Viscosities, Free Energies of Activation and their Excess Properties in the Binary Mixtures of Some Monoalkanolamines with Acetonitrile between 303.15 and 323.15 K: Experimental and Correlative Approach

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Abstract

Viscosities (η) *of three binary non-aqueous systems of ACN + MEA, + MMEA and + MEEA have been measured in the whole range of compositions at temperatures ranging between 303.15 and 323.15 K at an interval of 5 K. At different compositions, deviations in viscosity* ($\Delta\eta$)*, free energy* ($\Delta G^{\ddagger}$) *of activation for viscous flow along its excess values* ($\Delta G^{\ddagger E}$) *were calculated from experimental* ρ *and* η *data. For all systems,* η *vs.* x_2 *initially changed very slowly, but with the increment of solute concentration* η *were found to rise quite rapidly. The values of* $\Delta\eta$ *were largely positive and they formed a sharp maximum invariably at the highly alkanolamine-rich regions. All positive values of* $\Delta\eta$ *followed the increasing order as: ACN + MMEA > ACN + MEA > ACN + MEEA. The order of* $\Delta G^{\ddagger E}$ *at the maximum point was ACN + MMEA > ACN + MEA > ACN + MEEA. For the correlative model, zero parameter relations: Bingham, Kendall- Munroe, Gambill, and Eyring relations, one parameter relations: Hind, Grunberg-Nissan, Frenkel, Wijk, Katti-Chaudhri, Tamura Kurata and two as well as three parameter-based models: Heric, Ausländer, McAllister (3-body) and McAllister (4-body) Equation and the Jouyban-Acree model (JA) were employed to correlate viscosities. Ausländer equation fit the best for: ACN + MEA. McAlliester 4-body fit the best for ACN + MMEA and ACN + MEEA. All the above results were attempted to be interpreted in terms of the strength and order of self-association, intra- as well as intermolecular hydrogen bonding via OH···O or OH···N and the effect due to steric hindrance of the concerned alkanolamine molecules and interstitial accommodation of ACN into alkanolamine network.*

Keywords: *Viscosity, Deviation in viscosity, Excess free energy of activation for viscous flow, Correlative model, Alkanolamine, Cross H-bonding.*

1. Introduction

Nowadays, global warming is a burning environment issue. Greenhouse gases, especially, CO_2 were responsible. Due to human activities, emission of CO_2 is increasing day by day [1]. Scientists all over the world are ceaselessly trying to find the ways to get rid of this problem. For carbon capture [2], utilization and storage (CCUS) and to make effective absorption columns they amass data of

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alkanolamine systems [3–5]. A good number of pure alkanolamines, important physical properties, such as density, viscosity, thermal conductivity and heat capacity have already been studied [6–15]. Density, viscosity and some excess properties of aqueous solutions of monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monomethylethanolamine (MMEA), dimethylethanolamine (DMEA), methyldiethanolamine (MDEA), ethyldiethanolamine (EDEA), diethylethanolamine (DEEA) have been studied by several researchers [16,17,26,27,18–25]. Also, densities and viscosities of aqueous solutions of some blended amines have been reported [28–30]. These observations of these data are in agreement with our findings. Our goal is to fill the gap between present status and scientists' expectations for research and development. For this purpose, we combat with CO_2 (searching absorber for making carbon capture machine) to reduce carbon level at atmosphere.

This report is a continuation of our systematic study on thermodynamic, optical and transport properties of binary mixtures of organic liquids including alkanols, amines, alkanolamines, etc. in aqueous and non-aqueous media [31–40]. We have reported densities, excess molar volumes, apparent molar volumes, partial molar volumes, thermal expansivities and their excess and/or deviation properties of alkanolamine in aqueous media [27]. At present, we are going to extend our study of alkanolamines in non-aqueous media where a literature survey revealed that no work has yet to be done with alkanolamines except for the paper we reported earlier about volumetric properties and refractive indices [41]. In this paper, we are going to report viscosities (η), deviation in viscosities ($\Delta\eta$), the free energy of activation for viscous flow ($\Delta G^{\ddagger}$) and their excess ($\Delta G^{\ddagger E}$) properties for the binary mixtures of ACN + MEA, ACN + MMEA and ACN + MEEA between 303.15 K and 323.15 K at 5 K interval. Liquid viscosity depends upon temperature which was pointed out first by J. deGuzmann Carrancio in 1913. It requires the requisite amount of energy to surmount the barrier in the flow process. The activation energy for viscous flow varies with molecular interactions present in the components of the liquids/liquid mixtures. It has been observed that significant specific interactions are present in the aqueous solutions of such bipolar compounds. For this reason, η, $\Delta\eta$, $\Delta G^{\ddagger}$ and $\Delta G^{\ddagger E}$ have been discussed with a range of temperatures.

Viscosity is a very useful property for the design of transport and process equipment in the chemical industries [42]. With the increased popularity of process and reservoir simulators, there is always an acute need for consistent and reliable data for viscosity calculations. Many correlations and prediction methods have until now been developed for the estimation of the viscosity of liquid mixtures. Generally, there are two different types of methods for this purpose: one is the predictive approach and the other is the correlative approach [43]. Correlative approaches usually lead to better results, even though some optimization techniques should be involved for the determination of interaction parameters (one or more). There are also other methods for estimating the viscosity of liquid mixtures that can be classified as semi-theoretical and empirical models [44]. A comparison of experimental data with their calculated values from various theoretical models of liquid mixtures is very useful from different points of view: i) it suggests which model is more suitable to the characteristics of the liquid system, ii) it may indicate which part should be improved in the equation and iii) it may allow the identification of some models as a convenient reference for the deviations observed [45]. In the present investigation, theoretical viscosities of non-aqueous binary systems: ACN + MEA, + MMEA and + MEEA have been evaluated using six standard models and the relative merits were analyzed. These estimations were made from correlative methods involving zero parameter relations: Bingham, Kendall- Munroe, Gambill, and Eyring relations; one parameter relations: Hind, Grunberg-Nissan, Frenkel, Wijk, Katti-Chaudhri, Tamura Kurata and two and three parameter based models: Heric, Ausländer, McAllister (3-body) and McAllister (4-body) equation and the Jouyban-Acree model (JA) were employed to correlate viscosities on the basis of experimental data.

2. Experimental Section

Acetonitrile (ACN) and different alkanolamines were used for the preparation of the binary solution. Monomethylethanolamine (MMEA) and monoethylethanolamine (MEEA) were procured from Merck-Schuchardt and monoethanolamine (MEA) was obtained from Aldrich Chemical Co. Ltd**.** Table 1 lists the specification of chemicals used in the present study.

Table 1: Specifications of the pure liquids

Liquids	**Molecular Formula**	**Source**	**CAS No.**	**Initial Purity (Mass Fraction) %**	**Molar Mass $(g\cdot mol^{-1})$**	**B.P. in ℃**
Acetonitrile (ACN)	C_2H_3N	Aldrich	75-05-8	>99.5	41.0519	82
Monoethanolamine (MEA)	C_2H_7NO	Aldrich	141-43-5	>99	61.0831	170
Monometylethanolamine (MMEA)	C_3H_9NO	Merck	109-83-1	>98	75.1097	259
Monoethylethanolamine (MEEA)	$C_4H_{11}NO$	Merck	110-73-6	>97	89.1362	169-170

ACN and MEA were used without further treatment but MMEA and MEEA were used after distillation. The middle portion of distillation was taken to prepare solutions. All the chemicals were kept under molecular sieves (4 Å) for 2-3 weeks prior to use.

Solutions of different alkanolamines with ACN at different compositions were made by the method of dilution using a Metler Toledo (Model: SAG285) electronic balance with an accuracy of ± 0.01 mg. In order to measure the viscosity of binary solutions at different compositions, the amount of each component used was later converted into its mole fraction. Special caution was taken to prevent evaporation and also the introduction of moisture into the experimental samples. Viscosities were measured using an automated SVM 3000 Anton Paar rotational Stabinger Viscometer. The temperature was adjusted automatically and calibrated with Millikelvin Thermometer, MKT controlled up to ± 0.005 K. Reproducibility of viscosity measurement was estimated less than ± 0.35 %.

In order to correlate measured η, general polynomial equation has been used:

$$\eta = \sum_{i=0}^{n} a_i x_2^i \tag{1}$$

Here, a_i is the fitting coefficient and x_2 be the mole fraction of alkanolamines.

The theoretical viscosities η_{id} of the mixtures were calculated by using the relation,

$$\eta_{id} = \exp\left(x_1 \ln \eta_1 + x_2 \ln \eta_2\right) \tag{2}$$

The deviation in viscosity $(\Delta\eta)$ was then calculated by subtracting the theoretical viscosity from the observed value of η, i.e,

$$\Delta\eta = \eta - \eta_{id} \tag{3}$$

And deviation in viscosity, $\Delta\eta$, has been correlated by Redlich-Kister polynomial equation of the form:

$$\Delta\eta = x_2(1-x_2)\sum_{i=0}^{n} A_i(1-2x_2)^{i-1} \qquad (4)$$

with standard deviation, σ, that has been calculated as follows:

$$\sigma(Y) = \left[\sum \frac{(\eta_{exp}-\eta_{cal})}{\mathrm{n-p}}\right]^{\frac{1}{2}} \qquad (5)$$

Here A_i is the i-th fitting coefficient and the other terms have their usual significance. And Y represents η or$\Delta\eta$, n the number of measurements and p the number of coefficients.

Eyring and co-workers [46] using absolute reaction rate theory and partition functions, correlated viscosity (η) as follows:

$$\eta = \frac{\hbar N}{V_m} \exp \Delta G^{\ddagger} / RT \qquad (6)$$

where, $\Delta G^{\ddagger}$ = Free energy of activation per mole for viscous flow, *h*= Planck's constant, *N*= Avogadro's number, V_m= The molar volume for pure liquids or mixture, *R*=Molar gas constant and *T*=Absolute temperature. Since, $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$, eq. (37) reduces to,

$$ln\frac{\eta V_m}{\hbar N} = \frac{\Delta H^{\ddagger}}{RT} - \frac{\Delta S^{\ddagger}}{R} \qquad (7)$$

where, $\Delta H^{\ddagger}$ = The enthalpy of activation for mole and $\Delta S^{\ddagger}$ The entropy of activation per mole for viscous flow. A plot $ln\frac{\eta V_m}{\hbar N}$ $vs.\frac{1}{T}$ will give a straight line. The slope and intercept $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be easily calculated. And the free energy of activation ($\Delta G^{\ddagger}$) for viscous flow has been calculated by using the simple thermodynamic relation,

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad (8)$$

And the excess free energy of activation ($\Delta G^{\ddagger E}$) for viscous flow was calculated as:

$$\Delta G^{\ddagger E} = \Delta G^{\ddagger} - (x_1\,\Delta G^{\ddagger}_1 + x_2\,\Delta G^{\ddagger}_2) \qquad (9)$$

3. Results and discussion

3.1. Viscosities (η)

The viscosities, η, of pure acetonitrile and alkanolamines at different temperatures along with their available literature values are given in Table 2.

Table 2: Experimental values with literature

Temp. T / K	ACN		MEA		MMEA		MEEA	
	This Work*	Lit.$^{\#}$	This Work*	Lit.$^{\#}$	This Work*	Lit.$^{\#}$	This Work*	Lit.$^{\#}$
303.15	3.324	0.3308[47] 0.3307[48] 0.3307[49] 0.35[50] 0.326[51] 0.3485[52] 0.333[53]	152.4	15.200[54] 14.88[55] 14.831[56]	89.60	8.535[57] 8.6122[58] 8.7976[59]	98.43	9.64[60] 9.9379[59] 10.157[61]
308.15	3.185	0.3165[48] 0.319[53] 0.3285[52]	123.1	11.966[54]	72.81	7.014[57] 7.0700[58] 7.3105[59]	79.34	7.96[60] 8.1387[59] 8.223[61]
313.15	3.077	0.2991[47] 0.3035[48] 0.3005[49] 0.3102[52]	100.7	9.702[54] 9.93[55] 9.890[56]	60.50	5.841[57] 5.883[58] 6.6098[59]	65.30	6.51[60] 6.5974[59] 6.748[61]
318.15	2.932	0.2912[48]	83.3	7.914[54]	50.91	4.919[57] 4.9526[58] 4.9956[59]	54.54	5.32[60] 5.5664[59] 5.608[61]
323.15	2.822	0.2720[47] 0.2746[49]	69.59	6.89[55] 6.872[56]	43.03	4.186[57] 4.2143[58] 4.3481[59]	45.89	4.28[60] 4.6264[59] 4.714[61]

*Units: $10^4\eta$ / kg $m^{-1}s^{-1}$, $^{\#}$Units: η / cP or mPa.s (1 cP = 1 mPa.s = 10^{-3} kg-$m^{-1}s^{-1}$)

The observed η values agreed quite satisfactorily with the available literature data. η for the binary mixtures of ACN+MEA, + MMEA and +MEEA measured between 303.15 K and 323.15 K at 5 K intervals are summarized in Table 3.

Table 3: Viscosities, $\eta.10^4/\,\mathrm{kg.m^{-1}.s^{-1}}$ and deviations in viscosities, $\Delta\eta.10^4/\,\mathrm{kg.m^{-1}.s^{-1}}$ of ACN + MEA, + MMEA and + MEEA systems for different molar ratios at different temperatures.

x_2	η	$\Delta\eta$	*H*	$\Delta\eta$	η	$\Delta\eta$	η	$\Delta\eta$	η	$\Delta\eta$
	303.15		**308.15**		**313.15**		**318.15**		**323.15**	
ACN + MEA										
0.0000	0.3324	0.0000	0.3185	0.0000	0.3077	0.0000	0.2932	0.0000	0.2822	0.0000
0.0576	0.4563	0.0420	0.4183	0.0252	0.4046	0.0284	0.4031	0.0475	0.3785	0.0391
0.0877	0.3655	-0.0994	0.3569	-0.0819	0.3432	-0.0747	0.3296	-0.0637	0.3175	-0.0563
0.1465	0.3561	-0.2261	0.3652	-0.1789	0.3397	-0.1732	0.3074	-0.1713	0.3014	-0.1499
0.1959	0.5062	-0.1970	0.4954	-0.1563	0.4499	-0.1595	0.4023	-0.1625	0.3850	-0.1437
0.2492	0.8148	-0.0475	0.7532	-0.0386	0.6768	-0.0572	0.6085	-0.0667	0.5649	-0.0623
0.3005	1.2425	0.1932	1.1084	0.1533	0.9934	0.1156	0.8971	0.0955	0.8165	0.0772
0.3509	1.7764	0.5041	1.5518	0.4036	1.3906	0.3440	1.2560	0.3072	1.1295	0.2606
0.3999	2.3945	0.8598	2.0661	0.6926	1.8511	0.6095	1.6668	0.5489	1.4879	0.4711
0.4516	3.1438	1.2735	2.6905	1.0314	2.4082	0.9212	2.1561	0.8270	1.9144	0.7144
0.4990	3.9119	1.6698	3.3307	1.3578	2.9754	1.2210	2.6462	1.0886	2.3409	0.9441
0.5504	4.8266	2.0973	4.0917	1.7112	3.6427	1.5437	3.2130	1.3631	2.8326	1.1855
0.5998	5.7813	2.4843	4.8827	2.0311	4.3264	1.8327	3.7834	1.6009	3.3247	1.3951
0.6490	6.8023	2.8225	5.7227	2.3094	5.0395	2.0788	4.3678	1.7946	3.8249	1.5657
0.6990	7.9092	3.0905	6.6242	2.5267	5.7875	2.2627	4.9697	1.9277	4.3345	1.6826
0.7498	9.1042	3.2519	7.5840	2.6505	6.5615	2.3533	5.5807	1.9751	4.8438	1.7229
0.8008	10.3751	3.2622	8.5864	2.6421	7.3416	2.3140	6.1850	1.9082	5.3365	1.6614
0.8501	11.6725	3.0833	9.5874	2.4696	8.0881	2.1170	6.7522	1.7082	5.7855	1.4814
0.8999	13.0542	2.6625	10.6257	2.0871	8.8237	1.7196	7.3004	1.3417	6.2023	1.1532
0.9499	14.5165	1.9344	11.6909	1.4405	9.5320	1.0743	7.8182	0.7741	6.5737	0.6471
1.0000	15.2400	0.0000	12.3100	0.0000	10.0730	0.0000	8.3300	0.0000	6.9590	0.0000
ACN + MMEA										
0.000	0.332	0.000	0.319	0.000	0.308	0.000	0.293	0.000	0.282	0.000
0.049	0.383	-0.008	0.366	-0.006	0.355	-0.002	0.345	0.008	0.331	0.009
0.098	0.461	0.001	0.434	0.001	0.413	0.000	0.395	0.007	0.376	0.007
0.150	0.551	0.006	0.513	0.004	0.479	-0.002	0.448	-0.002	0.423	-0.002
0.199	0.640	0.001	0.595	0.002	0.550	-0.006	0.504	-0.013	0.473	-0.012
0.247	0.746	-0.004	0.693	0.003	0.636	-0.006	0.578	-0.016	0.539	-0.014

0.296	0.893	0.011	0.826	0.021	0.756	0.012	0.684	0.000	0.634	0.001
0.350	1.128	0.076	1.034	0.082	0.941	0.069	0.849	0.053	0.780	0.048
0.400	1.455	0.213	1.314	0.200	1.187	0.174	1.067	0.148	0.970	0.131
0.449	1.900	0.440	1.690	0.391	1.509	0.336	1.349	0.292	1.213	0.253
0.500	2.519	0.792	2.203	0.679	1.942	0.577	1.723	0.500	1.531	0.428
0.550	3.277	1.245	2.825	1.046	2.459	0.878	2.161	0.753	1.901	0.640
0.599	4.201	1.807	3.576	1.498	3.075	1.241	2.677	1.054	2.332	0.887
0.650	5.279	2.450	4.444	2.009	3.780	1.648	3.259	1.384	2.814	1.156
0.700	6.440	3.104	5.374	2.526	4.527	2.052	3.868	1.705	3.316	1.415
0.750	7.612	3.682	6.307	2.979	5.272	2.402	4.468	1.975	3.807	1.631
0.800	8.712	4.079	7.175	3.284	5.959	2.628	5.017	2.142	4.253	1.759
0.850	9.595	4.128	7.864	3.311	6.502	2.634	5.446	2.128	4.599	1.740
0.900	10.080	3.635	8.230	2.905	6.789	2.299	5.670	1.843	4.777	1.500
0.944	10.020	2.582	8.157	2.056	6.730	1.620	5.623	1.290	4.736	1.047
1.000	8.960	0.000	7.281	0.000	6.047	0.000	5.091	0.000	4.303	0.000
ACN + MEEA										
0.0000	0.3324	0.0000	0.3185	0.0000	0.3077	0.0000	0.2932	0.0000	0.2822	0.0000
0.0499	0.4280	0.0344	0.3815	0.0076	0.3517	-0.0067	0.3233	-0.0160	0.3010	-0.0233
0.1000	0.5141	0.0476	0.4616	0.0223	0.4220	0.0044	0.3873	-0.0055	0.3581	-0.0149
0.1500	0.6117	0.0591	0.5633	0.0474	0.5159	0.0293	0.4769	0.0223	0.4424	0.0136
0.1997	0.7361	0.0822	0.6896	0.0843	0.6314	0.0651	0.5861	0.0605	0.5453	0.0528
0.2498	0.8996	0.1247	0.8448	0.1337	0.7697	0.1097	0.7131	0.1045	0.6628	0.0964
0.2998	1.1080	0.1901	1.0290	0.1939	0.9299	0.1610	0.8555	0.1512	0.7911	0.1400
0.3501	1.3660	0.2775	1.2450	0.2633	1.1140	0.2174	1.0150	0.1991	0.9302	0.1810
0.3997	1.6700	0.3823	1.4900	0.3386	1.3210	0.2777	1.1890	0.2458	1.0780	0.2177
0.4495	2.0220	0.4976	1.7650	0.4136	1.5530	0.3382	1.3840	0.2930	1.2380	0.2495
0.4986	2.4150	0.6147	2.0680	0.4855	1.8100	0.3987	1.5980	0.3386	1.4110	0.2774
0.5500	2.8720	0.7293	2.4200	0.5531	2.1100	0.4587	1.8480	0.3844	1.6110	0.3027
0.6001	3.3620	0.8229	2.7980	0.6048	2.4360	0.5116	2.1210	0.4266	1.8280	0.3236
0.6463	3.8540	0.8846	3.1810	0.6366	2.7680	0.5519	2.4010	0.4616	2.0510	0.3397
0.7000	4.4760	0.9141	3.6720	0.6480	3.1950	0.5839	2.7620	0.4929	2.3410	0.3532

0.7494	5.1060	0.8951	4.1750	0.6305	3.6280	0.5915	3.1290	0.5074	2.6380	0.3566
0.7995	5.8130	0.8230	4.7430	0.5789	4.1090	0.5703	3.5350	0.4999	2.9700	0.3465
0.8475	6.5740	0.7028	5.3570	0.4980	4.6150	0.5175	3.9560	0.4637	3.3190	0.3197
0.8957	7.4420	0.5292	6.0540	0.3805	5.1660	0.4184	4.4060	0.3853	3.6960	0.2652
0.9500	8.5860	0.2769	6.9590	0.2033	5.8450	0.2408	4.9420	0.2297	4.1500	0.1583
1.0000	9.8430	0.0000	7.9340	0.0000	6.5290	0.0000	5.4540	0.0000	4.5890	0.0000

Table 4: Free energy, $\Delta G^{\ddagger}$ / kJ.mol^{-1} and excess free energy, $\Delta G^{\ddagger E}$ / kJ.mol^{-1} of activation for ACN + MEA, + MMEA and + MEEA systems for different molar ratios at different temperatures.

x_2	$\Delta G^{\ddagger}$	$\Delta G^{\ddagger E}$	$\Delta G^{\ddagger}$	$\Delta G^{\ddagger E}$	$\Delta G^{\ddagger}$	$\Delta G^{\ddagger E}$	$\Delta G^{\ddagger}$	$\Delta G^{\ddagger E}$	$\Delta G^{\ddagger}$	$\Delta G^{\ddagger E}$
	303.15		**308.15**		**313.15**		**318.15**		**323.15**	
					ACN + MEA					
0.000	9.561	0.000	9.628	0.000	9.694	0.000	9.761	0.000	9.828	0.000
0.058	10.332	0.198	10.411	0.225	10.489	0.252	10.568	0.278	10.646	0.305
0.088	9.850	-0.583	9.934	-0.543	10.018	-0.503	10.102	-0.463	10.186	-0.424
0.147	9.861	-1.157	9.906	-1.141	9.950	-1.125	9.995	-1.109	10.040	-1.093
0.196	10.718	-0.792	10.708	-0.818	10.699	-0.843	10.690	-0.868	10.680	-0.893
0.249	11.866	-0.174	11.824	-0.219	11.781	-0.263	11.738	-0.308	11.695	-0.353
0.301	12.894	0.344	12.839	0.300	12.784	0.256	12.729	0.213	12.674	0.169
0.351	13.775	0.723	13.716	0.688	13.657	0.653	13.597	0.619	13.538	0.584
0.400	14.519	0.979	14.458	0.955	14.397	0.932	14.336	0.908	14.275	0.885
0.452	15.206	1.151	15.143	1.139	15.080	1.127	15.017	1.115	14.954	1.103
0.499	15.765	1.240	15.699	1.237	15.634	1.234	15.568	1.231	15.502	1.228
0.550	16.313	1.275	16.242	1.281	16.171	1.286	16.100	1.292	16.028	1.297
0.600	16.792	1.263	16.714	1.274	16.636	1.286	16.558	1.297	16.480	1.309
0.649	17.231	1.213	17.144	1.228	17.057	1.243	16.970	1.258	16.883	1.274
0.699	17.647	1.131	17.548	1.147	17.449	1.164	17.350	1.180	17.251	1.197

0.750	18.041	1.020	17.927	1.035	17.814	1.050	17.700	1.064	17.587	1.079
0.801	18.411	0.883	18.280	0.893	18.149	0.904	18.017	0.914	17.886	0.925
0.850	18.747	0.728	18.596	0.731	18.444	0.734	18.292	0.737	18.141	0.740
0.900	19.065	0.551	18.890	0.543	18.714	0.534	18.538	0.526	18.362	0.518
0.950	19.362	0.350	19.158	0.327	18.954	0.303	18.750	0.280	18.546	0.257
1.000	19.511	0.000	19.317	0.000	19.123	0.000	18.930	0.000	18.736	0.000
ACN + MMEA										
0.000	9.561	0.000	9.628	0.000	9.694	0.000	9.761	0.000	9.828	0.000
0.049	9.957	-0.061	10.047	-0.027	10.136	0.007	10.226	0.042	10.316	0.076
0.098	10.473	-0.004	10.530	0.010	10.587	0.023	10.645	0.037	10.702	0.050
0.150	10.979	0.021	11.000	0.010	11.020	-0.001	11.041	-0.012	11.061	-0.023
0.199	11.416	0.004	11.415	-0.017	11.414	-0.038	11.413	-0.059	11.412	-0.081
0.247	11.854	-0.007	11.843	-0.026	11.833	-0.046	11.822	-0.066	11.811	-0.085
0.296	12.358	0.036	12.343	0.024	12.328	0.012	12.313	-0.001	12.298	-0.013
0.350	12.995	0.176	12.974	0.170	12.953	0.164	12.932	0.158	12.911	0.152
0.400	13.679	0.391	13.646	0.384	13.613	0.378	13.579	0.372	13.546	0.366
0.449	14.394	0.648	14.344	0.637	14.294	0.625	14.244	0.614	14.194	0.602
0.500	15.149	0.927	15.079	0.908	15.009	0.888	14.939	0.869	14.869	0.849
0.550	15.857	1.176	15.767	1.148	15.677	1.121	15.588	1.093	15.498	1.065
0.599	16.531	1.386	16.422	1.351	16.313	1.316	16.204	1.281	16.096	1.246
0.650	17.156	1.540	17.030	1.499	16.904	1.459	16.777	1.418	16.651	1.377
0.700	17.708	1.625	17.567	1.581	17.426	1.537	17.284	1.493	17.143	1.450
0.750	18.181	1.635	18.027	1.590	17.874	1.546	17.720	1.501	17.566	1.457
0.800	18.574	1.562	18.410	1.519	18.247	1.476	18.083	1.433	17.919	1.390
0.850	18.873	1.393	18.701	1.354	18.530	1.315	18.358	1.276	18.186	1.237
0.900	19.054	1.109	18.878	1.077	18.702	1.045	18.526	1.013	18.349	0.981
0.944	19.090	0.739	18.913	0.717	18.737	0.695	18.560	0.672	18.383	0.650
1.000	18.877	0.000	18.709	0.000	18.542	0.000	18.374	0.000	18.206	0.000

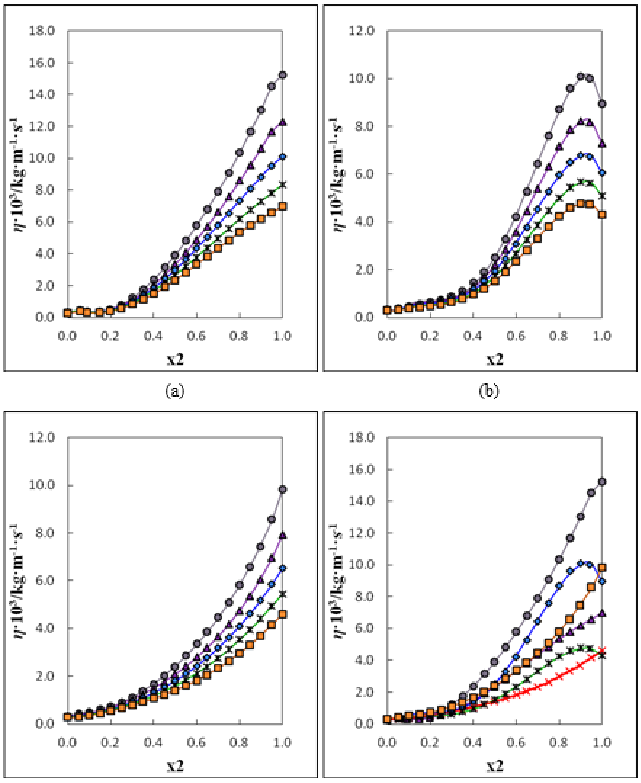
					ACN + MEEA					
0.000	9.561	0.000	9.628	0.000	9.694	0.000	9.761	0.000	9.828	0.000
0.050	10.240	0.177	10.193	0.076	10.146	-0.026	10.100	-0.127	10.053	-0.229
0.100	10.793	0.227	10.747	0.138	10.701	0.050	10.655	-0.039	10.609	-0.128
0.150	11.333	0.264	11.318	0.218	11.302	0.173	11.287	0.127	11.272	0.081
0.200	11.896	0.327	11.904	0.317	11.911	0.306	11.919	0.295	11.926	0.284
0.250	12.491	0.419	12.503	0.424	12.515	0.430	12.527	0.436	12.539	0.442
0.300	13.097	0.522	13.098	0.529	13.098	0.535	13.099	0.541	13.099	0.548
0.350	13.702	0.621	13.681	0.619	13.661	0.616	13.640	0.613	13.619	0.611
0.400	14.283	0.704	14.237	0.688	14.191	0.672	14.145	0.656	14.099	0.640
0.450	14.839	0.759	14.769	0.731	14.698	0.703	14.628	0.674	14.558	0.646
0.499	15.360	0.786	15.268	0.749	15.177	0.712	15.086	0.674	14.995	0.637
0.550	15.873	0.783	15.765	0.741	15.657	0.700	15.549	0.658	15.441	0.616
0.600	16.345	0.751	16.225	0.710	16.106	0.669	15.987	0.629	15.867	0.588
0.646	16.757	0.699	16.631	0.663	16.506	0.627	16.381	0.591	16.255	0.556
0.700	17.212	0.614	17.084	0.589	16.956	0.563	16.827	0.537	16.699	0.512
0.749	17.615	0.520	17.486	0.506	17.356	0.491	17.227	0.476	17.097	0.461
0.800	18.013	0.414	17.882	0.411	17.752	0.407	17.621	0.403	17.491	0.400
0.848	18.390	0.309	18.256	0.314	18.123	0.319	17.990	0.324	17.856	0.329
0.896	18.768	0.203	18.628	0.213	18.488	0.223	18.349	0.233	18.209	0.244
0.950	19.202	0.091	19.048	0.100	18.894	0.109	18.740	0.118	18.586	0.128
1.000	19.614	0.000	19.439	0.000	19.263	0.000	19.088	0.000	18.913	0.000

Table 5: Coefficients, a_i, of Equation 1, expressing viscosities, η, free energies, $\Delta G^{\ddagger}$ and standard deviation, σ, (Eqn. 5) of ACN + MEA, + MMEA and + MEEA systems for different molar ratios at different temperatures.

System	Property	**T (K)**	a_0	a_1	a_2	a_3	a_4	σ
ACN + MEA	$\eta.10^4$ (kg m^{-1}s^{-1})	303.15	0.8077	-8.2322	38.2826	-22.5375	7.7414	4.17E-5
		308.15	0.6674	-5.8806	27.6451	-11.0418	1.3867	1.75E-5
		313.15	0.6407	-5.4882	24.5431	-7.2159	-2.2798	2.67E-5
		318.15	0.6719	-6.2051	27.5541	-15.0915	1.3672	1.93E-5
		323.15	0.6029	-5.1792	22.8934	-10.7547	-0.6737	1.71E-5
	$\Delta G^{\ddagger}$	303.15	10.4039	-13.4186	111.3908	-162.8560	74.8970	0.2279
		308.15	10.5724	-14.8026	114.3943	-165.5960	75.6073	0.2203

	(kJ mol^{-1})	313.15	10.7408	-16.1868	117.3985	-168.3370	76.3184	0.2129
		318.15	10.9091	-17.5694	120.3965	-171.0690	77.0247	0.2057
		303.15	11.0775	-18.9522	123.3941	-173.7990	77.7303	0.1987
ACN + MMEA	$\eta.10^4$ (kg.m^{-1}.s^{-1})	303.15	-0.3216	15.2224	-80.4657	170.2566	-94.9685	0.0967
		308.15	-0.1897	11.9828	-62.6973	134.4402	-75.6635	0.0754
		313.15	-0.0623	9.0493	-47.3504	104.2349	-59.3933	0.0550
		318.15	0.0411	6.7156	-35.6943	81.6276	-47.3055	0.0374
		323.15	0.0927	5.3057	-28.0202	65.4961	-38.3506	0.0281
	$\Delta G^{\ddagger}$ (kJ mol^{-1})	303.15	9.7015	6.5661	7.4635	9.0951	-14.0582	0.0635
		308.15	9.8353	5.4789	10.5936	4.3567	-11.6421	0.0587
		313.15	9.9690	4.3912	13.7264	-0.3858	-9.2242	0.0541
		318.15	10.1027	3.3045	16.8549	-5.1229	-6.8084	0.0499
		323.15	10.2365	2.2165	19.9886	-9.8667	-4.3897	0.0459
ACN + MEEA	$\eta.10^4$ (kg.m^{-1}.s^{-1})	303.15	0.4873	-1.1970	13.5459	-10.3941	7.2301	0.0241
		308.15	0.3766	-0.1212	9.7304	-8.6069	6.4851	0.0093
		313.15	0.2956	0.8826	3.9607	0.0616	1.3321	0.0014
		318.15	0.2413	1.3560	1.4834	2.6078	-0.1874	0.0073
		323.15	0.2244	1.1868	2.3378	-0.6687	1.5625	0.0084
	$\Delta G^{\ddagger}$ (kJ mol^{-1})	303.15	9.7999	8.3791	15.5954	-26.2099	12.0864	0.0100
		308.15	9.6671	10.0063	9.5604	-18.7137	8.9634	0.0070
		313.15	9.5343	11.6350	3.5190	-11.2076	5.8353	0.0137
		318.15	9.4013	13.2653	-2.5285	-3.6923	2.7025	0.0229
		323.15	9.2686	14.8919	-8.5622	3.8033	-0.4208	0.0324

Correlating the concentration dependence of η with the polynomial Equation 1, relevant coefficients and standard deviations as obtained by Eqn. 5 are shown in Table 5.



(a) (b)

(c) (d)

Figure 1: Viscosities, η of (a) ACN + MEA, (b) ACN + MMEA, (c) ACN + MEEA systems against mole fraction, x_2 at 303.15 K (●), 308.15 K(▲), 313.15 K(◆), 318.15 K (⁎) and 323.15 K(■) and (d) comparative curves of ACN + MEA(●), + MMEA(◆) and + MEEA(■) at 303.15 K and curves of ACN + MEA (▲), + MMEA (⁎) and + MEEA(×) at 323.15 K for different molar ratios. Solid lines represent polynomial fitting values.

The values of η have been plotted in Figure 1(a-c). From Figure 1(a), it can be observed that with the addition of MEA to ACN, the initial rise of η up to $x_2 = 0.25$ was apparently very poor and the effect of temperature on η also seemed to be small. On further addition of MEA, η rose sharply, and with the rising of concentration of MEA, temperature effect increased. On the other hand, Figure 1(b) shows that η for the mixtures of ACN+MMEA ran almost linearly up to about $x_2 = 0.3$, and likewise, the effect of temperature also appeared to be insignificant in this region. But beyond that, η increased in a forking manner up to $x_2 = 0.85$ and afterwards a well-defined maximum was formed nearly at $x_2 = 0.9$. Then, again η decreased to reach its value. Thus, at all concentrations where, $x_2 > 0.8$, isotherms of η showed significant variations for this particular system. As Figure 1(c) shows, the addition of MEEA to ACN η initially went close up to $x_2 = 0.25$ as in ACN + MEA. Above this concentration, η rose again rather sharply but this time forming concave curves with respect to the composition axis. With ACN+MMEA, the effect of temperature on η was also quite large in the solute-rich region. Figure 1(d) is plotted to show the comparative curves of η *vs.* x_2 at 303.15 K and 323.15 K. For the present systems, the following characteristics were observed: (a) Up to $x_2 = 0.25$, viscosities apparently were very close to each other with more or less linear fashion for all the systems. But, beyond this composition η curves were well separated from each other. (b) For the mixtures of ACN+MMEA, the formation of a maximum was distinct at $x_2 = 0.9$, but there was no maximum for

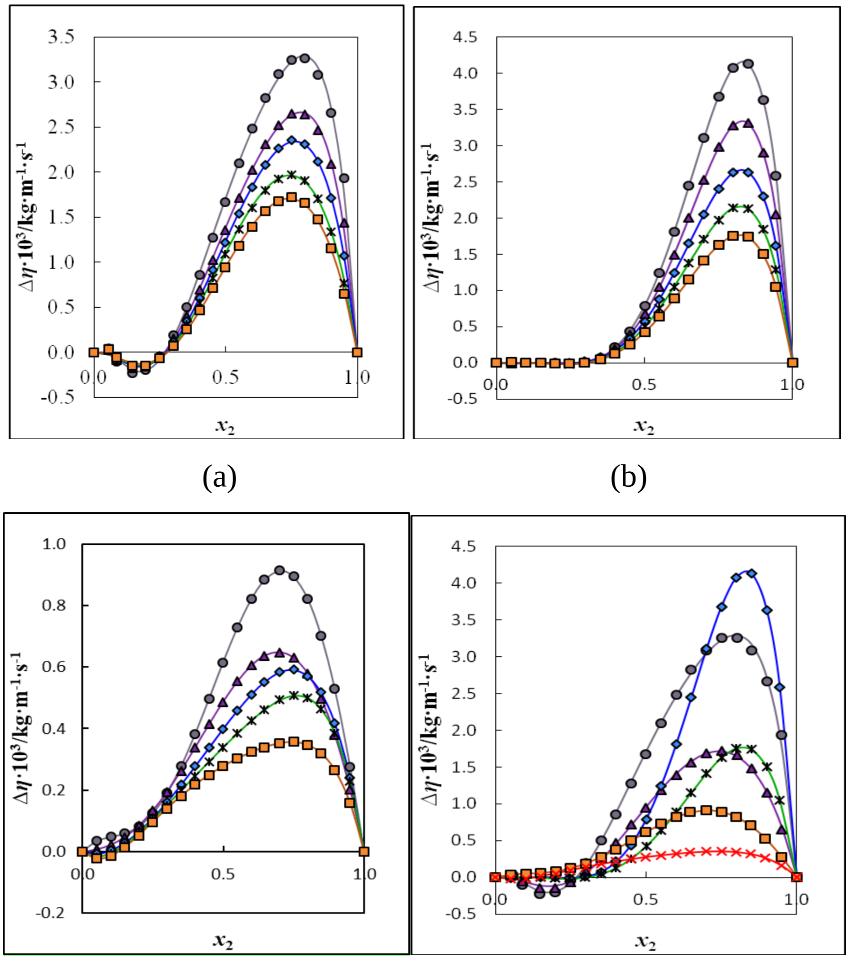
ACN+MEEA. (c) The increasing order of η was as follows: ACN +MEA > ACN+MMEA > ACN+MEEA. (d) $\frac{d\eta}{dT}$ values were negative for all the systems and large in magnitude, especially above $x_2 \approx 0.6$.

As alkanolamines were generally associated, viscosities of the pure liquids under the present investigation were thought to be influenced mainly by the following factors: strength of self-association, molar mass, size and shape of the molecules/flowing species as well as their steric hindrance. While the first four factors were said to enhance the viscosity of these aminoethanols, the last one was usually reduced η by decreasing the capacity of self-association. It is well known that the steric hindrance due to alkyl groups in the alkanolamines follows the order: H < $-CH_3$ < $-C_2H_5$. Considering structural features for MEA, MMEA and MEEA, their self-association though thought to be comparable, steric hindrance affected the respective η values significantly. Eventually, the order of variation η has to follow: ACN + MEA > ACN+MMEA > ACN+MEEA.

3.2. Deviations in viscosity($\Delta\eta$)

Deviations in viscosity ($\Delta\eta$) for the systems of ACN + MEA, + MMEA and + MEEA were calculated according to Eqn. 3 at different temperatures between 303.15 K to 323.15 K as presented in Table 3. All the $\Delta\eta$ values were fitted well to the Redlich-Kister equation (Eqn. 4). The coefficients along with the standard deviations (Eqn. 5) are as listed in Table 6. Figure 2(a-c) represents the plots of $\Delta\eta$ of ACN + MEA, + MMEA and + MEEA, respectively at different temperatures as a function of mole fraction of alkanolamines.

In the highly ACN-rich region [Figure 2(a)], the magnitudes of $\Delta\eta$ were small negative with a shallow minimum nearly at $x_2 = 0.1$. Then, $\Delta\eta$ rose sharply and showed well defined maximum at ~ $x_2 = 0.75$. The variation patterns of $\Delta\eta$ for ACN + MMEA and ACN + MEEA [Figure 2(b-c)] were somehow more or less similar in nature. In both cases, changes in $\Delta\eta$ with solute concentration were found apparently negligible, particularly at lower mole fractions of solutes. The (+)ve $\Delta\eta$ rose sharply after $x_2 = 0.4$ and $x_2 = 0.2$ exhibiting maxima at ~ $x_2 = 0.85$ and 0.7 for ACN+MMEA and ACN+MEEA, respectively. The effect of temperature was noticeable at or around the maximum. Figure 2(d) shows the plots of deviations in viscosity at 303.15 K against the mole fraction of alkanolamines for comparison. The order of increasing $\Delta\eta$ at least at the composition of maximum was: ACN+MMEA > ACN+MEA > ACN+MEEA. It was thought that in the solute-rich region alkanolamines were associated through H-bonding *via* OH⋯O or OH⋯N, favourably at low temperatures. But, at higher temperatures, these associated structures became mostly segregated or broken down into smaller species, so that all the η values were lowered down. Previously, Kipkemboi and Easteal [47] have found that the addition of BuOH or *tert*-butylamine to H_2O made viscosities to rise sharply to form large maxima, but the maxima were at compositions, which were usually in the highly water-rich regions. They have explained this by the formation of the so-called ‘associated complexes’ *via* H-bonding of solutes with water. Earlier [48,49] the concept of ‘associated complex’ formation was also used to describe the viscosity maxima observed for aqueous mixtures of different organic solutes. However, for the present systems, all the $\Delta\eta$ *vs.* x_2 curves were showing their asymmetric sharp maxima in the solute-rich regions. Obviously, some factors other than cross H-bonding between acetonitrile and alkanolamines might have to reinforce them. In this regard, any factor that favoured the formation of bulkier species in the solute-rich region should be considered important. At this stage, due to the interstitial accommodation effect, there was a high possibility of the formation of bulkier species, whereby the smaller ACN molecules were to remain trapped inside the network structures of alkanolamines so that, all the flowing species were not only becoming bulkier but were also showing the tendency to flow as a whole. Therefore, $\Delta\eta$ *vs.* x_2 curves were characterized by sharp maxima and they were all in the solute-rich regions of the respective alkanolamines as found experimentally. Again, though MEA was the most associated solute followed by MMEA and MEEA, the flowing species formed with MMEA (due to interstitial accommodation effect) seemed to be the largest as well as the most bulky. That is why high maxima followed this order: ACN + MMEA > ACN + MEA. On the other hand, due to greater steric hindrance by the –CH_2-CH_3 group of MEEA all the binary flowing species of the system of ACN + MEEA seemed to be least structured. Therefore, for this system the height of maxima of $\Delta\eta$ *vs.* x_2 curves decreased drastically compared to those of ACN + MEA and ACN + MMEA.



(a) (b)

(c) (d)

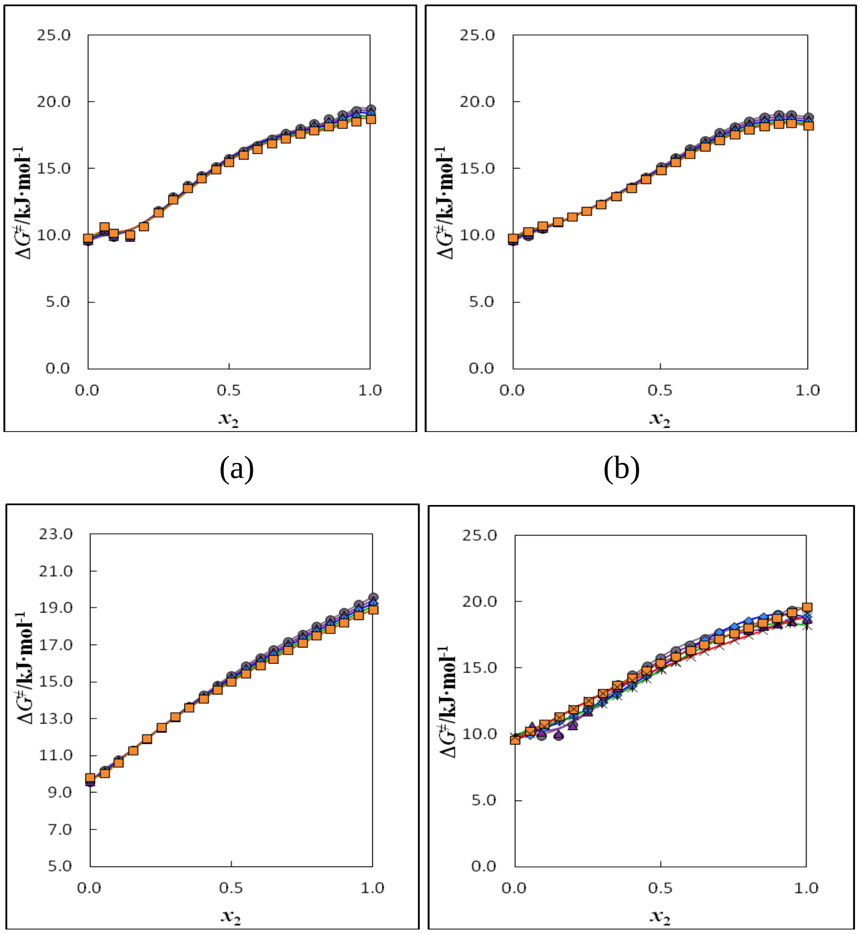
Figure 2: Deviation in viscosities, $\Delta\eta$ of (a) ACN + MEA, (b) ACN + MMEA, (c) ACN + MEEA systems against mole fraction, x_2 at 303.15 K (●), 308.15 K (▲), 313.15 K (◆), 318.15 K (×) and 323.15 K (■) and (d) comparative curves of ACN + MEA (◆), + MMEA (●) and + MEEA (■) at 303.15 K and curves of ACN + MEA (✳), + MMEA (▲) and + MEEA (×) at 323.15 K for different molar ratios. Solid lines represent polynomial fitting values.

3.3. Free energy of activation for viscous flow, $\Delta G^{\ddagger}$ and their excess values, $\Delta G^{\ddagger E}$

Free energies ($\Delta G^{\ddagger}$) and excess free energies ($\Delta G^{\ddagger E}$) of activation for viscous flow for the systems, ACN + MEA, + MMEA and + MEEA, for different molar ratios at different temperatures, are as listed in Table 4. All the $\Delta G^{\ddagger}$ *vs.* x_2 isothermal were fitted to approximate polynomial equations (like Eqn.1 where η is replaced by $G^{\ddagger}$), whereas $\Delta G^{\ddagger E}$ have been fitted to the Redlich-Kister equation (as like Eqn.4 where $\Delta\eta$ is replaced by $\Delta G^{\ddagger E}$). The relevant coefficients along with the standard deviations of $\Delta G^{\ddagger}$ and $\Delta G^{\ddagger E}$ are listed in Tables 5 and 6, respectively.

Table 6: Coefficients, A_i, of Equation 4, expressing deviation in viscosities, ($\Delta\eta$), excess free energies, ($\Delta G^{\ddagger E}$) and standard deviation, (σ), of Eqn. 5 of ACN + MEA, + MMEA and + MEEA systems for different molar ratios at different temperatures.

System	**Property**	**T(K)**	**A_0**	**A_1**	**A_2**	**A_3**	**A_5**	**σ**
ACN + MEA	$\Delta\eta.10^4$ (kg.m^{-1}.s^{-1})	303.15	6.8537	-16.3982	2.4248	-4.9654	15.0868	0.0586
		308.15	5.5469	-13.7228	2.9539	-2.5044	9.4887	0.0340
		313.15	4.9571	-12.9202	3.1560	0.4441	5.3375	0.0194
		318.15	4.4104	-11.3870	1.6173	2.3187	3.9379	0.0254
		323.15	3.8194	-10.0413	1.6538	2.3864	2.8282	0.0234
	$\Delta G^{\ddagger E}$ (kJ.mol^{-1})	303.15	5.4038	-4.5904	-18.5539	-6.4221	16.0168	0.2317
		308.15	5.3892	-5.1536	-18.9482	-5.1585	16.9098	0.2314
		313.15	5.3745	-5.7169	-19.3426	-3.8946	17.8030	0.2314
		318.15	5.3599	-6.2801	-19.7368	-2.6308	18.6958	0.2316
		323.15	5.3453	-6.8432	-20.1309	-1.3672	19.5886	0.2321
ACN + MMEA	$\Delta\eta.10^4$ (kg.m^{-1}.s^{-1})	303.15	3.1564	-16.1036	26.6242	-14.2787	0.0470	0.0009
		308.15	2.7077	-13.1277	20.9981	-11.0126	0.0073	0.0004
		313.15	2.3014	-10.8415	16.3633	-8.0051	0.0071	0.0002
		318.15	1.9944	-9.2573	12.9440	-5.4629	0.0001	0.0002
		323.15	1.7088	-7.7482	10.4226	-4.0971	-0.0080	0.0002
	$\Delta G^{\ddagger E}$ (kJ.mol^{-1})	303.15	3.6121	-9.8565	2.5528	3.6185	2.0904	0.0420
		308.15	3.5505	-9.7227	1.8340	3.8253	3.1247	0.0334
		313.15	3.4889	-9.5890	1.1150	4.0322	4.1591	0.0248
		318.15	3.4274	-9.4553	0.3962	4.2391	5.1934	0.0163
		323.15	3.3658	-9.3216	-0.3227	4.4460	6.2278	0.0081
ACN + MEEA	$\Delta\eta.10^4$ (kg.m^{-1}.s^{-1})	303.15	2.4721	-4.6729	0.9834	2.2705	0.0111	0.0003
		308.15	1.9510	-2.8015	0.3424	0.6280	-0.0064	0.0004
		313.15	1.6010	-2.4179	1.0777	-0.5941	-0.0105	0.0004
		318.15	1.3586	-1.8262	1.0918	-1.2855	0.0042	0.0002
		323.15	1.1126	-1.0537	0.3826	-1.3230	-0.0060	0.0002
	$\Delta G^{\ddagger E}$ (kJ.mol^{-1})	303.15	3.1680	-0.8279	-3.6335	1.5249	3.6937	0.0149
		308.15	3.0061	-0.3308	-2.4021	-0.2418	1.0797	0.0060
		313.15	2.8443	0.1662	-1.1708	-2.0086	-1.5341	0.0030
		318.15	2.6825	0.6632	0.0606	-3.7755	-4.1478	0.0118
		323.15	2.5207	1.1602	1.2918	-5.5422	-6.7614	0.0207



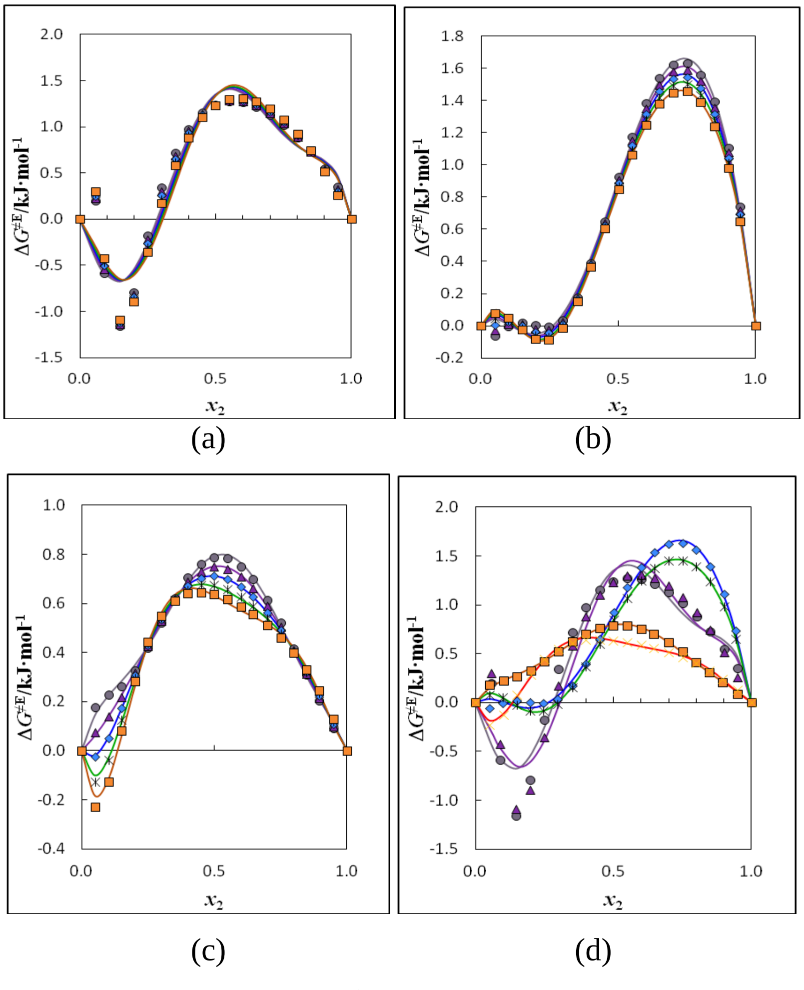
(a) (b)

(c) (d)

Figure 3: Free energy of activation, $\Delta G^{\ddagger}$ of (a) ACN + MEA, (b) ACN + MMEA, (c) ACN + MEEA systems against mole fraction, x_2 at 303.15 K (●), 308.15 K(▲), 313.15 K(♦), 318.15 K(×) and 323.15 K(■) and (d) comparative curves of ACN + MEA (◆), + MMEA (●) and + MEEA (■) at 303.15 K and curves of ACN + MEA (✳), + MMEA (▲) and + MEEA (×) at 323.15 K for different molar ratios. Solid lines represent polynomial fitting values.

Figs. 3(a-c) and 4(a-c) represent the variations of $\Delta G^{\ddagger}$ and $\Delta G^{\ddagger E}$ at different temperatures against mole fractions, x_2 for ACN + MEA, ACN + MMEA and ACN + MEEA, respectively. Fig. 3(d) and 4(d) show the comparisons of $\Delta G^{\ddagger}$ and $\Delta G^{\ddagger E}$ at 303.15 K. for these systems, respectively. From Figs. 3(a-d) and 4(a-d), the following characteristics are observed. All the variational patterns of $\Delta G^{\ddagger}$ for the systems were quite similar except for ACN + MMEA, where an ill-defined maximum was observed at the extremely solute-rich region as in Fig. 3(a-c). In all cases, $\Delta G^{\ddagger}$ rose gradually and the temperature effect was significant in the extremely solute-rich region. Figure 3(d) shows all the lines gradually rising in a similar fashion with some exceptions. For ACN + MEA, with the addition of MEA into ACN, the $\Delta G^{\ddagger E}$ value decreased forming a negative lobe with its minimum at $x_2 \sim 0.1$. Afterwards, it rose and formed a positive lobe with a maximum at $x_2 \sim 0.65$. Also, it formed three temperature invariant points at $x_2 = 0.25$, 0.6 and 0.8; otherwise, the effect of temperature was only prominent at the maximum and minimum compositions. For ACN + MMEA system, initially $\Delta G^{\ddagger E}$ ran almost linearly up to $x_2 = 0.25$; beyond this concentration, it rose to give a sharp maximum at $x_2 = 0.8$ and then fell. The temperature effect was more or less significant at or around the maximum. In the case of ACN + MEEA, a single positive lobe with a maximum at $x_2 = 0.55$ was formed with two temperature invariant points at $x_2 \sim 0.35$ and 0.85. With the temperature rise the values of $\Delta G^{\ddagger E}$ decreased, *i.e.*, $\delta\Delta G^{\ddagger E}/\delta T$ was negative. Also, at their maxima the values of $\Delta G^{\ddagger E}$ followed: ACN + MMEA > ACN + MEA > ACN + MEEA.

The positive $\Delta G^{\ddagger}$ as well as $\Delta G^{\ddagger E}$ could be regarded as an additional energy barrier, which the molecules must have to surmount to set them in the flow process. For all the above systems, the larger positive $\Delta G^{\ddagger E}$ thus led to suggest that for each of the systems, the additional energy barriers were reasonably higher, especially in its alkanolamine-rich regions. Here, due to the interstitial incorporation of smaller ACN into the associated structures of alkanolamines, the flowing species formed were quite bulkier. As a result, they had to encounter larger resistance to flow which was always greater than what was ideally expected.



(a) (b)

(c) (d)

Figure 4: Excess free energy of activation, $\Delta G^{\ddagger E}$ of (a) ACN + MEA, (b) ACN + MMEA, (c) ACN + MEEA systems against mole fraction, x_2 at 303.15 K (●), 308.15 K(▲), 313.15 K(♦), 318.15 K(×) and 323.15 K(■) and (d) comparative curves of ACN + MEA(▲), + MMEA(♦) and + MEEA(■) at 303.15 K and curves of CN + MEA (●), + MMEA (×) and + MEEA (×) at 323.15 K for different molar ratios. Solid lines represent Redlich-Kister polynomial fitting values.

4. Correlative models

Based upon the linear function of composition (expressed as - volume fraction, mole fraction or mass fraction) ideal mixing relations of the liquid mixture viscosity with zero parameters are given. Models of these kinds found in the literature are Bingham, Kendall- Munroe, Gambill, and Eyring relations. The proposed relations are represented as follows.

Bingham relation (BH):

$$y = x_1 y_1 + x_2 y_2 \qquad (10)$$

For mixture viscosity, *Kendall-Munroe (KM)* proposed the following relation:

$$ln\, y = x_1\, ln\, y_1 + x_2\, ln\, y_2 \qquad (11)$$

where, x_1 and x_2 are the mole fractions of the mixture, which holds good for several cases of mixtures consisting of non-polar and non-associated liquids.

Gambill relation (GM)

$$y^{1/3} = x_1 y_1^{1/3} + x_2 y_2^{1/3} \qquad (12)$$

Eyring (ER)

$$ln\, \eta V = x_1\, ln(\eta_1 V_1) + x_2\, ln(\eta_2 V_2) \qquad (13)$$

Where. x_1 and x_2 represent the mole fractions of two components and y_1 and y_2 represent their viscosities in the pure state.

One parameter-based model is as follows:
For η, the Grunberg and Nissan (GN) model suggest [50] the following relation:

$$ln\, y = x_1\, ln\, y_1 + x_2\, ln\, y_2 + x_1 x_2 G_{12} \qquad (14)$$

Where, G_{12} is an adjustable parameter. As G_{12} is dependent on the composition of the mixture and temperature, this model is widely applicable with reasonable accuracies, except for aqueous solutions. The temperature variation of this interaction coefficient is found to be similar to that of pure liquid viscosity.

Hind, McLaughlin and Ubbelohde [51] attempted to describe the viscosities of binary liquid mixtures in terms of viscosities of pure liquid components, their mole fraction, and a single parameter attributed to the interaction between them. In literature, the proposed relation is known as Hind's equation (HND) as shown below:

$$y = {x_1}^2 y_1 + {x_2}^2 y_2 + 2 x_1 x_2 H_{12} \qquad (15)$$

Here, η_{12} represents an interaction parameter.

Frenkel (FR)

$$ln\, y = x_1^2\, ln\, y_1 + x_2^2\, ln\, y_2 + x_1 x_2 F_{12} \qquad (16)$$

Wijk (WJ)

$$log\, y = x_1^2\, log\, y_1 + x_2^2\, log\, y_2 + 2x_1x_2 \log\,(W_{12}) \tag{17}$$

Katti-Chaudhri (KC)

$$ln\, \eta V = x_1\, ln(\eta_1 V_1) + x_2\, ln(\eta_2 V_2) + x_1 x_2 K_{12} \tag{18}$$

Tamura Kurata (TK)

$$ln\, \eta V = x_1 \phi_1 \eta_1 + x_2 \phi_2 \eta_2 + 2(x_1 \phi_1 x_2 \phi_2 \eta_2)^{1/2} T_{12} \tag{19}$$

In this equation, the notation is the same as in the earlier equations. Additionally, ϕ_1 and ϕ_2 are the volume fractions of the components 1 and 2 in the mixture. The interaction coefficient T_{12} is constant at a chosen temperature.

Here, G_{12}, H_{12}, F_{12}, W_{12}, K_{12}, and K_{12} are adjustable parameters for GN, HND, FR, WJ, KC, TK models, respectively and all the symbols have their usual meaning.

Two and three parameter-based models**:** The two-parameter Heric equation (HRC) is of the following form [52]:

$$ln\, y = x_1\, ln\, y_1 + x_2\, ln\, y_2 + x_1\, ln\, M_1 + x_2\, ln\, M_2 - ln(\, x_1 M_1 + x_2 M_2) + x_1 x_2 \{H_{12} + H_{21}(x_1 - x_2)\} \tag{20}$$

where, H_{12} and H_{21} are the requisite adjustable parameters.

The McAllister's multi-body interaction model [53] based on the Eyring theory [54,55] of absolute reaction rates have been widely used to correlate η and v. The McAllister three-body model (MAC3) has been defined as:

$$\begin{aligned} ln\, y = {} & x_1^3\, ln\, y_1 + 3x_1^2 x_2\, ln\, Z_{12} + 3x_1 x_2^2\, ln\, Z_{21} + x_2^3\, ln\, y_2 - ln[x_1 + x_2(M_2/M_1)] + \\ & 3x_1^2 x_2\, ln[\,(2 + M_2/M_1)/3] + 3x_1 x_1^2\, ln[\,(1 + 2M_2/M_1)/3] + x_2^3\, ln(\, M_2/M_1) \end{aligned} \tag{21}$$

Whereas, the McAllister four-body (MAC4) model is given by,

$$\begin{aligned} ln\, y = {} & x_1^4\, ln\, y_1 + 4x_1^3 x_2\, ln\, Z_{1112} + 6x_1^2 x_2^2\, ln\, Z_{1122} + 4x_1 x_2^3\, ln\, Z_{2221} + x_2^4\, ln\, y_2 - ln[x_1 \\ & + x_2(M_2/M_1)] + 4x_1^3 x_2\, ln[\,(3 + M_2/M_1)/4] + 6x_1^2 x_2^2\, ln[\,(1 \\ & + M_2/M_1)/2] + 4x_1 x_2^3\, ln[\,(1 + 3M_2/M_1)/4] + x_2^4\, ln(\, M_2/M_1) \end{aligned} \tag{22}$$

Here, Z_{12}, Z_{21}, Z_{1112}, Z_{1122}, and Z_{2221} represent the relevant interaction parameters, and M_i is the molar mass of pure component *i*.

The Ausländer equation [56] (AUS) representing binary interaction depends on three adjustable parameters, B_{12}, B_{21}, and A_{21}, and the resulting expression follows:

$$y = \frac{x_1 y_1 (x_1 + B_{12} x_2) + x_2 y_2 A_{21} (B_{21} x_1 + x_2)}{x_1 (x_1 + B_{12} x_2) + x_2 A_{21} (B_{21} x_1 + x_2)} \tag{23}$$

The Jouyban-Acree model (JA) [57,58] is used for correlating the viscosities of liquid mixtures at various temperatures. The equation is proposed to be

$$ln\, y_{m,T} = x_1\, ln\, y_{1,T} + x_2\, ln\, y_{2,T} + x_1 x_2 \sum [j_i (x_1 - x_2)^i / T] \tag{24}$$

where, $y_{m,T}$, $y_{1,T}$, and $y_{2,T}$ are the η values at temperature T for the mixture, components 1 and components 2, respectively, and j_i is the relevant model constant.

Correlating ability of each of Eqns. 10-24 was tested by calculating the percentage of standard deviation, σ and AAD between the experimental and calculated viscosities. The percentage of standard deviation, σ and AAD were calculated for the binary systems: ACN + MEA, + MMEA and + MEEA. The relevant coefficients of Equations 10-24 were obtained by the non-linear regression analysis. Table 7 summarizes all the results obtained. The σ values for the systems are as shown in Figure 5(a-c)**.** Comparison of all these values indicated that the McAllister (4-body) and the Ausländer equations correlated the viscosities excellently. For the systems ACN+MEEA, all the six models were observed outstanding estimation of η values and for ACN+MEA system, Ausländer equation predicted η the best. The McAlliester (4-body) equation fit the best for**:** ACN + MMEA and ACN + MEEA. The McAllister (4-body) equation for correlating v was better than the results obtained from the McAllister (3-body) equation. It is also to remark that, Z_{1122} parameter in McAllister's formula represents values practically transitional to the Z_{1112} and Z_{2221} parameters except at 323.15 K for ACN+MEA system.

Table 7: Different correlative models parameter

Systems	***T* / K**	**BH**		**GM**		**KM**		**ER**	
		σ(%)	**AAD%**	**σ(%)**	**AAD%**	**σ(%)**	**AAD%**	**σ(%)**	**AAD%**
ACN + MEA	303.15	235.170	153.542	49.476	28.017	32.909	28.665	31.373	27.296
	308.15	192.975	129.278	41.172	24.604	30.110	26.307	28.394	24.859
	313.15	169.806	111.804	39.630	24.464	30.646	26.747	28.967	25.283
	318.15	153.033	98.772	39.017	23.933	31.162	27.150	29.526	25.654
	323.15	131.998	85.058	35.313	22.867	30.144	26.301	28.414	24.752
ACN + MMEA	303.15	122.503	88.935	29.206	25.399	29.202	21.750	28.663	21.287
	308.15	103.659	76.001	26.377	23.160	28.575	21.413	28.003	20.869
	313.15	90.640	66.701	24.740	21.637	27.514	20.559	26.895	20.050
	318.15	81.094	59.606	23.645	20.562	26.698	20.135	26.056	19.675
	323.15	71.060	52.581	22.160	19.294	25.821	19.514	25.136	19.017
ACN + MEEA	303.15	117.166	95.564	17.426	14.698	16.785	14.685	17.885	15.626
	308.15	99.998	83.196	14.617	12.983	15.629	13.374	16.729	14.311
	313.15	88.075	72.962	13.020	11.069	15.024	12.829	16.087	13.722
	318.15	77.545	64.463	11.286	9.318	14.824	12.846	15.844	13.707
	323.15	69.022	58.237	10.634	8.940	13.681	11.920	14.674	12.772

Systems	***T* / K**	**GN**				**HND**		**FR**		
		G12	**σ(%)**	**AAD%**	**η12**	**σ(%)**	**AAD%**	**F12**	**σ(%)**	**AAD%**
ACN + MEA	303.15	2.328	40.732	20.392	0.259	28.899	16.583	1.975	40.732	20.392
	308.15	2.231	35.323	18.689	0.557	28.706	16.904	1.798	35.323	18.689
	313.15	2.261	37.426	19.943	0.946	38.450	22.184	1.696	37.426	19.943
	318.15	2.211	38.702	19.898	1.069	43.352	24.314	1.552	38.702	19.898
	323.15	2.196	37.036	19.630	1.159	44.417	25.797	1.435	37.036	19.630
ACN + MMEA	303.15	3.017	45.509	33.839	2.134	57.161	43.247	2.054	45.509	33.839
	308.15	2.880	41.875	31.468	1.993	53.195	40.561	1.860	41.875	31.468
	313.15	2.701	39.035	29.359	1.794	48.961	37.388	1.661	39.035	29.359
	318.15	2.561	37.076	27.604	1.617	45.999	35.017	1.481	37.076	27.604
	323.15	2.420	34.471	25.763	1.469	42.430	32.527	1.307	34.471	25.763
ACN + MEEA	303.15	1.028	2.646	2.154	-0.365	18.725	12.426	1.107	2.646	2.154
	308.15	0.905	2.479	2.039	-0.089	15.366	10.863	0.916	2.479	2.039
	313.15	0.952	2.989	1.695	0.192	9.121	6.367	0.825	2.989	1.695
	318.15	0.946	3.765	1.782	0.337	5.973	4.171	0.708	3.765	1.782
	323.15	0.810	4.404	2.438	0.368	5.928	4.300	0.534	4.404	2.438

Systems	***T* / K**	**WJK**			**KC**			**TK**		
		W12	**σ(%)**	**AAD%**	**K12**	**σ(%)**	**AAD%**	**T12**	**σ(%)**	**AAD%**
ACN + MEA	303.15	0.858	40.732	20.392	2.151	39.291	19.920	-0.232	21.408	12.471

	308.15	0.781	35.323	18.689	2.046	33.960	18.215	0.167	22.428	13.640
	313.15	0.737	37.426	19.943	2.072	36.008	19.389	0.630	32.975	19.375
	318.15	0.674	38.702	19.898	2.017	37.216	19.374	0.815	38.733	22.005
	323.15	0.623	37.036	19.630	1.995	35.555	19.052	0.951	40.653	23.517
ACN + MMEA	303.15	0.892	45.509	33.839	2.952	44.762	33.244	1.109	45.127	34.589
	308.15	0.808	41.875	31.468	2.814	41.132	30.875	1.169	43.085	33.395
	313.15	0.721	39.035	29.359	2.631	38.243	28.725	1.121	40.316	31.349
	318.15	0.643	37.076	27.604	2.490	36.310	26.991	1.060	38.504	29.808
	323.15	0.568	34.471	25.763	2.347	33.713	25.148	1.006	36.019	28.076
ACN + MEEA	303.15	0.481	2.646	2.154	1.122	2.896	2.304	-1.645	40.488	26.006
	308.15	0.398	2.479	2.039	0.996	2.570	2.133	-1.103	33.494	22.433
	313.15	0.358	2.989	1.695	1.039	3.412	1.939	-0.644	24.697	16.491
	318.15	0.307	3.765	1.782	1.029	4.171	1.980	-0.355	19.170	13.011
	323.15	0.232	4.404	2.438	0.891	4.684	2.480	-0.201	16.773	12.004

Systems	***T* / K**	**HRC**				**MAC3**			
		H12	**H21**	**σ(%)**	**AAD%**	**Z1112**	**Z1122**	**σ(%)**	**AAD%**
ACN + MEA	303.15	2.147	-0.645	33.457	15.701	1.927	10.621	33.457	15.701
	308.15	2.035	-0.701	27.631	13.400	1.650	8.915	27.631	13.400
	313.15	2.063	-0.740	29.152	14.272	1.502	7.881	29.152	14.272
	318.15	2.057	-0.642	31.679	15.724	1.408	6.600	31.679	15.724
	323.15	2.002	-0.775	28.578	14.469	1.214	5.934	28.578	14.469
ACN + MMEA	303.15	1.664	-4.166	7.409	4.025	0.415	20.096	7.409	4.025
	308.15	1.625	-4.021	7.258	4.125	0.390	16.227	7.258	4.125
	313.15	1.566	-3.795	6.419	3.626	0.378	12.890	6.419	3.626
	318.15	1.535	-3.582	5.888	3.071	0.368	10.422	5.888	3.071
	323.15	1.481	-3.422	5.680	2.951	0.351	8.569	5.680	2.951
ACN + MEEA	303.15	1.439	0.368	4.373	2.804	1.749	4.281	4.373	2.804
	308.15	1.331	0.419	3.472	2.129	1.552	3.467	3.472	2.129
	313.15	1.262	0.108	3.209	1.695	1.253	3.262	3.209	1.695
	318.15	1.222	0.014	3.536	1.690	1.093	2.899	3.536	1.690
	323.15	1.136	0.161	4.727	2.326	1.026	2.361	4.727	2.326

Systems	***T* / K**	**MAC4**					**AUS**				
		Z1112	**Z1122**	**Z2221**	**σ(%)**	**AAD %**	**A21**	**B12**	**B21**	**σ(%)**	**AAD %**
ACN + MEA	303.15	0.811	6.296	10.550	25.318	11.699	0.709	1.053	-0.107	11.135	5.547
	308.15	0.656	5.748	8.566	18.438	8.802	0.751	1.045	-0.101	8.770	4.236
	313.15	0.499	6.114	7.036	16.436	7.900	0.890	1.080	-0.129	9.289	3.919
	318.15	0.409	6.183	5.614	16.644	7.932	1.130	1.331	-0.151	11.253	4.447
	323.15	0.358	5.562	4.903	14.076	6.831	1.086	1.100	-0.142	9.844	3.867
ACN + MMEA	303.15	0.549	2.256	17.504	3.764	2.348	0.132	-0.245	0.940	5.518	3.539
	308.15	0.540	1.891	14.336	2.982	1.910	0.131	-0.254	1.100	5.032	3.357
	313.15	0.498	1.707	11.450	2.815	1.773	0.137	-0.254	1.133	4.602	3.015
	318.15	0.442	1.606	9.203	3.584	2.102	0.148	-0.253	1.087	4.454	2.997
	323.15	0.420	1.423	7.629	3.457	2.005	0.153	-0.255	1.147	4.038	2.758
ACN + MEEA	303.15	0.843	3.544	4.846	2.056	0.965	1.012	2.743	0.044	4.413	2.344
	308.15	0.871	2.691	4.047	1.080	0.629	1.196	3.235	0.062	1.496	0.808
	313.15	0.794	2.189	3.760	2.125	1.055	0.728	1.681	0.180	0.642	0.321
	318.15	0.764	1.798	3.363	3.438	1.633	0.555	1.164	0.325	2.551	1.286
	323.15	0.728	1.561	2.767	4.745	2.291	1.041	2.349	0.151	2.797	1.546

Systems	**JA**					
	j0	**j1**	**j2**	**j3**	**σ(%)**	**MAAD%**
ACN + MEA	679.903	-403.437	-1321.527	-1232.844	10.531	4.759
ACN + MMEA	469.416	-1108.349	133.819	-117.874	5.129	3.609
ACN + MEEA	353.180	-44.216	-266.090	-33.026	2.323	1.897

Fitting capabilities of simple polynomial equations and viscosity correlations were tested for different degrees of polynomials by calculating the standard percentage deviation, $\sigma\%$, as:

$$\sigma\% = \left[\frac{1}{n-p}\sum\left(100\times\frac{y_{exp}-y_{cal}}{y_{exp}}\right)^{2}\right]^{\frac{1}{2}} \qquad (25)$$

Here, y_{cal} *and* y_{exp} refer to calculated and experimental ρ, η, and v. n is the number of data used at each temperature. p is the number of coefficients taken.

The suitability and efficacy of each of the models are expressed by measuring the average absolute deviation percentage, AAD%, are computed as follows:

$$\mathrm{AAD\%} = \frac{100}{n}\sum_{i}^{1}\left(\frac{|y_{exp}-y_{cal}|}{y_{exp}}\right) \qquad (26)$$

Here, y_{cal} and y_{exp} refer to calculated and experimental ρ, η, or v and n is the number of data used at each temperature.

Mean average absolute deviation percentage, MAAD%*:* Calculated by taking the temperature average of AAD%s for each system.

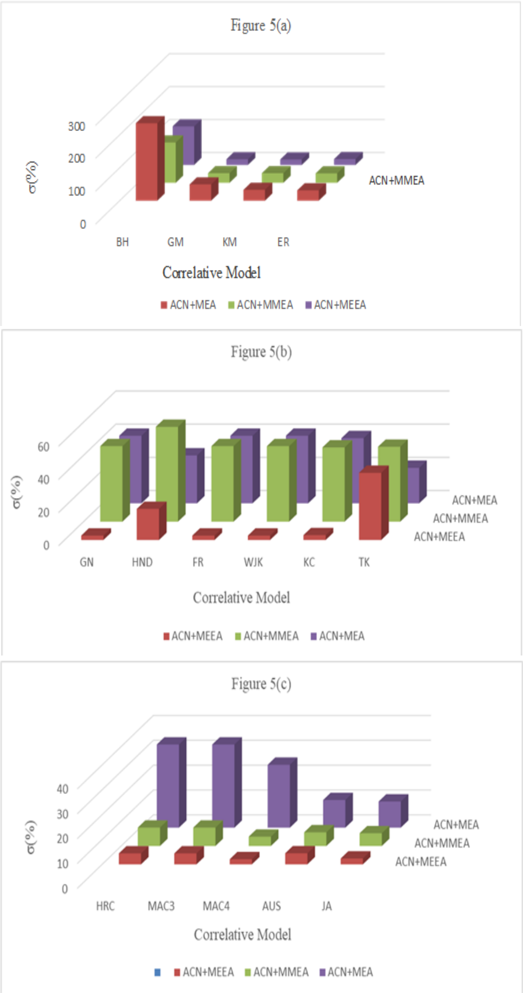


Figure 5: Comparative standard percentage deviation, σ %, for different correlative models: (a) Bingham (BH), Gambill (GM), Kendall- Munroe (KM), and Eyring relations (ER); (b) Grunberg-

Nissan (GN), Hind (HND), Frenkel (FR), Wijk (WJK), Katti-Chaudhri (KC), Tamura Kurata (TK) and (c) Heric (HRC), McAllister (3-body) (MAC3), McAllister (4-body) (MAC4), Ausländer (AUS), and the Jouyban-Acree (JA) models of ACN + MEA, + MMEA and + MEEA systems at 303.15 K.

5. Conclusions

Dynamic viscosities η for binary non-aqueous systems, (i) ACN + MEA, (ii) ACN + MMEA and (iii) ACN + MEEA were measured in the range, $0 \le x_2 \le 1$, at 5 different temperatures between 303.15 and 323.15 K. From experimental data of η deviations in viscosities ($\Delta\eta$) were calculated. To get the relevant coefficients (a_i / A_i) and σ, η was correlated to 5-parameter polynomials, whereas, $\Delta\eta$ was fitted to the Redlich-Kister type equations. $\Delta G^{\ddagger}$ and $\Delta G^{\ddagger E}$ of activation for viscous flow for the studied systems for different molar ratios at different temperatures are also derived. The experimental η were tested to some correlative models (Bingham, Kendall- Munroe, Gambill, and Eyring relations, Hind, Grunberg-Nissan, Frenkel, Wijk, Katti-Chaudhri, Tamura Kurata, Heric, Ausländer, McAllister (3-body) and McAllister (4-body) Equations and the Jouyban-Acree model).

Initially, η *vs.* x_2 varied very closely, but with the increasing amount of alkanolamines, η lines separated widely. The order of increasing η was: ACN + MEA > ACN + MMEA > ACN + MEEA. Whereas, $\Delta\eta$ lines exhibit slight/no minima in the ACN-rich region but show large maxima in the solute-rich region and vary accordingly.

Analysis of the above results revealed that, when the alkanolamines under consideration were mixed with liquid ACN, all effects due to intra- and intermolecular hydrogen bonding, the substitution of aminic hydrogens by alkyl groups had significantly influenced all types of interactions as well as the structural integrity of the heteromolecular complexes/species formed.

Finally, considerations of all such factors led to conclude that, self-association through both intra- & intermolecular H-bonding of the solutes, cross H-bonding between the ACN and alkanolamines and interstitial accommodation of the ACN into the cavities of the structural networks of associated components, i.e., the alkanolamines were mainly responsible for the variations in all the properties studied.

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