

Studies on Molecular Interaction of Cyclohexane with Some Protic and Aprotic Solvents

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Abstract: The specific and non specific inter molecular interactions are sensitive to composition, temperature and presence of different functional groups in the mixture under investigation. Group contribution methods are powerful tools for the prediction of thermodynamic and transport properties of liquid mixtures, for studying the excess molar volume and deviation function in the viscosity. In order to investigate the presence of specific and non specific interactions between the constituent molecules of binary mixtures of Cyclohexane with some Protic and aprotic solvents for measurement of densities and viscosities as the function of mole fractions are carried out. From the measured values excess molar volume and deviation in viscosity is calculated.

Keywords: Excess volume, Deviation in viscosity, Molecular interactions.

INTRODUCTION

Thermodynamic and transport properties of liquid mixtures have been extensively used to study the departure of a real liquid mixture behaviour from ideality^{1, 2} which leads to the intermolecular interaction between the components present in liquid mixtures^{3, 4}. Alcohols are highly polar in nature and hence form azeotropes easily. Ethanol forms azeotropes with Cyclohexane at 337.8 K while propanol forms at 347.7 K. Thermodynamic study used for understanding the different types of intermolecular interactions like dipole-dipole⁵, dipole-induced dipole⁶ in polar-polar⁷ and polar-non polar⁸ systems. In the present paper work, density and viscosity are determined for the binary systems of Cyclohexane with some protic and aprotic solvents at room temperature from these excess parameters are calculated over entire temperature range of composition.

EXPERIMENTAL DETAILS

All the chemicals were used of AR grade having purity more than 99% were directly used. Purity of Solvents Cyclohexane (CH), Ethanol (ET), Propan-1-ol (PR), Butan-1-ol (BUT), Ether (ETH), Tetrahydrofuran (THF), Toluene(TE), m-Xylene (m-Xy) and N, N, Dimethylformamide (DMF) was checked by comparing the experimental values of densities (ρ) and viscosities (η) from literature (Table 1). Our experimentally calculated densities and viscosities of chemicals were well matched with reported values in the literature. Binary mixtures were prepared by mixing of known mass of each liquid in air tight, stoppered glass bottle. The masses were recorded on digital balance (SHIMADZU, AUX 220) having an accuracy of $\pm 1 \times 10^{-4}$ g. A bicapillary pycnometer with a bulb volume of 15 CC was chosen⁹ for determination of densities of pure liquids and mixtures. The viscosities were measured using Ubbelodhe Viscometer¹⁰ calibrated

with conduction water. The accuracy of viscosity measurement was 0.001mpas. An electronic digital stop watch with accuracy of ± 0.01 Second was used for flow time measurement.

The experimental values of densities and viscosities at 301K over the entire temperature range composition for various binary mixtures are tabulated in table.2. The V^E is calculated from the experimental data using the relation (V^E - Excess Molar Volume)

$$V^E = X_1 \cdot M_1 \left[\frac{1}{\rho_M} - \frac{1}{\rho_1} \right] + X_2 \cdot M_2 \left[\frac{1}{\rho_M} - \frac{1}{\rho_2} \right] \quad (1)$$

Where x_i , M_i & ρ_i indicate the mole fraction, the molecular weight, density of the components and ρ_M is the density of the mixture.

From density (ρ) and flow time (t) the viscosity is determined by using the relation

$$\eta = \rho (A \cdot t - B \cdot t) \quad (2)$$

Where, A & B are the viscosity constants. Deviations in viscosity ($\Delta\eta$) were obtained as

$$\Delta\eta = \eta_{\text{mix}} - (x_1 \eta_1 - x_2 \eta_2) \quad (3)$$

Where η_{mix} is the viscosity of the mixture while η_1 and η_2 are the viscosities of pure components for first and second respectively. Linear regression analysis of a plot of $(\eta \cdot t)/\rho$ against t^2 for pure water at four different temperatures provide the estimates of the constants 'a' and 'b'.

RESULTS AND DISCUSSIONS

CH exhibit conformations and exists either in rigid chair form or in boat form and also in skew – boat form¹¹ which undergo rapid inter conversion at room temperature which

leads to breaking up of hydrogen bonds¹². A higher density or Viscosity of a molecule is due to higher intramolecular interactions¹³ experimental density and Viscosity values of binary liquid mixtures are summarized in Table – 2. The table shows decreasing trend in density and Viscosity for all three systems with increase in mole fraction (x_1) of CH. Fig. 1(a) shows the variation of V^E with x_1 (CH) for systems CH + Alkanols. For system CH + ET the V^E shows both positive and negative values. Positive V^E indicates the disruption of alkanol multimers through the breaking of hydrogen bonds while the negative V^E value indicates the contraction of volume on mixing and its magnitude becomes more negative due to several attracting effects thus results in to the formation of new complex between CH and ET. It shows maxima at $x_1 \approx 0.1$ and minima at $x_1 \approx 0.9$. For CH + PR system V^E shows negative values over entire composition results from the attracting effects between them. It also shows maxima at $x_1 \approx 0.1$ and minima at $x_1 \approx 0.9$. For CH + BUT system the V^E values are negative and becomes more negative as concentration increases. The negative V^E values for the binary mixtures follow the decreasing order as CH + ET > CH + PR > CH + BUT.

Fig.2(a) represents V^E with mole fraction (x_1) of CH for the systems CH + ETH/aromatic ethers. The system CH + ETH shows negative V^E values and becomes more negative as the concentration increases it shows maxima at $x_1 \approx 0.1$ while minima at $x_1 \approx 0.9$. For the system CH + THF the V^E shows both positive and negative values Positive V^E value indicates the decrease in double bond character and negative V^E value indicates the increase in attraction of CH and becomes more negative as the concentration of CH increases. It shows maxima at $x_1 \approx 0.1$ while minima at $x_1 \approx 0.9$. The negative V^E values for the binary mixtures follow the decreasing order as CH + ETH > CH + THF. It concludes that there is strong interaction between CH + ETH than CH + THF.

Fig. 3(a) represents V^E with mole fraction (x_1) of CH for the system CH+ substituted aromatic rings. For the system CH + TE the V^E value shows both positive and negative values. The negative V^E value results in the interaction between π electron of TE and CH. Hence it shows attraction between them it shows maxima at $x_1 \approx 0.1$ while minima at $x_1 \approx 0.9$. For CH + m- Xy the V^E values are negative over entire composition range results in the interaction between π electron of m-Xy and CH which shows attraction between them. The negative V^E values with increasing concentration of x_1 (CH) for the binary system follow the decreasing order as CH+ m-Xy > CH + TE.

Fig. 4(a) represents V^E with mole fraction (x_1) of CH for the system CH + DMF the V^E value shows both positive and negative values as the concentration of CH increases the V^E values become more negative results in the attraction between them due to the formation of hydrogen bond. It shows maxima at $x_1 \approx 0.1$ and minima at $x_1 \approx 0.9$. Fig. 1(b) represents variation of $\Delta\eta$ with (x_1) for binary mixtures of CH + alkanols.

For the system CH + ET $\Delta\eta$ are negative over entire composition range which shows maxima at $x_1 \approx 0.9$ and minima at $x_1 \approx 0.5$ as it becomes more negative from $x_1 \approx 0.1$ to $x_1 \approx 0.5$ clearly results due to the presence of attractive forces between them. For the system CH + PR $\Delta\eta$ are negative and increases from $x_1 \approx 0.0$ to $x_1 \approx 0.4$ results due to the attraction between them. It shows maxima at $x_1 \approx 0.9$ while minima at $x_1 \approx 0.4$. For CH + BUT $\Delta\eta$ shows positive and negative values and as concentration increases $\Delta\eta$ value becomes more negative from $x_1 \approx 0.2$ to $x_1 \approx 0.6$ resulting from the attracting forces between them it shows maxima at $x_1 \approx 0.1$ while minima at $x_1 \approx 0.6$. The positive $\Delta\eta$ values for the binary mixtures follow the decreasing order has CH + ET > CH + PR > CH + BUT.

Fig. 2(b) represents variation of $\Delta\eta$ with mole fraction (x_1) for binary mixtures of CH + ETH /aromatic ethers for CH + ETH system the $\Delta\eta$ values are negative over entire composition range shows minima at $x_1 \approx 0.7$ while maxima at $x_1 \approx 0.1$. For CH + THF $\Delta\eta$ values are also negative and becomes more negative as concentration increases from $x_1 \approx 0.1$ to $x_1 \approx 0.8$ results from π electron donation from THF to CH. It shows maxima at $x_1 \approx 0.1$ while minima at $x_1 \approx 0.8$. The negative $\Delta\eta$ values for the binary mixtures follows the decreasing order as CH + ETH > CH + THF. It concludes that there is strong interaction between CH + ETH than CH + THF.

Fig 3(b) represents variation of $\Delta\eta$ with mole fraction (x_1) for binary mixtures of CH + substituted aromatic rings. For CH + TE $\Delta\eta$ values are negative clearly indicates the π electron donation takes place from TE to CH It shows maxima at $x_1 \approx 0.1$ while minima at $x_1 \approx 0.7, 0.8$. For CH + m-Xy $\Delta\eta$ values are negative over the entire composition range indicates the π electron donation from m-Xy to CH which shows maxima at $x_1 \approx 0.2$ and minima at $x_1 \approx 0.7$.

The negative $\Delta\eta$ values for the binary mixtures follow the decreasing order as CH + m-Xy \geq CH + TE. It concludes that there is slight effect of addition of alkyl substituent on aromatic ring in presence of CH.

Fig. 4(b) represents variation of $\Delta\eta$ with mole fraction (x_1) for binary mixture CH + DMF $\Delta\eta$ values becomes positive after $x_1 \approx 0.3$ and its magnitude is more indicates specific interaction between CH + DMF shows presence of weak hydrogen bonding between them. It shows maxima at $x_1 \approx 0.5$ while minima at $x_1 \approx 0.3$.

Regression result for V^E & $\Delta\eta$ of binary liquids at various temperatures along with the correlation coefficient (R^2) are illustrated in Table.3

The dependence of $V^E / \Delta\eta$ on x_1 has been established using a polynomial equation as:-

$$V^E / \Delta\eta = \sum A_i X_1^i \quad (i = 0,1,2,3) \quad (4)$$

The coefficients A_i along with the correlation coefficient R^2 are listed in Table.3.

Table.1 Densities and Viscosities of pure liquids with literature values at 301K

Liquids	$\rho \times 10^{-3}(\text{kgm}^{-3})$		$\eta \times 10^{-3}(\text{kgm}^{-3})$	
	Experimental	Literature	Experimental	Literature
CH	0.7699	0.7695 ¹⁷	1.0493	1.0496
ET	0.7848	0.7686 ¹⁷	1.3269	
PR	0.7995		2.4344	2.4340
BUT	0.8389	0.8095 ¹⁶	3.0154	
TE	0.8547		0.6296	
m-Xy	0.8863		0.6718	0.6708
ETH	0.7275		0.3586	
THF	0.8745	0.8782 ¹⁵	0.5141	0.4683 ¹⁵
DMF	0.9437		0.8518	

Table.2 Values of ρ and η of various binary mixtures over an entire mole fraction at 301K

CH + ET			CH + ETH		
x_1	ρ	η	x_1	ρ	η
0.0000	0.7848	1.3269	0.0000	0.7225	0.3586
0.0988	0.7799	1.2496	0.1033	0.7336	0.3882
0.0199	0.7772	1.1924	0.2039	0.7425	0.3978
0.3010	0.7737	1.1542	0.3025	0.7461	0.4198
0.4041	0.7728	1.1065	0.3976	0.7514	0.4540
0.5506	0.7719	1.0779	0.4951	0.7589	0.4912
0.6013	0.7715	1.0684	0.5948	0.7656	0.5389
0.7049	0.7714	1.0207	0.6972	0.7737	0.5933
0.8005	0.7709	1.0207	0.8022	0.7809	0.7030
0.9046	0.7721	1.0493	0.9064	0.7881	0.8318
1.0000	0.7699	1.0493	1.0000	0.7699	1.0493

CH + PR			CH + THF		
x_1	ρ	η	x_1	ρ	η
0.0000	0.7995	2.4344	0.0000	0.8745	0.5141
0.1079	0.7943	2.1940	0.1006	0.8220	0.5475
0.2008	0.7920	1.9441	0.1992	0.7999	0.5685
0.2995	0.7883	1.7457	0.3016	0.7680	0.6019
0.3969	0.7850	1.5578	0.4002	0.7400	0.6324
0.5036	0.7817	1.4309	0.5012	0.7225	0.6696
0.6030	0.7793	1.3326	0.6035	0.7019	0.7040
0.6934	0.7777	1.2305	0.6978	0.6936	0.7431
0.7977	0.7755	1.1437	0.8015	0.6785	0.7936
0.9090	0.7749	1.1304	0.9020	0.6623	0.8490
1.0000	0.7699	1.0493	1.0000	0.7699	1.0493

CH + BUT			CH + TE		
x_1	ρ	η	x_1	ρ	η
0.0000	0.8389	3.0154	0.0000	0.8745	0.5141
0.1033	0.8325	2.8590	0.1006	0.8220	0.5475
0.2039	0.8269	2.4110	0.1992	0.7999	0.5685
0.3025	0.8231	1.9965	0.3016	0.7680	0.6019
0.3976	0.8184	1.7535	0.4002	0.7400	0.6324
0.4951	0.8144	1.5724	0.5012	0.7225	0.6696
0.5948	0.8099	1.3265	0.6035	0.7019	0.7040
0.6972	0.8056	1.2808	0.6978	0.6936	0.7431
0.8022	0.8013	1.2389	0.8015	0.6785	0.7936
0.9064	0.7847	1.1550	0.9020	0.6623	0.8490
1.0000	0.7699	1.0493	1.0000	0.7699	1.0493

CH + m-Xy		
x_1	ρ	η
0.0000	0.8863	0.6718
0.1033	0.8863	0.6718
0.2039	0.8863	0.6718
0.3025	0.8863	0.6718
0.3976	0.8863	0.6718
0.4951	0.8863	0.6718
0.5948	0.8863	0.6718
0.6972	0.8863	0.6718
0.8022	0.8863	0.6718
0.9064	0.8863	0.6718
1.0000	0.8863	0.6718

x_1	ρ	η	CH + DMF		
0.0000	0.8863	0.6718	x_1	ρ	η
0.1024	0.8780	0.6728	0.0000	0.9437	0.8518
0.2012	0.8677	0.6852	0.1059	0.8885	0.8242
0.2976	0.8600	0.6909	0.2090	0.8600	0.8404
0.4048	0.8552	0.7071	0.3021	0.8250	0.8270
0.5082	0.8446	0.7147	0.3994	0.8100	0.9367
0.5972	0.8425	0.7233	0.4980	0.8092	1.0426
0.7006	0.8371	0.7328	0.6002	0.7806	1.0369
0.7998	0.8321	0.8024	0.7053	0.7778	1.0588
0.8997	0.8273	0.8481	0.8057	0.7743	1.0665
1.0000	0.7699	1.0493	0.9019	0.7723	1.0760
			1.0000	0.7699	1.0493

Table 3 Regression result for the V^E and $\Delta\eta$ of binary mixtures at 301K along with the Correlation coefficient (R^2)

Systems		A_0	A_1	A_2	A_3	A_4	A_5	R^2
CH + ET	V^E	-0.401	1690	-3938	3289	-1166	125.2	0.981
	$\Delta\eta$	-0.0000	3.269	-5.629	2.775	0.206	-0.503	0.970
CH + PR	V^E	-0.448	1141	-2412	1775	-565.8	61.77	0.960
	$\Delta\eta$	0.004	0.817	-3.471	4.172	-0.427	-1.087	0.980
CH + BUT	V^E	-0.392	1227	-2623	1936	-577	36.26	0.973
	$\Delta\eta$	0.012	13.68	-44.14	49.65	-20.74	1.544	0.972
CH + ETH	V^E	-0.362	1210	-2570	1875	-533.1	17.07	0.976
	$\Delta\eta$	0.001	2.788	-5.453	4.223	-1.172	-0.387	0.997
CH + THF	V^E	-0.272	1287	-2788	2116	-697.9	82.76	0.974
	$\Delta\eta$	-0.0000	5.817	-12.26	9.121	-2.685	0.013	0.993
CH + TE	V^E	-0.380	1133	-2428	1844	-622.4	72.81	0.971
	$\Delta\eta$	-0.001	2.243	-2.893	0.285	0.998	-0.623	0.992
CH+m-Xy	V^E	-0.445	1196	-2559	1898	-579.5	43.31	0.969
	$\Delta\eta$	-0.006	4.038	-8.522	7.144	-2.809	0.150	0.953
CH+DMF	V^E	-0.313	1221	-2609	1957	-643.8	74.81	0.976
	$\Delta\eta$	0.004	2.772	-4.451	-0.310	2.885	-0.893	0.849

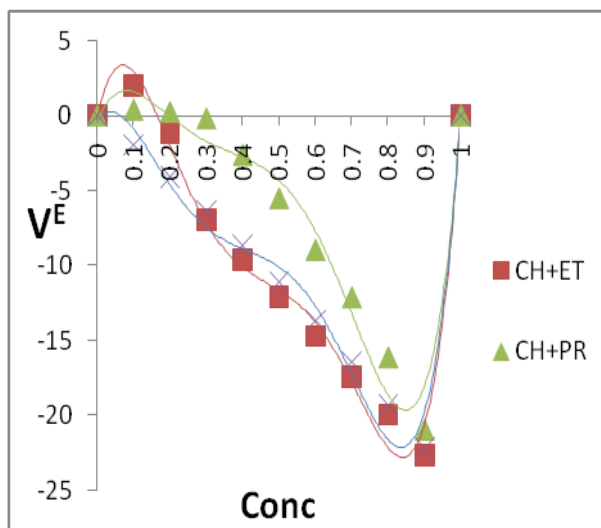


Fig.1.a. V^E for CH+ET (■), CH+PR (▲), CH+BUT (×) at 301K

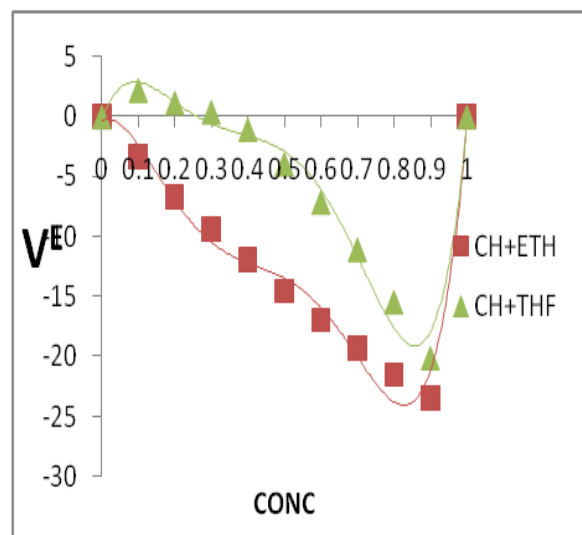


Fig.2.a. V^E for CH+ETH (▲), CH+THF (■)

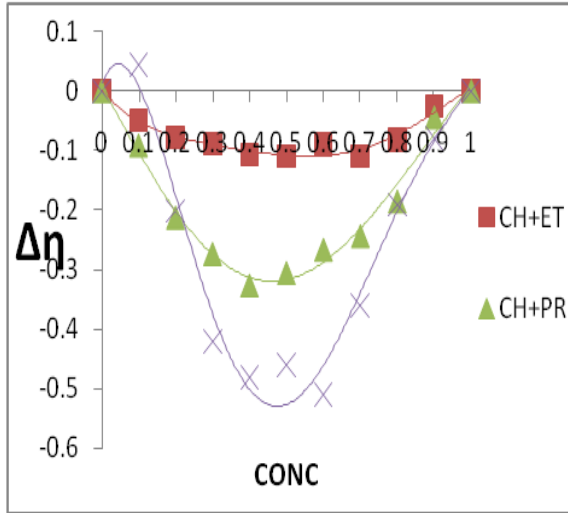


Fig.1.b. $\Delta\eta$ for CH+ET (■), CH+PR (▲), CH+BUT (×) at 301K

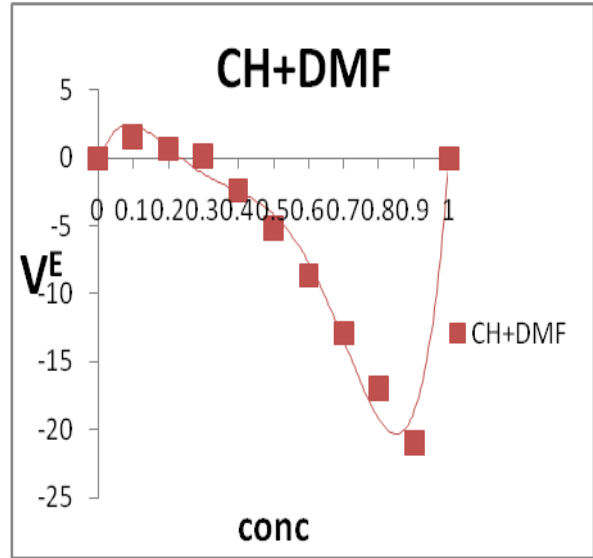


Fig.4.a. V^E for CH+DMF (■) at 301K

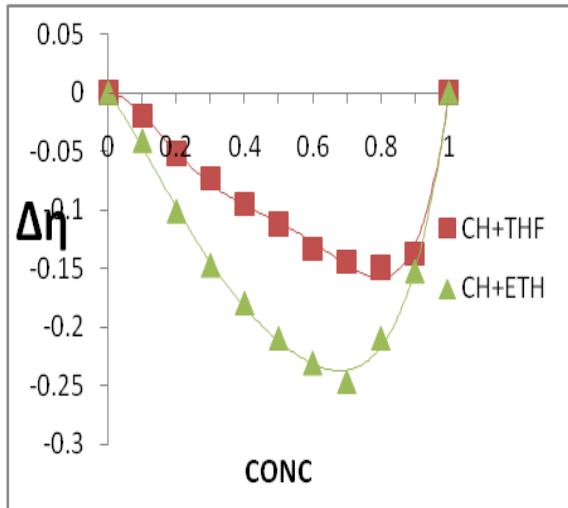


Fig.2.b. $\Delta\eta$ for CH+ETH (▲), CH+THF (■) at 301K

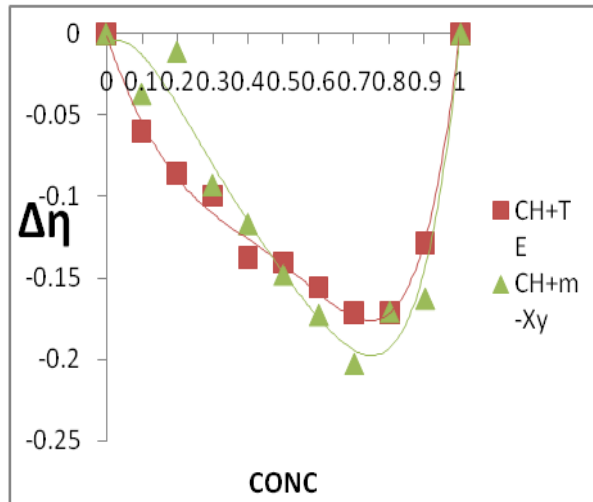


Fig.3.b. $\Delta\eta$ for CH+TE (■), CH+ m-Xy (▲) at 301K

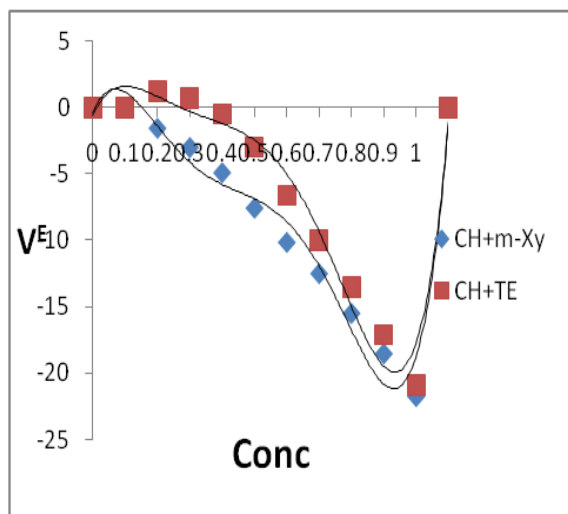


Fig.3.a. V^E for CH+TE (■), CH+ m Xy (▲) at 301K

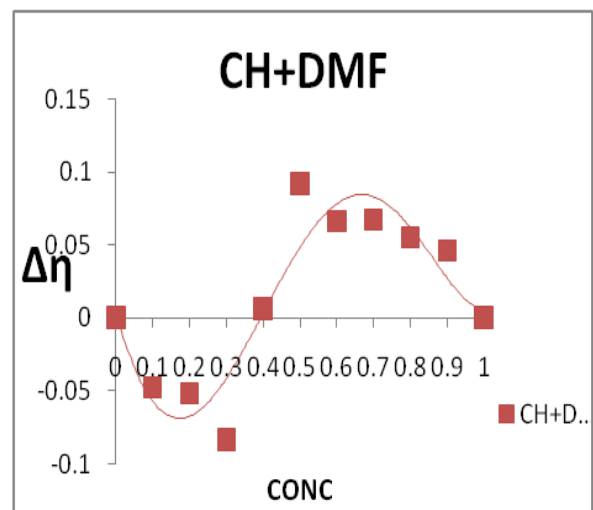


Fig.4.b. $\Delta\eta$ for CH+DMF (■) at 301K

CONCLUSIONS

For the system CH + alkanols the homo intermolecular Hydrogen bond between the alkanols weakens strongly due to the addition of CH (For short chain alkanols) resulting into the formation of new complex between them. As chain length of alkanols increases the hydrogen bonding decreases. For the system CH + substituted aromatic ring some interactions are present between them due to π -electron donation from aromatic ring to CH but it will remain unaffected as the alkyl substituent on aromatic ring are increases. For the system CH + ETH / aromatic ethers strong interaction is present between them due to the formation of Hydrogen bond as well as π -electron donation from aromatic ethers to CH. For the system CH + DMF some interactions are observed due to the presence of weak hydrogen bond in between them.

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