



ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2018, 10(3): 99-105
(<http://www.derpharmachemica.com/archive.html>)

Thermo-physical Studies on Molecular Interactions in Liquid Binaries of Diethyl Malonate and Isomeric Xylenes at Various Temperatures

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ABSTRACT

Densities and viscosities of binary liquid mixtures of diethyl malonate with isomeric xylenes were reported at (303.15, 308.15, 313.15 and 318.15 K). From the experimental data, deviation in Viscosity ($\Delta\eta$) and excess Gibbs free energy of activation of Viscous flow (ΔG^{*E}) were evaluated. The deviations in viscosity and excess Gibbs free energy of activation of viscous flow were correlated with Redlich-Kister polynomial equation. Viscosity theories like Grunberg-Nissan, Katti-Chaudhri, Heric-Brewer, Hind et al. and McAllister four body models have been applied to correlate the viscosity of binary mixtures.

Keywords: Density, Viscosity, Gibbs free energy, Molecular interaction

INTRODUCTION

Density and viscosity play a vital role in analyzing the theoretical and physical properties of binary liquids. The experimental results of these properties of the binary liquids attracted the attention of large number of engineering and chemical industries [1]. The viscosity of binary liquids is a tremendous tool in many chemical applications such as molecular structure, mass, liquid stream, heat transfer and capillary electrophoresis [2]. Moreover, the investigation of excess thermodynamics and transport properties for binary mixture gives essential data concerning the deeper understanding of the molecular liquid structure and intermolecular interactions [3]. Xylenes are habitually utilized as octane enhancer in vehicles [4]. They likewise have different applications in printing, elastic, petrochemical ventures and leather industries. Diethyl Malonate (DEM) is a diethyl ester of malonic acid.

In this study, viscosities and densities are measured at four temperatures (303.15, 308.15, 313.15 and 318.15) K for binary mixtures of Diethyl Malonate (DEM) with *o*-Xylene (OX), *m*-xylene (MX) and *p*-Xylene (PX). Deviation in Viscosity ($\Delta\eta$) and excess Gibbs free energy of activation of Viscous flow (ΔG^{*E}) have been computed from Density (ρ) and Viscosity (η) information to understand the nature of forces working between them. Semi-empirical viscosity models, for example, Grunberg and Nissan [5], Katti and Chaudhri [6], Heric and Brewer [7], Hind et al., [8] and McAllister [9] four body models are utilized to compare the investigational results with the theoretical viscosities.

EXPERIMENTAL SECTION

Materials and methods

Diethyl malonate and isomeric xylenes provided from Merck were purified as depicted in the literature [10,11]. The unadulterated chemicals were stored over activated molecular sieves to decrease water content before utilize. All the binary liquid mixtures are prepared gravimetrically utilizing an electronic balance (Shimadzu AY 120) with an uncertainty of $\pm 1 \times 10^{-7}$ kg and stored in sealed shut containers. The uncertainty on mole fraction is evaluated to be 1×10^{-4} . It is guaranteed that the mixtures are appropriately mixed and the estimation of the required parameters was done within one day of preparation. The densities (ρ) of unadulterated liquids and their mixtures are determined utilizing a 10^{-5} m³ double-arm Pycnometer and the values from triplicate replication at every temperature are reproducible within 2×10^{-1} kg.m⁻³ and the uncertainty in the estimation of density is observed to be 2 parts in 10^4 parts. The reproducibility in mole fractions was within ± 0.0002 . Temperature control for the estimation of viscosity and density is accomplished by utilizing a microprocessor assisted circulating water bath regulated to ± 0.01 K, utilizing a corresponding temperature controller. Satisfactory precautionary measures were taken to limit evaporation losses during the genuine estimations. Exploratory estimations of density and viscosity at 303.15-318.15 K with those detailed in the literature [12-15,4] are provided in Table 1.

Table 1: Comparison of density (ρ) and Viscosity (η) of the pure liquids with literature data

303.15 K				308.15 K				313.15 K				318.15 K			
ρ (10^{-3} kg m $^{-3}$)		η (m Pa s)		ρ (10^{-3} kg m $^{-3}$)		η (m Pa s)		ρ (10^{-3} kg m $^{-3}$)		η (m Pa s)		ρ (10^{-3} kg m $^{-3}$)		η (m Pa s)	
Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
1.044 ₃	1.0443 _a	1.73	1.732 ^b	1.038 ₅	1.0387 _a	1.602	1.602 ^b	1.033 ₅	1.0336 _a	1.456	1.458 ^b	1.031 ₃		1.424 ₄	1.425 ^b
0.870 ₄	0.8707 _c	0.706 ₁	0.7051 _c	0.869 ₅	0.8694 _c	0.665	0.6652 _c	0.867 ₈	0.8677 _c	0.622 ₆	0.6211 _c	0.865 ₈	0.8659 _c	0.569	0.5691 _c
0.855 ₅	0.8557 _c	0.555	0.5530 _d	0.848 ₅	0.8487 _c	0.522 ₄	0.523 ^d	0.845 ₅	0.8458 _c	0.493	0.493 ^d	0.840 ₃	0.8405 _c	0.468 ₆	0.468 ^d
0.852 ₉	0.8529 _e	0.577	0.5782 _c	0.846 ₈	0.8460 _c	0.551	0.5501 _c	0.842 ₈	0.8430 _c	0.505	0.5065 _c	0.837	0.8369 _c	0.492	0.4912 _c

since a=12, b=13, c=14, d=15, e=16

Theoretical considerations

The viscosity deviations ($\Delta\eta$) were calculated utilizing:

$$\Delta\eta = \eta_{12} - x_1\eta_1 - x_2\eta_2 \quad (1)$$

Where, η_{12} is the viscosity of the binary mixture, x_1 , x_2 and η_1 , η_2 are the mole fraction and the viscosities of unadulterated segments 1 and 2, respectively. The dynamic viscosities of the liquid mixtures have been computed utilizing observational relations given by Grunberg-Nissan, Katti-Chaudari, Heric-Brewer, Hind et al. and McAllister four body models. Grunberg and Nissan [5] proposed the following equation for the estimation of viscosity of liquid mixtures:

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

Where, G_{12} is an interaction parameter, which is an element of viscosity of segment liquids 1 and 2 and temperature. Katti and Chaudhri [6] equation for the dynamic viscosity of the liquid mixture is:

$$\ln[\eta V] = x_1 \ln[\eta_1 V_1] + x_2 \ln[\eta_2 V_2] + x_1 x_2 W_{vis} / RT \quad (3)$$

Where, W_{vis} is an interaction term, Heric and Brewer [7] determined the following equation to calculate the viscosity of the binary liquid mixtures:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln(x_1 M_1 + x_2 M_2) + x_1 x_2 \Delta_{12} \quad (4)$$

Where, Δ_{12} is the association term and other symbols have their typical importance. The expression to determine the viscosity of the binary liquid mixtures proposed by Hind et al. [8] is given by:

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1 x_2 H_{12} \quad (5)$$

Where, H_{12} is an association term, McAllister [9] four body interaction model was generally used to correlate kinematic viscosity (ν) information. The 2 parameter McAllister equation based on Eyring's theory of absolute reaction rates, considered collaborations of both like and unlike molecules by a two dimensional four body model. The four body model was characterized by the connection:

$$\begin{aligned} \ln \nu = & x_1^4 \ln \nu_1 + 4x_1^3 x_2 \ln Z_{1112} + 6x_1^2 x_2^2 \ln Z_{1122} + 4x_1 x_2^3 \ln Z_{2221} + x_2^4 \ln \nu_2 - \ln[x_1 + x_2 (M_2 / M_1)] \\ & + 4x_1^3 x_2 \ln[(3 + M_2 / M_1) / 4] + 6x_1^2 x_2^2 \ln[(1 + M_2 / M_1) / 2] + 4x_1 x_2^3 \ln[(1 + 3M_2 / M_1) / 4] \\ & + x_2^4 \ln(M_2 / M_1) \end{aligned} \quad (6)$$

Where, Z_{1112} , Z_{1122} and Z_{2221} are model parameters and M_i and ν_i are the molecular mass and kinematic viscosity of pure component i . To perform a numerical comparison of the correlating capability of above equations, we have calculated the standard percentage deviation (σ %) utilizing the connection:

$$\sigma \% = [1 / (\eta_{\text{expt}} - k) \times \sum (100(\eta_{\text{expt}} - \eta_{\text{cal}}) / \eta_{\text{expt}})^2]^{1/2} \quad (7)$$

Where, k speaks to the quantity of numerical coefficients in the respective equation. These parameters assessed by a non-linear regression analysis based on a least-squares strategy and given their standard percentage deviation (σ %) in Table 2

On the premise of the theories of absolute reaction rates [16], the excess Gibbs free energy of activation of viscous flow was computed by utilizing the connection:

$$\Delta G^{*E} = RT[\ln(\eta V_m) - x_1(\ln \eta_1 V_1) - x_2(\ln \eta_2 V_2)] \quad (8)$$

Where, η and V_m are the dynamic viscosity and molar volume of the mixture. η_1 , η_2 and V_1, V_2 are viscosity and molar volume of pure components 1 and 2 individually. R is the real gas constant and T is the absolute temperature. The composition dependence of $\Delta\eta$ and ΔG^{*E} (Y_{cal}^E) for each mixture are fitted to Redlich-Kister polynomial equation [17]:

$$Y_{cal}^E = X_1 X_2 \sum_{i=1}^n A_{i-1} (X_2 - X_1)^{i-1} \quad (9)$$

The coefficients of A_{i-1} in the above equation alongside the standard deviation σ (Y^E) have been ascertained. These coefficients are the adjustable parameters to get best - fit values of Y_{cal}^E . The standard deviations σ of Y_{cal}^E were computed by utilizing the connection:

$$\sigma = [\sum (Y_{exp}^E - Y_{cal}^E)^2 / (m - n)]^{1/2} \quad (10)$$

Where, m is the quantity of experimental data points and n is the number of coefficients considered and Y_{exp}^E, Y_{cal}^E are the values of experimental and calculated property ($\Delta\eta$ and ΔG^{*E}) separately.

RESULTS AND DISCUSSION

Diethyl malonate is an aprotic solvent which has a solid inclination to pull electron in carbon – oxygen bond towards itself. It has a dynamic methylene gathering and shows dipole-dipole interactions in the unadulterated state. The investigational values of viscosity and computed estimations of deviation in viscosity and excess Gibbs free energy of activation of viscous flow for three binary mixtures (DEM+OX/MX/PX) at various temperatures (303.15, 308.15, 313.15 and 318.15) K are displayed in Table 3. Excess/deviation quantities are correlated by Redlich-Kister polynomial as an element of temperature. The fitting coefficients A_{i-1} for all the three binary mixtures are recorded in Table 4 along with their standard deviation σ (root mean square deviation).

Viscosity deviation

The value and magnitude of $\Delta\eta$ depend on molecular size and shape of the components in addition to intermolecular forces. It is observed (Table 3) that deviation in viscosity is positive for all the systems (DEM+OX/MX/PX) and at all the temperatures. The absolute value of viscosity deviation of (DEM+OX/MX/PX) systems builds directly and scopes to a greatest incentive at $x_1 \sim 0.5440$ for (DEM+OX), $x_1 \sim 0.5483$ for (DEM+MX), $x_1 \sim 0.5490$ for (DEM+PX), after which step by step diminishes until pure condition of diethyl malonate is arrived. By and large, negative estimations of $\Delta\eta$ demonstrate the presence of dispersion forces or mutual loss of specific interactions in molecules working in the systems and positive estimations of deviation in viscosity show solid particular collaborations [18-21]. As indicated by Kauzmann and Eyring [22], the viscosity of a mixture unequivocally relies upon the entropy of mixture, which is connected with the structure of the liquid. Vogel and Weiss [23] clarified that mixtures with solid communications between various molecules and negative deviations from Raoult's law display positive viscosity deviations while for mixtures with positive deviations of Raoult's law and without particular connections, the viscosity deviations are negative.

Table 2: Interaction Parameters and the corresponding standard deviations (σ) for the binary mixtures of diethyl malonate and studied isomeric xylenes at various temperatures

T/K	G ₁₂	σ	W _{vis} /RT	σ	Δ_{12}	σ	H ₁₂	σ	Z ₁₁₁₂	Z ₁₁₂₂	Z ₂₂₂₁	σ
Diethyl malonate + o-xylene												
303.15	1.5107	0.0638	1.4823	0.064	1.5957	0.065	1.8831	0.0178	1.7387	1.7718	1.4772	0.0045
308.15	1.4092	0.0522	1.3756	0.0523	1.4943	0.0533	1.7068	0.0175	1.5858	1.6464	1.327	0.0062
313.15	1.3491	0.0437	1.312	0.0439	1.4343	0.0447	1.5497	0.0163	1.433	1.5215	1.1926	0.0058
318.15	1.2889	0.0371	1.2477	0.0372	1.3741	0.0381	1.4214	0.0189	1.3447	1.4864	1.0561	0.0034
Diethyl malonate + m-xylene												
303.15	1.8886	0.0921	1.8215	0.0916	1.9731	0.0932	1.8147	0.0172	1.7369	1.6312	1.4696	0.005
308.15	1.7753	0.0761	1.7041	0.0754	1.86	0.0771	1.6418	0.0165	1.5816	1.5156	1.3125	0.0057
313.15	1.6888	0.0627	1.614	0.0621	1.7735	0.0636	1.4897	0.0158	1.4256	1.4121	1.1678	0.0057
318.15	1.5748	0.0509	1.4945	0.0504	1.6597	0.0519	1.3796	0.0188	1.3406	1.4054	1.036	0.003
Diethyl malonate + p-xylene												
303.15	1.8996	0.0932	1.8235	0.0925	1.9841	0.0943	1.8712	0.0173	1.763	1.6646	1.519	0.0048
308.15	1.7834	0.0773	1.7059	0.0766	1.868	0.0784	1.7081	0.0169	1.6089	1.5587	1.3698	0.0056
313.15	1.6945	0.0629	1.616	0.0623	1.7793	0.0639	1.518	0.0158	1.4389	1.43	1.1904	0.0056
318.15	1.5821	0.0517	1.4988	0.0512	1.667	0.0527	1.4291	0.0187	1.3614	1.4385	1.0769	0.003

Table 3: Viscosity, η (m Pa s), deviation in viscosity, $\Delta\eta$ (m Pa s) and excess Gibbs free energy of activation of viscous flow, ΔG^{*E} (Jmol⁻¹) for the binary mixtures of diethyl malonate and isomeric xylenes at various temperatures

x_1	303.15 K			308.15 K			313.15 K			318.15 K		
	η	$\Delta\eta$	ΔG^{*E}	η	$\Delta\eta$	ΔG^{*E}	η	$\Delta\eta$	ΔG^{*E}	η	$\Delta\eta$	ΔG^{*E}
Diethyl malonate + <i>o</i>-xylene												
0.0000	0.706	0	0	0.665	0	0	0.623	0	0	0.569	0	0
0.0812	0.875	0.086	352.37	0.808	0.067	309.93	0.752	0.061	303.83	0.684	0.046	282.21
0.1658	1.051	0.175	618.62	0.971	0.151	584.6	0.889	0.128	546.14	0.812	0.101	523.5
0.2542	1.236	0.27	824.02	1.14	0.237	792.16	1.046	0.211	768.99	0.953	0.167	726.62
0.3465	1.387	0.326	901.74	1.275	0.285	866.4	1.164	0.252	838.05	1.076	0.211	817.98
0.443	1.509	0.349	894.81	1.384	0.304	857.61	1.266	0.274	841.71	1.186	0.238	839.49
0.544	1.615	0.352	838.28	1.479	0.304	800.66	1.35	0.274	786.3	1.274	0.24	784.32
0.6498	1.696	0.325	724.34	1.555	0.281	692.46	1.414	0.25	675.16	1.345	0.22	673.44
0.7608	1.722	0.237	515.06	1.586	0.208	496.9	1.441	0.184	483.34	1.377	0.157	471.21
0.8774	1.724	0.12	260.02	1.591	0.104	248.83	1.447	0.093	243.98	1.395	0.076	231.03
1.0000	1.73	0	0	1.602	0	0	1.456	0	0	1.424	0	0
Diethyl malonate + <i>m</i>-xylene												
0.0000	0.555	0	0	0.522	0	0	0.493	0	0	0.469	0	0
0.0825	0.74	0.088	472.99	0.68	0.069	423.02	0.635	0.063	407.75	0.596	0.048	371.23
0.1683	0.93	0.177	793.77	0.858	0.154	762.6	0.785	0.13	707.73	0.733	0.103	655
0.2575	1.13	0.272	1021.78	1.039	0.239	989.05	0.954	0.213	956.34	0.884	0.169	879.72
0.3504	1.295	0.328	1093.74	1.187	0.287	1057.89	1.084	0.254	1021.68	1.017	0.213	971.64
0.4473	1.433	0.352	1068.98	1.311	0.306	1031.7	1.199	0.276	1008.74	1.137	0.241	979.29
0.5483	1.555	0.356	986.74	1.422	0.308	950.82	1.297	0.276	927.99	1.238	0.245	907.81
0.6537	1.651	0.328	839.19	1.511	0.283	807.27	1.375	0.252	786.17	1.317	0.224	766
0.764	1.692	0.239	590.45	1.557	0.21	573.44	1.415	0.186	557.6	1.358	0.159	531.52
0.8793	1.71	0.122	297.23	1.578	0.106	287.36	1.435	0.095	280.83	1.387	0.078	261.8
1.0000	1.73	0	0	1.602	0	0	1.456	0	0	1.424	0	0
Diethyl malonate + <i>p</i>-xylene												
0.0000	0.577	0	0	0.551	0	0	0.505	0	0	0.492	0	0
0.0827	0.768	0.096	473.89	0.716	0.078	425.56	0.65	0.066	409.14	0.624	0.055	374.79
0.1687	0.964	0.193	797.81	0.899	0.171	763.36	0.802	0.137	708.82	0.764	0.115	656.99
0.2581	1.166	0.291	1022.1	1.084	0.262	990.36	0.973	0.223	957.19	0.918	0.185	882.3
0.3511	1.332	0.35	1094.5	1.232	0.312	1057.98	1.103	0.264	1021.82	1.051	0.232	972.78
0.448	1.469	0.375	1070.01	1.354	0.332	1032.1	1.218	0.287	1010.11	1.17	0.26	981.11
0.549	1.588	0.378	988.2	1.461	0.333	951.95	1.314	0.287	929.02	1.268	0.264	909.89
0.6544	1.678	0.346	839.45	1.543	0.304	808.05	1.389	0.262	787.44	1.341	0.239	766.61
0.7645	1.712	0.254	591.76	1.58	0.226	574.2	1.425	0.193	557.96	1.375	0.17	531.68
0.8796	1.721	0.13	298.1	1.59	0.115	287.39	1.441	0.1	282.18	1.397	0.085	263.46
1.0000	1.73	0	0	1.602	0	0	1.456	0	0	1.424	0	0

Table 4: Redlich-Kister coefficients $A_{i,1}$ and corresponding standard deviations (σ) computed for excess/deviation properties of the binary mixtures of diethyl Malonate + isomeric xylenes (*o*-xylene, *m*-xylene, *p*-xylene) at various temperatures

Property	Temp(K)	A_0	A_1	A_2	A_3	A_4	σ
Diethyl malonate + <i>o</i>-xylene							
$\Delta\eta$ (m Pa s)	303.15	1.4137	-0.0236	0.2506	0.2247	-1.1151	0.0077
	308.15	1.225	0.0259	0.3229	0.0528	-1.2314	0.0057
	313.15	1.1038	0.0407	0.1659	0.0183	-0.9088	0.0069

	318.15	0.9739	-0.0597	-0.2052	0.1073	-0.46	0.0042
ΔG^{*E} (Jmol ⁻¹)	303.15	3465.29	1253.547	1370.517	471.6292	-2093.47	13.6779
	308.15	3307.13	1293.438	1648.547	46.7655	-2884.83	12.0507
	313.15	3249.124	1273.93	1323.686	0.4554	-2381.6	17.9204
	318.15	3270.533	1110.997	395.3116	61.7989	-1486.61	10.1959
Diethyl malonate + <i>m</i>-xylene							
$\Delta\eta$ (m Pa s)	303.15	1.4268	-0.0539	0.2302	0.2311	-1.0576	0.0078
	308.15	1.2339	0.0043	0.3129	0.0502	-1.179	0.0054
	313.15	1.1127	0.0198	0.1582	0.0199	-0.8612	0.0069
	318.15	0.9873	-0.0972	-0.2063	0.1445	-0.4366	0.0045
ΔG^{*E} (Jmol ⁻¹)	303.15	4120.746	1740.811	1707.524	758.8105	-1968.94	15.2292
	308.15	3960.967	1800.282	2018.676	212.267	-2892.19	12.0754
	313.15	3876.974	1750.618	1695.694	129.119	-2486.33	19.1586
	318.15	3799.511	1470.171	587.1788	233.1599	-1372.62	11.5816
Diethyl malonate + <i>p</i>-xylene							
$\Delta\eta$ (m Pa s)	303.15	1.517	-0.028	0.2076	0.2096	-1.0199	0.0068
	308.15	1.3352	0.0363	0.3368	0.0291	-1.2142	0.0055
	313.15	1.1558	0.0257	0.2	0.0019	-0.9231	0.0074
	318.15	1.0615	-0.0761	-0.2174	0.1295	-0.4061	0.0046
ΔG^{*E} (Jmol ⁻¹)	303.15	4127.674	1735.429	1671.676	742.463	-1909.63	13.834
	308.15	3965.943	1787.299	2015.433	238.7783	-2868.52	12.3211
	313.15	3885.783	1739.739	1669.768	124.6681	-2434.53	19.3599
	318.15	3808.254	1469.713	567.8503	234.8453	-1293.3	12.192

The less positive $\Delta\eta$ esteems for diethyl malonate + *o*-xylene system show that associations are weaker over diethyl malonate + *m*-xylene and diethyl malonate + *p*-xylene systems [24], which recommends that the position of $-\text{CH}_3$ groups on the aromatic ring assumes a generous part in choosing the extent $\Delta\eta$ and, thus, the order of collaboration between the component molecules of the mixtures. The stereo normality of methyl groups in *o*-xylene is such that the steric repulsion is more. So that the $\Delta\eta$ esteems for *o*-xylene are observed to be lower than the *m*-xylene and *p*-xylene. On account of *p*-xylene, the two methyl groups disperse similarly the π -electron cloud on the benzene ring, in this manner the charge transfer complex development between diethyl malonate and *p*-xylene brings about higher positive $\Delta\eta$ esteems. The diethylmalonate + *p*-xylene mixtures are described by more positive $\Delta\eta$ esteems than the mixtures of diethylmalonate + *m*-xylene and diethylmalonate + *o*-xylene, regardless of the way that *p*-xylene very nearly a zero dipole moment and thus dipole-induced dipole associations are not anticipated. One conceivable explanation behind this could be that *p*-xylene molecule is planar and flat type and can shape closer and parallel $n-\pi$ complexes with slightest steric hindrance. The $\Delta\eta$ esteems diminish with increment of temperature for all the three systems. This might be clarified as takes after: viscosity is principally the force exhibited by one layer of molecules on the neighboring layer of molecules. With the temperature rise, the cluster breakage causes weak associations and hence less force is exhibited on the adjacent layers which bring about the bringing down of deviation in viscosities. In this manner, the molecular communication follows the order:



Excess Gibbs free energy of activation of viscous flow

The excess Gibbs free energy of activation of viscous flow like viscosity deviation can be utilized to detect molecular communications [25]. The excess Gibbs free energy of activation of viscous flow is positive for (DEM+OX/MX/PX) systems over the whole composition range and at all the temperatures. This shows the nearness of appealing strengths between the constituent molecules in the binary mixtures under examination. ΔG^{*E} values diminishes with temperature ascend for all the three systems. This shows the debilitating of intermolecular communications at hoisted temperatures [26] and this is might be credited to detachment of related molecules through breakage of clusters both in the mixtures and immaculate solvents.

Analysing viscosity of fluid mixtures by semi observational models

In this article, we utilize the conditions of Grunberg-Nissan, Katti-Chaudhri, Heric-Brewer, Hind et al. furthermore, McAllister four body models to connect the viscosities of binary mixtures of (DEM+OX/MX/PX). Experimental and computed estimations of viscosity (η) for the binary mixtures of (DEM+OX/MX/PX) at 303.15 K are displayed in Table 5. Interaction (adjustable) Parameters computed from equations 2-6 and the relating standard deviations (σ) for all the binary mixtures are appeared in Table 2. An examination of information in Table 5 demonstrates that all the observational relations gave a sensible fit, but the viscosity values computed utilizing McAllister 4 body models are in great concurrence with the experimental values. Examination of information in Table 2 demonstrates that the estimations of interaction parameters (d) computed from various viscosity theories are positive for the systems: (DEM+OX/MX/PX) at the four distinct temperatures.

Table 5: Experimental and computed estimations of viscosity, η (m Pa s) for the binary mixtures of diethyl malonate + *o*-xylene, diethyl malonate + *m*-xylene, diethyl malonate + *p*-xylene at 303.15 K

303.15 K						
x_1	η Expt	η GN	η KC	η HB	η H	η Mc
Diethyl malonate + <i>o</i>-xylene						
0.0000	0.706	0.706	0.706	0.706	0.706	0.706
0.0812	0.875	0.85	0.85	0.849	0.888	0.873
0.1658	1.051	1.009	1.009	1.008	1.06	1.036
0.2542	1.236	1.181	1.181	1.18	1.218	1.188
0.3465	1.387	1.356	1.357	1.355	1.362	1.324
0.443	1.509	1.525	1.525	1.524	1.488	1.441
0.544	1.615	1.672	1.673	1.673	1.593	1.54
0.6498	1.696	1.783	1.783	1.784	1.674	1.624
0.7608	1.722	1.838	1.838	1.84	1.727	1.69
0.8774	1.724	1.823	1.824	1.825	1.748	1.731
1.0000	1.73	1.73	1.73	1.73	1.73	1.73
Diethyl malonate + <i>m</i>-xylene						
0.0000	0.555	0.555	0.555	0.555	0.555	0.555
0.0825	0.74	0.703	0.704	0.703	0.754	0.738
0.1683	0.93	0.875	0.876	0.874	0.941	0.933
0.2575	1.13	1.067	1.067	1.066	1.115	1.123
0.3504	1.295	1.271	1.27	1.27	1.273	1.297
0.4473	1.433	1.472	1.471	1.472	1.413	1.443
0.5483	1.555	1.653	1.651	1.653	1.532	1.556
0.6537	1.651	1.79	1.787	1.791	1.627	1.638
0.764	1.692	1.86	1.859	1.862	1.695	1.691
0.8793	1.71	1.843	1.844	1.845	1.731	1.72
1.0000	1.73	1.73	1.73	1.73	1.73	1.73
Diethyl malonate + <i>p</i>-xylene						
0.0000	0.577	0.577	0.577	0.577	0.577	0.577
0.0827	0.768	0.73	0.731	0.729	0.781	0.767
0.1687	0.964	0.906	0.907	0.905	0.973	0.966
0.2581	1.166	1.102	1.102	1.101	1.149	1.16
0.3511	1.332	1.308	1.307	1.307	1.309	1.334
0.448	1.469	1.51	1.508	1.509	1.449	1.479
0.549	1.588	1.688	1.685	1.688	1.565	1.589
0.6544	1.678	1.819	1.817	1.821	1.656	1.665
0.7645	1.712	1.881	1.88	1.883	1.717	1.711
0.8796	1.721	1.854	1.855	1.855	1.743	1.731
1.0000	1.73	1.73	1.73	1.73	1.73	1.73

As indicated by Fort and Moore [27], G_{12} is dealt with as a precise estimation to discover the quality of association between the components. On the off chance that G_{12} is positive, at that point the system shows property of solid connection, on the off chance that it is negative; it is having the property of feeble communication. So also, Nigam and Mahl [28] inferred that: (i) If $\Delta\eta > 0$, $G_{12} > 0$ and the magnitudes of the above are large then solid particular cooperation's would happen; (ii) If $\Delta\eta < 0$, $G_{12} > 0$ then feeble associations would exist; (iii) If $\Delta\eta < 0$, $G_{12} < 0$ and the extents of both are huge then the dispersion force would be predominant. In the present binary systems (DEM+OX/MX/PX), G_{12} esteems in the Table 5 are positive and viscosity deviation is positive ($\Delta\eta > 0$) consequently one could state that solid particular cooperation's would display in the present binary mixtures.

CONCLUSION

From the estimations of viscosity and density, deviation in viscosity and excess Gibbs free energy of activation of viscous flow are computed. The exploratory estimations of viscosity were associated with the semi exact relations of viscosity like Grunberg-Nissan, Katti-Chaudhri, Heric-

Brewer, Hind et al., and McAllister four body models. Among the entire relations McAllister four body model gave great concurrence with the experimental values. From the watched positive estimations of $\Delta\eta$, ΔG^{*E} and G_{12} interaction parameter, it is presumed that strong molecular interactions are available among the concentrated binary mixtures.

REFERENCE

- [1] K. Lal, N. Tripathi, G.P. Dubey, *J. Chem. Eng. Data.*, **2000**, 45, 961.
- [2] V. Shkolnikov, G.S. Daniel, P.F. David, G.S. Juan, *Sensors and Actuators B.*, **2010**, 150, 556.
- [3] J.H. Yang, L.Y. Dai, X.Z. Wang, Y.Q. Chen, *J. Chem. Eng. Data.*, **2009**, 54, 2332.
- [4] M.V. Rathnam, S. Mohite, M.S.S. Kumar, *Ind. J. Chem. Tech.*, **2008**, 15, 409.
- [5] L. Grunberg, A.H. Nissan, *Nature.*, **1949**, 164, 799.
- [6] P.K. Katti, M.M. Chaudhri, *J. Chem. Eng. Data.*, **1964**, 9, 442.
- [7] E.L. Heric, J.G. Brewer, *J. Chem. Eng. Data.*, **1967**, 12, 574.
- [8] R.K. Hind, E. McLaughlin, A.R. Ubbelohde, *Trans. Faraday Soc.*, **1960**, 56, 328.
- [9] R.A. McAllister, *AIChE Journal.*, **1960**, 6, 427.
- [10] J.A. Riddick, W.B. Bunger, T.K. Sakano, *Organic Solvents, Physical Properties and Methods of Purification, Techniques of Chemistry*, 4th Edn., Wiley Interscience, New York, USA, **1986**, 2.
- [11] B.S. Furniss, A.J. Hannaford, P.W.G. Smith, A.R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, 5th Edn., Wiley, New York, USA, **1989**.
- [12] M.V. Rathnam, M. Sudhir, M.S. Kumar, *J. Serb. Chem. Soc.*, **2011**, 76, 1.
- [13] C.H. Udayalakshmi, K.A.K. Raj Kumar, V.N.S.R Venkateswararao, P.B. Sandhyasri, G.R. Satyanarayana, C. Rambabu, *Der Pharma Chemica.*, **2016**, 8, 209.
- [14] K. Narendra, Ch. Srinivasu, P. Narayana Murthy, *J. Appl. Sci.*, **2012**, 12, 136.
- [15] A. Jouyban, S.H. Maljaei, Sh. Soltanpour, M.A.A. Fakhree, *J. Mol. Liq.*, **2011**, 162, 50.
- [16] S. Glasstone, K.J. Laidler, H. Eyring, *The Theory of Rate Process*, McGraw- Hill, New York, USA, 1941.
- [17] O. Redilch, A.T. Kister, *Ind. Eng. Chem.*, **1948**, 40, 345.
- [18] M.R. Islam, S.K. Quadri, *Thermochimica Acta.*, **1987**, 115, 335.
- [19] K. Tiwari, C. Patra, V. Chakravorty, *Acoustics Letters.*, **1995**, 19, 53.
- [20] M. Kondaiah, K. Sreekanth, D.S. Kumar, S.M. Nayeem, D.K. Rao, *J. Therm. Anal. Calorim.*, **2014**, 118, 475.
- [21] S.C. Bhatia, R. Bhatia, G.P. Dubey, *J. Mol. Liq.*, **2009**, 144, 163.
- [22] W. Kauzmann, H. Eyring, *J. Am. Chem. Soc.*, **1940**, 62, 3113.
- [23] H. Vogel, A. Weiss, *Ber. Bunsenges. Phys. Chem.*, **1982**, 86, 193.
- [24] M.V. Rathnam, M. Sudhir, *J. Chem. Eng. Data.*, **2005**, 50, 325.
- [25] A. Mariano, M. Postigo, *Fluid Phase Equilib.*, **2006**, 239, 146.
- [26] G.R. Satyanarayana, D. Bala Karuna Kumar, K. Sujatha, G. Lakshmanarao, C. Rambabu, *J. Mol. Liq.*, **2016**, 216, 526.
- [27] R.J. Fort, W.R. Moore, *Trans. Faraday Soc.*, **1966**, 62, 1112.
- [28] R.K. Nigam, B.S. Mahl, *Ind. J. Chem.*, **1971**, 9, 1255.