2Cl_2 and CH_2ClCH_2Cl can act as σ-acceptors toward, and be involved in the formation of hydrogen bonds with, acetone. The system of acetone with c-C_6H_{12}, in which case only the dispersion, dipolar, and induction forces are believed to be present between the components, 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 acetone with CCl_2CCl_2, $CHClCCl_2$, CH_2Cl_2, CH_2ClCH_2Cl, and c-C_6H_{12}, and the results obtained have been interpreted in this paper.

Table I. Values of Ultrasonic Velocities in, and Adiabatic Compressibilities for, Various Pure Liquids at 293.15 K

	u, m s^{-1}		$10^{12}k_s$, pa^{-1}	
liquid	this work	lit.[a]	this work	lit.[a]
benzene	1325	1324	648	649
toluene	1327	1327.5	655	655.5
acetone	1190	1190	893	893.3
chlorobenzene	1285	1284.5	547	547.7
chloroform	1001	1002.5	670	668.3

[a] See ref *9*.

Experimental Section

Materials. Electronic-grade acetone (Rechem) and reagent-grade cyclohexane (BDH) were purified in a manner similar to that described earlier (*3*). Electronic-grade trichloroethylene (S. Merck), spectral-grade tetrachloroethylene (E. Merck, Darmstadt), and methylene chloride (E. Merck, Darmstadt) of GR quality were placed over anhydrous calcium chloride overnight and then subjected to fractional distillations. 1,2-Dichloroethane (BDH) was purified by the method described by Foster and Fyfe (*4*). The densities of the purified components measured at 303.15 K were found to be in good agreement with the available data (*5*).

Methods. Excess Volumes. Excess volumes (V^E) which are accurate to ± 0.002 cm^3 mol^{-1}, were measured by using a two-limbed dilatometer as described by Rastogi, Nath, and Misra (*6*). The working of the dilatometer was tested as described earlier (*7*).

Ultrasonic Velocities and Adiabatic Compressibilities. The ultrasonic velocities, u, in pure liquids and their binary mixtures at the temperatures 298.15 and 308.15 K (controlled with an accuracy of ± 0.01 K), were measured with a single-crystal interferometer (supplied by Mittal Enterprises, New Delhi) at a frequency of 2 MHz s^{-1}. The accuracy in the values of u is of the order of ± 1.0 m s^{-1}. The adiabatic compressibilities, k_s, were calculated from the relation (*1*, *8*)

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

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 (*5*), whereas the densities used to calculate k_s for mixtures were estimated from the densities of pure liquids, and the data on excess volumes for the various mixtures reported in this paper. The data on excess volumes used to calculate ρ for mixtures of acetone with c-C_6H_{12} at 298.15 K were those reported earlier (*3*). The accuracy in the values of $10^{12}k_s$ is of the order of ± 1.0 Pa^{-1}.

The working of the interferometer was tested by making measurements for pure samples of benzene, toluene, chloroform, chlorobenzene, and acetone at 293.15 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 (*9*).

0021-9568/84/1729-0313$01.50/0

Table II. Experimental Values of the Excess Volumes V^E for the Various Systems of Acetone

temp = 298.15 K		temp = 308.15 K	
x_1[a]	V^E, cm^3 mol^{-1}	x_1[a]	V^E, cm^3 mol^{-1}
	Acetone–CCl_2CCl_2		
0.1293	0.074	0.1573	0.107
0.1760	0.087	0.1980	0.119
0.2039	0.093	0.2231	0.125
0.2501	0.095	0.2453	0.128
0.3714	0.095	0.3384	0.133
0.4482	0.089	0.4747	0.118
0.5714	0.065	0.5350	0.108
0.7305	0.040	0.6615	0.085
0.7335	0.039	0.6700	0.076
0.8040	0.031	0.7311	0.068
0.8124	0.030	0.7968	0.052
0.8261	0.029	0.9162	0.022
0.8482	0.022		
	Acetone–$CHClCCl_2$		
0.1042	−0.062	0.1626	−0.093
0.1684	−0.091	0.1820	−0.099
0.2123	−0.105	0.2334	−0.121
0.2646	−0.121	0.3129	−0.134
0.3079	−0.128	0.3460	−0.141
0.3715	−0.134	0.4746	−0.139
0.4431	−0.136	0.5651	−0.123
0.5000	−0.134	0.6646	−0.105
0.5900	−0.118	0.6760	−0.103
0.6539	−0.098	0.7196	−0.088
0.7210	−0.081	0.7294	−0.085
0.7550	−0.070	0.7888	−0.065
0.8122	−0.053		
0.9160	−0.020		
	Acetone–CH_2ClCH_2Cl		
0.0906	−0.013	0.1196	−0.025
0.1496	−0.019	0.1875	−0.042
0.1614	−0.020	0.2341	−0.048
0.3056	−0.029	0.2876	−0.056
0.3714	−0.031	0.3000	−0.057
0.4339	−0.035	0.4186	−0.069
0.4960	−0.037	0.4243	−0.071
0.6115	−0.035	0.5339	−0.075
0.6881	−0.033	0.6846	−0.066
0.8033	−0.024	0.7580	−0.061
0.8220	−0.023	0.7855	−0.054
0.9238	−0.013	0.8551	−0.043

temp = 293.15 K		temp = 303.15 K	
x_1[a]	V^E, cm^3 mol^{-1}	x_1[a]	V^E, cm^3 mol^{-1}
	Acetone–CH_2Cl_2		
0.0914	0.035	0.1166	0.030
0.1064	0.041	0.1769	0.044
0.1573	0.061	0.2392	0.062
0.2070	0.075	0.3007	0.076
0.2267	0.080	0.4960	0.100
0.4032	0.113	0.5441	0.110
0.4514	0.116	0.5891	0.104
0.5054	0.119	0.6178	0.103
0.5563	0.116	0.6358	0.098
0.5960	0.113	0.6786	0.094
0.6957	0.100	0.7065	0.091
0.7001	0.100	0.7780	0.075
0.8771	0.053	0.8163	0.062
0.8805	0.048	0.8744	0.044
0.9087	0.043		

temp = 308.15 K		temp = 308.15 K	
x_1[a]	V^E, cm^3 mol^{-1}	x_1[a]	V^E, cm^3 mol^{-1}
	Acetone–c-C_6H_{12}		
0.1491	0.640	0.5148	1.133
0.1837	0.735	0.6551	1.036
0.2144	0.816	0.7286	0.920
0.3192	1.019	0.7343	0.907
0.4162	1.111	0.8106	0.743

[a] x_1 refers to the mole fraction of acetone.

Results and Discussion

The experimental values of the excess molar volumes V^E for binary mixtures of acetone with CCl_2CCl_2, $CHClCCl_2$, and CH_2ClCH_2Cl at 298.15 and 308.15 K, for mixtures of acetone with CH_2Cl_2 at 293.15 and 303.15 K, and for mixtures of acetone with c-C_6H_{12} at 308.15 K are given in Table II, whereas the values of u and k_s for binary mixtures of acetone with CCl_2CCl_2, $CHClCCl_2$, CH_2ClCH_2Cl, CH_2Cl_2, and c-C_6H_{12} at 298.15 and 308.15 K are given in Table III. The values of V^E have been fitted by least squares to the following equation:

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

In eq 2, x_1 refers to the mole fraction of acetone, x_2 refers to the mole fraction of the halo compound or c-C_6H_{12}, and A_0, A_1, and A_2 are constants characteristic of a system at a given temperature. The values of the constants A_0, A_1, and A_2 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 following equation:

$$k_s^E = x_1x_2[B_0 + B_1(x_1 - x_2) + B_2(x_1 - x_2)^2] \quad (3)$$

In eq 3, x_1 refers to the mole fraction of acetone, and B_0, B_1, and B_2 are constants characteristic of a system of a given temperature. The values of the constants B_0, B_1, and B_2 along with the standard deviations $\delta(k_s^E)$ are given in Table V.

At both temperatures, 298.15 and 308.15 K, the values of V^E have been found to be positive for acetone–CCl_2CCl_2 and negative for acetone–$CHClCCl_2$ and acetone–CH_2ClCH_2Cl. The values of V^E have been found to be positive for acetone–CH_2Cl_2 at 293.15 and 303.15 K. Also the values of V^E at 308.15 K have been found to be highly positive for acetone–c-C_6H_{12}. The negative values of V^E for the systems acetone–$CHClCCl_2$ and acetone–CH_2ClCH_2Cl indicate the existence of specific interaction between the components of these systems, leading to the formation of molecular complexes in the liquid state. The data show that the values of V^E for acetone–CCl_2CCl_2 and acetone–CH_2Cl_2, though positive, are much lower in magnitude than the values of V^E for acetone–c-C_6H_{12}. This behavior can also be attributed to the existence of specific interaction between the components of the binary systems acetone–CCl_2CCl_2 and acetone–CH_2Cl_2. The temperature coefficient $(\partial V^E/\partial T)_P$ which is found to be positive for acetone–CCl_2CCl_2 further confirms that acetone forms a molecular complex with CCl_2CCl_2 in the liquid state. The data show that at both temperatures, 298.15 and 308.15 K, the values of k_s^E are negative for acetone–CCl_2CCl_2, acetone–$CHClCCl_2$, and acetone–CH_2ClCH_2Cl and positive for acetone–CH_2Cl_2, and acetone–c-C_6H_{12}. The negative values of k_s^E for acetone–CCl_2CCl_2, acetone–$CHClCCl_2$, and acetone–CH_2ClCH_2Cl further give evidence in favor of the fact that acetone forms molecular complexes with CCl_2CCl_2, $CHClCCl_2$, and CH_2ClCH_2Cl. The negative values of the temperature coefficients $(\partial V^E/\partial T)_P$ and $\partial k_s^E/\partial T$ for acetone–$CHClCCl_2$, acetone–CH_2ClCH_2Cl, and acetone–CH_2Cl_2 can be attributed to the fact that molecules of $CHClCCl_2$, CH_2ClCH_2Cl, and CH_2Cl_2 are self-associated through hydrogen bonding (*10*).

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

temp = 298.15 K				temp = 308.15 K			
x_1[a]	u, m s^{-1}	$10^{12}k_s$, Pa^{-1}	$10^{12}k_s^E$, Pa^{-1}	x_1[a]	u, m s^{-1}	$10^{12}k_s$, Pa^{-1}	$10^{12}k_s^E$, Pa^{-1}
			Acetone–CCl_2CCl_2				
0.0000	1040	573		0.0000	1010	613	
0.0875	1038	595	−10	0.0517	1008	628	−7
0.2002	1038	624	−22	0.2026	1008	670	−27
0.3004	1039	654	−29	0.2225	1006	679	−27
0.3620	1042	671	−34	0.2400	1007	683	−30
0.5117	1052	719	−41	0.3937	1012	733	−44
0.5584	1057	735	−42	0.5020	1016	776	−46
0.5749	1059	740	−43	0.5285	1018	786	−47
0.6740	1072	779	−41	0.6357	1029	831	−47
0.8080	1098	837	−32	0.6781	1035	849	−47
0.8087	1098	838	−31	0.7320	1043	876	−42
0.9097	1126	891	−15	0.7855	1053	903	−38
0.9539	1143	914	−8	0.8143	1059	919	−34
1.0000	1165	939		0.8159	1059	920	−33
				0.8790	1076	954	−26
				0.9078	1085	971	−21
				0.9357	1094	989	−14
				0.9591	1102	1005	−8
				1.0000	1120	1030	
			Acetone–$CHClCCl_2$				
0.0000	1030	646		0.0000	1000	693	
0.0725	1032	661	−6	0.1287	1003	725	−11
0.1265	1035	672	−11	0.2115	1006	747	−17
0.1534	1037	677	−14	0.3950	1017	798	−28
0.2577	1043	701	−21	0.4517	1022	815	−30
0.3154	1045	717	−22	0.5533	1031	850	−29
0.3792	1050	734	−23	0.5881	1034	864	−27
0.4410	1056	750	−25	0.6435	1041	884	−26
0.4742	1060	758	−27	0.6750	1046	894	−26
0.6110	1075	801	−24	0.7326	1056	915	−25
0.6483	1079	814	−22	0.7422	1058	918	−25
0.6730	1084	821	−22	0.7552	1060	924	−24
0.7226	1091	839	−19	0.8669	1084	968	−17
0.8493	1118	884	−11	0.9344	1100	1000	−8
0.9613	1150	926	−2	1.0000	1120	1030	
1.0000	1165	939					
			Acetone–CH_2ClCH_2Cl				
0.0000	1194	563		0.0000	1156	608	
0.0606	1189	580	−6	0.1148	1147	643	−13
0.1476	1183	605	−13	0.1935	1140	670	−20
0.1536	1182	607	−14	0.3427	1131	722	−31
0.2384	1176	633	−20	0.4516	1127	762	−37
0.2723	1174	644	−21	0.5636	1122	809	−37
0.4446	1164	703	−27	0.6531	1118	851	−33
0.4673	1163	712	−27	0.6973	1117	871	−31
0.5776	1161	751	−29	0.7852	1115	916	−23
0.7027	1158	802	−25	0.8037	1116	924	−23
0.7967	1158	843	−20	0.9324	1118	991	−10
0.8614	1159	873	−14	0.9623	1119	1008	−6
0.8808	1160	881	−13	1.0000	1120	1030	
0.9265	1160	905	−6				
0.9814	1164	929	−3				
1.0000	1165	939					
			Acetone–CH_2Cl_2				
0.0000	1071	622		0.0000	1033	722	
0.0288	1072	670	0	0.2390	1031	812	16
0.1120	1068	702	9	0.3263	1032	846	23
0.1791	1066	728	16	0.3777	1035	863	25
0.2061	1066	737	18	0.5707	1052	922	24
0.2463	1068	749	19	0.5858	1054	926	24
0.3031	1070	767	21	0.6726	1064	951	22
0.4459	1079	810	24	0.7265	1071	966	20
0.4515	1080	811	24	0.7570	1076	973	18
0.6353	1098	863	25	0.7824	1081	978	15
0.6563	1102	867	23	0.8692	1094	1002	12
0.6724	1104	871	23	0.9311	1106	1015	6
0.6811	1105	873	22	0.9430	1108	1018	6
0.8656	1134	917	15	1.0000	1120	1030	
0.9128	1144	926	11				
1.0000	1165	939					

Table III (Continued)

temp = 298.15 K				temp = 308.15 K			
x_1[a]	u, m s^{-1}	$10^{12}k_s$, Pa^{-1}	$10^{12}k_s^E$, Pa^{-1}	x_1[a]	u, m s^{-1}	$10^{12}k_s$, Pa^{-1}	$10^{12}k_s^E$, Pa^{-1}
			Acetone–c-C_6H_{12}				
0.0000	1256	819		0.0000	1209	895	
0.0800	1238	845	16	0.1099	1188	930	20
0.1000	1234	851	20	0.1808	1172	957	38
0.1086	1233	853	21	0.2480	1161	976	48
0.1445	1226	863	27	0.3232	1151	994	55
0.2021	1217	877	34	0.3928	1145	1005	57
0.2378	1211	886	38	0.4231	1141	1012	60
0.2667	1206	894	43	0.4728	1135	1023	64
0.3336	1197	908	49	0.5283	1131	1030	64
0.3623	1193	914	52	0.8225	1114	1053	47
0.4236	1186	925	55	0.9513	1115	1044	21
0.4341	1185	926	55	1.0000	1120	1030	
0.4772	1181	932	56				
0.6175	1168	951	58				
0.6859	1164	956	55				
0.7951	1160	959	45				
0.8773	1160	955	31				
0.9116	1160	953	25				
1.0000	1165	939					

[a] x_1 refers to the mole fraction of acetone.

Table IV. Values of the Constants A_0, A_1, and A_2 of Eq 2, and the Standard Deviations $\delta(V^E)$ for the Various Systems of Acetone

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}
acetone–CCl_2CCl_2	298.15	0.3121	−0.3172	0.1957	0.0016
	308.15	0.4601	−0.3616	0.1965	0.0022
acetone–$CHClCCl_2$	298.15	−0.5258	0.2407	0.0892	0.0015
	308.15	−0.5484	0.2349	0.0516	0.0021
acetone–CH_2ClCH_2Cl	298.15	−0.1401	−0.0123	−0.0374	0.0013
	308.15	−0.2960	−0.0583	−0.0011	0.0017
acetone–CH_2Cl_2	293.15	0.4705	0.0300	−0.0118	0.0018
	303.15	0.4188	0.0820	−0.1293	0.0025
acetone–c-C_6H_{12}	308.15	4.5268	−0.0868	0.8732	0.0044

Table V. Values of the Constants B_0, B_1, and B_2 of Eq 3, and the Standard Deviations $\delta(k_s^E)$ for the Various Systems of Acetone at 298.15 and 308.15 K

system	T, K	$10^{12}B_0$, Pa^{-1}	$10^{12}B_1$, Pa^{-1}	$10^{12}B_2$, Pa^{-1}	$10^{12}\delta(k_s^E)$, Pa^{-1}
acetone–CCl_2CCl_2	298.15	−168.36	−44.79	19.37	1.7
	308.15	−192.71	−51.52	6.18	1.3
acetone–$CHClCCl_2$	298.15	−105.46	15.61	34.59	1.0
	308.15	−115.32	−23.16	−3.50	1.5
acetone–CH_2ClCH_2Cl	298.15	−110.12	−11.79	−9.41	1.2
	308.15	−141.70	−16.35	−0.23	1.3
acetone–CH_2Cl_2	298.15	109.42	31.76	−24.48	3.2
	308.15	98.54	2.12	0.86	1.3
acetone–c-C_6H_{12}	298.15	230.38	51.49	45.35	0.7
	308.15	259.11	97.00	95.67	3.4

Acknowledgment

We are extremely grateful to Professor R. P. Rastogi, Chemistry Department, Gorakhpur University, Gorakhpur, for encouragement during this investigation.

Registry No. Acetone, 67-64-1; tetrachloroethylene, 127-18-4; trichloroethylene, 79-01-6; methylene chloride, 75-09-2; 1,2-dichloroethane, 107-06-2; cyclohexane, 110-82-7.

Literature Cited

(1) Nath, J.; Dubey, S. N. *J. Phys. Chem.* **1980**, *84*, 2166–70.
(2) Rastogi, R. P.; Nath, J.; Singh, B. *J. Chem. Thermodyn.* **1977**, *9*, 831–4.
(3) Nath, J.; Dixit, A. P. *J. Chem. Eng. Data* **1983**, *28*, 190–1.
(4) Foster, R.; Fyfe, C. A. *J. Chem. Soc. B* **1966**, 926–9.
(5) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: Amsterdam, 1950.
(6) Rastogi, R. P.; Nath, J.; Misra, R. R. *J. Chem. Thermodyn.* **1971**, *3*, 307–17.
(7) Nath, J.; Dubey, S. N. *J. Chem. Thermodyn.* **1979**, *11*, 1163–5.
(8) Reddy, K. S.; Naidu, P. R. *J. Chem. Thermodyn.* **1976**, *8*, 1208–10.
(9) Freyer, E. B.; Hubbard, J. C.; Andrews, J. H. *J. Am. Chem. Soc.* **1929**, *51*, 759–70.
(10) McClellan, A. L.; Nicksic, S. W. *J. Phys. Chem.* **1965**, *69*, 446–9.

Received for review March 28, 1983. Revised manuscript received October 17, 1983. Accepted December 1, 1983. Thanks are also due to the University Grants Commission, New Delhi, for financial support.