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Ultrasonic Study of binary mixtures of $C_2H_4Cl_2$ or CH_2Cl_2 with C_3H_7NO or C_2H_6OS at 308.15 K

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ABSTRACT

The densities, ρ and viscosities, η of binary mixtures of $C_2H_4Cl_2 + C_3H_7NO$, $C_2H_4Cl_2 + C_2H_6OS$, $CH_2Cl_2 + C_3H_7NO$ and $CH_2Cl_2 + C_2H_6OS$ have been measured over the entire composition range at 308.15 K. From this experimental data, deviation in viscosity, $\Delta\eta$, excess free volume, V_f^E , excess internal pressure, π_i^E , excess enthalpy, H^E and excess Gibbs free energy, ΔG^E have been measured. From the positive and negative values of excess properties strong interactions such as hydrogen bond formation between the dissimilar molecules, dipole-dipole interactions exist between the unlike molecules. The experimental viscosity data of all of these binary liquid mixtures have been correlated with viscosity models.

Keywords: Density, Viscosity, Redlich–Kister type polynomial, Excess internal pressure, Theoretical viscosity model

INTRODUCTION

The volumetric and viscometric study of liquid mixtures enables the determination of some useful thermodynamic and other properties that are highly sensitive to molecular interactions [1-4]. Many engineering and technological problems require quantitative data on the density and viscosity of liquid mixtures. Volumetric properties of liquid binary mixtures enable the important information for the characterization of the interactions between components. *N,N*-Dimethyl formamide is used as a solvent in peptide coupling for pharmaceuticals, in the development and production of pesticides, in the manufacture of adhesives, synthetic leathers, fibers, films, and surface coatings and other applications of pure solvents. It has a large dipole moment $\mu = 3.82D$ [5] and, in view of this, dipole–dipole interactions are expected to play an important role in molecular interactions present in the liquid mixtures. Dimethyl sulfoxide having highly polar S=O group and two hydrophobic CH_3 groups. It is a typical aprotic highly polar ($\mu = 4.06D$) self-associated solvent, is an important solvent in chemistry, biotechnology, and medicine and it is able to participate in hydrogen bonding [6]. Dichloromethane used as a cleaning agent, paint remover and in extraction technology; paraffin extraction, recovery of specialty pharmaceuticals [7]. 1,2-Dichloroethane mostly used in the production of vinyl chloride which is used to make a variety of plastic and vinyl products including polyvinyl chloride. The present work focuses on the study of thermodynamic behavior of binary mixtures of *N,N*-Dimethyl formamide (C_3H_7NO)+Dichloromethane (CH_2Cl_2), *N,N*-Dimethyl formamide (C_3H_7NO)+1,2-Dichloroethane ($C_2H_4Cl_2$), Dimethyl sulfoxide (C_2H_6OS) +Dichloromethane (CH_2Cl_2) and Dimethyl sulfoxide (C_2H_6OS) +1,2-Dichloroethane ($C_2H_4Cl_2$).

A survey of literature indicates that Radhamma *et al.* [8], Ali and Tariq [9], Subash C Bhatia *et al.* [10], Radhey Shyam Sah *et al.* [11], Satyanarayana *et al.* [12], Oana Cioclirlan and Olga Iulian [13] Harish Kumar and Deepika [14] Vijayakumar Naidu *et al.* [15], Fabio Comelli *et al.* [16] and others [17] reported the various excess properties of the liquid mixtures containing Dichloromethane, 1,2-Dichloroethane, Dimethyl sulfoxide as one component. In the present investigation, we report data related to densities, ρ and viscosities, η of binary liquid mixtures of $C_2H_4Cl_2 + C_3H_7NO$, $C_2H_4Cl_2 + C_2H_6OS$, $CH_2Cl_2 + C_3H_7NO$ and $CH_2Cl_2 + C_2H_6OS$ over the entire composition range at 308.15 K. The experimental data of ρ and η were used to calculate the free volume, V_f , internal pressure, π_i , relaxation time, τ , enthalpy, H and deviation in viscosity, $\Delta\eta$, excess free volume, V_f^E , excess internal pressure, π_i^E , excess enthalpy, H^{*E} , excess Gibbs free energy, ΔG^{*E} have been measured. The variation of these properties with composition has been discussed in terms of molecular interactions.

MATERIALS AND METHODS

C_3H_7NO , C_2H_6OS , CH_2Cl_2 and $C_2H_4Cl_2$, all of Analytical Reagent grade (AR grade) are used in the present investigation and are further purified by standard methods [18]. $C_2H_4Cl_2 + C_3H_7NO$, $C_2H_4Cl_2 + C_2H_6OS$, $CH_2Cl_2 + C_3H_7NO$ and $CH_2Cl_2 + C_2H_6OS$ were prepared so that the entire composition range is covered. The mixtures were prepared by mass in air-tight bottles. The mass measurements were performed with a METTLER TOLEDO (Switzerland) ABB5-S/FACT digital balance with an accuracy ± 0.01 mg. The uncertainty in the mole fraction is 10^{-4} .

The density and viscosity measurements of liquid mixtures have been measured using a two stem double-walled Parker & Parker type pycnometer [19] and Ostwald viscometer respectively. The detailed description of measurements of density and viscosity were presented in our previous papers [20-22]. The reproducibility in the measured parameters of density and viscosity are 3 in 10^5 parts and ± 0.2 %, respectively. The experimental values of ρ and η of pure liquids at $T = 308.15$ K along with their literature [10,12,15,23,24,25,26] values are presented in Table 1. These results are in good agreement with the reported data.

Table 1 Comparison of densities, ρ , and viscosities, η , of pure liquids with literature data at 308.15 K

Liquid	$\rho/(\text{kg.m}^{-3})$		$\eta/(10^{-3}\text{N.m}^{-2}\text{s})$	
	In this work	Literature	In this work	Literature
Dichloromethane	1297.2	1297.2 ^[23]	0.364	0.362 ^[23]
1,2-Dichloroethane	1230.2	1230.8 ^[12]	0.738	0.779 ^[10]
N,N-Dimethyl formamide	935.6	935.717 ^[24]	0.707	0.710 ^[25]
Dimethyl sulphoxide	1085.2	1085.48 ^[15]	1.614	1.645 ^[26]

3. Theory and Calculation

From the experimental data the following parameters are computed.

$$\text{Free volume } V_f = \left[\frac{M_{\text{eff}} u}{K \eta} \right]^{3/2} \quad (1)$$

Where $M_{\text{eff}} = \sum M_i X_i$; M_i and X_i are molecular weight and mole fraction of the individual molecules of liquid mixture. K is a temperature-independent constant equal to 4.28×10^9 for all liquids.

$$\text{Internal pressure } \pi_i = bRT \left[\frac{K \eta}{u} \right]^{1/2} \left[\frac{\rho^{2/3}}{M_{\text{eff}}^{7/6}} \right] \quad (2)$$

$$\text{Enthalpy } H = \pi_i V_m \quad (3)$$

$$\text{Gibbs free energy } \Delta G^* = RT \left[\ln(\eta V_m) \right] \quad (4)$$

$$\text{Relaxation time } \tau = \frac{4}{3} \beta \eta \quad (5)$$

The symbols used in the above expressions are their usual meanings.

The experimental values of densities, ρ , viscosities, η , and calculated values of free volume, V_f , internal pressure, π_i , relaxation time, τ and enthalpy, H of all binary systems are furnished in Table 2.

Table 2 Experimental values of densities, ρ (kg.m^{-3}), viscosities, η ($10^{-3}\text{N.m}^{-2}\text{s}$), free volume, V_f ($10^{-7}\text{m}^3\text{.mol}^{-1}$), internal pressure, π_i (10^6 Pa), relaxation time, τ (10^{-12} s) and enthalpy, H (J.mol^{-1}) of all binary systems at 308.15 K with mole fraction, x_1 of $\text{C}_2\text{H}_4\text{Cl}_2$ or CH_2Cl_2

x_1	ρ	η	V_f	π_i	τ	H
$\text{C}_2\text{H}_4\text{Cl}_2 + \text{C}_3\text{H}_7\text{NO}$						
0.0000	935.6	0.707	0.9865	838.0	0.4897	40339.9
0.0633	964.5	0.728	1.0056	809.3	0.5204	40657.1
0.1341	993.6	0.742	1.0500	773.6	0.5446	40696.6
0.2048	1020.1	0.753	1.1028	739.0	0.5635	40627.6
0.2923	1052.2	0.759	1.1864	697.7	0.5780	40314.9
0.3771	1080.5	0.762	1.2732	660.9	0.5898	39984.8
0.4823	1111.1	0.766	1.3869	619.1	0.6013	39583.8
0.5829	1138.2	0.770	1.4962	584.0	0.6114	39237.2
0.7123	1170.2	0.762	1.6805	539.9	0.6129	38503.8
0.8393	1198.1	0.758	1.8684	502.3	0.6118	37858.8
1.0000	1230.2	0.738	2.2000	455.5	0.5912	36638.8
$\text{C}_2\text{H}_4\text{Cl}_2 + \text{C}_2\text{H}_6\text{OS}$						
0.0000	1085.2	1.614	0.6869	722.9	0.9017	52050.3
0.0902	1100.7	1.432	0.8052	681.3	0.8502	49521.2
0.1653	1113.8	1.315	0.9065	651.6	0.8121	47722.9
0.2383	1126.2	1.227	1.0004	627.4	0.7831	46294.0
0.3546	1145.3	1.108	1.1590	592.7	0.7423	44254.3
0.4762	1164.3	1.002	1.3438	559.4	0.7028	42304.2
0.5782	1179.4	0.926	1.5171	533.3	0.6698	40776.1
0.6794	1192.4	0.866	1.6864	510.7	0.6442	39522.5
0.7798	1205.2	0.808	1.8836	488.4	0.6165	38241.7
0.8787	1216.6	0.762	2.0719	469.3	0.5955	37196.6
1.0000	1230.2	0.738	2.2000	455.5	0.5912	36639.1
$\text{CH}_2\text{Cl}_2 + \text{C}_3\text{H}_7\text{NO}$						
0.0000	935.6	0.707	0.9865	838.0	0.4897	40339.9
0.0728	967.6	0.716	0.9909	820.8	0.5266	40668.6
0.1536	1002.2	0.714	1.0353	792.9	0.5478	40482.1
0.2399	1038.0	0.712	1.0819	765.9	0.5697	40293.0
0.3325	1074.4	0.702	1.153	734.5	0.5845	39856.6
0.425	1109.3	0.688	1.2401	703.0	0.5927	39284.2
0.5682	1159.6	0.654	1.4369	650.0	0.5846	37951.5
0.6343	1181.8	0.634	1.5539	625.2	0.5754	37211.8
0.7568	1221.7	0.578	1.8884	572.7	0.5384	35267.5
0.8734	1258.4	0.510	2.4112	517.3	0.4822	32839.6
1.0000	1297.2	0.364	4.2317	420.1	0.3500	27388.9
$\text{CH}_2\text{Cl}_2 + \text{C}_2\text{H}_6\text{OS}$						
0.0000	1085.2	1.614	0.6869	722.9	0.9017	52047.4
0.1048	1106.2	1.446	0.7484	707.3	0.8969	50412.5
0.2114	1128.2	1.286	0.8405	685.3	0.8627	48329.0
0.3184	1150.6	1.136	0.9612	659.9	0.8154	46052.4
0.4228	1173.1	0.998	1.1137	632.7	0.7614	43692.4
0.5259	1195.5	0.881	1.2906	606.5	0.7073	41454.3
0.6256	1217.8	0.766	1.5377	576.1	0.6428	38970.4
0.7241	1239.0	0.658	1.8699	543.0	0.5760	36399.3
0.8236	1260.4	0.556	2.3366	507.2	0.5059	33692.2
0.9079	1277.7	0.462	3.0248	467.5	0.4316	30844.5
1.0000	1297.2	0.364	4.2317	420.1	0.3500	27507.4

In order to study the non-ideality of the liquid mixtures, the difference between the values of the real mixture and those corresponding to an ideal mixture namely the deviation/excess parameters are computed from the experimental data.

$$\text{Deviation in viscosity } \Delta\eta = \eta - (x_1\eta_1^* + x_2\eta_2^*) \quad (6)$$

$$\text{Excess free volume } V_f^E = V_f - (x_1V_{f1}^* + x_2V_{f2}^*) \quad (7)$$

$$\text{Excess internal pressure } \pi_i^E = \pi_i - (x_1\pi_{i1}^* + x_2\pi_{i2}^*) \quad (8)$$

$$\text{Excess enthalpy } H^E = H - (x_1H_1^* + x_2H_2^*) \quad (9)$$

Excess Gibbs free energy of activation for viscous flow

$$\Delta G^{*E} = RT \left[\ln(\eta V) - x_1 \ln(\eta_1^* V_1^*) - x_2 \ln(\eta_2^* V_2^*) \right] \quad (10)$$

where $\eta_1^*, V_{f1}^*, \pi_{i1}^*, H_1^*, V_1^*$ are the viscosities, free volumes, internal pressures, enthalpy's and molar volumes of pure component 1 ($\text{C}_2\text{H}_4\text{Cl}_2$ or CH_2Cl_2) and $\eta_2^*, V_{f2}^*, \pi_{i2}^*, H_2^*, V_2^*$ are the viscosities, free volumes, internal pressures, enthalpy's and molar volumes of pure component 2 ($\text{C}_3\text{H}_7\text{NO}$ or $\text{C}_2\text{H}_6\text{OS}$) respectively and x_i represents the mole fraction of the component 'i' in the mixture. The values of deviation in viscosity, $\Delta\eta$, excess free volume, V_f^E , excess internal pressure, π_i^E , excess enthalpy, H^E and excess Gibbs free energy activation for viscous flow, ΔG^{*E} for all binary systems are presented in Table 3.

Table 3 Deviation in viscosity, $\Delta\eta$ ($10^{-3}\text{N.m}^{-2}\text{s}$), excess free volume, V_f^E ($10^{-7}\text{m}^3\text{.mol}^{-1}$), excess internal pressure, π_i^E (10^6Pa), excess enthalpy, H^E (J.mol^{-1}) and excess Gibbs free energy, ΔG^{*E} (kJ.mol^{-1}) of all binary systems at 308.15 K with mole fraction, x_1 of $\text{C}_2\text{H}_4\text{Cl}_2$ or CH_2Cl_2

x_1	$\Delta\eta$	V_f^E	π_i^E	H^E	ΔG^{*E}
$\text{C}_2\text{H}_4\text{Cl}_2 + \text{C}_3\text{H}_7\text{NO}$					
0.0000	0.000	0.0000	0.0	0.0	0.000
0.0633	0.019	-0.0578	-4.4	551.5	0.094
0.1341	0.031	-0.0993	-13.1	853.0	0.160
0.2048	0.040	-0.1322	-20.6	1045.7	0.210
0.2923	0.043	-0.1548	-28.5	1056.8	0.233
0.3771	0.043	-0.1709	-32.8	1040.6	0.240
0.4823	0.044	-0.1849	-34.4	1029.0	0.245
0.5829	0.045	-0.1977	-31.0	1054.7	0.242
0.7123	0.033	-0.1703	-25.6	800.1	0.183
0.8393	0.025	-0.1366	-14.6	625.3	0.131
1.0000	0.000	0.0000	0.0	0.0	0.000
$\text{C}_2\text{H}_4\text{Cl}_2 + \text{C}_2\text{H}_6\text{OS}$					
0.0000	0.000	0.0000	0.0	0.0	0.000
0.0902	-0.103	-0.0182	-17.5	-1139.0	-0.127
0.1653	-0.154	-0.0305	-27.1	-1779.9	-0.197
0.2383	-0.178	-0.0470	-31.8	-2083.9	-0.230
0.3546	-0.195	-0.0645	-35.4	-2331.2	-0.260
0.4762	-0.195	-0.0637	-36.2	-2407.3	-0.276
0.5782	-0.181	-0.0447	-35.0	-2363.4	-0.275
0.6794	-0.153	-0.0285	-30.5	-2057.4	-0.241
0.7798	-0.123	0.0168	-26.0	-1790.9	-0.216
0.8787	-0.082	0.0555	-18.6	-1311.9	-0.165
1.0000	0.000	0.0000	0.0	0.0	0.000

CH ₂ Cl ₂ +C ₃ H ₇ NO					
0.0000	0.000	0.0000	0.0	0.0	0.000
0.0728	0.034	-0.2318	13.3	1271.6	0.173
0.1536	0.060	-0.4497	19.1	2131.5	0.316
0.2399	0.087	-0.6831	28.1	3060.1	0.465
0.3325	0.109	-0.9125	35.4	3822.9	0.592
0.4250	0.127	-1.1257	42.6	4448.4	0.700
0.5682	0.142	-1.3935	49.4	4970.3	0.814
0.6343	0.145	-1.4910	52.2	5086.7	0.844
0.7568	0.131	-1.5540	51.0	4728.9	0.806
0.8734	0.103	-1.4097	44.3	3811.1	0.669
1.0000	0.000	0.0000	0.0	0.0	0.000
CH ₂ Cl ₂ + C ₂ H ₆ OS					
0.0000	0.000	0.0000	0.0	0.0	0.000
0.1048	-0.037	-0.3100	16.1	936.9	0.118
0.2114	-0.064	-0.5958	26.3	1469.4	0.223
0.3184	-0.080	-0.8544	33.4	1818.6	0.313
0.4228	-0.087	-1.0719	37.8	2020.5	0.377
0.5259	-0.076	-1.2605	42.9	2312.5	0.450
0.6256	-0.066	-1.3668	42.6	2275.2	0.470
0.7241	-0.051	-1.3838	39.3	2121.3	0.457
0.8236	-0.029	-1.2698	33.6	1855.9	0.407
0.9079	-0.017	-0.8804	19.4	1076.9	0.257
1.0000	0.000	0.0000	0.0	0.0	0.000

The values of $\Delta\eta$, H^{*E} and ΔG^{*E} have been fitted to a Redlich-Kister [27] type polynomial equation.

$$Y^E = x(1-x) \sum A_i (1-2x)^i \quad (11)$$

where Y^E is $\Delta\eta$, H^{*E} and ΔG^{*E} . The subscript 'i' in the summation of the above equation takes values from 0 to 4. The values of coefficients A_i in the above equation have been determined using the least square method and are compiled in Table 4 along with the standard deviations $\sigma(Y^E)$ calculated using the expression.

$$\sigma(Y^E) = [\sum (Y_{\text{exp}}^E - Y_{\text{cal}}^E)^2 / (m-n)]^{1/2} \quad (12)$$

where 'm' is the total number of experimental points and 'n' is the number of coefficients in the eq. (11). The value of 'n' in the present study is 5.

Table 4 Coefficients A_i of Redlich-Kister type polynomial equation eq 6 and the corresponding standard deviations (σ) of all the systems

	A_0	A_1	A_2	A_3	A_4	σ
C ₂ H ₄ Cl ₂ + C ₃ H ₇ NO						
$\Delta\eta$ (10 ⁻³ N.m ⁻² .s)	0.178	0.033	0.050	0.053	0.084	0.002
H^{*E} (J.mol ⁻¹)	4168.4	840.3	2177.6	2058.3	2624.11	40.1
ΔG^{*E} (kJ.mol ⁻¹)	0.982	0.199	0.211	0.186	0.305	0.007
C ₂ H ₄ Cl ₂ +C ₂ H ₆ OS						
$\Delta\eta$ (10 ⁻³ N.m ⁻² .s)	-0.768	-0.238	-0.201	-0.076	-0.299	0.002
H^{*E} (J.mol ⁻¹)	-9609.5	-1477.2	-3341.5	1086.5	-4114.2	38.3
ΔG^{*E} (kJ.mol ⁻¹)	-1.104	-0.091	-0.299	0.2	-0.745	0.005
CH ₂ Cl ₂ +C ₃ H ₇ NO						
$\Delta\eta$ (10 ⁻³ N.m ⁻² .s)	0.552	-0.196	0.079	-0.188	0.334	0.001
H^{*E} (J.mol ⁻¹)	19298.8	-7021.5	3542.2	-8019.8	14342.1	44.3
ΔG^{*E} (kJ.mol ⁻¹)	3.095	-1.448	0.899	-1.643	2.061	0.008
CH ₂ Cl ₂ + C ₂ H ₆ OS						
$\Delta\eta$ (10 ⁻³ N.m ⁻² .s)	-0.324	-0.16	0.062	0.058	-0.021	0.002
H^{*E} (J.mol ⁻¹)	8821.9	-3046.0	4142.5	1575.4	521.7	57.9
ΔG^{*E} (kJ.mol ⁻¹)	1.713	-1.002	0.733	-0.229	-0.008	0.008

The dynamic viscosities of the binary liquid mixtures have been calculated using the following empirical relations. Grunberg and Nissan [28] model is based on Arrhenious equation for the measurement of viscosity of liquid mixtures

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \quad (13)$$

where G_{12} is an interaction parameter which is function of the components 1 and 2 as well as temperature. Hind and Ubbelohde [29] suggested an equation for the viscosity of binary liquid mixtures as

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1 x_2 H_{12} \quad (14)$$

where H_{12} is an interaction parameter and is attributed to unlike pair interactions. Frenkel relation [30] for viscosity theoretical calculation is given by

$$\ln \eta = x_1^2 \ln \eta_1 + x_2^2 \ln \eta_2 + 2x_1 x_2 \ln \eta_{12} \quad (15)$$

The terms G_{12} , H_{12} , and η_{12} are adjustable parameters representing the binary interactions presented in Table 5 along with the standard deviations, σ .

Table 5 Various interaction parameters calculated from theoretical viscosity models and the corresponding standard deviations σ (10^3 N.s.m⁻²) at 308.15 K

Binary solution	G_{12}	σ	H_{12}	σ	η_{12}	σ
C ₂ H ₄ Cl ₂ + C ₃ H ₇ NO	0.2920	0.009	0.0008	0.011	0.0008	0.012
C ₂ H ₄ Cl ₂ +C ₂ H ₆ OS	-0.4870	0.014	0.0007	0.043	0.0009	0.022
CH ₂ Cl ₂ +C ₃ H ₇ NO	1.2410	0.044	0.0008	0.025	0.0010	0.054
CH ₂ Cl ₂ + C ₂ H ₆ OS	0.7700	0.041	0.0008	0.020	0.0011	0.035

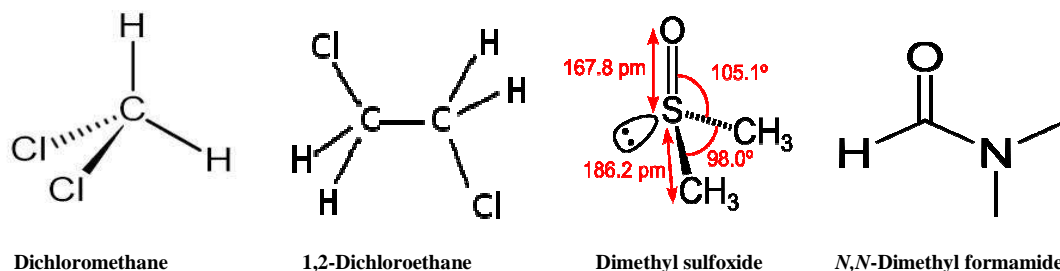
RESULTS AND DISCUSSION

It is noticed from the Table 2, that the density, free volume increases in all binary systems and relaxation time increases in C₂H₄Cl₂+ C₃H₇NO binary systems linearly, where as internal pressure, enthalpy, relaxation time (except C₂H₄Cl₂+ C₃H₇NO) decreases linearly in all systems. The viscosity behavior shows non-linearly for the presented binary systems. This clearly indicates the existence of intermolecular interaction between the unlike molecules. To understand the nature of molecular interactions exist in the liquid mixtures, it is of interest to discuss the properties in term of excess properties rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their physical behavior with respect to concentration and these have been interpreted as arising from the presence of strong or weak interactions.

The close perusal of Table 3 reveals that, $\Delta\eta$ values are positive for C₂H₄Cl₂+ C₃H₇NO, CH₂Cl₂+C₃H₇NO systems and negative for C₂H₄Cl₂+C₂H₆OS, CH₂Cl₂+ C₂H₆OS systems. Generally, negative values of $\Delta\eta$ indicate the presence of dispersion forces or mutual loss of specific interactions in like molecules operating in the systems arising due to weak intermolecular interactions and positive values of deviation in viscosity indicate strong specific interactions [30,31]. The sign and magnitude of $\Delta\eta$ depend on the combined effect of factors such as physical, chemical and structural factors [32–34].

The physical interactions are generally weak and the sign of $\Delta\eta$ may be negative or positive. Positive values of $\Delta\eta$ signify strong intermolecular interaction and the negative $\Delta\eta$ values are indicative of weaker interactions between unlike molecules. The chemical interactions involving H-bond formation, charge-transfer complex formation and the dipole-dipole interactions between components of liquid mixtures make the structure more compact and result in positive viscosity deviations $\Delta\eta$ of the liquid mixtures. The sign and magnitude of $\Delta\eta$ also varies with the structural characteristics of the liquid components arising from the geometrical fitting of one component into other component structure due to difference in the molecular size [36-38]. In the present work, dispersion forces are dominant in the C₂H₄Cl₂+C₂H₆OS and CH₂Cl₂+ C₂H₆OS binary systems and strong interactions are present in C₂H₄Cl₂+ C₃H₇NO and CH₂Cl₂+C₃H₇NO binary systems. The strength of interaction follows the order CH₂Cl₂+C₃H₇NO > C₂H₄Cl₂+ C₃H₇NO > CH₂Cl₂+ C₂H₆OS > C₂H₄Cl₂+C₂H₆OS.

When $\text{C}_2\text{H}_6\text{OS}$ mixed with $\text{C}_2\text{H}_4\text{Cl}_2$ ($\mu=1.86$ D and $\epsilon=10.36$) which is polar but practically unassociated, specific interaction could be donor-acceptor type between the oxygen atom of $\text{S}=\text{O}$ group of $\text{C}_2\text{H}_6\text{OS}$ with its unshared pairs of electrons, acts as electron-donor towards electron-acceptor chlorine atoms of $\text{C}_2\text{H}_4\text{Cl}_2$. In case of $\text{C}_3\text{H}_7\text{NO} + \text{C}_2\text{H}_4\text{Cl}_2$ a new hydrogen bond between the chlorine atom of $\text{C}_2\text{H}_4\text{Cl}_2$ and hydrogen atom of $\text{C}_3\text{H}_7\text{NO}$ ($\text{C}-\text{Cl} \cdots \text{H}$), hydrogen atom of $\text{C}_2\text{H}_4\text{Cl}_2$ and oxygen atom of carbonyl group of $\text{C}_3\text{H}_7\text{NO}$ ($-\text{H} \cdots \text{C}=\text{O}$) may be formed. The hydrogen bond formation is easy in between $\text{C}_3\text{H}_7\text{NO}$ and $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_4\text{Cl}_2$ molecules compared to $\text{C}_2\text{H}_6\text{OS}$. In $\text{C}_3\text{H}_7\text{NO}$ molecules hydrogen is attached to carbonyl group which is more favourable for the formation of hydrogen bond with chlorine atom in $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_4\text{Cl}_2$ molecules.



The negative values of excess Gibbs' free energy of activation of viscous flow indicate absence of specific and strong interactions in the system and also indicate that weak interactions are operative in the systems investigated [39,40]. Large negative excess values of ΔG^{*E} indicates the presence of weak interactions, whereas a large positive excess values of ΔG^{*E} suggests the specific strong interactions between the molecules in the liquid molecules reported by several authors [12,41].

The positive values of H^E for the mixtures are attributed to the fact that the physical forces are the dominant interactions between the dissimilar molecules than the chemical forces. From the negative values of excess free volume, V_f^E , positive and negative values of excess internal pressure, π_i^E concluded that strong interactions such as hydrogen bond, dipole-dipole interactions exist between the mixing liquids. The strength of interaction follows the order $\text{CH}_2\text{Cl}_2 + \text{C}_3\text{H}_7\text{NO} > \text{CH}_2\text{Cl}_2 + \text{C}_2\text{H}_6\text{OS} > \text{C}_2\text{H}_4\text{Cl}_2 + \text{C}_3\text{H}_7\text{NO} > \text{C}_2\text{H}_4\text{Cl}_2 + \text{C}_2\text{H}_6\text{OS}$.

Figs. 1,2,3 and 4 represent the percentage deviations of theoretical viscosity of $\text{C}_2\text{H}_4\text{Cl}_2 + \text{C}_3\text{H}_7\text{NO}$, $\text{C}_2\text{H}_4\text{Cl}_2 + \text{C}_2\text{H}_6\text{OS}$, $\text{CH}_2\text{Cl}_2 + \text{C}_3\text{H}_7\text{NO}$ and $\text{CH}_2\text{Cl}_2 + \text{C}_2\text{H}_6\text{OS}$. On the examination of these figures the viscosity models are well correlated to the experimental viscosity values. From table 5, the interaction parameters corresponding to the viscosity models are very small which further support the correlation of theoretical values of viscosity.

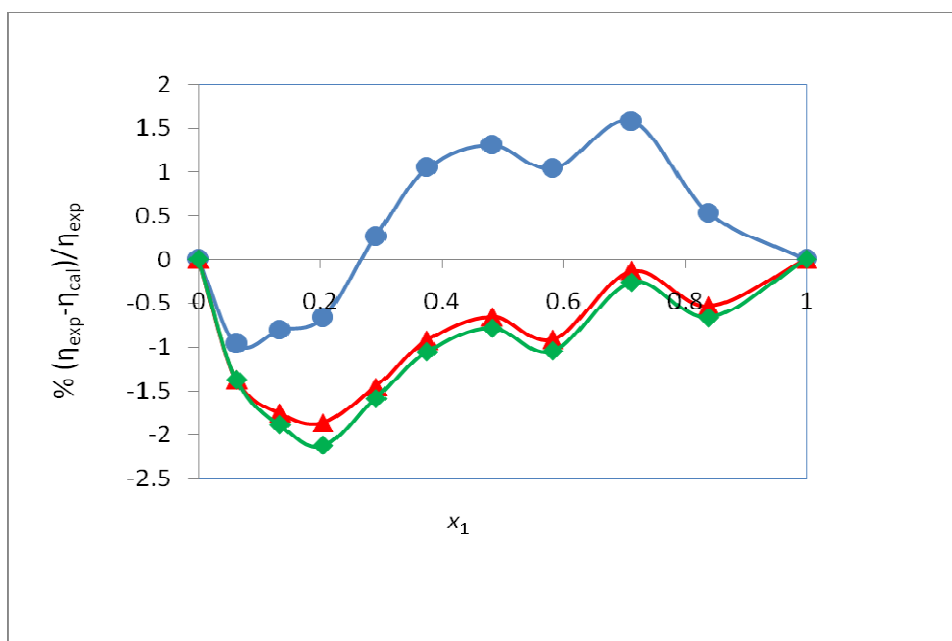


Figure 1 Plots of percentage deviations of theoretical viscosity of $C_2H_4Cl_2 + C_3H_7NO$ solution against mole fraction, x_1 of $C_2H_4Cl_2$; Grunberg (●), Hind (▲), Frenkel (◆)

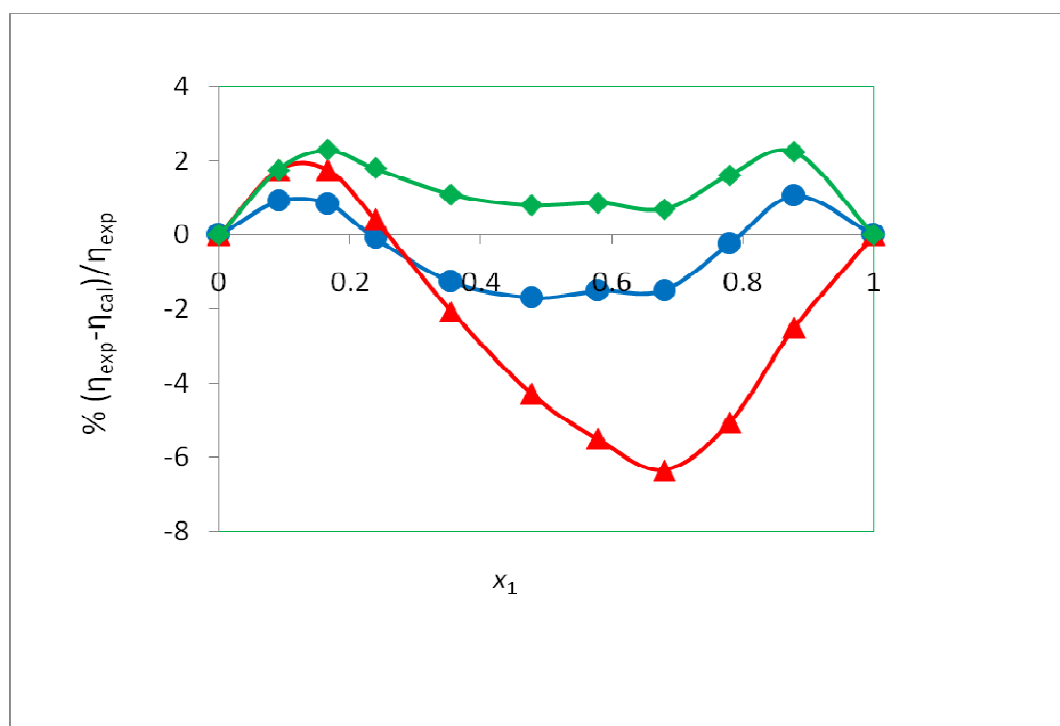


Figure 2 Plots of percentage deviations of theoretical viscosity of $C_2H_4Cl_2 + C_2H_6OS$ solution against mole fraction, x_1 of $C_2H_4Cl_2$; Grunberg (●), Hind (▲), Frenkel (◆)

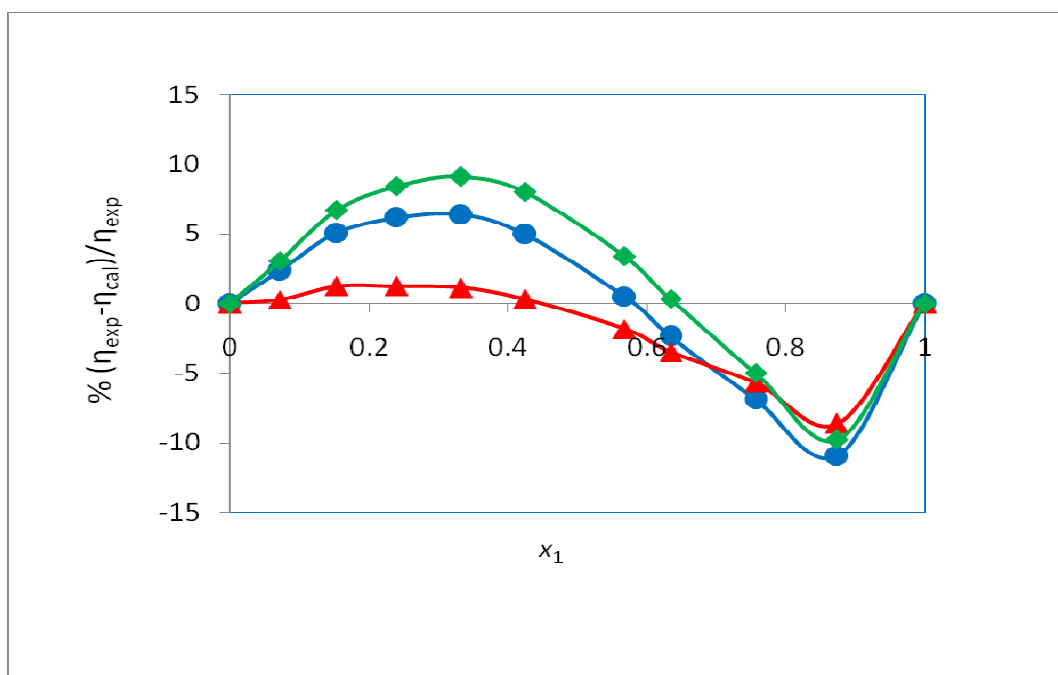


Figure 3 Plots of percentage deviations of theoretical viscosity of $\text{CH}_2\text{Cl}_2 + \text{C}_3\text{H}_7\text{NO}$ solution against mole fraction, x_1 of CH_2Cl_2 ; Grunberg (●), Hind (▲), Frenkel (◆)

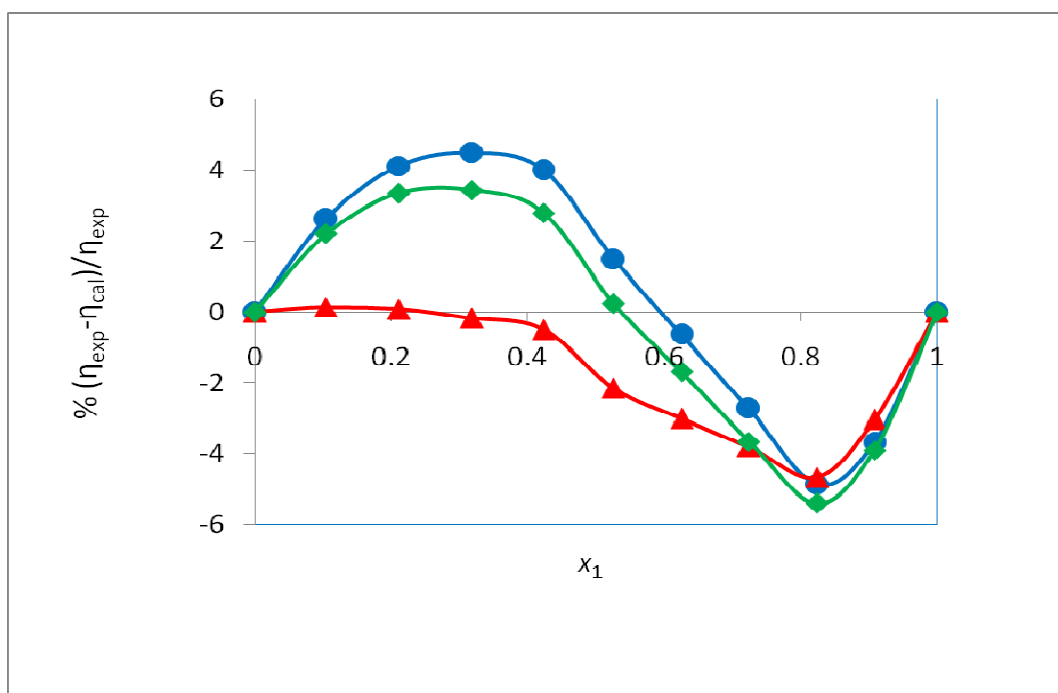


Figure 4 Plots of percentage deviations of theoretical viscosity of $\text{CH}_2\text{Cl}_2 + \text{C}_2\text{H}_6\text{OS}$ solution against mole fraction, x_1 of CH_2Cl_2 ; Grunberg (●), Hind (▲), Frenkel (◆)

CONCLUSION

- Densities, ρ and viscosities η of binary mixtures of $\text{C}_2\text{H}_4\text{Cl}_2 + \text{C}_3\text{H}_7\text{NO}$, $\text{C}_2\text{H}_4\text{Cl}_2 + \text{C}_2\text{H}_6\text{OS}$, $\text{CH}_2\text{Cl}_2 + \text{C}_3\text{H}_7\text{NO}$ and $\text{CH}_2\text{Cl}_2 + \text{C}_2\text{H}_6\text{OS}$ have been measured over the entire composition range at 308.15 K.
- From this experimental data, deviation in viscosity, $\Delta\eta$, excess free volume, V_f^E , excess internal pressure, π_i^E , excess enthalpy, H^E and excess Gibbs free energy, ΔG^E have been measured.
- The deviation/excess properties have been fitted to Redlich-Kister type polynomial and the corresponding standard deviations have been calculated.
- From the positive and negative values of excess properties strong interactions such as hydrogen bond formation between the dissimilar molecules, dipole-dipole interactions and interstitial accommodation of unlike molecules are the favorable factors for the responsible properties.
- The strength of interaction in the mixtures follow the order $\text{CH}_2\text{Cl}_2 + \text{C}_3\text{H}_7\text{NO} > \text{CH}_2\text{Cl}_2 + \text{C}_2\text{H}_6\text{OS} > \text{C}_2\text{H}_4\text{Cl}_2 + \text{C}_3\text{H}_7\text{NO} > \text{C}_2\text{H}_4\text{Cl}_2 + \text{C}_2\text{H}_6\text{OS}$.
- The experimental viscosity data of all of these binary liquid mixtures have been correlated with viscosity models.

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