

Viscometric studies on the molecular interactions of diethyl malonate with higher alkanes

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ABSTRACT

In this analysis, experimental values of densities (ρ) and dynamic viscosities (η) in the binary mixtures of n-hexane, n-heptane and n-octane with diethyl malonate are reported over the whole range of mixture composition at $T = (303.15, 308.15, 313.15 \text{ and } 318.15)$ K. From these experimental data, deviations in viscosity ($\Delta\eta$) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) have been evaluated. These results were fitted to Redlich–Kister polynomial equation to estimate the fitting coefficients and standard deviation. The results of the viscosity composition are discussed in the light of various viscosity equations suggested by Grunberg–Nissan, Katti–Chaudhri, Heric–Brewer and Hind et al. The deviation of the experimental values of the viscosity of the mixture from the mole fraction mixture law rules, are found to be negative and follow the order n-hexane < n-heptane < n-octane. The experiments on the constituted binaries are analyzed to discuss the nature and strength of intermolecular interactions in these mixtures.

Introduction

The investigation of the physico-chemical behaviour of liquid systems, which includes measurement of density, dynamic viscosity and related excess properties, provides important and useful information focused on intermolecular interactions in liquids and their mixtures. Such thermophysical data is significant both for formulating models and theories of solutions and testing the reliability of the existing methods for prediction of the system behaviour. It is obvious that compiling experimental data is valuable for industrial objectives as well as for theoretical and applied thermodynamics.

The binary mixtures containing alkanes are important series of homologous, non-polar and organic solvents. They have often been used in the study of solute dynamics because their physicochemical properties as a function of chain length are well-known [1]. They are also employed in a large range of chemical processes [2] and these are used in paints, coatings and gasoline.

Diethyl malonate (DEM) is the diethyl ester of malonic acid. DEM is a colourless liquid. The odour of DEM is like that of apple juice. It is used in perfumes, synthesizing the compounds such as barbiturates, vitamin B₁, Vitamin B₆ and artificial flavorings. Diethyl malonate can be prepared by treating the sodium salt of chloroacetic acid with sodium cyanide, following by the base hydrolysis of the resultant nitrile to give the sodium salt of malonic acid. Fischer esterification gives diethyl malonate.

In the present analysis, we explore viscosity, deviation in viscosity and excess Gibbs free energy of activation of viscous flow data for the binary mixtures of diethyl malonate with alkanes and are correlated with some of the semi-empirical viscosity models such as Grunberg and Nissan [3], Katti and

Chaudhri [4], Heric and Brewer [5] and Hind et al. [6] and the results are compared with the experimental results. Literature survey reveals that much work available on different physical properties of ester like liquids, but no such work is available on diethyl malonate with alkanes. The present analysis gives elaborative information about the physical properties of diethyl malonate with three alkanes including the reinvestigation of diethyl malonate (DEM) with hexane at 308.15 K. However, certain parameters such as deviation in viscosity and adiabatic compressibilities for diethyl malonate and n-hexane were already reported at a temperature of 308.15 K. But in those the deviation in viscosity values did not show any maxima or minima to indicate the nature of forces operative.

In this study, experimental viscosities and densities are reported at four temperatures (303.15, 308.15, 313.15 and 318.15) K for binary mixtures of diethyl malonate with n-hexane, n-heptane and n-octane. Deviation in viscosity ($\Delta\eta$) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) have been calculated from the density (ρ) and viscosity (η) data.

Materials and Methods

Diethyl malonate and alkanes supplied from Merck were purified as described in the literature [7, 8]. The pure chemicals were stored over activated molecular sieves to reduce water content before use. All the binary liquid mixtures are prepared gravimetrically using an electronic balance (Shimadzu AY 120) with an uncertainty of $\pm 1 \times 10^{-7}$ kg and stored in airtight bottles. The uncertainty on mole fraction is estimated to be 1×10^{-4} . It is ensured that the mixtures are properly mixed and the measurement of the required parameters was done within one day of preparation.

The densities (ρ) of pure liquids and their mixtures are determined using a 10^{-5} m^3 double-arm pycnometer and the values from triplicate replication at each temperature are reproducible within $2 \times 10^{-1} \text{ kg m}^{-3}$ and the uncertainty in the measurement of density is found to be 2 parts in 10^4 parts. The reproducibility in mole fractions was within ± 0.0002 . Temperature control for the measurement of viscosity and density is achieved by using a microprocessor assisted circulating water bath regulated to $\pm 0.01 \text{ K}$, using a proportional temperature controller. Adequate precautions were taken to minimize evaporation losses during the actual measurements. Experimental values of density and viscosity, at 303.15 K with those reported in the literature, as presented in the Table 1.

Theoretical Considerations:

The viscosity deviations ($\Delta\eta$) were calculated using

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

where η_{12} is the viscosities of the binary mixture. x_1, x_2 and η_1, η_2 are the mole fraction and the viscosities of pure components 1 and 2, respectively.

There are several semi-empirical relations used to correlate the viscosity of binary liquid mixtures, which help us to know the strength of molecular interactions. The dynamic viscosities have been calculated by the following empirical relations. The dynamic viscosities of the liquid mixtures have been calculated using empirical relations given by Grunberg-Nissan, Katti-Chaudari, Heric-Brewer and Hind *et al.* Grunberg and Nissan [3] proposed the following equation for the measurement of viscosity of liquid mixtures:

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

where G_{12} is an interaction parameter, which is a function of viscosity of component liquids 1 and 2 and temperature. Katti and Chaudhri [4] equation for the dynamic viscosity of the liquid mixture is

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

where W_{vis} is an interaction term.

Heric and Brewer [5] derived the following equation to calculate the viscosity of the binary liquid mixtures:

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

Δ_{12} is the interaction term and other symbols have their usual meaning.

The expression to determine the viscosity of the binary liquid mixtures proposed by Hind *et al.* [6] is given by

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

where H_{12} is an interaction term.

On the basis of the theories of absolute reaction rates [14], the excess Gibbs free energy of activation of viscous flow was calculated by using

$$\Delta G^{*E} = RT[\ln(\eta V_m) - x_1(\ln \eta_1 V_1) - x_2(\ln \eta_2 V_2)] \quad (6)$$

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. R is the real gas constant and T is the absolute temperature.

The composition dependence of $\Delta\eta$ and $\Delta G^{*E}, Y_{\text{cal}}^E$ for each mixture are correlated by Redlich-Kister polynomial equation [15]

$$Y_{\text{cal}}^E = X_1 X_2 \sum_{i=1}^n A_{i-1} (X_2 - X_1)^{i-1} \quad (7)$$

The coefficients of A_{i-1} in the above equation along with the standard deviation $\sigma (Y^E)$ have been calculated. These coefficients are the adjustable parameters to get best - fit values of Y_{cal}^E . The standard deviations σ of Y_{cal}^E were calculated by using the relation:

$$\sigma = [\sum (Y_{\text{expt}}^E - Y_{\text{cal}}^E)^2 / (m - n)]^{1/2} \quad (8)$$

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

Results and Discussion

Diethyl malonate is an aprotic, polar solvent since it has the group $\text{C}=\text{O}$ and oxygen is far more electro negative than carbon, it has a strong tendency to pull electron in carbon - oxygen bond towards itself.

The experimental values of dynamic viscosity, deviation in viscosity and excess Gibbs free energy of activation of viscous flow for three binary mixtures (diethyl malonate + n-hexane, diethyl malonate + n-heptane and diethyl malonate + n-octane) at different temperatures (303.15, 308.15, 313.15 and 318.15) K are presented in Table 2. Excess/deviation quantities are correlated by using Redlich-kister polynomial Eq. (7) as a function of temperature. The fitting coefficients A_{i-1} for all the three binary mixtures are listed in Table 3 along with their standard deviation σ (root mean square deviation) by using Eq. (8). From the excess/deviation properties, molecular interaction among the diethyl malonate (1) + n-hexane (2) + n-heptane (2) + n-octane (2) has been interpreted.

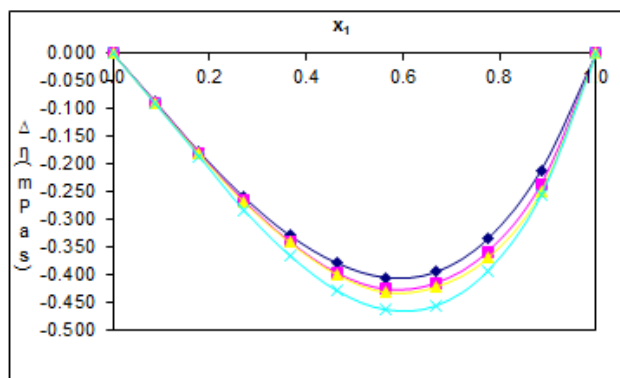
Viscosity Deviation

The variation of deviation in viscosity, $\Delta\eta$, with mole fraction of diethyl malonate (x_1) for the binary mixtures of n-hexane, n-heptane, n-octane with diethyl malonate at $T = (303.15, 308.15, 313.15 \text{ and } 318.15) \text{ K}$ is shown in Figure 1. The value and magnitude of $\Delta\eta$ depend on molecular size and shape of the components in addition to intermolecular forces. It is observed from the Figure 1(a - c) that deviation in viscosity is negative for all the binaries and at all the temperatures. The absolute value of viscosity deviation of diethyl malonate + n-hexane, diethyl malonate + n-heptane and diethyl malonate + n-octane systems increases linearly and reaches to a maximum value at $x_1 \sim 0.5644$ for (diethyl

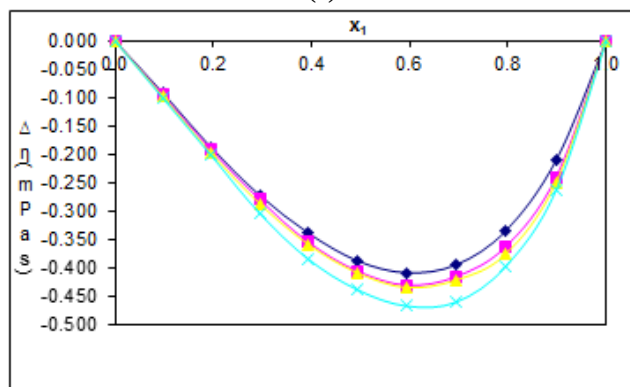
Table 1. Comparison of density (ρ) and Viscosity (η) of the pure liquids with literature data at 303.15 °K.

Compound	$\rho (10^{-3} \text{ kg m}^{-3})$		$\eta (\text{m Pa s})$	
	Expt.	Lit.	Expt.	Lit.
diethyl malonate	1.0443	1.0443 ^[9]	1.730	1.732 ^[10]
n-hexane	0.6506	0.6504 ^[11]	0.280	0.284 ^[13]
n-heptane	0.6719	0.6713 ^[12]	0.375	0.370 ^[13]
n-octane	0.6940	0.6945 ^[11]	0.484	0.481 ^[13]

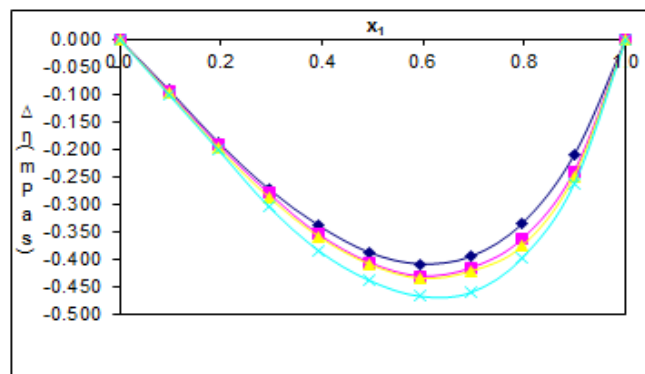
malonate + n-hexane), $x_1 \sim 0.5933$ for (diethyl malonate + n-heptane), $x_1 \sim 0.6168$ for (diethyl malonate + n-octane), after which gradually decreases until to a pure state of diethyl malonate.



(a)



(b)



(c)

Figure 1. Plot of variation of deviation in viscosity ($\Delta\eta/\text{mPa s}$) with mole fraction of diethyl malonate (x_1) for the systems

(a)diethylmalonate(1)+nhexane(2)(b)diethylmalonate(1)+n-heptane(2) (c)diethylmalonate(1)+n-octane(2) at (♦) 303.15°K, (■) 308.15°K, (▲) 313.15°K and (×) 318.15°K.

According to Baragi [16], increase in size of alkanes (chain length) causes larger volume expansion which indicates the presence of dispersion type of interactions between the component liquids.

According to Kauzmann and Eyring [17], the viscosity of a mixture strongly depends on the entropy of mixture, which is related to the structure of the liquid. Vogel and Weiss [18] explained that mixtures with strong interactions between different molecules and negative deviations from Raoult's law exhibit positive viscosity deviations; whereas, for mixtures with positive deviations of Raoult's law and without specific interactions the viscosity deviations are negative.

Table 2. Dynamic 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) the binary mixtures diethyl malonate and alkanes at different temperatures.

diethyl malonate + n-hexane												
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}
0.0000	0.280	0.000	0	0.265	0.000	0.00	0.250	0.000	0.00	0.240	0.000	0.00
0.0876	0.320	-0.087	-17.19	0.294	-0.088	-90.63	0.266	-0.090	-194.05	0.253	-0.091	-227.40
0.1776	0.360	-0.177	-97.80	0.323	-0.179	-230.04	0.283	-0.181	-411.80	0.265	-0.185	-495.40
0.2701	0.413	-0.259	-152.68	0.361	-0.265	-348.74	0.308	-0.268	-593.48	0.278	-0.282	-782.51
0.3654	0.482	-0.328	-187.78	0.415	-0.339	-418.46	0.350	-0.341	-685.65	0.309	-0.364	-939.76
0.4634	0.574	-0.378	-194.94	0.489	-0.396	-447.65	0.410	-0.399	-721.19	0.361	-0.428	-987.90
0.5644	0.694	-0.404	-187.05	0.595	-0.425	-417.48	0.500	-0.431	-674.62	0.446	-0.462	-911.01
0.6683	0.855	-0.394	-154.78	0.745	-0.414	-336.62	0.635	-0.421	-544.87	0.576	-0.455	-739.46
0.7755	1.070	-0.334	-106.32	0.945	-0.357	-245.67	0.816	-0.369	-407.36	0.766	-0.392	-513.58
0.8860	1.355	-0.210	-51.55	1.215	-0.235	-143.31	1.070	-0.249	-240.20	1.034	-0.255	-271.44
1.0000	1.730	0.000	0.00	1.602	0.000	0.00	1.456	0.000	0.00	1.424	0.000	0.00
diethyl malonate + n-heptane												
0.0000	0.375	0.000	0.00	0.347	0.000	0.00	0.330	0.000	0.00	0.310	0.000	0.00
0.0975	0.415	-0.092	-74.90	0.373	-0.096	-151.63	0.342	-0.098	-238.49	0.318	-0.101	-280.82
0.1956	0.452	-0.188	-206.03	0.400	-0.192	-325.99	0.352	-0.198	-511.62	0.326	-0.202	-580.12
0.2942	0.502	-0.272	-301.11	0.436	-0.280	-471.62	0.374	-0.287	-715.04	0.334	-0.304	-894.21
0.3933	0.569	-0.339	-356.42	0.486	-0.355	-571.16	0.414	-0.359	-823.04	0.363	-0.385	-1063.41
0.4930	0.655	-0.388	-383.17	0.560	-0.406	-596.03	0.476	-0.409	-842.47	0.420	-0.439	-1077.26
0.5933	0.770	-0.409	-367.61	0.661	-0.431	-570.06	0.563	-0.435	-798.61	0.503	-0.468	-1010.24
0.6941	0.920	-0.395	-321.58	0.802	-0.416	-483.31	0.690	-0.422	-672.35	0.622	-0.461	-868.67
0.7955	1.118	-0.335	-242.48	0.982	-0.363	-383.34	0.850	-0.376	-542.18	0.798	-0.398	-639.12
0.8975	1.380	-0.211	-135.21	1.232	-0.241	-231.72	1.091	-0.250	-316.09	1.046	-0.264	-363.87
1.0000	1.730	0.000	0.00	1.602	0.000	0.00	1.456	0.000	0.00	1.424	0.000	0.00
diethyl malonate + n-octane												
0.0000	0.484	0.000	0.00	0.443	0.000	0.00	0.423	0.000	0.00	0.403	0.000	0.00
0.1065	0.524	-0.093	-95.86	0.463	-0.103	-192.07	0.428	-0.105	-266.44	0.405	-0.107	-297.27
0.2115	0.559	-0.189	-241.17	0.484	-0.204	-396.03	0.432	-0.210	-551.93	0.406	-0.213	-611.83
0.3150	0.604	-0.273	-358.37	0.520	-0.288	-533.53	0.445	-0.303	-789.26	0.407	-0.318	-932.79
0.4171	0.664	-0.340	-436.18	0.570	-0.356	-622.94	0.488	-0.366	-866.66	0.431	-0.398	-1111.76
0.5176	0.740	-0.389	-482.88	0.636	-0.407	-670.85	0.548	-0.410	-886.50	0.485	-0.447	-1134.10
0.6168	0.843	-0.410	-477.35	0.726	-0.432	-663.05	0.624	-0.436	-872.04	0.560	-0.473	-1089.40
0.7146	0.978	-0.396	-429.32	0.854	-0.417	-581.20	0.738	-0.423	-761.98	0.670	-0.463	-953.85
0.8111	1.159	-0.336	-333.21	1.019	-0.364	-468.09	0.884	-0.377	-622.60	0.831	-0.400	-726.07
0.9062	1.401	-0.212	-188.93	1.251	-0.242	-283.58	1.108	-0.251	-368.83	1.062	-0.266	-423.34
1.0000	1.730	0.000	0.00	1.602	0.000	0.00	1.456	0.000	0.00	1.424	0.000	0.00

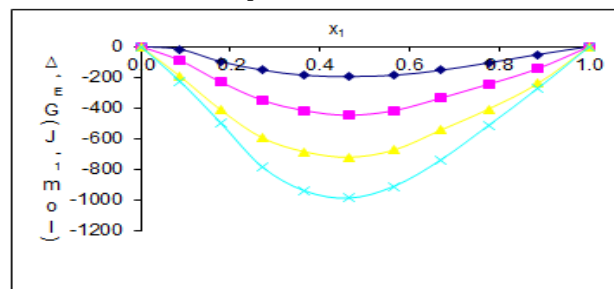
The sign and magnitude of $\Delta\eta$ depend on the combined effect of various factors such as molecular size, shape and intermolecular forces. Nayeem et al. [19] presented negative values of viscosity deviation in the binary systems of 1,4-dioxane with n-alkanes. The variation in $\Delta\eta$ with the mole fraction of diethyl malonate is presented in Table 2. The deviation in viscosity variation gives a qualitative estimation of the strength of the intermolecular interactions. In the present study, the observed $\Delta\eta$ is negative for the systems over whole concentration range at all the temperatures, and such values are found to increase with increasing temperature. The negative deviations in viscosity ($\Delta\eta$) indicate the presence of dispersive forces [20–22] and steric hindrance [23] in the systems. Further, the magnitude of negative $\Delta\eta$ values for n-octane is larger than the other two systems to an appreciable amount at all temperatures. This may be due to the increase in length of carbon chain n-octane, offering resistance to flow process in binary mixtures and this flow process causes to an increase in $\Delta\eta$ values. Thus, negative $\Delta\eta$ follows the trend: (diethyl malonate + n-octane) > (diethyl malonate + n-heptane) > (diethyl malonate + n-hexane). Therefore, the observed negative deviations in $\Delta\eta$ suggest the presence of weak interaction between the component molecules.

The magnitude of negative $\Delta\eta$ values for the three systems indicates that the strength of interactions between the components follow the order n-hexane > n-heptane > n-octane.

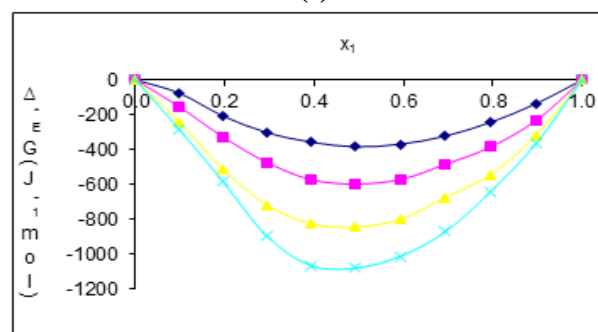
Excess Gibbs free energy of activation of viscous flow:

In order to elucidate the forces that are acting between unlike molecules, the help of excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) is quite essential. Figures 2a, 2b and 2c show the variation in (ΔG^{*E}) with mole fraction of diethyl malonate at $T = (303.15, 308.15, 313.15, \text{ and } 318.15) \text{ K}$.

According to Reed [24], the positive values of (ΔG^{*E}) may be attributed to specific interactions such as hydrogen bonding and charge transfer, while negative values may be ascribed to the dominance of physical (dispersion forces) interactions [25]. This suggests existence of weak interactions in the present systems. It can be seen that the ΔG^{*E} values increase with increasing number of carbon atoms of the alkanes. It may be due to the increasing difficulty to form cross associates between different molecules with increasing steric hindrance between them and the aliphatic chain of the alkanes.



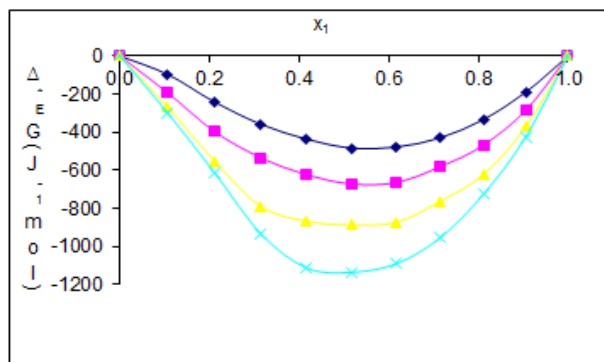
(a)



(b)

Table 3. Redlich-Kister coefficients A_{i-1} and corresponding standard deviations (σ) computed for excess/ deviation properties of the binary mixtures of diethyl malonate + alkanes (n-hexane, n-heptane, n-octane) at different temperatures.

Property	Temp(K)	A_0	A_1	A_2	A_3	A_4	σ
diethyl malonate + n-hexane							
$\Delta\eta$ (m Pa s)	303.15	-1.5623	0.5873	-0.1533	0.0490	0.1419	0.0007
	308.15	-1.6385	0.6305	-0.0497	0.2367	-0.1775	0.0011
	313.15	-1.6513	0.6462	-0.1283	0.3361	-0.2368	0.0019
	318.15	-1.7768	0.7660	-0.0933	0.1733	-0.0600	0.0014
ΔG^{*E} (Jmol ⁻¹)	303.15	-767.6883	-227.0455	19.2880	546.7951	906.6817	5.1553
	308.15	-1760.7475	-601.1327	754.3866	1166.5362	-99.0322	5.1059
	313.15	-2829.1151	-1035.1020	741.4359	1532.7547	-239.1913	8.8695
	318.15	-3887.9307	-1287.8758	1609.5636	1714.5499	100.2299	11.2035
diethyl malonate + n-heptane							
$\Delta\eta$ (m Pa s)	303.15	-1.5615	0.6630	-0.2118	0.1845	0.0559	0.0009
	308.15	-1.6342	0.7052	-0.1331	0.3994	-0.3488	0.0015
	313.15	-1.6458	0.6837	-0.2711	0.5065	-0.2540	0.0027
	318.15	-1.7679	0.8306	-0.3848	0.3890	-0.0048	0.0030
ΔG^{*E} (Jmol ⁻¹)	303.15	-1532.5898	-30.8086	199.8808	636.9055	582.3600	4.6828
	308.15	-2382.2761	-175.7358	739.8599	1050.0906	-539.3292	5.1474
	313.15	-3361.8806	-623.7435	310.3576	1673.5635	190.1805	10.7368
	318.15	-4302.4542	-537.9816	466.7400	1557.5963	1022.9666	20.2629
diethyl malonate + n-octane							
$\Delta\eta$ (m Pa s)	303.15	-1.5296	0.7914	-0.2915	0.2331	-0.0085	0.0008
	308.15	-1.6018	0.7890	-0.3015	0.4606	-0.3623	0.0027
	313.15	-1.6170	0.6897	-0.5608	0.7036	-0.0637	0.0032
	318.15	-1.7588	0.8744	-0.4787	0.5688	-0.0890	0.0034
ΔG^{*E} (Jmol ⁻¹)	303.15	-1916.2053	511.7318	283.8000	415.8913	333.8530	3.6961
	308.15	-2674.1187	366.5639	273.2098	706.2447	-379.4529	9.3097
	313.15	-3557.6454	-242.8431	-1014.8285	1927.6798	1665.4938	17.0863
	318.15	-4534.1824	229.8406	242.3959	1509.9588	898.0310	20.6749



(c)

Figure 2 . Plot of variation of excess Gibbs free energy of activation of viscous flow ΔG^{*E} (Jmol^{-1}) with mole fraction of diethyl malonate(x_1) for the systems (a)diethyl malonate(1)+n-hexane(2) (b)diethyl malonate(1)+n-heptane(2) (c)diethyl malonate(1)+n-octane(2) at (♦) 303.15°K, (■) 308.15°K, (▲) 313.15°K and (×) 318.15°K.

Analysing Viscosity of Liquid Mixtures by Semi Empirical Models

To interpret the molecular interaction in the liquid mixture, several empirical and semi empirical models (equations) have been put forth for correlating the viscosity of liquid mixtures. In this article, we use the equations of Grunberg–Nissan, Katti–Chaudhri, and Heric- Brewer and Hind et al. to correlate the viscosities of binary mixtures of diethyl malonate + alkanes (n-hexane, n-heptane, n-octane). Experimental and calculated values of viscosity (η) for the binary mixtures of diethyl malonate + alkanes (n-hexane/ n-heptane/ n-octane) at temperatures (303.15, 308.15, 313.15 and 318.15) K are presented in Tables 4a – 4c. Interaction (adjustable) parameters calculated from Eqs. (2-5) and the corresponding standard deviations (σ) for the binary mixtures of diethyl malonate + alkanes (n-hexane/ n-heptane/ n-octane) at temperatures (303.15, 308.15, 313.15 and 318.15) K are shown in Table 5.

Table 4a.Experimental and calculated values of dynamic viscosity, η (m Pa s), for the binary mixtures of diethyl malonate and n-hexane at different temperatures.

diethyl malonate + n-hexane										
x_1	η Expt	η GN	η KC	η HB	η H	η Expt	η GN	η KC	η HB	η H
303.15K						308.15K				
0.0000	0.280	0.280	0.280	0.280	0.280	0.265	0.265	0.265	0.265	0.265
0.0876	0.320	0.341	0.329	0.330	0.291	0.294	0.331	0.320	0.320	0.268
0.1776	0.360	0.414	0.389	0.390	0.325	0.323	0.410	0.387	0.386	0.294
0.2701	0.413	0.501	0.462	0.464	0.385	0.361	0.505	0.467	0.467	0.345
0.3654	0.482	0.606	0.552	0.554	0.472	0.415	0.617	0.564	0.563	0.423
0.4634	0.574	0.730	0.663	0.664	0.590	0.489	0.745	0.679	0.677	0.530
0.5644	0.694	0.876	0.798	0.799	0.740	0.595	0.892	0.815	0.813	0.670
0.6683	0.855	1.047	0.964	0.965	0.926	0.745	1.055	0.974	0.972	0.843
0.7755	1.070	1.245	1.169	1.170	1.151	0.945	1.231	1.158	1.155	1.054
0.8860	1.355	1.473	1.421	1.421	1.418	1.215	1.416	1.368	1.366	1.306
1.0000	1.730	1.730	1.730	1.730	1.730	1.602	1.602	1.602	1.602	1.602
313.15K						318.15K				
0.0000	0.250	0.250	0.250	0.250	0.250	0.240	0.240	0.240	0.240	0.240
0.0876	0.266	0.321	0.311	0.311	0.252	0.253	0.316	0.306	0.305	0.246
0.1776	0.283	0.408	0.385	0.384	0.275	0.265	0.409	0.387	0.385	0.272
0.2701	0.308	0.511	0.474	0.472	0.321	0.278	0.521	0.484	0.481	0.320
0.3654	0.350	0.631	0.578	0.575	0.391	0.309	0.650	0.598	0.593	0.390
0.4634	0.410	0.765	0.699	0.695	0.487	0.361	0.793	0.727	0.721	0.486
0.5644	0.500	0.911	0.835	0.830	0.612	0.446	0.945	0.869	0.861	0.609
0.6683	0.635	1.062	0.984	0.978	0.769	0.576	1.097	1.019	1.011	0.761
0.7755	0.816	1.211	1.142	1.136	0.960	0.766	1.237	1.169	1.161	0.946
0.8860	1.070	1.346	1.302	1.298	1.188	1.034	1.351	1.308	1.303	1.166
1.0000	1.456	1.456	1.456	1.456	1.456	1.424	1.424	1.424	1.424	1.424

Table 4b. Experimental and calculated values of dynamic viscosity, η (m Pa s), for the binary mixtures of diethyl malonate and n-heptane at different temperatures.

diethyl malonate + n-heptane										
x_1	η Expt	η GN	η KC	η HB	η H	η Expt	η GN	η KC	η HB	η H
303.15K						308.15K				
0.0000	0.375	0.375	0.375	0.375	0.375	0.347	0.347	0.347	0.347	0.347
0.0975	0.415	0.465	0.449	0.455	0.378	0.373	0.442	0.428	0.433	0.344
0.1956	0.452	0.568	0.536	0.548	0.409	0.400	0.553	0.522	0.534	0.369
0.2942	0.502	0.686	0.636	0.655	0.468	0.436	0.678	0.630	0.647	0.421
0.3933	0.569	0.817	0.750	0.775	0.557	0.486	0.816	0.751	0.774	0.501
0.4930	0.655	0.959	0.878	0.908	0.675	0.560	0.962	0.882	0.911	0.610
0.5933	0.770	1.111	1.021	1.055	0.824	0.661	1.111	1.023	1.055	0.748
0.6941	0.920	1.268	1.178	1.213	1.003	0.802	1.257	1.169	1.202	0.916
0.7955	1.118	1.428	1.349	1.380	1.214	0.982	1.393	1.318	1.346	1.114
0.8975	1.380	1.583	1.534	1.554	1.456	1.232	1.510	1.463	1.482	1.343

1.0000	1.730	1.730	1.730	1.730	1.730	1.602	1.602	1.602	1.602	1.602
313.15K						318.15K				
0.0000	0.330	0.330	0.330	0.330	0.330	0.310	0.310	0.310	0.310	0.310
0.0975	0.342	0.433	0.419	0.424	0.326	0.318	0.417	0.404	0.409	0.314
0.1956	0.352	0.553	0.522	0.533	0.346	0.326	0.545	0.516	0.526	0.341
0.2942	0.374	0.688	0.640	0.656	0.392	0.334	0.690	0.643	0.658	0.391
0.3933	0.414	0.833	0.767	0.790	0.464	0.363	0.845	0.780	0.802	0.464
0.4930	0.476	0.981	0.902	0.929	0.561	0.420	1.003	0.924	0.950	0.562
0.5933	0.563	1.125	1.037	1.068	0.686	0.503	1.152	1.064	1.093	0.684
0.6941	0.690	1.253	1.167	1.198	0.837	0.622	1.279	1.194	1.222	0.831
0.7955	0.850	1.357	1.285	1.311	1.015	0.798	1.372	1.302	1.327	1.003
0.8975	1.091	1.427	1.383	1.400	1.221	1.046	1.423	1.381	1.396	1.200
1.0000	1.456	1.456	1.456	1.456	1.456	1.424	1.424	1.424	1.424	1.424

Table 4c. Experimental and calculated values of dynamic viscosity, η (m Pa s), for the binary mixtures of diethyl malonate and n-octane at different temperatures.

diethyl malonate + n-octane										
x_1	η Expt	η GN	η KC	η HB	η H	η Expt	η GN	η KC	η HB	η H
303.15K						308.15K				
0.0000	0.484	0.484	0.484	0.484	0.484	0.443	0.443	0.443	0.443	0.443
0.1065	0.524	0.605	0.584	0.598	0.478	0.463	0.571	0.552	0.565	0.430
0.2115	0.559	0.738	0.695	0.724	0.504	0.484	0.714	0.674	0.700	0.450
0.3150	0.604	0.880	0.816	0.859	0.561	0.520	0.866	0.804	0.845	0.500
0.4171	0.664	1.028	0.944	1.000	0.648	0.570	1.021	0.940	0.994	0.579
0.5176	0.740	1.175	1.077	1.143	0.764	0.636	1.172	1.076	1.139	0.686
0.6168	0.843	1.318	1.212	1.284	0.907	0.726	1.309	1.207	1.275	0.820
0.7146	0.978	1.449	1.347	1.417	1.076	0.854	1.427	1.329	1.395	0.980
0.8111	1.159	1.564	1.481	1.538	1.271	1.019	1.517	1.438	1.492	1.164
0.9062	1.401	1.659	1.608	1.644	1.489	1.251	1.577	1.529	1.562	1.372
1.0000	1.730	1.730	1.730	1.730	1.730	1.602	1.602	1.602	1.602	1.602
313.15K						318.15K				
0.0000	0.423	0.423	0.423	0.423	0.423	0.403	0.403	0.403	0.403	0.403
0.1065	0.428	0.560	0.542	0.554	0.409	0.405	0.548	0.531	0.542	0.397
0.2115	0.432	0.714	0.675	0.700	0.423	0.406	0.714	0.675	0.700	0.418
0.3150	0.445	0.877	0.816	0.855	0.466	0.407	0.889	0.829	0.867	0.465
0.4171	0.488	1.039	0.958	1.010	0.536	0.431	1.064	0.983	1.034	0.536
0.5176	0.548	1.188	1.094	1.155	0.631	0.485	1.222	1.127	1.188	0.631
0.6168	0.624	1.315	1.216	1.281	0.751	0.560	1.352	1.252	1.316	0.748
0.7146	0.738	1.410	1.317	1.379	0.895	0.670	1.441	1.348	1.409	0.887
0.8111	0.884	1.467	1.393	1.443	1.061	0.831	1.484	1.411	1.459	1.047
0.9062	1.108	1.482	1.439	1.469	1.248	1.062	1.477	1.435	1.464	1.226
1.0000	1.456	1.456	1.456	1.456	1.456	1.424	1.424	1.424	1.424	1.424

Table 5. Interaction Parameters and the corresponding standard deviations (σ) for the binary mixtures of diethyl malonate and studied alkanes at different temperatures.

diethyl malonate + n-hexane								
T/K	G_{12}	σ	W_{vis}/RT	σ	Δ_{12}	σ	H_{12}	σ
303.15	0.4601	0.1287	0.2666	0.0729	0.2705	0.0737	0.2770	0.0458
308.15	0.8059	0.2102	0.6183	0.1563	0.6135	0.1546	0.2215	0.0622
313.15	1.2129	0.2911	1.0303	0.2386	1.0191	0.2351	0.2059	0.0856
318.15	1.4876	0.3506	1.3117	0.2982	1.2949	0.2930	0.2230	0.1161
diethyl malonate + n-heptane								
303.15	0.7412	0.2405	0.5631	0.1774	0.6326	0.2015	0.3172	0.0545
308.15	1.0620	0.3183	0.8874	0.2572	0.9529	0.2797	0.2635	0.0742
313.15	1.4324	0.3975	1.2606	0.3375	1.3228	0.3587	0.2455	0.0955
318.15	1.6901	0.4561	1.5234	0.3968	1.5808	0.4168	0.2723	0.1326
diethyl malonate + n-octane								
303.15	0.9131	0.3339	0.7364	0.2605	0.8576	0.3102	0.3763	0.0647
308.15	1.2309	0.4121	1.0575	0.3415	1.1748	0.3887	0.3077	0.0809
313.15	1.5738	0.4906	1.4047	0.4221	1.5175	0.4671	0.2859	0.1008
318.15	1.8259	0.5578	1.6614	0.4896	1.7697	0.5339	0.3121	0.1387

An examination of data in Table 4 shows that all the empirical relations gave a reasonable fit, but the viscosity values calculated using Hind et al. are in good agreement with the experimental values. Perusal of data in Table 5 shows that the values of interaction parameters (G_{12}) calculated from different viscosity theories are positive for the systems: diethyl malonate + alkanes (n-hexane, n-heptane, n-octane) at the four different temperatures.

According to Fort and Moore [20] G_{12} is treated as an accurate measurement to find the strength of interaction between the components. If G_{12} is positive, then the system exhibits the property of strong interaction else it is negative and having the property of weak interaction. Similarly Nigam and Mahl [26] give some statements from the study of binary mixtures dimethyl sulphoxide with chloroethanes, that

- i. if $\Delta\eta > 0$, $G_{12} > 0$ and the magnitudes of the above are large then strong specific interactions would take place.
- ii. if $\Delta\eta < 0$, $G_{12} > 0$ then weak interaction would exist.
- iii. if $\Delta\eta < 0$, $G_{12} < 0$ and the magnitudes of both are large then the dispersion force would be dominant.

Interaction parameter W_{vis}/RT and G_{12} exhibit almost equal trend. One could say that G_{12} and W_{vis}/RT show the similar behavior, but it is different by considering the logarithmic nature of the two equations. In the present binary systems diethyl malonate + alkanes (n-hexane, n-heptane, n-octane) G_{12} values in the Table 5, are less positive and viscosity deviation is negative ($\Delta\eta < 0$), hence one could say that weak specific interactions would be present in current binary mixtures.

Conclusion

In the present analysis, the density and dynamic viscosity of the binary mixtures of diethyl malonate with alkanes (n-hexane, n-heptane, n-octane) have been experimentally measured at $T = (303.15, 308.15, 313.15, 318.15)$ K. From the values of viscosity and density, deviation in viscosity and excess Gibbs free energy of activation of viscous flow are determined. The experimental values of viscosity were correlated with the semi empirical relations of viscosity like Grunberg-Nissan, Katti-Chaudhri, Heric-Brewer, and Hind et al. Among all the relations Hind et al. relation gave good agreement with the experimental values. From the observed negative values of $\Delta\eta$, negative values of ΔG^*E and low positive values of G_{12} interaction parameter, it is concluded that weak specific interactions are present among the studied binary mixtures.

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