

# Excess thermodynamic properties of binary organic liquids mixtures involving dimethylaniline and polar and non-polar solvents

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## Abstract

Densities and viscosities of binary liquid mixture of dimethyl aniline with polar and non-polar solvents, viz. methyl alcohol, ethyl alcohol, n-propyl alcohols, n-butyl alcohol, acetone, methyl ethyl ketone, carbon tetrachloride, benzene and toluene have been measured at 293.15, 303.15 and 313.15K. From density and viscosity data the values of viscosity derivations ( $\Delta\eta$ ) and the thermodynamic excess properties viz. the excess molar volume ( $V_o^E$ ) and the excess Gibbs free energy of activation of viscous flow ( $\Delta G^{\#E}$ ) have been determined. The values of ( $\Delta\eta$ ),  $V_o^E$  and ( $\Delta G^{\#E}$ ) have been fitted to Redlich-Kister polynomial equation to estimate the binary coefficients and standard deviation between the experimental and theoretical (calculated) values.

From the small magnitude of the values of standard deviation it is concluded that the experimental values of ( $\Delta\eta$ ),  $V_o^E$  and ( $\Delta G^{\#E}$ ) Compare fairly well with the theoretical values predicted by Redlich-Kister equation. The effect of increasing temperature on the values of ( $\Delta\eta$ ),  $V_o^E$  and ( $\Delta G^{\#E}$ ) as well as the nature of molecular interactions between the mixing components of the binaries has also been discussed.

## Keywords

Densities, viscosities, excess thermodynamic properties, binary mixtures.

## Introduction

In recent years, much attention has been paid to the viscosities of liquid mixtures because quantitative knowledge of this transport property is often required in chemical engineering design. Experimental transport property data are important because they have not been studied as much as other properties of liquid mixtures.

The excess thermodynamic properties are useful in understanding the strength and the nature of interaction among the molecules of the binary liquid mixtures<sup>1</sup>.

So far as the studies relating to the thermodynamic and transport property of binary organic liquid mixtures of aliphatic amines with polar and non-polar solvents are concerned, A survey of literature reveals that Oswal and Patel<sup>2-4</sup> have reported studies on viscosities and excess molar volumes for binary mixtures of triethylamine and tri-n-butylamine with n-hexane-octane, iso-octane, n-propylamine, n-butylamine, n-hexylamine and n-octylamine.

Papaioannou et al<sup>5</sup> have measured the densities and viscosities of the binary mixtures of n-butylamine with 1-alkanols (Methanol, ethanol, 1-propanol and 1-butanol) at 25°C. The results of the study reveal that all binary systems studied exhibit relatively large negative excess volumes, which persist over the pressure range studied here.  $V^E$  is especially large (negative) in the mixture with methanol and decreases as the chain length of the alcohol increases. This is certainly indicative of the relative strength of the specific interactions between the hydroxyl and the amino groups in the above four mixtures. The large negative excess volume in the mixture with methanol indicates that a most efficient packing of molecules occurs in the mixture. Aside from the strength of the  $\text{OH}\cdots\text{NH}_2$  interactions (compared to the strength of the  $\text{OH}\cdots\text{OH}$ ,  $\text{NH}_2\cdots\text{NH}_2$  interactions), this efficiency arises also from the relative sizes of the methanol and butylamine molecules.

Ethylene diamine is a polar liquid and can form intermolecular hydrogen bonds<sup>6</sup>. It is a base with dissociation constant,  $K_b = 0.85 \times 10^{-4}$ . From the survey of literature, it is seen that studies on the measurement of densities, viscosities and excess thermodynamic properties of binary liquid mixtures involving ethylene diamine are still lacking with this aim in view, comprehensive studies on the measurement of densities, viscosities, viscosity deviations ( $\Delta\eta$ ) and excess thermodynamic properties ( $V^E$  and  $\Delta G^{\#E}$ ) at 293.15, 303.15 and 313.15 K.

The density and viscosity data at these temperatures would be used for determining viscosity deviation  $\Delta\eta$  and excess thermodynamic properties and interaction parameters of the following binary liquid mixtures:

Dimethylaniline + Methyl alcohol, Dimethylaniline + Ethyl alcohol, Dimethylaniline + n-Propyl alcohol, Dimethylaniline + n-Butyl alcohol, Dimethylaniline + Benzyl alcohol, Dimethylaniline + Acetone, Dimethylaniline + Methyl ethyl ketone, Dimethylaniline + Acetophenone, Dimethylaniline + Chloroform, Dimethylaniline + Chlorobenzene, Dimethylaniline + Bromobenzene, Dimethylaniline + Carbon tetrachloride, Dimethylaniline + Benzene, Dimethylaniline + Toluene.

## Material and Method

All the organic liquids used in the study were of analytical grade. Ethyl enediamine, methyl alcohol, ethyl alcohol, n-propyl alcohol, n-butyl alcohol, acetone, methyl ethyl ketone, carbon tetrachloride, benzene and toluene were obtained from Merck. The organic liquids were further purified for purity better than 99% , as reported in literature<sup>7-8</sup> .

Liquid mixtures of various compositions were prepared by mass in a 25 cm<sup>3</sup> flask using a Mettler analytical balance. The average uncertainty in the mole fraction of the mixtures was estimated to be less than  $\pm 0.0001$ . Density and viscosity measurements were carried out using a thermostatically controlled, well-stirred water-bath to maintain temperature, which was measured with a digital thermometer with an uncertainty of  $\pm 0.01$  K .

Densities of pure liquids and their binary liquid mixtures were measured at 293.15, 303.15 and 313.15 K. with a digital vibrating tube densitometer (model 60/602, Anton Parr, Austria). The densitometer was calibrated with degassed water and dehumidified air at atmospheric pressure. The uncertainty of the density measurements was estimated to be  $\pm 1 \times 10^{-5}$  g.cm<sup>-3</sup> .

The viscosities ( $\eta$ ) of pure organic liquids and their binary mixtures were determined using an Ostwald viscometer which was suspended in a thermostat maintained at (293.15, 303.15 & 313.15  $\pm$  0.01 ) K . The details of the procedure have been reported in an earlier publication was  $\pm 1 \times 10^{-14}$  mPa.s.

## Result and Discussion:

The various excess thermodynamic properties viz.,  $\eta^E$ ,  $V^E$ ,  $\Delta G^{#E}$ ,  $\Delta H^{#E}$  and  $\Delta S^{#E}$  of binary organic liquid mixtures of dimethylaniline with polar and non-polar solvents have been determined from density and viscosity data at 293.15, 303.15 and 313.15K. The result have been presented in Tables and are discussed below:

### 1.Excess Viscosity ( $\eta^E$ ) :

It is seen that for all the binary liquid mixtures the value of  $\eta^E$  are positive over the entire range of composition at different temperatures. The positive value may be attributed to the presence of strong molecular interaction between the mixing components of the binary liquid mixtures.

The plots of  $\eta^E$  versus  $X_1$  are of parabolic shape in each case and are symmetrical about the mid value of the composition range i.e.  $X_1 \approx 0.5$ . These plots are characterized by the presence of well-defined maxima

occurring at  $X_1 \approx 0.5$ . Which in the present of complex formation<sup>9</sup> between the molecules of mixing component in the ratio of 1:1. On comparing of  $\eta^E$  corresponding to the maxima at different temperatures. It is seen that the values follows the following order:

(i) Mixtures of dimethylaniline with alcohol:

n-Butyl alcohol > Ethyl alcohol > Benzyl alcohol > n-Propyl alcohol > Methyl alcohol

(ii) Mixtures of dimethylaniline with ketone:

Acetone > Methyl ethyl ketone > Acetophenone

(iii) Mixtures of dimethylaniline with polar halogen liquids:

Chloroform > Bromobenzene > Chlorobenzene

(iv) Mixtures of dimethylaniline with nonpolar solvents:

Toluene > Carbon tetrachloride > Benzene

A perusal of the values of  $\eta^E$  at different temperatures shows that the values are rendered smaller and smaller as the temperature rises from 293.15 to 313.15K. This is further supported by the negative values of  $\left[ \frac{\partial \eta^E}{\partial T} \right]_P$ . As  $\eta^E$  is approximately proportional to the strength of molecular interaction<sup>10</sup>. It follows that at elevated temperature the strength of molecular interaction gates decreased.

## 2. Excess Molar Volume ( $V^E$ ):

It is seen that the value of  $V^E$  for all the binary mixtures of dimethyl aniline are negative over the entire range of composition at different temperatures. The negative value of  $V^E$  may be attributed<sup>11</sup> to the specific molecular interaction between the mixing components of the binary liquid mixtures under discussion.

The plots of  $V^E$  versus  $X_1$  are of parabolic shape in each case and are characterized by well-defined minima which occur at composition  $X_1 \approx 0.5$ . These minima indicate<sup>12</sup> the complex formation between the mixing component with 1:1 composition. It is seen that with the rise of temperature the value of  $V^E$  are

rendered increasingly more negative which is further supported by negative value of  $\left[ \frac{(\partial V^E)}{\partial T} \right]_P$  presented in the Table.

### 3 Excess Gibbs Free Energy of Activation of Flow ( $\Delta G^{\#E}$ ):

For all the binary liquid mixtures the value of  $\Delta G^{\#E}$  at different temperatures are positive over the entire range composition. The positive value of  $\Delta G^{\#E}$  may be attributed to specific interaction<sup>5</sup> between the mixing components.

The plots of  $\Delta G^{\#E}$  versus  $X_1$  have been presented in the figs. In each case the plots are of parabolic shape and are characterized by the presence of well-defined maxima which indicate the composition at which maximum interaction<sup>13</sup> between the mixing components are expected to occur. However these plots are unsymmetrical for the binary mixtures of dimethyl aniline with n- butyl alcohol and benzyl alcohol, where maxima gets shifted to dimethylaniline rich region of the composition, while in the case of binary mixture with acetone, chloroform and carbon tetrachloride the maxima gets shifted towards the second components rich region

With the rise of temperature of  $\Delta G^{\#E}$  decreases which is supported by the negative value of temperature coefficient of  $\Delta G^{\#E}$  i.e.  $\left[ \frac{(\partial \Delta G^{\#E})}{\partial T} \right]_P$  presented in the table.

### 4. Excess enthalpy ( $\Delta H^{\#E}$ ) and Excess Entropy ( $\Delta S^{\#E}$ ) of Activation of Flow:

The value of  $\Delta H^{\#E}$  and  $\Delta S^{\#E}$  have been calculated and presented in the table. It is seen that for all the binary liquid mixtures the value are positive over the entire range of composition at different temperatures which indicate that the molecular interaction between the mixing components of the binary liquid mixtures are of endothermic nature<sup>14-19</sup>. It is further seen that both  $\Delta H^{\#E}$  and  $\Delta S^{\#E}$  increase with the rise of temperature. This is further supported the positive value of temperature of  $\Delta H^{\#E}$  and  $\Delta S^{\#E}$ , i.e.  $\left[ \frac{\partial(\Delta H^{\#E})}{\partial T} \right]_P$

and.  $\left[ \frac{\partial(\Delta S^{\#E})}{\partial T} \right]_P$  presented in the Table 1 .

<b>Table 1 : Value of <math>\left(\frac{\partial(\eta^E)}{\partial T}\right), \left(\frac{\partial(V^E)}{\partial T}\right)_P, \left(\frac{\partial(\Delta G^{\#E})}{\partial T}\right)_P</math> &amp; <math>\left(\frac{\partial(\Delta H^{\#E})}{\partial T}\right)_P</math> &amp; <math>\left(\frac{\partial(\Delta S^{\#E})}{\partial T}\right)_P</math></b> <b>for binary organic liquid mixtures of Dimethylaniline with polar and non-polar solvents</b>					
Binary Mixtures	$\left(\frac{\partial(\eta^E)}{\partial T}\right), \left(\frac{\partial(V^E)}{\partial T}\right)_P, \left(\frac{\partial(\Delta G^{\#E})}{\partial T}\right)_P$ & $\left(\frac{\partial(\Delta H^{\#E})}{\partial T}\right)_P$ & $\left(\frac{\partial(\Delta S^{\#E})}{\partial T}\right)_P$				
Dimethylaniline +					
Methyl alcohol	-0.0010	-0.0189	-2.6167	0.0078	0.0304
Ethyl alcohol	-0.0042	-0.0194	-3.7973	0.0101	0.0401
n-Propyl alcohol	-0.0025	-0.0042	-2.4595	0.0061	0.0246
n-Butyl alcohol	-0.0075	-0.0053	-4.6716	0.0118	0.0473
Benzyl alcohol	-0.0041	-0.0206	-3.6797	0.0101	0.0397
Acetone	-0.0014	-0.0386	-5.5694	0.0147	0.0586
Methyl ethyl ketone	-0.0005	-0.0676	-3.1470	0.0081	0.0322
Acetophenone	-0.0004	-0.0087	-0.4709	0.0011	0.0044
Chloroform	-0.0016	-0.0101	-4.1578	0.0105	0.0420
Chlorobenzene	-0.0009	-0.0228	-2.4203	0.0055	1.2324
Bromobenzene	-0.0011	-0.0426	-2.3615	0.0050	0.0205
Carbon tetrachloride	-0.0009	-0.0484	-1.4592	0.0037	0.0146
Benzene	-0.0003	-0.0621	-2.1573	0.0052	0.0210
Toluene	-0.0060	-0.0479	-8.7371	0.0215	0.0865

TABLE- 2 : Coefficients $A_i$ and Standard Deviation $s(\Delta G)$ for representation of Excess Gibb's Free Energy of activation of flow by Redlich, Kister Eqn. at different temperatures for the binary systems involving Dimethylaniline and polar and non-polar solvents									
System	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$A_5$	$A_6$	$A_7$	$\sigma(\Delta G^{#E})$ (J.mol <sup>-1</sup> )
Dimethylaniline +									
Methyl alcohol	2781.07	-1033.02	-452.82	-3625.46	-1929.73	11434.98	22825.75	11692.16	1.32
Ethyl alcohol	2751.70	-897.90	-1340.66	3048.58	21695.79	6741.10	-44661.61	-35987.88	0.40
n-Propyl alcohol	1388.81	-27.26	389.72	386.37	-2601.30	-4093.26	4809.14	7208.87	0.24
n-Butyl alcohol	2773.62	397.65	-296.94	653.25	7226.14	3826.51	-10679.46	-7935.53	1.91
Benzyl alcohol	2886.80	1423.70	533.55	-1008.74	725.90	4236.12	-138.67	-2926.24	1.18
Acetone	3573.70	-1950.38	1638.76	-415.88	-4032.30	-4222.63	7691.80	7441.96	1.22
Methyl ethyl ketone	1855.28	-721.91	324.68	-301.36	905.19	925.28	-1156.61	-1346.86	1.56
Acetophenone	185.57	-35.01	-48.07	-38.45	287.05	503.24	-222.60	-718.58	0.88
Chloroform	2272.52	-1067.67	843.70	899.81	-3081.06	-6217.71	5642.12	8227.48	1.91
Chlorobenzene	823.74	-160.36	127.75	-277.53	-61.26	1021.64	113.28	-1068.71	0.98
Bromobenzene	397.23	-10.01	284.55	-77.72	-1001.07	-102.58	954.09	116.26	0.28
Carbon tetrachloride	775.76	-190.90	314.40	-993.88	-581.87	3133.49	826.58	-2780.09	0.71
Benzene	1009.96	-309.47	20.32	256.09	486.81	-1128.32	-554.45	908.78	0.80
Toluene	4214.95	-1907.25	3238.42	2451.29	-9583.57	-7905.82	11996.74	4724.01	0.06
<b>Temperature 303.15 K</b>									
Dimethylaniline +									
Methyl alcohol	2613.6	-1010.63	1947.591	7223.3	5151.999	-25972.5	-48223.2	-22738.07	1.8812
Ethyl alcohol	2601.19	-989.193	-1294.32	3490.11	19560.12	5730.416	-41351.8	-33020.23	1.0679
n-Propyl alcohol	1300.85	-109.715	5.687753	760.219	-1599.57	-3600.97	3692.567	5468.512	1.0109
n-Butyl alcohol	2591.62	353.3257	596.0739	1324.76	-1068.32	-5362.11	206.2307	5080.823	1.5912
Benzyl alcohol	2824.71	1239.537	478.5761	-434.94	372.6957	2574.982	-210.224	-2422.445	0.6032
Acetone	3225.49	-1691.73	177.4493	-2622.8	6631.869	11763.7	-10521	-15870.27	2.2013
Methyl ethyl ketone	1605.82	-600.151	118.4824	458.683	485.2028	-2303.81	-3.27804	2277.151	0.0269
Acetophenone	161.44	-34.1411	41.34798	109.742	-114.971	-266.857	52.64158	72.95023	0.4882
Chloroform	2117.92	-967.742	299.4329	746.471	1321.316	-2074.06	-1903.28	462.1063	0.8352
Chlorobenzene	654.528	-98.369	0.214622	-742.72	426.2279	4059.401	-749.291	-4721.183	0.2403
Bromobenzene	290.977	-83.0769	72.20763	-132.05	-744.655	1679.164	986.3514	-2336.885	0.0477
Carbon tetrachloride	724.147	-229.325	-162.255	-577.88	1384.167	2905.172	-1347.43	-3456.068	0.7779
Benzene	842.931	-296.591	252.8469	660.834	-1489.8	-3842.47	2428.804	4837.796	0.7917
Toluene	3865.37	-1256.25	3268.569	-5108.3	-10850.6	18364.3	12848.85	-18895.83	0.521
<b>Temperature 313.15 K</b>									
Dimethylaniline +									
Methyl alcohol	2517.64	-821.432	795.5191	3024.91	2379.222	-10461.6	-20096.5	-9766.747	0.0416
Ethyl alcohol	2350.42	-780.144	325.4245	3011.62	-878.922	-7119.18	35.31692	4676.753	1.5973
n-Propyl alcohol	1112.74	-69.4033	-1046.22	-773.97	7543.361	7152.422	-11987.4	-11904.88	1.2067
n-Butyl alcohol	2244.92	-15.3438	153.4149	1864.07	-1363.37	-7393.56	1121.368	6968.109	1.1302
Benzyl alcohol	2435.74	952.7946	626.4971	100.078	-1209.48	16.1308	1644.636	533.2855	0.1475

Acetone	3002.2	-1514.22	558.3161	-571.31	1421.154	1387.276	-1778.04	-1982.943	0.4636
Methyl ethyl ketone	1490.38	-445.004	280.4193	-1353.9	100.91	4505.138	-463.287	-4402.599	1.625
Acetophenone	126.711	-70.2086	79.62976	273.24	-381.733	-940.732	370.0096	872.7658	0.669
Chloroform	1830.91	-923.384	345.3573	1635.89	-2260.83	-9669.53	4343.368	12973.16	0.6085
Chlorobenzene	528.006	-93.3505	-25.3589	465.727	9.155745	-1869.37	237.1841	2126.962	0.5777
Bromobenzene	104.348	-84.4986	158.1234	966.707	-1216.87	-3860.23	1483.944	3895.084	0.0527
Carbon tetrachloride	600.365	-272.112	332.0913	530.196	-627.229	-1354.71	376.9612	796.0057	0.5594
Benzene	728.214	-264.53	202.119	-5.3755	-781.931	-621.648	1041.958	1250.238	0.5923
Toluene	3260.89	-1253.95	1323.725	-2113.6	-4402.21	6540.534	6051.576	-6983.692	0.5645

**TABLE- 3 : Coefficients  $A_i$  and Standard Deviation  $s(\Delta S^{\#E})$  for the representation of Excess.Entropy of activation of flow by Redlich-Kister Eqn. at different temperatures**

System	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$A_5$	$A_6$	$A_7$	$\sigma(\Delta S^{\#E})$
<b>Temperature 293.15 K</b>									
Dimethylaniline +									
Methyl alcohol	11.72	-9.68	-58.33	-310.49	-201.27	1022.42	2004.07	1001.87	0.060
Ethyl alcohol	18.18	-5.32	-77.69	1.07	1051.92	647.28	-2082.38	-1895.53	0.056
n-Propyl alcohol	12.62	1.98	67.13	54.23	-474.27	-525.48	785.14	893.08	0.068
n-Butyl alcohol	24.14	19.24	-21.02	-56.82	400.47	524.34	-550.03	-695.86	0.036
Benzyl alcohol	20.48	21.73	-4.47	-51.68	90.43	196.60	-83.44	-161.29	0.048
Acetone	25.97	-19.99	50.21	7.37	-254.38	-261.66	441.58	439.53	0.079
Methyl ethyl ketone	16.68	-12.80	2.00	49.33	37.45	-167.76	-32.20	143.32	0.149
Acetophenone	2.71	1.66	-5.97	-14.58	31.24	67.48	-27.69	-74.33	0.010
Chloroform	20.18	-6.52	23.14	-34.65	-37.72	162.92	59.56	-223.92	0.061
Chlorobenzene	13.66	-3.10	7.14	-34.73	-3.28	135.10	-5.82	-149.35	0.019
Bromobenzene	13.62	3.49	5.86	-48.87	10.32	175.91	-25.01	176.90	0.015
Carbon tetrachloride	8.04	3.84	-0.90	-71.12	2.25	209.40	20.87	-166.78	0.007
Benzene	12.97	-2.04	-8.51	12.18	59.28	-23.47	-74.60	-16.18	0.010
Toluene	43.74	-30.16	88.91	213.13	-240.43	-674.46	275.66	546.97	0.024
<b>Temperature 303.15 K</b>									
Dimethylaniline +									
Methyl alcohol	13.31	-10.32	-68.34	-357.70	-231.94	1183.31	2312.03	1152.30	0.0601
Ethyl alcohol	19.93	-5.40	-80.80	0.34	1099.81	674.24	-2174.56	-1978.22	0.0531
n-Propyl alcohol	13.66	2.31	70.77	54.93	-494.35	-545.97	816.71	930.94	0.0674
n-Butyl alcohol	26.20	20.14	-24.75	-60.82	443.15	573.41	-607.15	-764.35	0.0495
Benzyl alcohol	22.05	23.41	-4.32	-55.57	94.85	209.76	-86.08	-169.13	0.0519
Acetone	28.82	-21.97	57.12	14.80	-299.16	-324.29	518.48	533.12	0.0929
Methyl ethyl ketone	18.49	-13.81	2.82	48.44	40.32	-162.62	-37.37	135.95	0.1596
Acetophenone	2.93	1.70	-6.48	-15.58	33.70	72.44	-29.59	-79.64	0.0116



Chloroform	21.89	-7.32	25.92	-35.12	-54.23	153.39	87.77	-204.06	0.0665
Chlorobenzene	14.88	-3.45	7.83	-34.44	-5.02	129.92	-3.15	-142.64	0.0233
Bromobenzene	14.53	3.85	6.82	-50.37	9.60	176.00	-25.75	-174.82	0.0166
Carbon tetrachloride	8.66	4.06	0.72	-75.15	-4.29	218.01	28.94	170.87	0.0122
Benzene	14.19	-2.22	-9.57	11.32	67.93	-15.58	-87.11	-29.48	0.0155
Toluene	47.35	-33.78	92.59	245.90	-246.65	-785.94	285.00	644.62	0.0224
<b>Temperature 313.15 K</b>									
Dimethylaniline +									
Methyl alcohol	15.10	-11.86	-68.70	-366.24	237.20	1205.75	2363.63	1181.76	0.0706
Ethyl alcohol	22.67	-6.67	-91.85	2.74	1245.32	763.11	-2466.06	-2242.54	0.0657
n-Propyl alcohol	15.48	2.31	78.99	63.85	-558.01	-618.85	924.03	1051.89	0.0795
n-Butyl alcohol	29.68	22.78	-24.81	-66.39	473.60	617.38	-650.84	-820.71	0.0435
Benzyl alcohol	25.43	26.20	-4.99	-61.15	106.51	232.83	-98.02	-190.75	0.0571
Acetone	32.21	-24.41	59.74	8.45	-300.56	-309.20	522.08	519.55	0.0929
Methyl ethyl ketone	20.47	-15.38	2.50	57.56	44.40	-196.50	-38.36	167.60	0.1755
Acetophenone	3.28	1.93	-7.03	-17.14	36.81	79.46	-32.61	-87.60	0.0119
Chloroform	24.78	-8.17	27.57	-40.24	-45.76	188.27	72.63	-258.91	0.0719
Chlorobenzene	16.44	-3.72	8.44	-40.90	-3.88	159.08	-6.78	-175.84	0.0222
Bromobenzene	16.18	4.09	7.01	-57.41	11.63	206.45	-28.90	-207.61	0.0181
Carbon tetrachloride	9.81	4.42	-0.90	-83.97	2.36	247.32	24.89	-197.12	0.0084
Benzene	15.71	-2.54	-9.98	14.42	69.82	-28.09	-87.84	-18.56	0.0118
Toluene	53.37	-36.33	105.94	251.38	-286.86	-795.58	329.38	644.38	0.0276

**TABLE- 4 : Coefficients  $A_i$  and Standard Deviation  $s(AH)$  for representation of Excess Enthalpy of activation of flow by Redlich, Kister Eqn. at different temperatures for the binary systems involving Dimethylaniline and polar and non -polar solvents.**

	$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$A_5$	$A_6$	$A_7$	$\sigma(\Delta S^{#E})$
									(K.J. Mol <sup>-1</sup> )
Dimethylaniline +									
Methyl alcohol	6.22	-3.87	-17.55	-94.65	-60.93	311.16	610.32	305.39	0.0188
Ethyl alcohol	8.08	-2.46	-24.12	3.36	330.07	196.49	-655.11	-591.66	0.0161
n-Propyl alcohol	5.09	0.55	20.07	16.28	-141.6	-158.1	234.97	269.02	0.0201
n-Butyl alcohol	5.85	6.04	-6.46	-16.00	124.62	157.54	-171.92	-211.93	0.0125
Benzyl alcohol	8.89	7.79	-0.78	-16.16	27.24	61.87	-24.60	-50.21	0.0153
Acetone	11.2	-7.81	16.36	1.74	-78.6	-80.93	137.14	136.29	0.0243
Methyl ethyl ketone	6.74	-4.48	0.91	14.16	11.88	-48.25	-10.60	40.67	0.0452
Acetophenone	0.98	0.45	-1.80	-4.31	9.45	20.28	-8.34	-22.51	0.0037
Chloroform	8.19	-2.98	7.63	-9.26	-14.14	41.54	23.10	-57.42	0.0196
Chlorobenzene	4.83	-1.07	2.22	-10.46	-1.02	40.62	-1.59	-44.85	0.0064
Bromobenzene	4.39	1.01	2.00	-14.40	2.02	51.46	-6.38	-51.74	0.0048
Carbon tetrachloride	3.13	0.94	0.05	-21.84	0.08	64.52	6.94	-51.67	0.0027
Benzene	4.81	-0.91	-2.48	3.83	17.86	-8.01	-22.42	-3.83	0.0037
Toluene	17	-10.75	29.30	64.93	-80.07	-205.6	92.81	165.07	0.0068

Temperature 303.15 K									
Dimethylaniline +									
Methyl alcohol	6.65	-4.14	-18.8	-101.2	-65.16	332.7	652.67	326.58	0.0201
Ethyl alcohol	8.64	-2.63	-25.8	3.59	352.97	210.13	-700.57	-632.72	0.0172
n-Propyl alcohol	5.44	0.59	21.46	17.41	-151.5	-169.1	251.28	287.68	0.0215
n-Butyl alcohol	10.53	6.46	-6.91	-17.11	133.27	168.47	-183.85	-226.63	0.0134
Benzyl alcohol	9.51	8.34	-0.83	-17.28	29.13	66.16	-26.31	-53.69	0.0164
Acetone	11.96	-8.35	17.49	1.86	-84.06	-86.54	146.66	145.75	0.026
Methyl ethyl ketone	7.21	-4.79	0.97	15.14	12.71	-51.6	-11.33	43.49	0.0483
Acetophenone	1.05	0.48	-1.92	-4.61	10.1	21.69	-8.92	-24.07	0.004
Chloroform	8.75	-3.19	8.16	-9.9	-15.12	44.43	24.71	-61.4	0.021
Chlorobenzene	5.16	-1.14	2.37	-11.18	-1.09	43.44	-1.7	-47.96	0.0068
Bromobenzene	4.70	1.08	2.14	-15.4	-2.16	55.03	-6.82	-55.33	0.0051
Carbon tetrachloride	3.35	1.00	0.06	-23.36	0.08	68.99	7.43	-55.26	0.0029
Benzene	5.15	-0.97	-2.65	4.09	19.1	-8.56	-23.98	-4.1	0.0039
Toluene	18.22	-11.50	31.34	69.44	-85.62	-219.9	99.25	176.52	0.0073
Dimethylaniline +	6.65	-4.14	-18.8	-101.2	-65.16	332.7	652.67	326.58	0.0201
Methyl alcohol	8.64	-2.63	-25.8	3.59	352.97	210.13	-700.57	-632.72	0.0172
Ethyl alcohol	5.44	0.59	21.46	17.41	-151.5	-169.1	251.28	287.68	0.0215
n-Propyl alcohol	10.53	6.46	-6.91	-17.11	133.27	168.47	-183.85	-226.63	0.0134
n-Butyl alcohol	9.51	8.34	-0.83	-17.28	29.13	66.16	-26.31	-53.69	0.0164
Benzyl alcohol	11.96	-8.35	17.49	1.86	-84.06	-86.54	146.66	145.75	0.026
Acetone	7.21	-4.79	0.97	15.14	12.71	-51.6	-11.33	43.49	0.0483
Temperature 313.15 K									
Dimethylaniline +									
Methyl alcohol	7.10	-4.42	-20.03	-108.00	-69.53	355.06	696.44	348.48	0.0215
Ethyl alcohol	9.22	-2.80	-27.52	3.84	376.64	224.22	-747.55	-675.15	0.0183
n-Propyl alcohol	5.81	0.63	22.90	18.58	-161.6	-180.5	268.13	306.97	0.0229
n-Butyl alcohol	11.24	6.89	-7.37	-18.26	142.21	179.77	-196.18	-241.83	0.0143
Benzyl alcohol	10.15	8.89	-0.89	-18.44	31.08	70.8	-28.07	-57.29	0.0174
Acetone	12.77	-8.91	18.67	1.99	-89.69	-92.65	156.49	155.52	0.0277
Methyl ethyl ketone	7.70	-5.11	1.04	16.16	13.56	-55.06	-12.09	46.41	0.0516
Acetophenone	1.12	0.51	-2.05	-4.92	10.78	23.15	-9.52	-25.68	0.0043
Chloroform	9.34	-3.40	8.70	-10.56	-16.13	47.41	26.36	-65.52	0.0224
Chlorobenzene	5.51	-1.22	2.53	-11.93	-1.17	46.26	-1.82	-51.18	0.0073
Bromobenzene	5.01	1.16	2.28	-16.44	2.31	58.73	-7.28	-59.04	0.0054
Carbon tetrachloride	3.57	1.07	0.06	-24.92	0.09	73.62	7.92	-58.96	0.0031
Benzene	5.49	-1.03	-2.82	4.37	20.39	-9.14	-25.59	-4.38	0.0042
Toluene	19.44	-12.27	33.44	74.09	-91.36	-234.6	105.9	188.36	0.0078

TABLE-5: Coefficients  $A_i$  and Standard Deviation  $\sigma(V^E)$  for representation of Excess Molar Volume by Redlich-Kister Eqn. at different temperatures for the binary systems involving Dimethylaniline and polar and non-polar solvents

System	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma(V^E)$ ( $\text{cm}^3 \cdot \text{mol}^{-1}$ )
<b>Temperature 293.15 K</b>					
Dimethylaniline +					
Methyl alcohol	-3.736	1.242	0.058	-0.691	0.0249
Ethyl alcohol	-2.976	0.172	0.269	0.661	0.0207
n-Propyl alcohol	-1.030	0.091	-0.062	-0.371	0.0091
n-Butyl alcohol	-2.093	0.423	0.204	0.052	0.0139
Benzyl alcohol	-4.535	0.714	0.207	0.530	0.0213
Acetone	-6.786	1.161	1.105	-0.512	0.0568
Methyl Ethyl ketone	-12.920	-0.380	0.239	0.288	0.1160
Acetophenone	-1.698	0.188	-0.377	-1.167	0.0124
Chloroform	-1.243	0.083	0.068	0.027	0.0105
Chlorobenzene	-3.253	0.375	0.059	0.300	0.0233
Bromobenzene	-9.358	0.194	-2.569	-5.098	0.0884
Carbon tetrachloride	-9.679	-2.971	2.874	1.627	0.0667
Benzene	-5.191	0.324	-0.838	-2.242	0.0682
Toluene	-5.376	-1.435	-1.613	-0.978	0.0934
<b>Temperature 303.15K</b>					
Dimethylaniline +					
Methyl alcohol	-4.878	1.753	0.345	0.570	0.0273
Ethyl alcohol	-4.061	0.836	-0.400	0.022	0.0375
n-Propyl alcohol	-1.292	0.114	-0.158	-0.026	0.0071
n-Butyl alcohol	-2.341	0.678	-0.011	-0.534	0.0142
Benzyl alcohol	-5.745	0.453	0.377	0.951	0.0361
Acetone	-9.020	1.664	0.613	1.305	0.0402
Methyl ethyl ketone	-17.436	1.308	-0.799	-1.449	0.0713
Acetophenone	-2.270	-0.007	-0.296	-0.833	0.0145
Chloroform	-1.782	0.333	-0.212	-0.283	0.0053
Chlorobenzene	-4.760	1.142	0.908	0.187	0.0251
Bromobenzene	-12.623	-0.861	-0.137	-0.639	0.0885
Carbon tetrachloride	-12.517	-3.845	2.289	-0.340	0.1535
Benzene	-8.647	-1.464	-1.373	0.610	0.0841
Toluene	-7.840	-0.424	-0.839	-2.396	0.0915
<b>Temperature 313.15 K</b>					
Dimethylaniline +					
Methyl alcohol	-6.138	2.022	-0.249	1.088	0.0375
Ethyl alcohol	-5.439	1.114	-0.161	0.923	0.0582

n-Propyl alcohol	-1.545	0.015	-0.275	0.059	0.0080
n-Butyl alcohol	-2.700	0.624	-0.235	-0.098	0.0076
Benzyl alcohol	-7.249	0.361	-0.040	1.596	0.0321
Acetone	-11.402	4.110	-1.204	-1.777	0.1334
Methyl ethyl ketone	-21.190	-0.054	-3.900	2.415	0.0903
Acetophenone	-2.824	-0.468	-0.538	-0.514	0.0334
Chloroform	-2.541	0.336	-0.175	0.066	0.0157
Chlorobenzene	-6.228	1.194	0.062	2.129	0.0410
Bromobenzene	-14.919	-0.677	-2.973	0.543	0.0568
Carbon tetrachloride	-16.061	-5.821	1.179	0.599	0.0582
Benzene	-13.463	-3.280	-1.741	4.264	0.0686
Toluene	-11.874	-0.040	-0.879	-3.429	0.0754

**TABLE- 6 : Values of McAllister parameters ( $Z_{12}$  and  $Z_{21}$ ) and Brewer parameters (a,b,c) at different temperatures**

System	$Z_{12}$	$Z_{21}$	a	b	c
			( $\text{cm}^2.\text{s}^{-1}$ )	( $\text{cm}^2.\text{s}^{-1}$ )	( $\text{cm}^2.\text{s}^{-1}$ )
<b>Temperature 293.15 K</b>					
Dimethylaniline +					
Methyl alcohol	1.05279	0.44385	0.06801	-0.03225	0.02881
Ethyl alcohol	1.58995	0.66443	1.05419	-0.20217	0.18023
n-Propyl alcohol	1.92882	0.76639	0.25498	-0.07739	0.06568
n-Butyl alcohol	2.85707	1.04766	1.68302	-0.35408	0.19655
Benzyl alcohol	4.21615	1.51370	1.18116	0.06266	0.02522
Acetone	0.97542	0.43550	0.40372	-0.20966	0.08671
Methyl ethyl ketone	1.11549	0.32850	0.15520	-0.05404	0.06675
Acetophenone	1.39960	0.46348	0.09460	-0.01019	0.02157
Chloroform	1.17623	0.41497	0.11586	-0.01437	0.03800
Chlorobenzene	1.25354	0.36794	0.09885	0.01874	0.03476
Bromobenzene	1.40051	0.44007	-0.07872	0.00130	0.00881
Carbon tetrachloride	1.34802	0.42947	-0.08180	-0.03078	0.06637
Benzene	1.18250	0.33817	0.10383	-0.03695	0.01110
Toluene	1.4705	0.6889	1.8293	-0.2548	0.1847
<b>Temperature 303.15 K</b>					
Dimethylaniline+					
Methyl alcohol	1.0375	0.211524615	-0.57581441	-0.42320963	-1.2019048
Ethyl alcohol	1.4528	0.3668	0.0557	-0.3661	-1.8119
n-Propyl alcohol	1.7857	0.3073	-1.3359	1.3521	-4.6461
n-Butyl alcohol	2.1497	0.4955	-0.5830	1.5315	-5.2856
Benzyl alcohol	2.8383	0.9870	-1.2594	2.0581	-5.5043

Acetone	0.7491	0.2860	-0.2244	-0.8530	-0.9192
Methyl ethyl ketone	0.8062	0.2303	-0.4590	-0.6602	-1.1270
Acetophenone	0.9019	0.4079	-0.5267	-0.5362	-1.4766
Chloroform	0.8866	0.2820	-0.4192	-0.6693	-1.0281
Chlorobenzene	0.8540	0.2787	-0.4996	-0.5717	-1.2906
Bromobenzene	0.9685	0.3053	-0.7269	-0.4775	-1.5216
Carbon tetrachloride	0.9831	0.2892	-0.6591	-0.5668	-1.3075
Benzene	0.8864	0.2178	-0.5682	-0.5292	-1.3658
Toluene	0.9762	0.4964	0.8648	-0.8636	-1.1504
<b>Temperature 313.15 K</b>					
Dimethylaniline +					
Methyl alcohol	1.0196	0.0849	-1.0274	-0.4123	-2.2750
Ethyl alcohol	1.3562	0.1588	-0.7487	0.1086	-3.6355
n-Propyl alcohol	1.6235	0.1441	-2.2706	2.3027	-7.4128
n-Butyl alcohol	1.8804	0.2337	-2.1911	3.2240	-9.1211
Benzyl alcohol	2.3490	0.5019	-3.4499	5.1233	-11.0859
Acetone	0.7282	0.1675	-0.6551	-1.0062	-1.5519
Methyl ethyl ketone	0.7140	0.1592	-0.8216	-0.8632	-1.8552
Acetophenone	0.7044	0.3896	-0.8267	-0.8153	-2.1472
Chloroform	0.7570	0.2118	-0.7412	-1.0052	-1.5905
Chlorobenzene	0.7257	0.1942	-0.9123	-0.7001	-2.1271
Bromobenzene	0.8025	0.2233	-1.1126	-0.6453	-2.3399
Carbon tetrachloride	0.8590	0.1976	-1.0147	-0.7569	-2.0895
Benzene	0.7896	0.1518	-0.9344	-0.7045	-2.1221
Toluene	0.7591	0.3325	0.1039	-1.0514	-2.0091

temperatures have been fitted to Redlich-Kister polynomial equation and result have been presented in the Tables 1 It is seen that in each case, the fit is good as revealed by very small values of corresponding standard deviations,  $\sigma(\eta^E)$ ,  $\sigma(V^E)$ ,  $\sigma(\Delta G^{\#E})$ ,  $\sigma(\Delta H^{\#E})$  and  $\sigma(\Delta S^{\#E})$ . From this it is concluded that the experimental value of various excess thermodynamic properties are theoretically predicated in a precise manner by Redlich-Kister polynomial equation.

### REFERENCES

1. V.K. Henry, S.K. Krystne and H.Regina 'Properties of Water - Acetone and Water - Isopropanol as a Solvent Mixtures', *J.Chem.Phys.*, 1971, **68**, 922.
2. S.L. Oswal and A.V. Rao, 'STUDIES ON VISCOSITY AND VOLUME OF MIXING OF BINARY-LIQUID MIXTURES OF TERTIARY-AMINES WITH CYCLOHEXANE AND BENZENE' *Indian J. Chem.*, Sect. A, 1985, 24, 1024.

- 3 S.L. Oswal and A . T . Patel ‘**Viscosity of binary mixtures. I. mono-, di-, and tri-*n*-butyl and -*n*-octylamine with cyclohexane**’, Int . J . Thermophys . 1991 ,12 821 .
4. S.L. Oswal and A . T . Patel ,’**Viscosity of binary mixtures. II. *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, and *n*-dodecylamine with benzene and *n*-hexyl, *n*-decyl, and *n*-dodecylamine with cyclohexane**’ Int . J . Thermophys. , 1992, 13 629.
5. D . Papaioannou , M . Bridakis and C . G . Panayiotou , ‘**Excess dynamic viscosity and excess volume of N-butylamine + 1-alkanol mixtures at moderately high pressures**’, C . G . Panayiotou , J . Chem . Eng . Data , 1993 , 38 , 370 .
6. R . T . Marrison and R . N . Boyd ‘organic chemistry’, **Sixty Edn. Prentice Hall of India** , New Delhi , 1999 , **824** .
7. R.J Fort and W.R. Moore ‘**Viscosities of binary liquid mixtures**’, Trans Faraday soc , 19.66, 62, 1112 ..
8. L Pikkarainen , ‘**Densities and viscosities of binary solvent mixtures of N-methylacetamide with aliphatic alcohols**’, J chem. Eng Data , 1983, 28, 381.
9. S. Glasstone , K. J. Laidler and H. Eyring , ‘**The Theory of Rate Processes The Kinetics of Chemical Reactions, Viscosity, Diffusion and Electrochemical Phenomena**’ The theory of Rate Processes (Mc Graw – Hill , New york ) 1941 .
10. O. Redlich and A .T. Kister ‘**Algebraic Representation of Thermodynamic Properties and the Classification of Solutions**’, Ind Eng Chem , 1948 , 40 , 345 .
11. G . Moumouzlas , D . K . Panopoulous and G . Ritzoulls , ‘**Excess properties of the binary liquid system propylene carbonate + acetonitrile**’, J . ChemEng . Data , 1991 , 36, 20 .
- 12 M . Ibrahim . Ph.D . Thesis , A . M . U . , Aligarh , 1979 .
13. J . M . G . Cowie and P . M . Toporowski , ‘**ASSOCIATION IN THE BINARY LIQUID SYSTEM DIMETHYL SULPHOXIDE – WATER**’, Can . J . Chem , 1961 , 39 , 2240 .
14. P . Assarson and F . R . Eirich , ‘**Properties of amides in aqueous solution. I. Viscosity and density changes of amide-water systems. An analysis of volume deficiencies of mixtures based on molecular size differences**’, J . Phys . Chem . 72 , 8 1968 , 2710 .
- 15 . D . Debashis , S . K . Ray and D .K . Hazara , **J . Indian Chem . Soc . , 2003 , 80 , 385 .**
- 16 A . Pal and G . Dass , ‘**Excess Molar Volumes and Viscosities of Diethylene Glycol Diethyl Ether with Dimethyl Carbonate, Diethyl Carbonate, and Propylene Carbonate at 298.15, 308.15, and 318.15 K**’, J . Chem Eng . Data , 2000 , 45, 487 ,2000.
- 17 K.Ramamoorthy, ‘**EXCESS FREE-ENERGY OF MIXING (DELTA-FM) AND STRENGTH OF INTERACTION IN BINARY-LIQUID MIXTURES FROM VISCOSITY STUDIES**’, J . pure and Appl.phys , 1973 , 11 ,554 .

18 A. Vogel, 'Potentiometric, spectrophotometric, conductimetric and thermodynamic studies on some transition metal complexes derived from 3-methyl-1-phenyl- and 1, 3-diphenyl-4-arylazo-5-pyrazolones', Practical Organic Chemistry, 4<sup>th</sup> Edn (Longman, London) 1978.

19 J. A. Reddick, W. B. Bunger and T. K. Sakano, 'Physical and Electrolytic Properties of Monofluorinated Ethyl Acetates and Their Application to Lithium Secondary Batteries', Techniques of Chemistry: Organic Solvents, 4<sup>th</sup> Edn (Wiley, New York) 1986)

