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Research Article

Viscometric Intermolecular Interaction studies in binary liquid mixture of carbon tetrachloride with benzene and its substituted products.

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ABSTRACT

Viscosities (η) of binary liquid mixtures of carbon tetrachloride with benzene and its substituted products viz. toluene, m-xylene, ethyl benzene and chlorobenzene have been measured at two different temperatures 293.15 k and 303.15k. Excess volume of mixing (V^E) and deviation of viscosities ($\Delta\eta$) of mixtures from ideal mole fraction law and parameter (d) as a measure of strength of intermolecular interaction between components of binary mixtures have been calculated from data of viscosities. Excess volumes have been found to be negative and positive in sign for binary mixtures of carbon tetrachloride with toluene and chlorobenzene and carbon tetrachloride with benzene, ethyl benzene and m-xylene respectively at entire mole fraction range and at both temperatures i.e. 293.15 k and 303.15 k. On the other hand, $\Delta\eta$ were found to be negative for binary mixtures of carbon tetrachloride with toluene, m-xylene and chlorobenzene, except the binary mixture of carbon tetrachloride with benzene at entire mole fraction range and temperature metntioned. Positive value of excess volumes for three mixtures (carbon tetrachloride with benzene, m-xylene and ethyl benzene) show weak intermolecular interactions between components. However, the negative value of $\Delta\eta$ for binary mixtures of carbon tetrachloride with toluene, m-xylene and chlorobenzene show weak interaction between components. The different average value of parameter d (d_{av}) for different binary systems show different extent of molecular

interactions present there in. The experimental values of V^E have been analyzed in the light of Flory`s theory.

Key words: Viscosities, excess volume, intermolecular interactions, Flory`s theory.

INTRODUCTION

In recent year's study of intermolecular interactions, in various binary liquid mixtures by several authors [1-9] through volumetric, densitometric, ultrasonic etc., studies have got considerable importance in framing theoretical models as well as its applications in a number of branches of science. In continuation with the earlier attempts [(1-3,7-9)] made by Gupta and et al on measurement of excess volumes, densities, ultrasonic velocities etc. of a number of binary mixtures to detect and deal with intermolecular interaction in binary systems both qualitatively and quantatively. The present work deals with viscometric studies of inter molecular interactions in carbon tetrachloride with benzene, toluene, m-xylene, ethyl benzene and chlorobenzene at entire mole fraction range at temperatures 293.15k and 303.15 k. The regular trend in variation of V^E and $\Delta\eta$ for binary mixtures[1] has not been found in present case. Some of the mixtures show positive sign while others show negative sign of V^E and $\Delta\eta$ both. The low positive value of V^E and $\Delta\eta$ show existence of some specific interactions there in . Negative values of both V^E and $\Delta\eta$ for carbon tetrachloride + toluene + chlorobenzene counterbalance their effects showing some weak specific interactions between unlike components. This is supported by low positive and negative values of parameter, 'd' for these binary mixtures. Excess volumes of mixing (V^E) calculated from density measurements have been compared with theoretical values calculated on the basis of Flory`s theory. [10]

EXPERIMENTAL

Carbon tetrachloride (AR, CDH) was fractionally distilled thrice and stored. Benzene (AR, CDH) was shaken with Conc. H_2SO_4 to remove trace of thiophene, present if any. It was then washed with 10% Na_2C0_3 followed by distilled water till all alkali was removed. It was then dried over anhydrous $CaCl_2$, fractionally distilled over P_2O_5 and stored over Na-wire. Toluene (AR, CDH) was shaken with conc. H_2SO_4 to remove thiophene (if present). It was subsequently shaken with distilled water to remove most of the acid and then with 10% solution of sodium carbonate. It was again shaken with distilled water till it became free from alkali. Further it was dried over anhydrous calcium chloride, fractionally distilled over P_2O_5 and stored over sodium wire. m-xyleme (AR, CDH) was fractionally distilled thrice and was stored over sodium wire. Ethyl benzene (AR, CDH) was fractionally distilled thrice and was stored over sodium wire. Chlorobenzene (AR, CDH) was fractionally distilled thrice and dried over calcium chloride, filtered and distilled using an air condenser. The purities of the different component liquids were verified from density measurement. Binary liquid mixtures of varying composition were prepared[1.] The densities were measured by the use of pyknometer thermostated at desired temperatures. The viscosities of binary liquid mixtures were measured by the use of calibrated Ostwald Viscometer designed properly to minimize the loss of liquid components through vaporization .All the measurements were carried out at temperatures 293.15k and 303.15k using thermostat.

RESULTS AND DISCUSSION

Excess volumes (V^E) of binary liquid mixtures of varying composition were calculated using relations.

$$V^E = V^{obs} - V^{id} \quad \text{... (1)}$$

Where V^{obs} = Experimental value of volume of binary liquid mixture

$$= \frac{M_1X_1 + M_2X_2}{\rho} \quad \text{... (2)}$$

Where ρ is the density of binary liquid mixture of given composition measured. V^{id} refers to the value for ideal binary mixture.

$$V^{id} = x_1 v_1^0 + x_2 v_2^0 = \frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2} \quad \text{... (3)}$$

Where M_1 and M_2 are molar masses and ρ_1 and ρ_2 are densities of component liquid in pure state x_1 and x_2 are mole fractions of first and second components in mixture.

Thus, $$V^E = \frac{M_1x_1 + M_1x_2}{\rho} - \left[\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right] \quad \text{... (4)}$$

Experimental values of different parameters for the pure component liquids at 303.15k have been recorded in **Table-1**

Table -1: Parameters for the pure component liquids at 30.3 15 K

Liquid	V/cm^{3}mol^{-1}	α x103/K^{-1}	γ /Cal.cm^{-3}K^{-1}	V /cm3.mol^{-1}	V*/cm3.mol^{-1}	T*/K	P*/Cal.cm^{-3}	T
Carbon								
Tetrachloride	097.68	1.240	0.263	1.2986	75.23	4748	137	0.06386
Benzene	089.95	1.233	0.92	1.2975	69.33	4730	149	0.06408
Toluene	107.424	1.085	0.278	1.2684	84.69	5046	135.5	0.06007
m-xylene	124.094	1.008	0.270	1.2527	99.06	5429	128.4	0.05775

The dynamic viscosity 'η', $\Delta\eta$ and parameters (d) for mentioned binary mixtures are given in Table-2. $\Delta\eta$ have been calculated using the formula

$$\Delta\eta = \eta(x_1\eta_1 + x_2\eta_2) \quad \text{... (5)}$$

Where $\Delta\eta$ is the deviation of viscosities of mixture from ideal mole fraction mixture law $\eta 1$ and $\eta 2$ refer to dynamic viscosities of pure components and x_1 and x_2 are their mole fractions. $\Delta\eta$ like V^E have been fitted in the following equation

$$\Delta\eta = x_1 x_2 [B_O + B_1 (x_1 - x_2) + B_2 (x_1 - x_2)^2] \quad \text{... (6)}$$

Table -2: Viscosities (η), $\Delta\eta$ and (d) at 293.25K and 303.15K

X_1	$10^3\eta$/kgm^{-1}s^{-1}	$10^3\ \Delta\eta$/kg m^{-1} s^{-1}	d	X_1	$10^3\eta$/kgm^{-1}s^{-1}	$10^3\ \Delta\eta$/kg m^{-1} s^{-1}	d
X_1 carbon tetrachloride + x_2 benzene							
293.15 K							*303.15 K*
0.0000	6.4800	0.000	0.0000	0.0000	5.7000	0.000	0.0000
0.1216	6.9359	0.064	0.1773	0.1068	5.9980	0.001	0.0894
0.2816	7.5471	0.160	0.1919	0.2353	6.3572	0.003	0.0869
0.3556	7.8103	0.185	0.1887	0.3173	6.5900	0.008	0.0879
0.4035	7.9935	0.214	0.1957	0.4148	6.8663	0.013	0.0880
0.5600	8.5156	0.232	0.1917	0.5334	7.2050	0.022	0.0900
0.6507	8.8108	0.235	0.1967	0.6092	7.4180	0.025	0.0905
0.7131	9.0056	0.229	0.2024	0.7076	7.6902	0.023	0.0888
0.8535	9.4358	0.207	0.2514	0.8216	7.9980	0.014	0.0842
0.9557	9.5983	0.137	0.2818	0.9143	8.2477	0.006	0.0800
1.0000	9.7005	0.000	0.0000	1.0000	8.4800	0.000	0.0000
X_1	$10^3\eta$/kgm^{-1}s^{-1}	$10^3\ \Delta\eta$/kg m^{-1} s^{-1}	d	X_1	$10^3\eta$/kgm^{-1}s^{-1}	$10^3\ \Delta\eta$/kg m^{-1} s^{-1}	d
X_1 carbon tetrachloride + x_2 toluene							
293.15 K							*303.15 K*
0.0000	5.9059	0.000	0.0000	0.0000	5.2505	0.000	0.0000
0.1570	6.2809	-0.221	-0.1234	0.1041	5.5457	-0.041	0.0514
0.2675	6.3310	-0.590	-0.3227	0.2074	5.8302	-0.090	0.0322
0.3251	6.4398	-0.700	-0.3408	0.3118	6.1436	-0.114	0.0354
0.4055	6.7189	-0.726	-0.2996	0.4188	6.4762	-0.127	0.0371

0.5279	7.2740	-0.635	-0.2150	0.5168	6.7696	-0.150	0.0255
0.6113	7.6936	-0.532	-0.1637	0.6213	7.1421	-0.115	0.0418
0.7046	8.1728	-0.407	-0.1190	0.7103	7.4394	-0.105	0.0399
0.8001	8.6869	-0.255	-0.0698	0.8029	7.7506	-0.093	0.0287
0.9120	9.2685	-0.098	-0.0235	0.9151	8.1508	0.055	0.0142
1.0000	9.7005	0.000	-0.0000	1.0000	8.4800	0.000	0.0000
			X_1 carbon tetrachloride + x_2 m-xylene				
293.15 K							*303.15 K*
0.0000	7.7021	0.000	0.0000	0.0000	6.6860	0.000	0.0000
0.1200	7.9150	-0.026	-0.0039	0.1198	6.8090	-0.091	- 0.0971
0.2005	8.0420	-0.601	-0.0191	0.2493	6.9410	-0.192	-0.1166
0.4100	8.3687	-0.153	-0.0478	0.3468	7.0360	-0.272	-0.1300
0.5008	8.5170	-0.185	-0.0598	0.4310	7.1140	-0.345	-0.1647
0.6502	8.8005	-0.201	- 0.0733	0.5186	7.2450	-0.371	-0.1721
0.8500	9.2590	-0.142	-0.9390	0.6270	7.3980	-0.41	-0.2045
0.9006	9.3989	-0.103	-0.0960	0.7100	7.5940	-0.36	-0.2011
1.0000	9.7005	0.000	0.0000	0.8585	8.0240		-0.1781
			X_1 carbon tetrachloride + x_2 chlorobenzene				
293.15 K						*303.15 K*	
0.0000	8.0322	0.000	0.0000	0.0000	7.0120	0.000	0.0000
0.1008	8.2005	0.000	0.0189	0.1214	7.1842	0.006	0.0111
0.2500	8.4340	-0.015	0.0080	0.2295	7.3339	-0.015	0.0071
0.4070	8.6856	-0.025	0.0057	0.3541	7.5078	-0.024	0.0044
0.5008	8.8415	-0.026	0.0059	0.4571	7.6510	-0.032	0.0013
0.6535	9.1025	-0.019	0.0077	0.5552	7.7911	-0.036	-0.0007
0.8005	9.3370	-0.031	0.0034	0.6646	7.9557	-0.032	-0.0002
1.0000	9.7005	-0.000	0.0000	0.7730	8.1247	0.022	0.0019

B_o B_1 and B_2 are fitting parameters along with standard deviation $\sigma(^{\Delta\eta})$ for binary mixtures are listed in Table -3.

Observed values of viscosities of binary mixtures have been fitted using following equation.

$$\eta = C_0 + C_1 x + C_2x^2 + C_3x^3 \quad \text{... (7)}$$

Where, x is the mole fraction of carbon tetrachloride. C_0, C_1, C_2 and C_3 are fitting constants. These constants have been calculated using method of least square and recorded in Table -4 along with standard deviation $\sigma(^{\Delta\eta})$. The parameter'd' representative of the strength of interaction between components of binary mixture were calculated using formula[5].

$$\text{In } \eta = X_1 \text{In } \eta_1 + X_2 \text{In } \eta_2 + X_1X_2d \quad \text{... (8)}$$

The value of 'd' at different mole fractions are recorded in Table-2. The average value of parameter 'd_{av}' have been recorded in **Table -3.**

Table -3: Values of constants B_0, B_1 and B_2 for the various binary liquid mixtures, standard deviation ($^{\Delta\eta}$) and d_{av} at 293.15k and 303.15k

System	10^3B_0/kg m^{-1}s^{-1}	10^3B_1/kg m^{-1}s^{-1}	10^3B_2/kg m^{-1}s^{-1}	$10^3\Delta\eta$/kg m^{-1}s^{-1}	d_{av}
			293.15k		
Carbon tetrachloride+ Benzene	0.8868	0.5174	0.5547	0.0185	0.2086
Carbon tetrachloride+ Toluene	-2.7679	0.9790	2.0015	-0.1863	-0.1863
Carbon tetrachloride+ m-xylene	-0.7336	-0.5591	0.0620	-0.0563	-0.0563
Carbon tetrachloride+ Chlorobenzene	-0.1024	-0.0701	-0.0085	0.0072	0.0072
			303.15k		
Carbon tetrachloride + Benzene	0.0803	0.0813	-0.0685	0.0873	0.0873
Carbon tetrachloride+ Toluene	-0.5034	-0.0352	-0.0281	0.0135	0.0340
Carbon tetrachloride + m-xylene	-1.5069	-0.7227	0.4182	0.0168	0.1591
Caron tetrachloride + Chlorobenzene	-0.1349	-0.0516	0.0881	0.0016	0.0032

The values for V^E for binary mixtures of carbon tetrachloride + benzene+m-xylene + ethyl benzene at both temperatures 293.15k and 303.15 k are small positive while negative values are found for carbon

tetrachloride+ toluene and + chlorobenzen. In general the dependence of V^E on X_1 (the mole fraction of carbon tetrachloride) is unsymmetrical. 10^6 V^E for equimolal binary mixtures of carbon tetrachloride with benzene, toluene, m-xylene, ethyl benzene and

Table - 4: Values of Constants C_0, C_1, C_2, C_3 and the standard deviation $6^{(\eta)}$ for the various binary liquid mixtures of Carbon Tetrachloride at 293.15k and 303.15k

System	$1\,0^3C_0$/kg m^{-1}s^{-1} 0^3	C_1/kg m^{-1}s^{-1}	10^3C_2/kg m^{-1}s^{-1}	10^3C_3/kg m^{-1}s^{-1}	$10^3\mathbf{6}^{(\eta)}$/kg m^{-1}s^{-1}
293.15k					
Carbon tetrachloride+					
Benzene	6.4800	3.70401	0.41589	-0.87081	0.02162
Carbon tetrachloride+					
Toulene	5.9059	0.35135	5.26985	-0.78959	0.08907
Carbon tetrachloride+					
m-xylene	8.0322	1.60055	-0.00481	0.07176	0.00411
Carbon tetrachloride+					
Chlorobenzene	7.7021	1.82400	-0.95682	1.13182	0.00627
System					
303.15k					
Carbon tetrachloride +					
Benzene	5.7000	2.76858	0.18344	-0.17503	0.00291
Carbon tetrachloride+					
Toluene	5.2505	2.71123	0.48655	0.02665	0.00985
Carbon tetrachloride +					
m-xylene	6.6860	1.08617	-0.82725	1.54998	0.01993
Carbon tetrachloride +					
Chlorobenzene	7.0120	1.40013	-0.04613	0.11606	0.00297

chlorobenzene at 303.15k are 0.0506.-0.0398, 0.1674, 0.0720 and -0.0579 m^3mol^{-1} respectively. The order of magnitude of V^E at X_1= 0.5 follow as :

Carbon tetrachloride + m-xylene>+ethyl benzene>+ benzene>+toluene>+chlorobenzene.

It can be seen from Table-2 that the values of viscosities $\Delta\eta$ increase with increasing mole fraction of common component (carbon tetrachloride) for binary mixtures carbon tetrachloride + benzene + toluene+ m-xylene + chlorobenzene. Small positive deviation from linear dependance on mole fraction, $\Delta\eta$ over the entire range of composition can be seen for binary mixtures of carbon tetrachloride with benzene while the mixture with toluene, m-xylene and chlorobenze show negative deviations.

10^3 $\Delta\eta$ / kg m^{-1} s^{-1} for equimolal mixtures vary in order

carbon tetrachloride + benzene>+ chlorobenzne > + toluene> + m-xylene.

The average value of parameter 'd_{av}' as a measure of the strength of interaction between components for binary mixtures of carbon tetrachloride with benzene, toluene, m-xylene and chlorobenzene at 303.15k are 0.0873, 0.0340, -0.1591 and 0.0032 respectively.

Comparatively larger positive value of V^E, large negative value of $\Delta\eta$ and negative value of d_{av} for bianry mixtures of carbon tetrachloride with m-xylene are indicative of very weak interaction between unlike components. Larger negative value of V^E, and smaller negative value of $\Delta\eta$ along with positive value of d_{av} for binary mixture of carbon tetrachloride with chlorobenzene show comparatively stronger interaction. Weaker but specific interaction between carbon tetrachloride and benzene shown by the data of V^E, $\Delta\eta$ and d_{av} may be due to the fact that they are nonpolar and dispersive forces as well may exist there in.

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