

Table III. Invariant Points in the System Caprolactam + H₂O at 1 atm

	wt % CAP	<i>t</i> , °C
stable eutectic (ice + phase b + solution)	52.4	-13.7
metastable eutectic (ice + phase a + solution)	60.3	-19.3
incongruent melting point (phase a + phase b + solution)	67.5	-7

we know the composition and nature of solid phase c, and are able to form it at will, this extension does not seem useful. We presume c to be a metastable phase since it proved to be so elusive and impossible to form again.

The presence of two eutectics, one stable and one metastable, would give no problems in a continuous eutectic freezing process in a stirred vessel as long as some phase b were introduced to the crystallizer during start-up. It should then produce ice and phase b continuously with no trouble by operating at a temperature somewhat below -13.7 °C (e.g., -16 °C) to give a driving force of 2.3 °C for crystallization. In a

batch process, however, this might not be true and either eutectic might first form, in which case the temperature might have to be either -16 or -22 °C to get reasonable rates depending on which eutectic first formed on cooling the feed. In this (batch) case, one might have to introduce some crystals of phase b at the beginning of each batch. A temperature of -16 °C would, of course, be more economical for operation than would -22 °C.

Literature Cited

- (1) Puffr, Rudolph, *Collect. Czech. Chem. Commun.* 1969, 34, 1421-8 (see Table VI, p 1427).
- (2) Barduhn, A. J. "Waste-Water Renovation", AWTR-4; US Public Health Service, Department of Health, Education, and Welfare: Washington, DC, 1963; Part 1, p 1-32 (original submitted July 1961).
- (3) Stepakoff, G. L.; Siegelman, D.; Johnson, R.; Gibson, W. *Desalination* 1974 14, 25-38.
- (4) Seidell, A.; Linke, W. F. "Solubilities"; American Chemical Society: Washington, DC, 1965; Vol. II, p 755 for (NH₄)₂SO₄ in water and pp 773-4 for CAP + (NH₄)₂SO₄ + water (at 30 and 50 °C only).

Received for review August 21, 1981. Accepted February 8, 1982. This work was supported in part by NSF Grant ENG 77-14894.

Binary Systems of Tetrachloroethylene with Benzene, Toluene, *p*-Xylene, Carbon Tetrachloride, and Cyclohexane. 1. Ultrasonic Velocities and Adiabatic Compressibilities at 293.15 and 303.15 K, Dielectric Constants at 298.15 and 308.15 K, and Refractive Indexes at 298.15 K

Jagan Nath* and B. Narain

Chemistry Department, Gorakhpur University, Gorakhpur 273001, India

Measurements of ultrasonic velocities and adiabatic compressibilities at 293.15 and 303.15 K, dielectric constants at 298.15 and 308.15 K, and refractive indexes at 298.15 K have been made for binary liquid mixtures of tetrachloroethylene (C₂Cl₄) with benzene, toluene, *p*-xylene, carbon tetrachloride, and cyclohexane. The values of the quantity k_s^E , which refers to the deviations of the adiabatic compressibilities of the mixtures from the ideal mole fraction mixture law values, have been calculated and have been fitted by the method of least squares to the equation $k_s^E = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2]$ where x_1 refers to the mole fraction of C₂Cl₄, x_2 refers to the mole fraction of aromatic hydrocarbon, CCl₄, or *c*-C₆H₁₂, and *A*, *B*, and *C* are constants which are characteristic of a system. For the systems C₂Cl₄-aromatics at 293.15 and 303.15 K, the values of k_s^E at $x_1 = 0.5$ have the sequence benzene > toluene > *p*-xylene. The values of the quantity $\Delta\epsilon$, which refers to the deviations of the dielectric constants of the mixtures from the ideal volume fraction mixture law values, have also been calculated. The values of $\Delta\epsilon$ at 298.15 K are found to be slightly negative or zero for all of the systems, and, at 308.15 K, the values are less negative or slightly positive. The values of the dipole moments of cyclohexane, carbon tetrachloride, and *p*-xylene, as determined from the dielectric constant and refractive index data for their dilute solutions in C₂Cl₄, have been found to be 0.04, 0.26, and 0.12 D, respectively.

Introduction

The binary systems of tetrachloroethylene (C₂Cl₄) with aromatic hydrocarbons, carbon tetrachloride (CCl₄), 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 C₂Cl₄ with aromatics and CCl₄ can be visualized to be due to the presence of four Cl atoms and an olefinic π -electron system in C₂Cl₄, on account of which it can act both as a σ - and π -type sacrificial electron acceptor toward aromatics and as a π -type electron donor toward CCl₄. The system of cyclohexane with C₂Cl₄, in which case only the dispersion 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. The measurements of excess volumes (V^E) for binary mixtures of C₂Cl₄ with benzene, toluene, *p*-xylene, CCl₄, and cyclohexane at 293.15 and 303.15 K have, however, been reported (1, 2). But these do not provide useful information concerning the existence of specific interaction between the components of the various systems. Hence, in the present program, the measurements of ultrasonic velocities in, and adiabatic compressibilities, dielectric constants, and refractive indexes of, binary liquid mixtures of C₂Cl₄ with benzene, toluene, *p*-xylene, CCl₄, and cyclohexane have been undertaken, and the results obtained have been interpreted in this paper.

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 (3). Carbon tetrachloride (AR, BDH) was purified as described by Rastogi and Nath (4). *p*-Xylene (E. Merck, Darmstadt) of synthesis quality was subjected to fractional crystallizations, placed over anhydrous calcium chloride overnight, and then fractionally distilled. Cyclohexane (E. Merck, Darmstadt) and tetrachloroethylene (E. Merck, Darmstadt), both of which were of spectral grade, were placed over anhydrous calcium chloride overnight and then subjected to distillations.

The densities of the purified samples of benzene, toluene, *p*-xylene, carbon tetrachloride, cyclohexane, and tetrachloroethylene, as measured at 303.15 K, were found to be 0.868 41, 0.857 75, 0.852 35, 1.574 76, 0.769 16, and 1.606 39 g cm⁻³, which are in good agreement with the literature values (5), 0.868 36, 0.857 70, 0.852 30, 1.574 80, 0.769 14, and 1.606 40 g cm⁻³, respectively, for the various liquids in the same order.

Methods. The ultrasonic velocities, u , in pure liquids and their binary mixtures were measured by using 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 (6)

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

where ρ refers to the density. The densities used to calculate k_s for pure liquids at 293.15 and 303.15 K were the same as those reported by Timmermans (5), whereas the densities used to calculate k_s for mixtures were estimated from the densities of the pure components and the measurements on excess volumes (1, 2).

The measurements of dielectric constants (ϵ), which are accurate to ± 0.001 , were made at 298.15 and 308.15 K, and at a frequency of 1.8 MHz s⁻¹, with a Dekameter (Type DK₀₃, Wissenschaftlich-Technische, Werkstätten, Germany), by using a cell (type MFL 1/S, Nr. 2078) of capacity of 10 cm³.

Refractive index (n) measurements were carried out at 298.15 K by using a thermostated Abbe refractometer. The values of refractive indexes were obtained for sodium D light.

Results and Discussion

The values of u and k_s for the various systems are given in Table I, whereas the values of the dielectric constants and refractive indexes are given in Tables II and III, respectively. The values of $10^9 k_s$ for benzene, toluene, and CCl₄ at 303.15 K have been found to be 71.4, 71.8, and 78.4 atm⁻¹, respectively, which can be compared with the corresponding values 71.5, 71.8, and 78.8 atm⁻¹ for the various liquids in the same order, as obtained by Freyer, Hubbard, and Andrews (7). The dielectric constants of benzene, toluene, *p*-xylene, CCl₄, and cyclohexane at 298.15 K have been found to be 2.274, 2.376, 2.260, 2.229, and 2.014, respectively, which are in good agreement with the corresponding literature (8) values 2.274, 2.379, 2.262, 2.228, and 2.015 for the various liquids in the same order. The values of the refractive indexes for benzene, toluene, *p*-xylene, CCl₄, and cyclohexane at 298.15 K have been found to be 1.4980, 1.4940, 1.4932, 1.4576, and 1.4236, respectively, which are in good agreement with the respective values 1.4981, 1.494 05, 1.493 20, 1.4576, and 1.423 54 available in the literature (5).

The values of the quantity k_s^E , which refers to the deviations of the values of k_s (as obtained from eq 1) for the various mixtures from the ideal mole fraction mixture law values, are also given in Table I and have been fitted by the method of least squares to the equation

$$k_s^E = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2] \quad (2)$$

where A , B , and C are constants characteristic of a system,

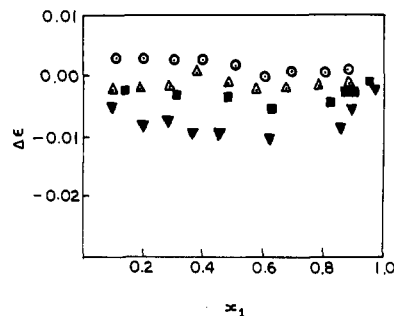


Figure 1. Plot of the values of $\Delta\epsilon$ vs. the mole fraction x_1 of C_2Cl_4 , for the systems of C_2Cl_4 with toluene and CCl_4 . C_2Cl_4 -toluene: (\blacktriangledown) 298.15 and (\circ) 308.15 K. C_2Cl_4 - CCl_4 : (\blacksquare) 298.15 and (\triangle) 308.15 K.

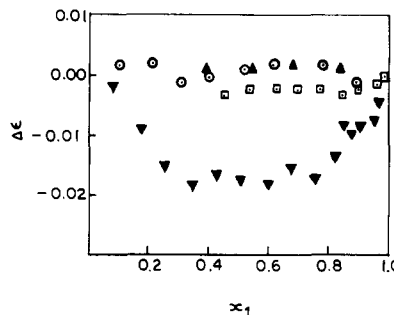


Figure 2. Plot of $\Delta\epsilon$ vs. the mole fraction x_1 of C_2Cl_4 , for the systems of C_2Cl_4 with cyclohexane and *p*-xylene. C_2Cl_4 -cyclohexane: (\blacktriangledown) 298.15 and (\circ) 308.15 K. C_2Cl_4 -*p*-xylene: (\square) 298.15 and (\blacktriangle) 308.15 K.

x_1 is the mole fraction of C_2Cl_4 , and x_2 is the mole fraction of the aromatic hydrocarbon, CCl_4 , or $c-C_6H_{12}$. The values of the constants A , B , and C for the various systems at 293.15 and 303.15 K are given in Table IV. The values of the refractive indexes, n_{12} , for the various systems have been fitted to the equation

$$n_{12} = x_1 n_1 + x_2 n_2 + x_1 x_2 D \quad (3)$$

where D is a constant characteristic of a system. The values of the constant D along with those of the standard deviations $\sigma(n)$ in the values of refractive indexes of the various systems are given in Table V.

The dielectric constants ϵ_{12} of the various mixtures have been used to calculate the values of the quantity $\Delta\epsilon$ from the relation

$$\Delta\epsilon = \epsilon_{12} - \varphi_1 \epsilon_1 - \varphi_2 \epsilon_2 \quad (4)$$

where φ_1 and φ_2 refer to volume fractions of components 1 and 2, respectively, and ϵ_1 and ϵ_2 are the dielectric constants of the two pure liquids. The values of $\Delta\epsilon$ for the systems C_2Cl_4 -toluene and C_2Cl_4 - CCl_4 at 298.15 and 308.15 K have been plotted vs. x_1 in Figure 1, whereas those for C_2Cl_4 -cyclohexane and C_2Cl_4 -*p*-xylene have been plotted in Figure 2. Figures 1 and 2 show that the values of $\Delta\epsilon$ at 298.15 K are slightly negative or zero in the case of all of the systems, and the values of $\Delta\epsilon$ for all of the systems become less negative or very slightly positive as the temperature changes from 298.15 to 308.15 K.

The values of k_s^E can be discussed from the viewpoint of intermolecular interactions (9). The various types of interactions that are present between the molecules in different systems are dispersion forces which should make a positive contribution to the values of k_s^E , and charge-transfer, hydrogen-bonding, dipole-dipole, and dipole-induced dipole interactions which are expected to make negative contributions. The data

Table I. Experimental Values of Ultrasonic Velocities in, and Adiabatic Compressibilities for, the Various Mixtures of Tetrachloroethylene at 293.15 and 303.15 K

temperature = 293.15 K				temperature = 303.15 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
C ₂ Cl ₄ -Benzene							
0.0000	1325	65.7		0.0000	1278	71.4	
0.0910	1274	65.4	0.6	0.0907	1229.5	71.1	0.7
0.1398	1250.5	65.2	0.8	0.1508	1202	70.8	1.1
0.2878	1195	63.8	0.8	0.2316	1170	70.2	1.3
0.3936	1162	62.9	0.9	0.3057	1146	69.4	1.4
0.4649	1143	62.3	1.0	0.4695	1103	67.4	1.2
0.5405	1124.5	61.6	1.0	0.5485	1086	66.4	1.0
0.6374	1105	60.5	0.9	0.6353	1072	65.0	0.6
0.7504	1085	59.3	0.7	0.7120	1058	64.2	0.6
0.8529	1071	58.0	0.4	0.8068	1045	62.9	0.4
1.0000	1054	56.2		0.8939	1035	61.6	0.0
				1.0000	1022	60.4	
C ₂ Cl ₄ -Toluene							
0.0000	1328	66.3		0.0000	1283	71.8	
0.0945	1285	65.6	0.3	0.2683	1181	69.1	0.4
0.1773	1250	65.1	0.6	0.4310	1134	67.2	0.3
0.3345	1198	63.5	0.6	0.5098	1113	66.5	0.5
0.4307	1170	62.5	0.6	0.5928	1094	65.5	0.5
0.5104	1149	61.7	0.6	0.6803	1077	64.3	0.3
0.6006	1129	60.6	0.4	0.7458	1065	63.4	0.1
0.6747	1111	60.0	0.5	0.8276	1049	62.5	0.1
0.8143	1085	58.3	0.2	1.0000	1022	60.4	
0.9117	1067	57.3	0.2				
1.0000	1054	56.2					
C ₂ Cl ₄ - <i>p</i> -Xylene							
0.0000	1327	66.8		0.0000	1288	71.7	
0.3760	1201	63.0	0.2	0.1209	1245.5	70.3	0.0
0.4707	1173	62.2	0.4	0.1978	1219	69.5	0.0
0.5462	1154	61.3	0.3	0.2910	1188	68.8	0.4
0.6232	1134	60.5	0.3	0.4738	1136.5	66.8	0.5
0.7036	1115.5	59.6	0.3	0.5511	1118	65.7	0.2
0.8508	1083	58.0	0.2	0.6326	1098	64.8	0.2
0.9294	1068	57.0	0.1	0.8340	1054	62.4	0.1
1.0000	1054	56.2		0.9028	1041	61.5	0.0
				1.0000	1022	60.4	
C ₂ Cl ₄ -CCl ₄							
0.0000	938	72.3		0.0000	906	78.4	
0.0899	948	70.6	-0.3	0.0853	916	76.6	-0.3
0.1630	957	69.2	-0.5	0.1584	924	75.1	-0.4
0.2420	965	68.0	-0.4	0.2404	933	73.6	-0.5
0.3087	973	66.8	-0.5	0.4802	964	68.6	-1.2
0.4114	986	64.9	-0.8	0.5671	972	67.3	-0.9
0.4903	995	63.6	-0.8	0.7367	994	64.2	-0.9
0.5692	1004	62.4	-0.7	0.8779	1010	62.0	-0.6
0.8223	1034	58.6	-0.5	1.0000	1022	60.4	
0.9081	1042	57.6	-0.1				
1.0000	1054	56.2					
C ₂ Cl ₄ -Cyclohexane							
0.0000	1279	79.6		0.0000	1228.5	87.3	
0.2581	1182	73.7	0.1	0.1005	1189	84.6	0.0
0.4194	1139.5	69.9	0.1	0.2610	1137	80.4	0.1
0.6731	1090	64.1	0.3	0.3304	1118.5	78.6	0.2
0.7288	1083	62.6	0.1	0.4223	1097	76.1	0.2
0.7964	1073	61.2	0.2	0.5705	1071.5	71.8	-0.2
0.8861	1064	58.9	0.0	0.6699	1056	69.1	-0.2
1.0000	1054	56.2		0.7343	1048	67.3	-0.2
				0.8302	1038	64.7	-0.3
				0.8997	1032	62.8	-0.3
				1.0000	1022	60.4	

^a x_1 refers to the mole fraction of C₂Cl₄.

show that for the systems of C₂Cl₄ with aromatics at both temperatures, k_s^E at $x_1 = 0.5$ has the sequence

benzene > toluene > *p*-xylene

This trend in the values of k_s^E for the systems of C₂Cl₄ with aromatics may be explained to be due to the increasing strength of interaction of C₂Cl₄ with the aromatic hydrocarbon having an increasing number of CH₃ substituents attached to

the aromatic ring. It has been pointed out by Thacker and Rowlinson (10), Reddy et al. (11), and Fort and Moore (9) that the difference in boiling points of the components can be taken as a measure of the strength of interaction between the components. For the systems C₂Cl₄-aromatics, the values of k_s^E at $x_1 = 0.5$ have been plotted vs. the difference (Δ (bp), K) in the boiling point of the second component and that of C₂Cl₄ in Figure 3, which supports the above viewpoint concerning the

Table II. Dielectric Constants for the Various Mixtures of Tetrachloroethylene at 298.15 and 308.15 K

temperature = 298.15 K		temperature = 308.15 K	
x_1^a	ϵ	x_1^a	ϵ
C ₂ Cl ₄ -Toluene			
0.0000	2.376	0.0000	2.356
0.1020	2.362	0.1110	2.349
0.2053	2.349	0.2078	2.340
0.2890	2.342	0.3089	2.331
0.3670	2.333	0.4061	2.322
0.4618	2.324	0.5115	2.311
0.6257	2.307	0.6081	2.300
0.8682	2.285	0.7046	2.292
0.9098	2.284	0.8046	2.283
0.9717	2.281	0.9018	2.273
1.0000	2.280	1.0000	2.263
C ₂ Cl ₄ - <i>p</i> -Xylene			
0.0000	2.260	0.0000	2.244
0.4622	2.265	0.3903	2.252
0.5427	2.268	0.5479	2.255
0.6331	2.270	0.6879	2.258
0.7002	2.271	0.8461	2.261
0.7783	2.273	1.0000	2.263
0.8538	2.274		
0.9080	2.276		
0.9604	2.278		
0.9845	2.280		
1.0000	2.280		
C ₂ Cl ₄ -CCl ₄			
0.0000	2.229	0.0000	2.210
0.1359	2.234	0.1005	2.214
0.3180	2.243	0.1942	2.219
0.4826	2.251	0.2862	2.224
0.6300	2.257	0.3889	2.232
0.8235	2.267	0.4935	2.236
0.8867	2.273	0.5828	2.240
0.9114	2.274	0.6777	2.245
0.9572	2.277	0.7882	2.251
1.0000	2.280	0.8929	2.257
		1.0000	2.263
C ₂ Cl ₄ -Cyclohexane			
0.0000	2.014	0.0000	1.999
0.0831	2.033	0.1063	2.028
0.1752	2.049	0.2090	2.054
0.2598	2.065	0.3077	2.076
0.3512	2.086	0.3988	2.101
0.4305	2.109	0.5265	2.135
0.5148	2.130	0.6219	2.162
0.6093	2.154	0.7884	2.206
0.6820	2.177	0.8980	2.234
0.7616	2.197	1.0000	2.263
0.8360	2.221		
0.8630	2.234		
0.8889	2.240		
0.9112	2.247		
0.9529	2.260		
0.9760	2.269		
1.0000	2.280		

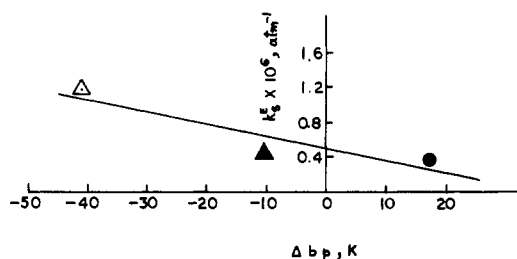
^a x_1 refers to the mole fraction of C₂Cl₄.Figure 3. Plot of k_s^E for equimolar mixtures at 303.15 K vs. the difference (Δ (bp), K) in the boiling points of the second component and C₂Cl₄: (Δ) C₂Cl₄-benzene; (\blacktriangle) C₂Cl₄-toluene; (\bullet) C₂Cl₄-*p*-xylene.

Table III. Values of the Refractive Indexes for the Various Systems at 298.15 K

x_1^a	n	x_1^a	n
C ₂ Cl ₄ -Benzene			
0.0000	1.4980	0.7382	1.5004
0.1699	1.4984	0.8483	1.5014
0.3061	1.4986	0.9373	1.5022
0.3721	1.4988	0.9691	1.5026
0.4863	1.4992	1.0000	1.5032
0.6074	1.4994		
C ₂ Cl ₄ -Toluene			
0.0000	1.4940	0.4993	1.4978
0.0592	1.4942	0.5687	1.4984
0.1040	1.4946	0.6868	1.4994
0.1879	1.4950	0.8011	1.5008
0.2568	1.4954	0.8810	1.5012
0.3379	1.4960	1.0000	1.5032
0.4048	1.4970		
C ₂ Cl ₄ - <i>p</i> -Xylene			
0.0000	1.4932	0.6030	1.4990
0.0978	1.4938	0.6891	1.4998
0.2115	1.4952	0.7498	1.5004
0.3734	1.4960	0.8324	1.5010
0.4336	1.4966	0.8897	1.5018
0.5554	1.4982	1.0000	1.5032
C ₂ Cl ₄ -CCl ₄			
0.0000	1.4576	0.4791	1.4804
0.0667	1.4608	0.5652	1.4848
0.0863	1.4620	0.6021	1.4860
0.1582	1.4654	0.7206	1.4916
0.2380	1.4692	0.8174	1.4956
0.3141	1.4726	0.8748	1.4980
0.3897	1.4764	1.0000	1.5032
C ₂ Cl ₄ -Cyclohexane			
0.0000	1.4236	0.5886	1.4648
0.0737	1.4282	0.7358	1.4772
0.1524	1.4332	0.8504	1.4884
0.2640	1.4396	1.0000	1.5032
0.4192	1.4520		

^a x_1 refers to the mole fraction of C₂Cl₄.Table IV. Values of the Constants A , B , and C of Eq 2 for the Various Systems at 293.15 and 303.15 K

system	T , K	$10^6 A$, atm ⁻¹	$10^6 B$, atm ⁻¹	$10^6 C$, atm ⁻¹
C ₂ Cl ₄ -benzene	293.15	3.70	-1.82	2.61
	303.15	4.62	-5.02	0.04
C ₂ Cl ₄ -toluene	293.15	2.24	-1.19	1.17
	303.15	1.79	-0.86	-1.54
C ₂ Cl ₄ - <i>p</i> -xylene	293.15	1.25	0.75	-0.51
	303.15	1.47	0.06	-2.35
C ₂ Cl ₄ -CCl ₄	293.15	-2.90	0.67	0.35
	303.15	-3.87	-1.48	-1.02
C ₂ Cl ₄ -cyclohexane	293.15	1.00	0.55	-1.82
	303.15	0.24	-2.06	-2.78

Table V. Values of the Constant D of Eq 3 and the Standard Deviations $\sigma(n)$ for the Various Systems at 298.15 K

system	D	$\sigma(n)$
C ₂ Cl ₄ -benzene	-0.007 45	0.0004
C ₂ Cl ₄ -toluene	-0.004 62	0.0003
C ₂ Cl ₄ - <i>p</i> -xylene	-0.002 57	0.0003
C ₂ Cl ₄ -CCl ₄	0.004 43	0.0002
C ₂ Cl ₄ -cyclohexane	-0.022 28	0.0005

Increased strength of interaction of C₂Cl₄ with the aromatic hydrocarbon having an increased number of CH₃ substituents in the aromatic ring. This fact further becomes quite evident when we examine the plot (see Figure 4) of the values of k_s^E vs. the excess volumes (V) for the equimolar mixtures of C₂Cl₄ with aromatics at 303.15 K. Figure 4 shows that the excess

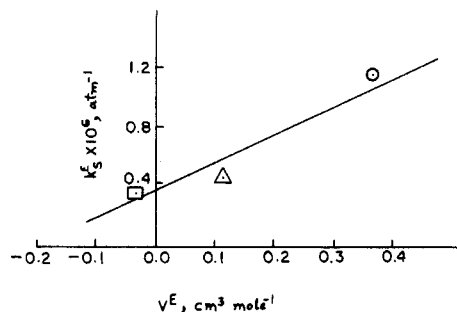


Figure 4. Plot of k_s^E vs. V^E for equimolar mixtures at 303.15 K: (O) C_2Cl_4 -benzene; (Δ) C_2Cl_4 -toluene; (\square) C_2Cl_4 -*p*-xylene.

volumes decrease as the number of CH_3 substituents attached to the aromatic ring increases, and these changes in V^E parallel the changes in the values of k_s^E .

In order to assess the perturbation that will be caused to the molecules of cyclohexane, CCl_4 , and *p*-xylene as a result of their interactions with C_2Cl_4 , we have estimated the dipole moments of cyclohexane, carbon tetrachloride, and *p*-xylene in C_2Cl_4 from the refractive index, dielectric constant, and specific volume (obtained by using data on excess volumes (1, 2)) for dilute solutions of cyclohexane, carbon tetrachloride, and *p*-xylene in C_2Cl_4 at 298.15 K, by using the method described by Halverstadt and Kumler (12). The dipole moments of cyclohexane, carbon tetrachloride, and *p*-xylene in tetrachloroethylene have been found to be 0.04, 0.26, and 0.12 D, respectively. The dipole moments (13) of these substances are normally zero. The value of the dipole moment, 0.04 D, of cyclohexane is negligibly small. The values 0.12 and

0.26 D of the dipole moments of *p*-xylene and carbon tetrachloride, respectively, in tetrachloroethylene suggest the formation of electron donor-acceptor species of C_2Cl_4 with *p*-xylene and CCl_4 in the liquid state.

Acknowledgment

We are extremely grateful to Professor R. P. Rastogi, Head of the Chemistry Department, Gorakhpur University, for invaluable suggestions and discussions. We are also thankful to Professor N. K. Sanyal, Head of the Physics Department, for providing a sodium lamp.

Literature Cited

- (1) Rastogi, R. P.; Nath, J.; Singh, B. *J. Chem. Thermodyn.* 1977, 9, 831.
- (2) Nath, J.; Singh, B. *J. Chem. Thermodyn.* 1978, 10, 307.
- (3) Rastogi, R. P.; Nath, J.; Misra, R. R. *J. Chem. Thermodyn.* 1971, 3, 307.
- (4) Rastogi, R. P.; Nath, J. *Indian J. Chem.* 1967, 5, 249.
- (5) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: Amsterdam, 1950.
- (6) Reddy, K. S.; Naidu, P. R. *J. Chem. Thermodyn.* 1976, 8, 1208.
- (7) Freyer, E. B.; Hubbard, J. C.; Andrews, J. H. *J. Am. Chem. Soc.* 1929, 51, 759.
- (8) Lange, N. A. "Hand-book of Chemistry"; McGraw-Hill: New York, 1967.
- (9) Fort, R. J.; Moore, W. R. *Trans. Faraday Soc.* 1965, 61, 2102.
- (10) Thacker, R.; Rowlinson, J. S. *J. Chem. Phys.* 1953, 21, 2242.
- (11) Reddy, K. C.; Subrahmanyam, S. V.; Bhimasenachar, J. *Trans. Faraday Soc.* 1962, 58, 2352.
- (12) Halverstadt, I. F.; Kumler, W. D. *J. Am. Chem. Soc.* 1942, 64, 2988.
- (13) McClellan, A. L. "Tables of Experimental Dipole Moments"; W. H. Freeman: San Francisco, CA, 1963.

Received for review September 14, 1981. Accepted April 6, 1982. Thanks are due to the Council of Scientific and Industrial Research, New Delhi, for financial support.

Densities and Refractive Indices of Pure Alcohols as a Function of Temperature

Juan Ortega

Escuela Técnica Superior de Ingenieros Industriales, Polytechnic University of Las Palmas, Canary Islands, Spain

Densities and refractive indices of normal alcohols from methanol to 1-decanol were measured in the temperature range from 20 to 80 °C for the refractive indices and from 20 to 45 °C for the densities. In both cases the data are discussed and compared to the results obtained by other scientists, having been correlated vs. temperature through an empirical relationship. To check the accuracy of experimental densities and refractive indices, the Eykman equation is used within the common interval of temperatures (20-45 °C).

The degree to which the velocity of propagation of an electromagnetic disturbance is affected by the medium through which it travels depends upon the molecular charge distributions that the radiation encounters per unit of its path length. Thus, in a liquid under ordinary ambient conditions, the packing degree of the molecules is one of the determining factors for the refractive index. Therefore, the effect of temperature on the usual refractive index of transparent liquids is primarily due to its influence on the degree of packing of the molecules in the liquid.

The refractive indices of all liquids decrease with increasing temperature. Most organic liquids have temperature coefficients

between -0.00035 and -0.00045 °C⁻¹. An average value of -0.00045 °C⁻¹ in applying temperature corrections to data is often recommended by some authors.

Density is a physical property of extreme importance in the characterization, identification and utilization of materials. The wide range of densities covered by the compounds provides a quick way of rough identification or classification of many substances with apparatus that can be carried into the field or plant. Densities of organic liquids range from about 3.3 to 0.6 g cm⁻³. In general, the density of a substance decreases with increasing temperature.

In this work both properties have been determined for the primary set of normal alcohols at temperatures higher than ambient conditions.

Normal alcohols have been the subject of a great deal of study. Actual investigations generally require highly accurate physical properties. Although several sets of density and refractive index data exist for normal alcohols at 20 and 25 °C, in the literature there are few data for higher temperatures. The present work was undertaken to resolve the densities of pure normal alcohols at temperatures higher than 25 °C at atmospheric pressure. Therefore, the densities of normal alcohols from methanol to 1-decanol were determined at 5 °C intervals from 20 to 45 °C. For the same alcohols the refractive indices