



Solvent Effect on the Stability Constants of Charge Transfer Complexes of Iodine and Certain Ethers at 303 K

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ABSTRACT

Ultrasonic velocity (U), density (ρ), and coefficient of viscosity (η) values are measured for solutions containing iodine and one of the following ethers in equimolar concentration in the range 0.001 - 0.01M at 303 K. Diphenyl ether, 4-chloroanisole, anisole and 1,4-dioxane are used as donors. Dichloromethane, chloroform, carbon tetrachloride and n-hexane have been used as solvents. Acoustical parameters such as adiabatic compressibility (β), absorption coefficient (α/f^2), internal pressure (π_i) and cohesive energy (CE) values are calculated from the values of u , ρ and η . The trend in the acoustical parameters establishes the formation of charge transfer complexes between iodine (acceptor) and ethers (donors). The formation constants (K) are calculated for these complexes. The free energy of formation of these complexes (ΔG) are also reported. Attempt has been made to correlate the formation constants with polarizability (α), dielectric strength (ϵ) and dipole moment (μ) of the donor and solvent molecules. The free energy of activation (ΔG^\ddagger) and viscous relaxation time (τ) are found to be almost constant for these complexes indicating the formation of similar charge transfer complexes in these systems.

Keywords: Solvent effect, formation constants, donor-acceptor complexes, iodine, ethers, ultrasonic method.

INTRODUCTION

Ultrasonic velocity measurements have been successfully employed to detect and assess weak and strong molecular interactions, in binary [1-5] and ternary [6-11] liquid mixtures. These studies can also be used to detect complexation and for the evaluation of stability constants of complexes [12-14], in particular the charge transfer complexes formed between organic compounds containing electron rich centers and electron deficient compounds. Ethers are Lewis bases as they contain electron rich ethereal oxygen and thus they can function as donors. Among halogens, iodine has basic character and it can function as electron acceptor. It forms charge transfer complexes with electron donors [15]. In the present work, charge transfer complexes are detected between iodine and ethers in four different solvents by ultrasonic method and the stability constants of these complexes are calculated using modified Bhat equation [16]. In this paper, we report the results obtained in the ultrasonic study of molecular interaction between iodine and four ethers namely, diphenyl ether, 4-chloroanisole, anisole and 1,4-dioxane in dichloromethane, chloroform, carbon tetrachloride and n-hexane at 303K.

These studies are made mainly to investigate the influence of structure of donor molecules and polarity of medium on the stability of this type of complexes and the factor which plays significant role in the complexation.

EXPERIMENTAL SECTION

Materials

Iodine (Merck-GR) was purified by sublimation. The solvents dichloromethane (bp 313 K), chloroform (bp 335 K), carbon tetrachloride (bp 350 K) and n-hexane (bp 341 K), are distilled before use. The four ethers diphenyl ether, 4-chloroanisole, anisole and 1,4-dioxane used as donors are of AnalaR grade (SDS). Accurately weighed amounts of donors and acceptor were dissolved in suitable solvent to obtain solution in the concentration range 1×10^{-3} - 1×10^{-2} M.

Methods

Ultrasonic velocity measurements were performed with ultrasonic interferometer (Model F81) supplied by 'Mittal Enterprises, New Delhi' operating at a frequency of 2 MHz. It has an accuracy of $\pm 0.1 \text{ ms}^{-1}$. Viscosities of pure compounds and their mixtures were determined using Oswald's viscometer calibrated with double distilled water. The densities of pure compounds and their solutions were measured accurately using specific gravity bottles with accuracy of 0.001 kg/m^3 . The temperature is maintained constant at 303 K with a precision of $\pm 0.1 \text{ K}$ with a thermostat. The ternary liquid mixtures containing n-hexane, equimolar concentration of donor and acceptor are thermostated at 303 K for 30 minutes before measuring ultrasonic velocity to attain equilibrium. Acoustical parameters such as adiabatic compressibility (β), absorption coefficient (α/f^2), free length (L_f), internal pressure (π_i), cohesive energy (CE), relaxation time (τ), stability constant (K) and the thermodynamic parameter free energy change (ΔG) for the complexation and free energy of activation (ΔG^\ddagger) were calculated using standard equations [15-20].

RESULTS AND DISCUSSION

The measured ultrasonic velocities, densities and viscosities at various equimolar concentrations of diphenyl ether, 4-chloroanisole, anisole and 1,4-dioxane with iodine in dichloromethane, chloroform, carbon tetrachloride and n-hexane at 303 K are given in Tables 1–3. The plots of ultrasonic velocity vs concentration of four ethers in four different solvents are presented in Figs.1-4. From the plots it is seen that the ultrasonic velocities vary non-linearly with concentration for all the sixteen systems. At a characteristic concentration, the ultrasound velocity of solution is less than that of ideal mixing indicating the formation of charge transfer complex between the donor and acceptor. The ultrasonic velocity is minimum at characteristic concentration indicating that the extent of complexation is maximum at this concentration. This concentration depends on the system. There is decrease in density (Table 2) at a specific concentration (3×10^{-3} - 6×10^{-3} M) and this also suggests that the complexation is concentration dependant. This is also supported by the trend in the viscosity values (Table 3).

The adiabatic compressibility is a measure of intermolecular association between the donor and acceptor. The plots of adiabatic compressibility vs concentration of four ethers are given in Figs.5–8. From these plots, it is evident that there is considerable variation in adiabatic compressibility values in the concentration range 3×10^{-3} – 9×10^{-3} M indicating that the complex formation is significant in this concentration range.

The calculated absorption coefficient (α/f^2), internal pressure (π_i) and cohesive energy (CE) for all the above systems are given in Tables [4-6]. The absorption coefficient (α/f^2) generally increases with increase in concentration and this trend suggest that the extent of complexation increases with increase in concentration.

The internal pressure (π_i) is a measure of cohesive forces between the constituent molecules in liquids. In order to assess the cohesive forces in the ternary liquids investigated; ' π_i ' values are calculated for all the systems (Table 5). It is found that the internal pressure in ternary solution is generally greater than that of pure solvent which shows that the intermolecular attractive forces between the molecules of components are strong in solution. Further, the internal pressure for a given system increases with increase in concentration which suggests that there is an increase in the extent of complexation with increase in concentration.

The stability constants are calculated from measured ultrasonic velocities using modified Bhat equation [16]. These values for all the donor-acceptor complexes are given in Table 7. It may be noted that the stability constant values are almost constant for a given system at a given temperature but are different for different donors indicating that the equilibrium constant depends on the structure of ethers. By comparing the values of equilibrium constant of four ethers in one solvent, the ease of complexation with iodine and ethers is found to be in the order of diphenyl ether >

4-chloroanisole \approx anisole $>$ 1,4-dioxane. During complexation between ether and iodine, ethereal oxygen being electron rich donates electron which is attracted by positive end of iodine molecule. Diphenyl ether contains electron releasing phenyl groups on either side of the donor atom and similarly in 4-chloroanisole, chlorine atom in the para position to methoxy group releases electron by mesomeric effect. But in anisole molecule the resonance effect is limited although methoxy group is directly attached to a phenyl ring. In dioxane molecule, absence of mesomeric effect is the reason for the least stability constant value.

From the stability constants obtained for the above systems, the free energy of formation (ΔG) are calculated at 303 K and they are given in Table 7. For all the systems, ΔG values are negative indicating that the charge transfer complexes are thermodynamically stable. The free energy of activation (ΔG^\ddagger) and relaxation time (τ) are intrinsic properties of a charge transfer complex. Since similar complexes are formed in the four systems these two properties are almost constant.

Table 1. ULTRASONIC VELOCITY (ms^{-1}) VALUES OF IODINE - ETHER SYSTEMS IN DIFFERENT SOLVENTS AT 303 K

Conc. M	Diphenylether				4-chloroanisole				anisole				1,4-dioxane			
	CH_2Cl_2	CHCl_3	CCl_4	C_6H_{14}	CH_2Cl_2	CHCl_3	CCl_4	C_6H_{14}	CH_2Cl_2	CHCl_3	CCl_4	C_6H_{14}	CH_2Cl_2	CHCl_3	CCl_4	C_6H_{14}
0.001	1049.1	965.1	905.2	1055.9	1051.6	966.4	904.6	1056.8	1052.8	965.8	900.4	1055.2	1052.2	965.2	907.0	1049.0
0.002	1050.8	966.6	907.6	1053.3	1052.0	967.2	906.6	1057.6	1051.2	966.0	901.6	1054.8	1049.8	965.6	908.4	1049.6
0.003	1052.4	965.3	906.4	1054.7	1051.0	967.8	904.8	1058.0	1050.4	966.4	899.6	1055.6	1050.2	963.2	905.4	1051.2
0.004	1049.7	965.5	905.2	1053.9	1052.0	966.4	906.0	1054.8	1050.6	965.0	903.6	1055.6	1050.6	964.1	904.0	1052.4
0.005	1049.5	965.2	906.5	1056.0	1052.6	966.0	907.2	1054.0	1050.9	967.2	905.4	1057.6	1055.2	964.0	906.6	1052.8
0.006	1049.4	964.9	906.0	1053.6	1052.4	967.4	905.6	1057.6	1052.0	965.1	903.0	1056.8	1050.0	965.0	907.0	1053.0
0.007	1048.6	964.8	905.4	1051.2	1051.8	966.2	908.2	1055.8	1051.6	965.8	904.4	1053.6	1049.2	963.4	905.4	1053.4
0.008	1048.4	966.0	904.8	1052.4	1051.2	966.0	905.6	1056.9	1050.4	966.2	906.4	1054.4	1051.0	966.8	904.0	1054.0
0.009	1047.6	966.4	904.9	1054.4	1050.6	967.8	907.6	1059.0	1050.8	966.4	906.4	1054.4	1051.6	963.3	905.2	1054.4
0.010	1047.2	967.6	906.1	1054.8	1050.1	967.8	901.6	1063.0	1052.0	965.6	904.4	1055.2	1051.0	963.8	905.4	1056.0

Table 2. DENSITY (kgm^{-3}) VALUES OF IODINE - ETHER SYSTEMS IN DIFFERENT SOLVENTS AT 303 K

Conc. M	Diphenylether				4-chloroanisole				anisole				1,4-dioxane			
	CH_2Cl_2	CHCl_3	CCl_4	C_6H_{14}	CH_2Cl_2	CHCl_3	CCl_4	C_6H_{14}	CH_2Cl_2	CHCl_3	CCl_4	C_6H_{14}	CH_2Cl_2	CHCl_3	CCl_4	C_6H_{14}
0.001	1268.9	1413.4	1518.6	640.4	1261.1	1408.3	1520.7	638.3	1258.3	1409.8	1519.8	634.3	1260.1	1408.3	1519.5	636.2
0.002	1264.1	1413.6	1514.2	638.5	1258.0	1407.0	1516.6	636.5	1257.8	1406.6	1515.0	637.0	1257.7	1407.2	1519.1	635.5
0.003	1270.5	1434.2	1514.8	640.1	1260.1	1406.2	1512.6	637.2	1263.2	1407.3	1516.1	635.2	1257.6	1405.8	1516.2	636.2
0.004	1269.4	1410.7	1519.6	643.6	1261.6	1405.9	1521.8	638.7	1258.2	1413.0	1520.1	633.3	1262.8	1411.0	1516.4	637.5
0.005	1259.8	1404.2	1519.0	636.1	1261.6	1410.9	1508.9	634.9	1260.1	1409.9	1518.0	637.6	1262.2	1408.0	1514.1	635.6
0.006	1267.5	1418.0	1520.0	641.4	1262.6	1409.5	1519.7	639.1	1258.7	1412.2	1523.0	636.7	1260.7	1409.7	1520.0	637.8
0.007	1263.3	1419.6	1514.9	639.0	1258.0	1408.0	1515.2	637.3	1260.7	1407.5	1516.8	638.5	1258.8	1407.0	1517.5	636.6
0.008	1269.8	1434.8	1520.3	643.0	1258.0	1406.7	1514.3	638.6	1264.5	1408.2	1516.1	635.4	1259.7	1406.5	1517.3	638.2
0.009	1269.5	1409.6	1514.9	643.6	1261.0	1413.5	1519.7	641.0	1258.6	1413.3	1521.8	633.5	1263.8	1410.9	1515.3	638.9
0.010	1261.5	1403.0	1518.9	637.8	1262.7	1405.6	1509.8	635.1	1259.7	1411.0	1519.5	637.9	1262.2	1407.8	1515.8	636.5

Table 3. VISCOSITY ($\times 10^{-4} \text{ Nsm}^{-2}$) VALUES OF IODINE - ETHER SYSTEMS IN DIFFERENT SOLVENTS AT 303 K

Conc. M	Diphenylether				4-chloroanisole				anisole				1,4-dioxane			
	CH_2Cl_2	CHCl_3	CCl_4	C_6H_{14}	CH_2Cl_2	CHCl_3	CCl_4	C_6H_{14}	CH_2Cl_2	CHCl_3	CCl_4	C_6H_{14}	CH_2Cl_2	CHCl_3	CCl_4	C_6H_{14}
0.001	5.63	6.71	8.57	3.39	5.59	6.73	8.70	3.35	5.42	6.58	8.66	3.31	5.57	6.65	8.70	3.34
0.002	5.63	6.71	8.63	3.39	5.57	6.63	8.70	3.32	5.43	6.62	8.58	3.29	5.54	6.63	8.80	3.34
0.003	5.67	6.90	8.66	3.41	5.64	6.59	8.63	3.33	5.47	6.61	8.68	3.30	5.55	6.62	8.76	3.31
0.004	5.66	6.75	8.61	3.40	5.50	6.60	8.70	3.35	5.47	6.69	8.60	3.27	5.63	6.65	8.73	3.34
0.005	5.61	6.70	8.55	3.36	5.61	6.62	8.67	3.31	5.48	6.57	8.65	3.29	5.52	6.60	8.68	3.34
0.006	5.64	6.83	8.64	3.37	5.56	6.56	8.73	3.37	5.51	6.62	8.73	3.29	5.56	6.60	8.67	3.32
0.007	5.63	6.84	8.54	3.39	5.56	6.57	8.70	3.34	5.53	6.68	8.70	3.32	5.61	6.68	8.75	3.34
0.008	5.65	6.83	8.67	3.39	5.57	6.66	8.66	3.33	5.52	6.63	8.67	3.29	5.59	6.66	8.76	3.34
0.009	5.69	6.76	8.43	3.40	5.53	6.57	8.78	3.34	5.46	6.64	8.78	3.27	5.58	6.65	8.76	3.33
0.010	5.60	6.74	8.67	3.35	5.62	6.54	8.72	3.32	5.50	6.59	8.70	3.31	5.55	6.62	8.76	3.31

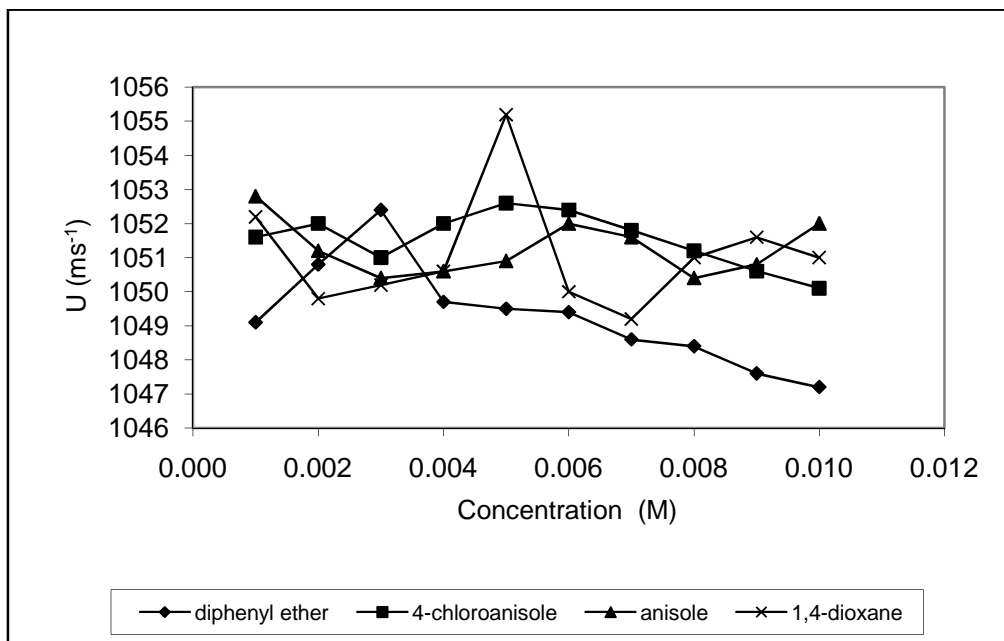


Fig.1 Plots of Ultrasonic velocity Vs Concentration of iodine and ethers in dichloromethane

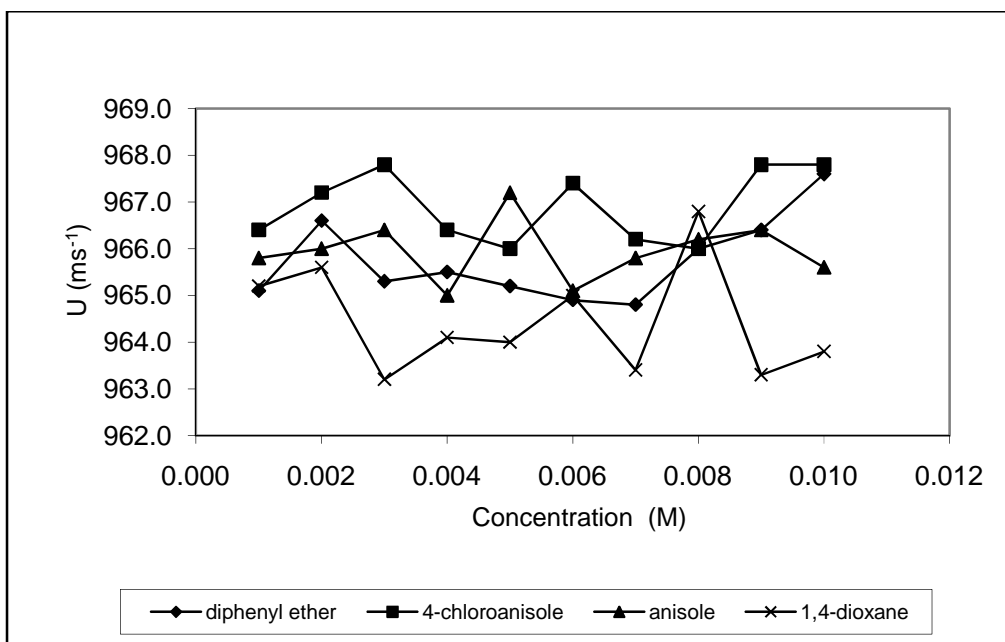


Fig.2 Plots of Ultrasonic velocity Vs Concentration of iodine and ethers in chloroform

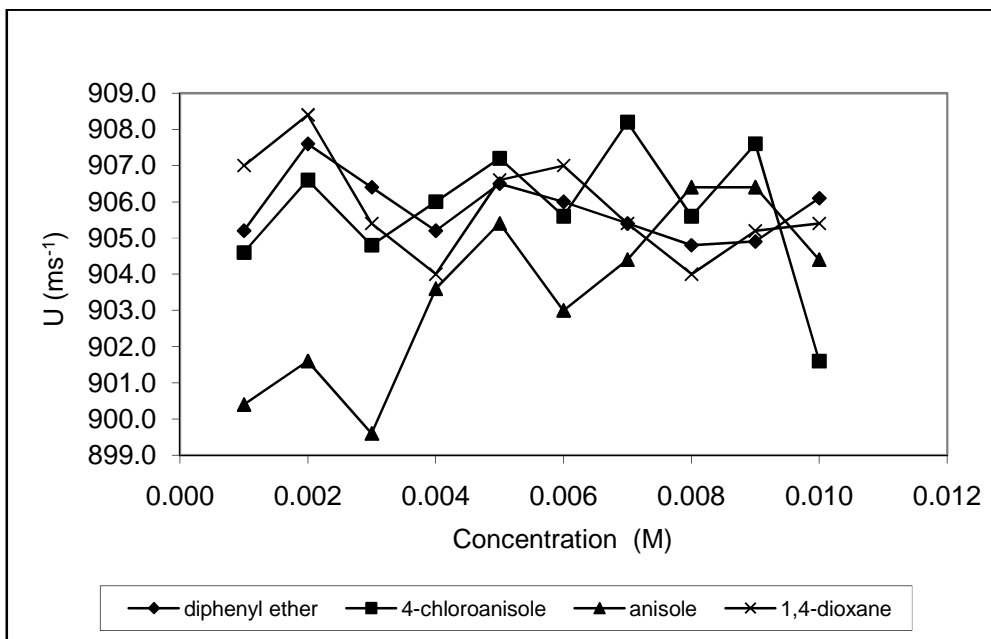


Fig.3 Plots of Ultrasonic velocity Vs Concentration of iodine and ethers in carbon tetrachloride

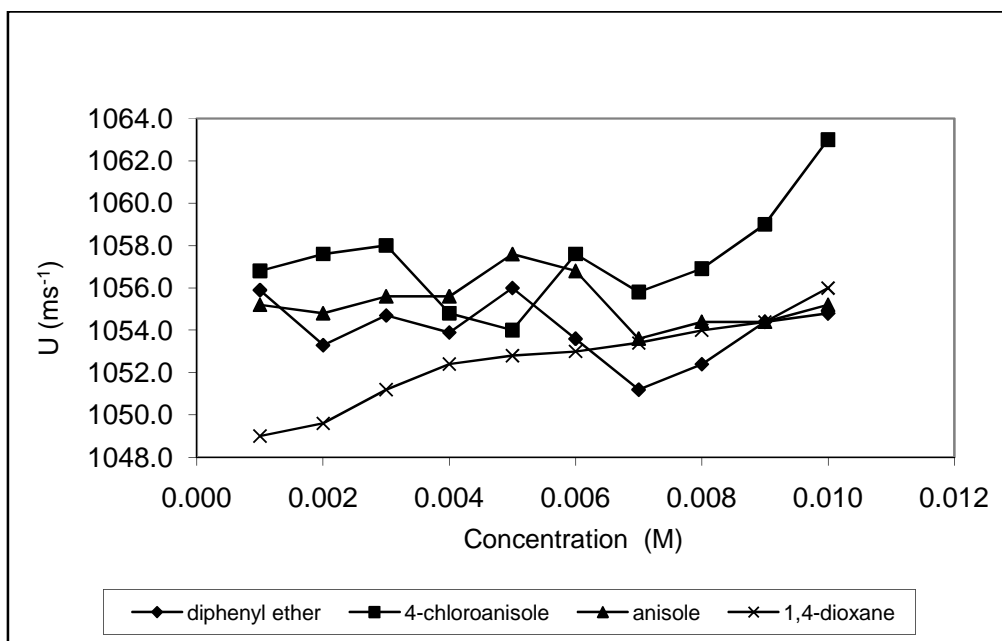


Fig.4 Plots of Ultrasonic velocity Vs Concentration of iodine and ethers in n-hexane

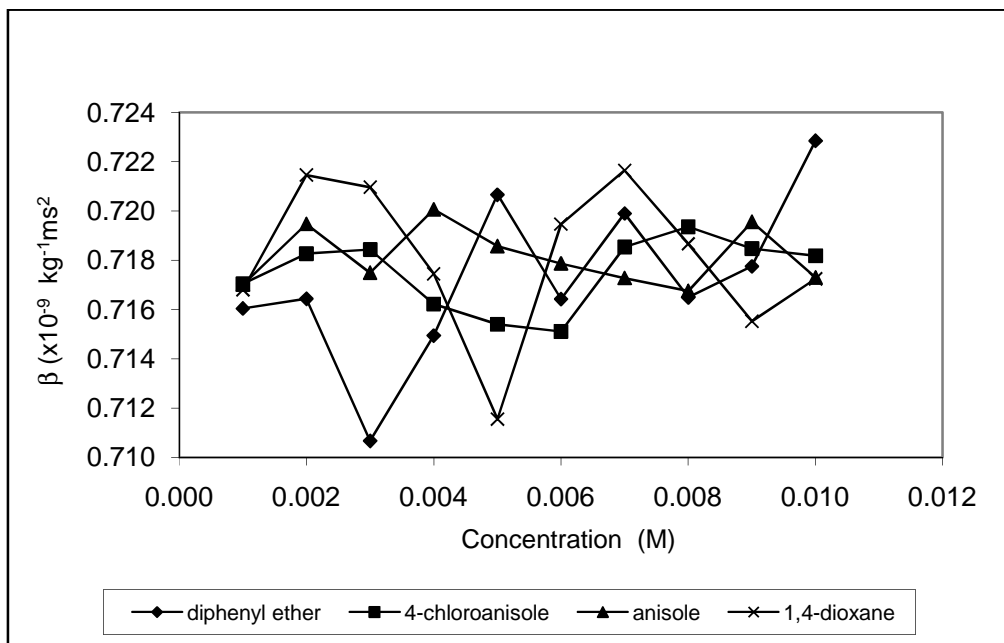


Fig.5 Plots of Adiabatic compressibility Vs Concentration of iodine and ethers in dichloromethane

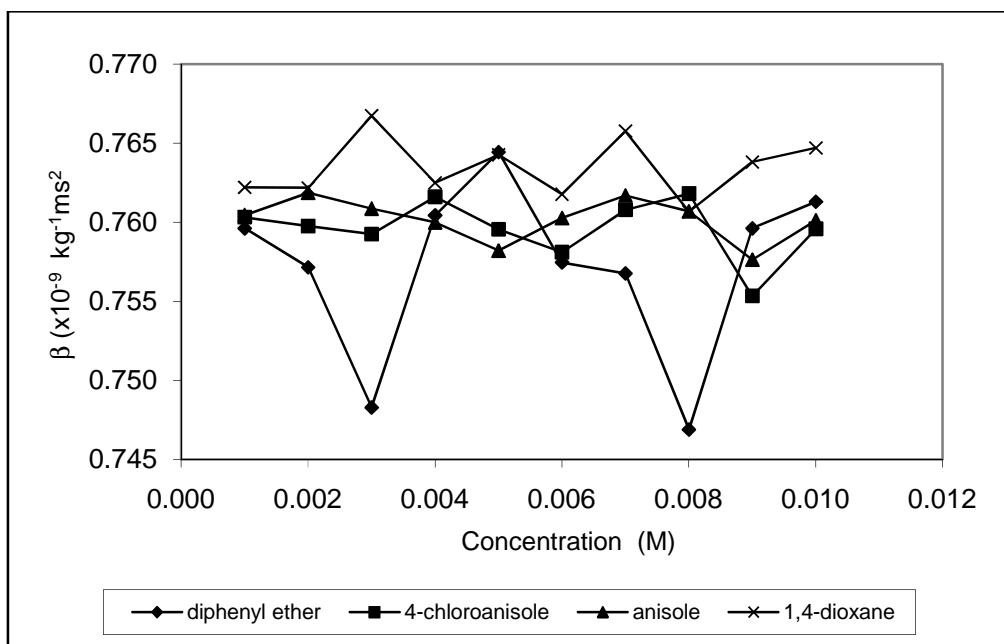


Fig.6 Plots of Adiabatic compressibility Vs Concentration of iodine and ethers in chloroform

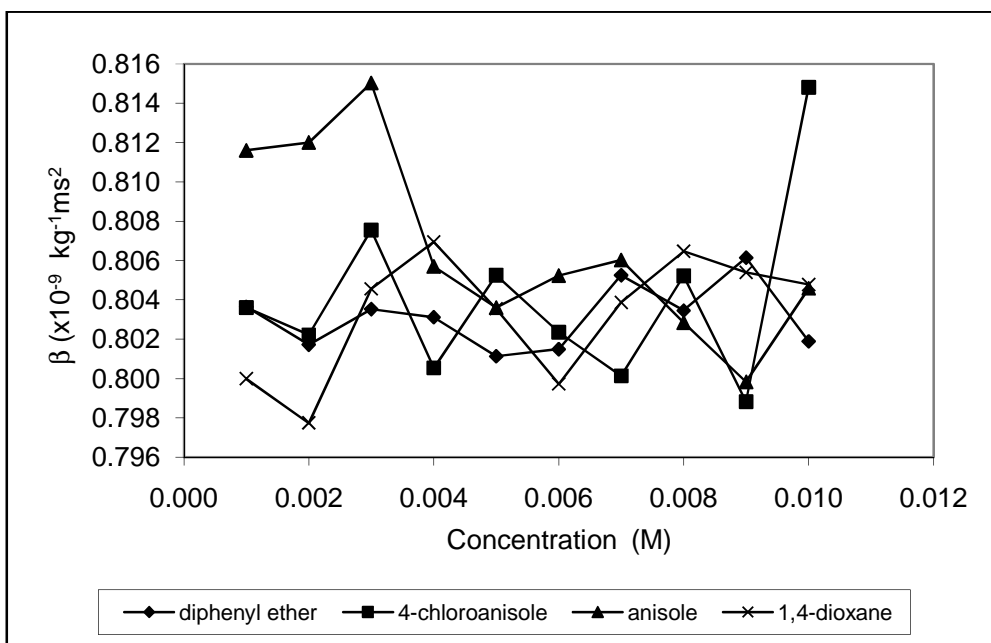


Fig.7 Plots of Adiabatic compressibility Vs Concentration of iodine and ethers in carbon tetrachloride

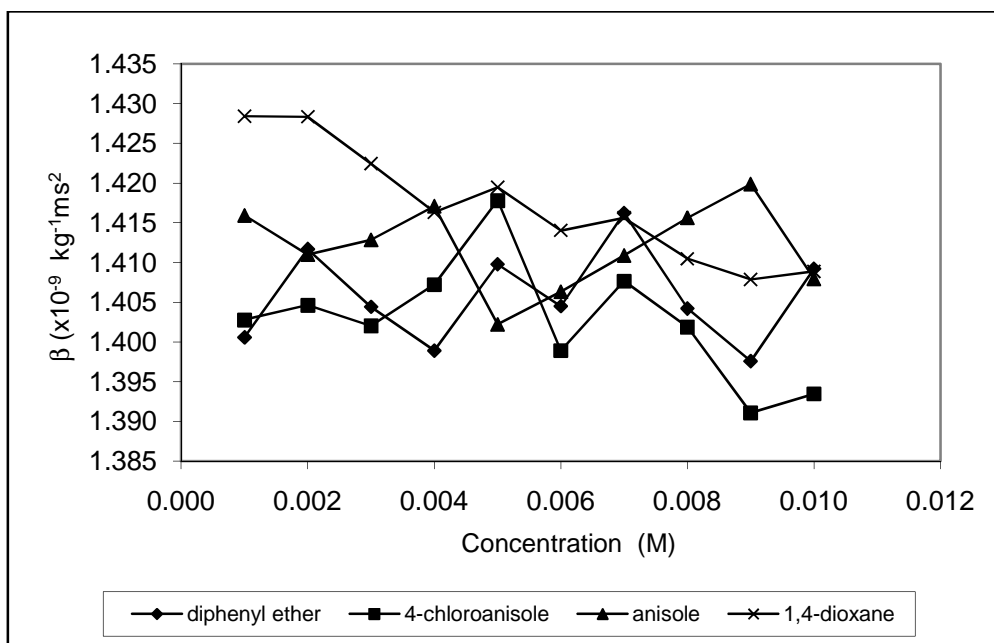


Fig.8 Plots of Adiabatic compressibility Vs Concentration of iodine and ethers in n-hexane

Table 4. ABSORPTION COEFFICIENT ($\times 10^{15} \text{ Npm}^{-1}\text{s}^{-2}$) VALUES OF IODINE - ETHER SYSTEMS IN DIFFERENT SOLVENTS AT 303 K

Conc. M	Diphenylether				4-chloroanisole				anisole				1,4-dioxane			
	CH ₂ Cl ₂	CHCl ₃	CCl ₄	C ₆ H ₁₄	CH ₂ Cl ₂	CHCl ₃	CCl ₄	C ₆ H ₁₄	CH ₂ Cl ₂	CHCl ₃	CCl ₄	C ₆ H ₁₄	CH ₂ Cl ₂	CHCl ₃	CCl ₄	C ₆ H ₁₄
0.001	10.106	13.884	19.994	11.822	10.026	13.927	20.311	11.706	9.703	13.620	20.526	11.671	9.978	20.143	20.175	11.950
0.002	10.089	13.827	20.041	11.952	10.002	13.699	20.231	11.607	9.779	13.730	20.314	11.564	10.017	20.044	20.311	11.935
0.003	10.067	14.056	20.186	11.948	10.133	13.600	20.261	11.604	9.828	13.679	20.669	11.621	10.019	20.224	20.464	11.778
0.004	10.134	13.973	20.093	11.863	9.852	13.679	20.205	11.744	9.870	13.858	20.171	11.548	10.111	20.229	20.497	11.814
0.005	10.126	13.955	19.857	11.808	10.027	13.676	20.227	11.708	9.849	13.532	20.196	11.480	9.781	20.109	20.218	11.856
0.006	10.121	14.098	20.085	11.803	9.927	13.512	20.347	11.718	9.878	13.714	20.457	11.511	10.017	20.025	20.105	11.707
0.007	10.158	14.102	19.977	11.994	9.981	13.609	20.148	11.692	9.918	13.844	20.387	11.682	10.138	20.385	20.435	11.801
0.008	10.148	13.893	20.232	11.903	10.022	13.812	20.240	11.625	9.902	13.722	20.186	11.627	10.044	20.033	20.551	11.739
0.009	10.259	13.964	19.754	11.859	9.949	13.488	20.315	11.538	9.828	13.689	20.380	11.574	9.974	20.304	20.494	11.679
0.010	10.156	13.949	20.181	11.781	10.099	13.502	20.711	11.436	9.852	13.629	20.341	11.613	9.962	20.173	20.464	11.618

Table 5. INTERNAL PRESSURE ($\times 10^3 \text{ atm}$) VALUES OF IODINE - ETHER SYSTEMS IN DIFFERENT SOLVENTS AT 303 K

Conc. M	Diphenylether				4-chloroanisole				anisole				1,4-dioxane			
	CH ₂ Cl ₂	CHCl ₃	CCl ₄	C ₆ H ₁₄	CH ₂ Cl ₂	CHCl ₃	CCl ₄	C ₆ H ₁₄	CH ₂ Cl ₂	CHCl ₃	CCl ₄	C ₆ H ₁₄	CH ₂ Cl ₂	CHCl ₃	CCl ₄	C ₆ H ₁₄
0.000	4.928	4.073	3.753	2.333												
0.001	4.980	4.093	3.727	2.399	4.936	4.088	3.760	2.380	4.849	4.045	3.760	2.356	4.923	4.065	3.754	2.378
0.002	4.960	4.091	3.728	2.397	4.917	4.053	3.749	2.363	4.858	4.051	3.731	2.355	4.909	4.055	3.771	2.374
0.003	4.991	4.189	3.738	2.405	4.953	4.037	3.732	2.366	4.890	4.047	3.759	2.354	4.911	4.055	3.764	2.364
0.004	4.988	4.097	3.738	2.409	4.894	4.042	3.758	2.378	4.877	4.086	3.741	2.337	4.958	4.071	3.762	2.376
0.005	4.940	4.070	3.719	2.375	4.939	4.056	3.728	2.355	4.881	4.036	3.744	2.353	4.894	4.052	3.740	2.372
0.006	4.973	4.136	3.741	2.391	4.917	4.032	3.763	2.382	4.887	4.062	3.773	2.349	4.921	4.053	3.749	2.366
0.007	4.958	4.141	3.714	2.393	4.906	4.036	3.743	2.366	4.903	4.068	3.754	2.367	4.937	4.073	3.765	2.371
0.008	4.983	4.166	3.750	2.403	4.912	4.060	3.737	2.367	4.910	4.054	3.742	2.349	4.926	4.058	3.769	2.372
0.009	5.004	4.093	3.690	2.405	4.904	4.042	3.768	2.372	4.866	4.066	3.776	2.334	4.930	4.071	3.763	2.369
0.010	4.939	4.073	3.746	2.371	4.945	4.017	3.750	2.344	4.881	4.046	3.757	2.358	4.916	4.055	3.763	2.355

Table 6. COHESIVE ENERGY (kJmol^{-1}) VALUES OF IODINE - ETHER SYSTEMS IN DIFFERENT SOLVENTS AT 303 K

Conc. M	Diphenylether				4-chloroanisole				anisole				1,4-dioxane			
	CH ₂ Cl ₂	CHCl ₃	CCl ₄	C ₆ H ₁₄	CH ₂ Cl ₂	CHCl ₃	CCl ₄	C ₆ H ₁₄	CH ₂ Cl ₂	CHCl ₃	CCl ₄	C ₆ H ₁₄	CH ₂ Cl ₂	CHCl ₃	CCl ₄	C ₆ H ₁₄
0.001	33.769	35.025	38.244	32.712	33.681	35.105	38.530	32.561	33.160	34.700	38.549	32.429	33.614	34.908	38.497	32.639
0.002	33.773	35.006	38.371	32.792	33.638	34.840	38.520	32.431	33.236	34.834	38.381	32.290	33.592	34.852	38.684	32.630
0.003	33.814	35.333	38.462	32.843	33.835	34.730	38.455	32.443	33.316	34.786	38.633	32.377	33.607	34.890	38.689	32.468
0.004	33.834	35.137	38.342	32.728	33.399	34.779	38.492	32.550	33.371	34.985	38.351	32.258	33.796	34.899	38.661	32.565
0.005	33.771	35.076	38.168	32.651	33.712	34.781	38.509	32.442	33.351	34.636	38.442	32.258	33.382	34.814	38.498	32.617
0.006	33.793	35.301	38.369	32.612	33.542	34.615	38.600	32.601	33.430	34.802	38.608	32.269	33.609	34.781	38.432	32.435
0.007	33.808	35.309	38.218	32.779	33.592	34.690	38.502	32.492	33.493	34.972	38.575	32.422	33.776	35.027	38.667	32.566
0.008	33.812	35.152	38.458	32.724	33.641	34.934	38.475	32.441	33.443	34.834	38.467	32.342	33.680	34.912	38.715	32.511
0.009	33.969	35.151	37.982	32.728	33.512	34.614	38.654	32.402	33.303	34.821	38.674	32.252	33.599	34.919	38.704	32.445
0.010	33.748	35.148	38.458	32.580	33.752	34.598	38.728	32.329	33.386	34.705	38.543	32.366	33.552	34.858	38.687	32.387

Table 7. STABILITY CONSTANT ($\text{dm}^{-3} \text{ mol}^{-1}$), FREE ENERGY (kJmol^{-1}), FREE ENERGY OF ACTIVATION (kJmol^{-1}) AND RELAXATION TIME ($\times 10^{13} \text{ s}$) VALUES OF CERTAIN CHARGE TRANSFER COMPLEXES OF IODINE - ETHER SYSTEMS AT 303 K

DONOR	K				ΔG				ΔG^\ddagger				τ			
	CH ₂ Cl ₂	CHCl ₃	CCl ₄	C ₆ H ₁₄	CH ₂ Cl ₂	CHCl ₃	CCl ₄	C ₆ H ₁₄	CH ₂ Cl ₂	CHCl ₃	CCl ₄	C ₆ H ₁₄	CH ₂ Cl ₂	CHCl ₃	CCl ₄	C ₆ H ₁₄
DIPHENYL ETHER	74.2	51.2	50.4	37.3	-10.7	-9.5	-9.7	-9.0	3.4	4.0	4.9	3.8	5.4	6.8	9.2	6.3
4-CHLORO ANISOLE	58.9	43.4	36.4	34.6	-10.1	-9.2	-9.0	-8.9	3.4	4.0	4.9	3.8	5.3	6.7	9.3	6.2
ANISOLE	53.3	37.6	35.5	31.2	-9.7	-9.0	-8.8	-8.6	3.3	4.0	4.9	3.8	5.2	6.7	9.3	6.2
1,4-DIOXANE	40.3	31.5	33.5	24.0	-9.2	-8.3	-8.8	-8.0	3.4	4.0	4.9	3.8	5.3	6.8	9.4	6.3

Correlation of stability constant with molecular properties

The complex formation is also influenced by the molecular properties such as polarizability (α), dipole moment (μ) and dielectric constant (ϵ) of donor molecules [21-23]. These parameters for the four ethers are listed in Table 8.

Plots of log K against polarizability of the donor in different solvents are given in Fig.9. These plots show that formation constant (K) increases with increase in polarizability of donor molecules. Thus, polarizability of donor molecules plays significant role during complexation.

Table 8. POLARIZABILITY, DIPOLE MOMENT AND DIELECTRIC STRENGTH FOR ETHERS AND SOLVENTS

	α	μ	ϵ		α	μ	ϵ
CH_2Cl_2	6.80	1.60	9.08	Diphenylether	20.86	1.03	2.68
CHCl_3	8.50	1.01	4.81	4-chloroanisole	14.75	1.62	7.84
CCl_4	10.50	0.00	2.24	Anisole	13.07	1.08	4.30
C_6H_{14}	11.60	0.08	1.89	n-hexane	10.00	0.00	2.22

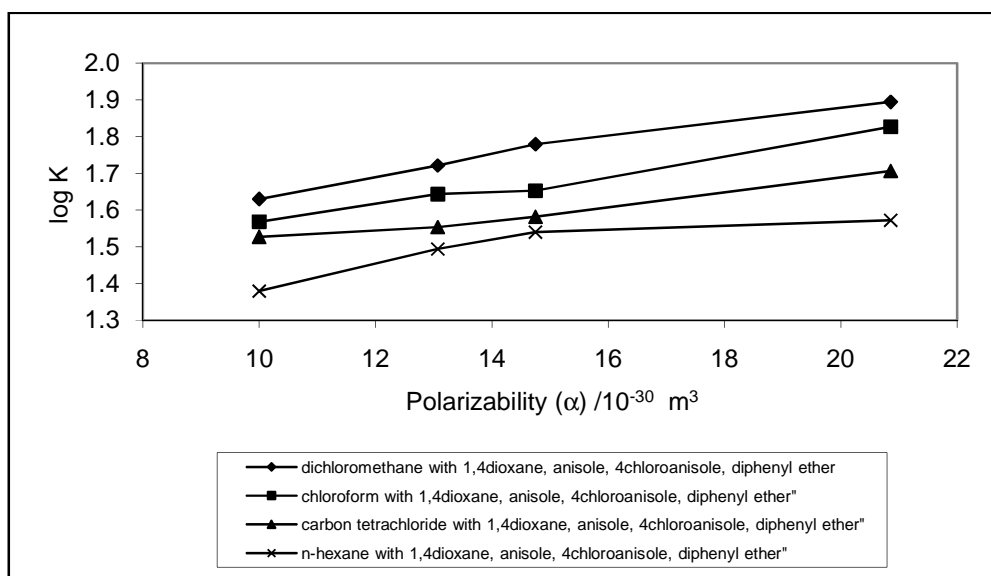
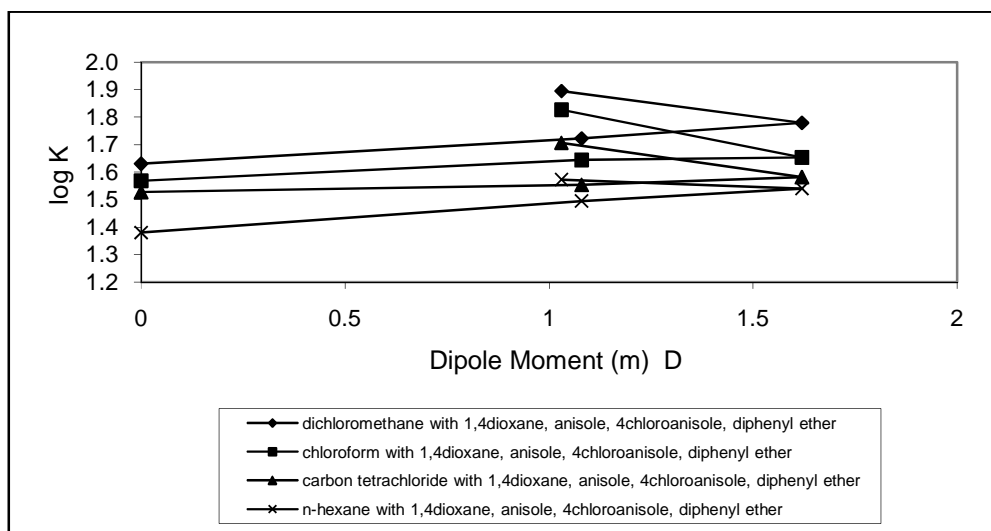
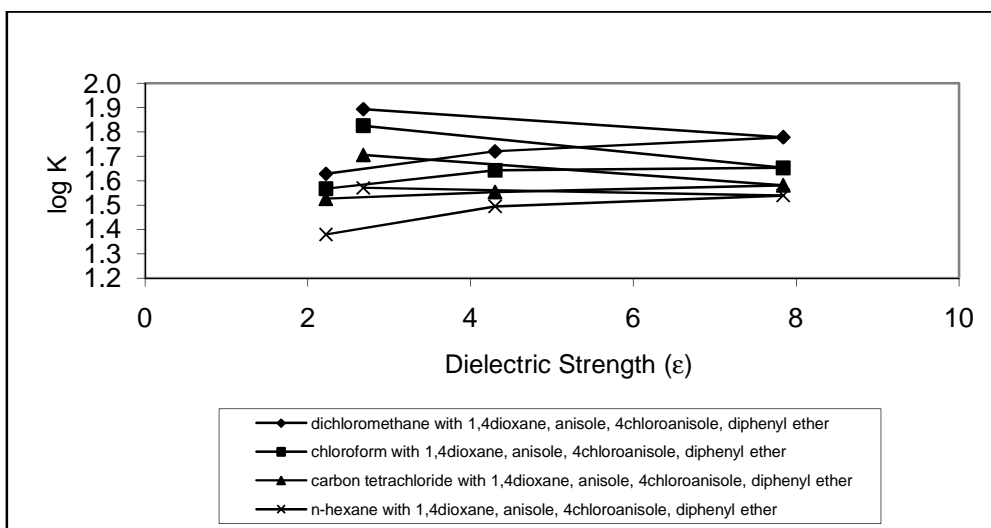


Fig.9. Plots of log K Vs Polarizability of ethers

The plots of log K against dipole moment of the donor are given in Fig.10. From these plots it is clear that stability constant K increase with dipole moment in three systems. But in the case of diphenyl ether, the stability constant is abnormally high even with different ethers having low dipole moment. This may be due to high π electron density in diphenyl ether. Plots of log K against dielectric constant of the donor are given in Fig.11. These plots also show that the stability constant value increases with increase in dielectric constant of donor molecules except diphenyl ether.

**Fig.10. Plots of log K Vs Dipole Moment of ethers****Fig.11. Plots of log K Vs Dielectric Strength of ethers**

These correlations of K with molecular properties indicate that it is the polarizability factor which mainly determines the ease of complexation. Thus, the acceptor molecule first polarizes the donor molecule during the formation of a charge transfer complex. The stability of charge transfer complex is also influenced by the polarity of the medium (Table 8). The plots of $\log K$ Vs dielectric strength of the solvents are presented in Fig.12. As the dielectric constant of the medium increases, the stability constant of the charge transfer complex also increases. This can be explained as follows. The charge transfer complex is more polar than the donor and acceptor molecules and hence it is more soluted. Therefore, high dielectric constant of the medium favours the formation of such a complex.

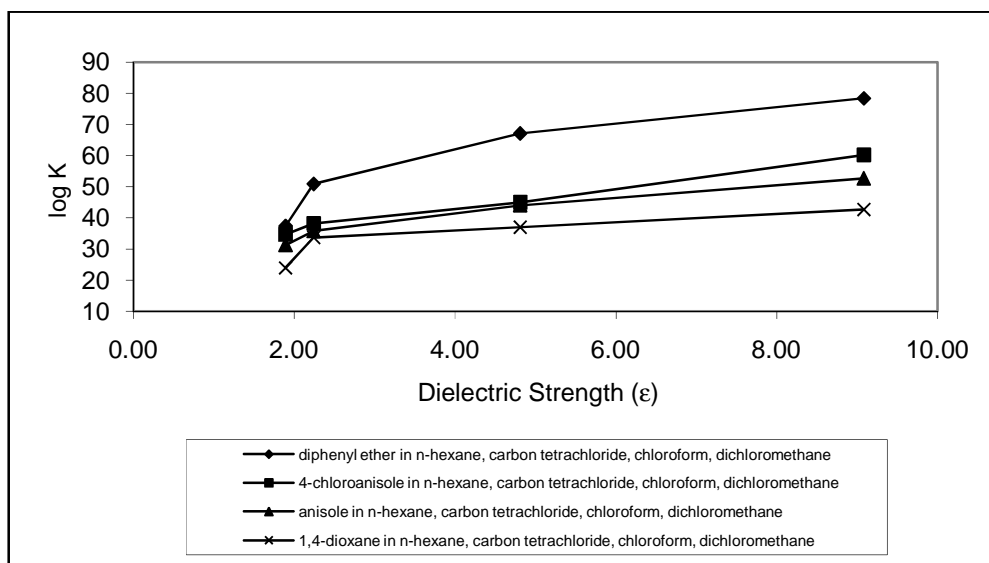


Fig.12. Plot of log K Vs Dielectric strength of solvents

CONCLUSION

Iodine forms thermodynamically stable charge transfer complexes with ethers. The formation constants correlate with the molecular properties of donor molecules and the correlation is better with polarizability. The stability of such complexes is also influenced by the dielectric constant of the medium.

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