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

Muhammad A. R. Khan*, M. Mehedi Hasan Rocky*, Md. Ariful Islam, Faisal I. Chowdhury*, M. Shamsuddin Ahmed and Shamim Akhtar*
Department of Chemistry, University of Chittagong, Chattogram-4331, Bangladesh
*Department of Natural Science, Port City International University, Chattogram, Bangladesh.

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 (Δη), free energy (ΔG‡) of activation for viscous flow along its excess values (ΔG‡E) were calculated from experimental ρ and η data. For all systems, η vs. x2 initially changed very slowly, but with the increment of solute concentration η were found to rise quite rapidly. The values of Δη were largely positive and they formed a sharp maximum invariably at the highly alkanolamine-rich regions. All positive values of Δη followed the increasing order as: ACN + MMEA > ACN + MEA > ACN + MEEA. The order of ΔG‡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, 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. McAllister 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, CO₂ were responsible. Due to human activities, emission of CO₂ 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...
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 CO₂ (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 (Δη), the free energy of activation for viscous flow (ΔG‡) and their excess (ΔG‡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, Δη, ΔG‡ and ΔG‡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.

| Liquids                        | Molecular Formula | Source      | CAS No.   | Initial Purity (Mass Fraction) % | Molar Mass (g·mol⁻¹) | B.P. in °C |
|-------------------------------|-------------------|-------------|-----------|---------------------------------|-----------------------|------------|
| Acetonitrile (ACN)            | C₂H₃N             | Aldrich     | 75-05-8   | >99.5                           | 41.0519               | 82         |
| Monoethanolamine (MEA)        | C₂H₇NO            | Aldrich     | 141-43-5  | >99                             | 61.0831               | 170        |
| Monometylethanolamine (MMEA)  | C₃H₉NO            | Merck       | 109-83-1  | >98                             | 75.1097               | 259        |
| Monoethylethanolamine (MEEA)  | C₄H₁₁NO           | 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 \( \eta \), general polynomial equation has been used:

\[
\eta = \sum_{i=0}^{n} a_i x_2^i
\]  
(1)

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

The theoretical viscosities \( \eta_{id} \) of the mixtures were calculated by using the relation,

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

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

\[
\Delta \eta = \eta - \eta_{id}
\]  
(3)

And deviation in viscosity, \( \Delta \eta \), has been correlated by Redlich-Kister polynomial equation of the
form:
\[ \Delta \eta = x_2 (1 - x_2) \sum_{i=0}^{n} A_i (1 - 2x_2)^{i-1} \]  
(4)

with standard deviation, \( \sigma \), that has been calculated as follows:
\[ \sigma(Y) = \left[ \frac{\sum \left( \eta_{exp} - \eta_{cal} \right)^2}{n - p} \right]^{\frac{1}{2}} \]  
(5)

Here, \( A_i \) is the i-th fitting coefficient and the other terms have their usual significance. And \( Y \) represents \( \eta \) 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 (\( \eta \)) as follows:
\[ \eta = \frac{kN}{V_m} \exp \frac{\Delta G^\ddagger}{RT} \]  
(6)

where, \( \Delta G^\ddagger \) = Free energy of activation per mole for viscous flow, \( k \) = 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,
\[ \ln \left( \frac{\eta_{exp}}{\eta_{cal}} \right) = \frac{\Delta H^\ddagger}{RT} \frac{\Delta S^\ddagger}{R} \]  
(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 \( \ln \left( \frac{\eta_{exp}}{\eta_{cal}} \right) \) 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,
\[ \Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \]  
(8)

And the excess free energy of activation (\( \Delta G^{\ddagger E} \)) for viscous flow was calculated as:
\[ \Delta G^{\ddagger E} = \Delta G^\ddagger - (x_1 \Delta G^\ddagger_1 + x_2 \Delta G^\ddagger_2) \]  
(9)

3. Results and discussion

3.1. Viscosities (\( \eta \))

The viscosities, \( \eta \), 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.#        |
| 303.15      | 3.324        | 0.3308[47]   | 152.4        | 15.200[54]   | 89.60        | 8.535[57]    | 98.43        | 9.64[60]     |
|             | 0.3307[48]   | 0.3307[49]   |              |              |              |              |              |              |
|             | 0.35[50]     | 0.326[51]    |              |              |              |              |              |              |
|             | 0.3485[52]   | 0.333[53]    |              |              |              |              |              |              |
| 308.15      | 3.185        | 0.3165[48]   | 123.1        | 11.966[54]   | 72.81        | 7.014[57]    | 79.34        | 7.96[60]     |
|             | 0.319[53]    | 0.3285[52]   |              |              |              |              |              |              |
| 313.15      | 3.077        | 0.2991[47]   | 100.7        | 9.702[54]    | 60.50        | 5.841[57]    | 65.30        | 6.51[60]     |
|             | 0.3035[48]   | 0.3005[49]   |              |              |              |              |              |              |
|             | 0.3102[52]   |              |              |              |              |              |              |              |
| 318.15      | 2.932        | 0.2912[48]   | 83.3         | 7.914[54]    | 50.91        | 4.919[57]    | 54.54        | 5.32[60]     |
|             |              |              |              |              |              |              |              |              |
| 323.15      | 2.822        | 0.2720[47]   | 69.59        | 6.89[55]     | 43.03        | 4.186[57]    | 45.89        | 4.28[60]     |
|             | 0.2746[49]   |              |              |              |              |              |              |              |

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

The observed $\eta$ values agreed quite satisfactorily with the available literature data. $\eta$ 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, $\eta \times 10^4$ kg m$^{-1}$ s$^{-1}$ and deviations in viscosities, $\Delta \eta \times 10^4$ kg m$^{-1}$ s$^{-1}$ of ACN + MEA, + MMEA and + MEEA systems for different molar ratios at different temperatures.

| $x_2$ | $\eta$ (303.15) | $\Delta \eta$ (303.15) | $H$ (308.15) | $\Delta \eta$ (308.15) | $\eta$ (313.15) | $\Delta \eta$ (313.15) | $\eta$ (318.15) | $\Delta \eta$ (318.15) | $\eta$ (323.15) | $\Delta \eta$ (323.15) |
|-------|-----------------|------------------------|--------------|------------------------|-----------------|------------------------|-----------------|------------------------|-----------------|------------------------|
| 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          | 0.0024                 | 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          | 2.6267                 | 4.9697          | 1.9277                 | 4.3345          | 1.6826                 |
| 0.7498 | 9.1042          | 3.2519                 | 7.5840       | 2.6505                 | 6.5615          | 2.3533                 | 5.8507          | 1.9751                 | 4.8438          | 1.7229                 |
| 0.8008 | 10.3751         | 3.6222                 | 8.5864       | 2.6421                 | 7.3416          | 2.3140                 | 6.1850          | 1.9082                 | 5.3365          | 1.6614                 |
| 0.8501 | 11.6725         | 3.8033                 | 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 |
| $x_2$ | $\Delta G^f$ | $\Delta G^{fE}$ | $\Delta G^i$ | $\Delta G^{iE}$ | $\Delta G^j$ | $\Delta G^{jE}$ | $\Delta G^k$ | $\Delta G^{kE}$ |
|------|--------------|----------------|-------------|----------------|------------|---------------|------------|---------------|
| 0.000 | 9.561        | 0.000          | 9.628       | 0.000          | 9.694      | 0.000         | 9.761      | 0.000         |
| 0.058 | 10.332       | 0.198          | 10.411      | 0.225          | 10.489     | 0.252         | 10.568     | 0.278         |
| 0.088 | 9.850        | -0.583         | 9.934       | -0.543         | 10.018     | -0.503        | 10.102     | -0.463        |
| 0.147 | 9.861        | -1.157         | 9.906       | -1.141         | 9.950      | -1.125        | 9.995      | -1.109        |
| 0.196 | 10.718       | -0.792         | 10.708      | -0.818         | 10.699     | -0.843        | 10.690     | -0.868        |
| 0.249 | 11.866       | -0.174         | 11.824      | -0.219         | 11.781     | -0.263        | 11.738     | -0.308        |
| 0.301 | 12.894       | 0.344          | 12.839      | 0.300          | 12.784     | 0.256         | 12.729     | 0.213         |
| 0.351 | 13.775       | 0.723          | 13.716      | 0.688          | 13.657     | 0.653         | 13.597     | 0.619         |
| 0.400 | 14.519       | 0.979          | 14.458      | 0.955          | 14.397     | 0.932         | 14.336     | 0.908         |
| 0.452 | 15.206       | 1.151          | 15.143      | 1.139          | 15.080     | 1.127         | 15.017     | 1.115         |
| 0.499 | 15.765       | 1.240          | 15.699      | 1.237          | 15.634     | 1.234         | 15.568     | 1.231         |
| 0.550 | 16.313       | 1.275          | 16.242      | 1.281          | 16.171     | 1.286         | 16.100     | 1.292         |
| 0.600 | 16.792       | 1.263          | 16.714      | 1.274          | 16.636     | 1.286         | 16.558     | 1.297         |
| 0.649 | 17.231       | 1.213          | 17.144      | 1.228          | 17.057     | 1.243         | 16.970     | 1.258         |
| 0.699 | 17.647       | 1.131          | 17.548      | 1.147          | 17.449     | 1.164         | 17.350     | 1.180         |

Table 4: Free energy, $\Delta G^f$/kJ.mol$^{-1}$ and excess free energy, $\Delta G^{fE}$/kJ.mol$^{-1}$ of activation for ACN + MEA, + MMEA and + MEEA systems for different molar ratios at different temperatures.
| 0.750 | 18.041 | 1.020 | 17.927 | 1.035 | 17.814 | 1.050 | 17.700 | 1.064 | 17.587 | 1.079 |
| 0.800 | 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 |
### Table 5: Coefficients, $a_i$, of Equation 1, expressing viscosities, $\eta$, free energies, $\Delta G^\ddagger$ and standard deviation, $\sigma$, (Eqn. 5) of ACN + MEA, + MMEA and + MEEA systems for different molar ratios at different temperatures.

| System     | Property  | $T$ (K) | $a_0$  | $a_1$  | $a_2$  | $a_3$  | $a_4$  | $\sigma$ |
|------------|-----------|---------|--------|--------|--------|--------|--------|----------|
| ACN + MEA  | $\eta \times 10^4$ (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 | 24.5311 | -7.2159  | 19.2798 | 2.76E-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 |
| Temperature (K) | ACN + MMEA (kg·m\(^{-1}\)·s\(^{-1}\)) | ACN + MMEA (kJ mol\(^{-1}\)) | ACN + MMEA | ACN + MMEA | ACN + MMEA | ACN + MMEA |
|----------------|----------------------------------------|-------------------------------|------------|------------|------------|------------|
| 303.15         | 0.4873                                 | 9.7304                        | -11.970    | 13.5459    | -10.3941   | 7.2301     |
| 308.15         | 0.3766                                 | -0.1212                       | 9.7304     | -11.970    | 13.5459    | -10.3941   |
| 313.15         | 0.2956                                 | 0.8826                        | 9.7304     | -11.970    | 13.5459    | -10.3941   |
| 318.15         | 0.2413                                 | 1.1868                        | 9.7304     | -11.970    | 13.5459    | -10.3941   |
| 323.15         | 0.2244                                 | 0.8826                        | 9.7304     | -11.970    | 13.5459    | -10.3941   |

**ΔG‡ (kJ mol\(^{-1}\))**

| Temperature (K) | ACN + MMEA (kJ mol\(^{-1}\)) | ACN + MMEA | ACN + MMEA | ACN + MMEA | ACN + MMEA |
|----------------|-------------------------------|------------|------------|------------|------------|
| 303.15         | -1.1970                       | 13.5459    | -10.3941   | 7.2301     | 0.0241     |
| 308.15         | -0.1212                       | 9.7304     | -11.970    | 13.5459    | -10.3941   |
| 313.15         | 0.8826                        | 9.7304     | -11.970    | 13.5459    | -10.3941   |
| 318.15         | 1.1868                        | 9.7304     | -11.970    | 13.5459    | -10.3941   |
| 323.15         | 0.8826                        | 9.7304     | -11.970    | 13.5459    | -10.3941   |

**η (10^4)**

| Temperature (K) | ACN + MMEA (kg·m\(^{-1}\)·s\(^{-1}\)) | ACN + MMEA (kJ mol\(^{-1}\)) | ACN + MMEA | ACN + MMEA | ACN + MMEA |
|----------------|----------------------------------------|-------------------------------|------------|------------|------------|
| 303.15         | 9.7015                                 | 6.5661                        | 7.4635     | 9.0951     | -14.0582   |
| 308.15         | 9.8353                                 | 5.4789                        | 10.5936    | 4.3567     | -11.6421   |
| 313.15         | 9.9690                                 | 4.3912                        | 13.7264    | -0.3858    | -9.2242    |
| 318.15         | 10.1027                                | 3.3045                        | 16.8549    | -5.1229    | -6.8084    |
| 323.15         | 10.2365                                | 2.2165                        | 19.9886    | -9.8667    | -4.3897    | 0.0459     |

**ΔG‡ (kJ mol\(^{-1}\))**

| Temperature (K) | ACN + MMEA (kJ mol\(^{-1}\)) | ACN + MMEA | ACN + MMEA | ACN + MMEA | ACN + MMEA |
|----------------|-------------------------------|------------|------------|------------|------------|
| 303.15         | 9.7015                        | 6.5661     | 7.4635     | 9.0951     | -14.0582   |
| 308.15         | 9.8353                        | 5.4789     | 10.5936    | 4.3567     | -11.6421   |
| 313.15         | 9.9690                        | 4.3912     | 13.7264    | -0.3858    | -9.2242    |
| 318.15         | 10.1027                       | 3.3045     | 16.8549    | -5.1229    | -6.8084    |
| 323.15         | 10.2365                       | 2.2165     | 19.9886    | -9.8667    | -4.3897    | 0.0459     |
Correlating the concentration dependence of $\eta$ with the polynomial Equation 1, relevant coefficients and standard deviations as obtained by Eqn. 5 are shown in Table 5.

![Graphs showing viscosity vs. mole fraction](image)

Figure 1: Viscosities, $\eta$ 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.

The values of $\eta$ 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 $\eta$ up to $x_2 = 0.25$ was apparently very poor and the effect of temperature on $\eta$ also seemed to be small. On further addition of MEA, $\eta$ rose sharply, and with the rising of concentration of MEA, temperature effect increased. On the other hand, Figure 1(b) shows that $\eta$ 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, $\eta$ 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 $\eta$ decreased to reach its value. Thus, at all concentrations where, $x_2 > 0.8$, isotherms of $\eta$ showed significant variations for this particular system. As Figure 1(c) shows, the addition of MEEA to ACN $\eta$ initially went close up to $x_2 = 0.25$ as in ACN + MEA. Above this concentration, $\eta$ rose again rather sharply but this time forming concave curves with respect to the composition axis. With ACN+MMEA, the effect of temperature on $\eta$ was also quite large in the solute-rich region. Figure 1(d) is plotted to show the comparative curves of $\eta$ 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 $\eta$ 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 $\eta$ was as follows: ACN + MEA > ACN+MMEA > ACN+MEEA. (d) $\frac{d\eta}{dx_2}$ 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 $\eta$ 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: $\text{H} < -\text{CH}_3 < -\text{C}_2\text{H}_5$. Considering structural features for MEA, MMEA and MEEA, their self-association though thought to be comparable, steric hindrance affected the respective $\eta$ values significantly. Eventually, the order of variation $\eta$ 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 $\sim x_2 = 0.75$. 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 $\sim x_2 = 0.85$ 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 $\eta$ values were lowered down. Previously, Kipkemboi and Easteal [47] have found that the addition of BuOH or tert-butylation to H$_2$O 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 –CH₂-CH₃ 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.

![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.](image)

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

Free energies ($\Delta G^f$) and excess free energies ($\Delta G^{fE}$) 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 $\Delta G^f$ vs. $x_2$ isothermal were fitted to approximate polynomial equations (like Eqn.1 where $\eta$ is replaced by $G^f$), whereas $\Delta G^{fE}$ have been fitted to the Redlich-Kister equation (as like Eqn.4 where $\Delta\eta$ is replaced by $\Delta G^{fE}$). The relevant coefficients along with the standard deviations of $\Delta G^f$ and $\Delta G^{fE}$ 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, ($\Delta G^{\text{E}}$) and standard deviation, ($\sigma$), of Eqn. 5 of ACN + MEA, + MMEA and + MEEA systems for different molar ratios at different temperatures.

| System       | Property | $T$(K) | $A_0$     | $A_1$     | $A_2$     | $A_3$     | $A_5$     | $\sigma$ |
|--------------|----------|--------|-----------|-----------|-----------|-----------|-----------|----------|
| 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    | 0.4444    | 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   |
|              | $\Delta G^{\text{E}}$ (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   | -8.0517   | 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   |
| ACN + MMEA   | $\Delta G^{\text{E}}$ (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   |
| ACN + MEEA   | $\Delta G^{\text{E}}$ (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   |
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 $x_2 \approx 0.1$. Afterwards, it rose and formed a positive lobe with a maximum at $x_2 \approx 0.65$. 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 $\Delta G^{IE}$ decreased, i.e., $\Delta \Delta G^{IE} / \delta T$ was negative. Also, at their maxima the values of $\Delta G^{IE}$ followed: ACN + MMEA > ACN + MEA > ACN + MEEA.

The positive $\Delta G^f$ as well as $\Delta G^{IE}$ 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 $\Delta G^{IE}$ 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.

![Excess free energy of activation](image)

Figure 4: Excess free energy of activation, $\Delta G^{IE}$ 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):

\[ y = x_1 y_1 + x_2 y_2 \]  \hspace{1cm} (10)

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

\[ \ln y = x_1 \ln y_1 + x_2 \ln y_2 \]  \hspace{1cm} (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)

\[ y^{1/3} = x_1 y_1^{1/3} + x_2 y_2^{1/3} \]  \hspace{1cm} (12)

Eyring (ER)

\[ \ln \eta V = x_1 \ln (\eta_1 V_1) + x_2 \ln (\eta_2 V_2) \]  \hspace{1cm} (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 \( \eta \), the Grunberg and Nissan (GN) model suggest [50] the following relation:

\[ \ln y = x_1 \ln y_1 + x_2 \ln y_2 + x_1 x_2 G_{12} \]  \hspace{1cm} (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:

\[ y = x_1^2 y_1 + x_2^2 y_2 + 2x_1 x_2 H_{12} \]  \hspace{1cm} (15)

Here, \( H_{12} \) represents an interaction parameter.

Frenkel (FR)

\[ \ln y = x_1^2 \ln y_1 + x_2^2 \ln y_2 + x_1 x_2 F_{12} \]  \hspace{1cm} (16)

Wijk (WJ)
In this equation, the notation is the same as in the earlier equations. Additionally, $\phi_1$ and $\phi_2$ 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]:

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

(18)

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 $\eta$ and $v$. The McAllister three-body model (MAC3) has been defined as:

$$
\ln y = x_1^2 \ln y_1 + x_2^2 \ln y_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln (x_1 M_1 + x_2 M_2) + x_1 x_2 \{H_{12} + \\
H_{21}(x_1 - x_2)\}
$$

(20)

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

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

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

(24)
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| 235.17 | 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 |
| ACN + MEEA       | 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 |

| Systems          | T / K | GN | HND | F12 | FR |
|------------------|-------|----|-----|-----|----|
|                  |       | 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 |
|------------------|-------|-----|----|----|
|                  |       | σ(%) | AAD% | 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 |

where, \( y_{mT} \), \( y_{1,T} \), and \( y_{2,T} \) are the \( \eta \) values at temperature \( T \) for the mixture, components 1 and components 2, respectively, and \( j \) is the relevant model constant.

Correlating ability of each of Eqsns. 10-24 was tested by calculating the percentage of standard deviation, \( \sigma \) and AAD between the experimental and calculated viscosities. The percentage of standard deviation, \( \sigma \) 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 \( \sigma \) 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 \( \eta \) values and for ACN+ME system, Ausländer equation predicted \( \eta \) the best. The McAllister (4-body) equation fit the best for: ACN + MMEA and ACN + MEA. The McAllister (4-body) equation for correlating \( \nu \) was better than the results obtained from the McAllister (3-body) equation. It is also to remark that, \( Z_{122} \) 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**: ACN + MEA, ACN + MMEA, ACN + MEEA
- **T / K**: Various temperatures (303.15 to 323.15 K)
- **BH, GM, KM, ER, GN, HND, F12, FR, WJK, KC, TK**: Correlative models parameters
- **σ(%)**: Standard deviation
- **AAD%**: Average absolute deviation
- **η12**: Viscosity parameter
- **AAD%**: Average absolute deviation
- **F12**: Correlation coefficient
- **σ(%)**: Standard deviation
- **AAD%**: Average absolute deviation
- **T12**: Viscosity parameter
- **σ(%)**: Standard deviation
- **AAD%**: Average absolute deviation
| Systems       | $T / K$ | HRC | ACN + MMEA | ACN + MEEA |
|--------------|---------|-----|------------|------------|
|               |         | H12 | H21        | σ(%)        | AAD %   | Z1112 | Z1122 | AAD %   | MAC4 | AUS | AAD % |
| ACN + MEA    | 303.15  | 2.147 | -0.645 | 33.457 | 15.701 | 1.927 | 10.621 | 33.457 | 15.701 |
|              | 308.15  | 2.063 | -0.740 | 29.152 | 14.272 | 1.502 | 7.881 | 29.152 | 14.272 |
|              | 313.15  | 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 + MEEA   | 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 | 3.261  | 4.727  | 2.326  |

| Systems       | $T / K$ | Z1112 | Z1122 | Z2212 | σ(%)        | AAD %   | A21   | B12   | B21   | AAD %   | MAC4 | AUS | 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 + MEEA   | 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       | $j$    | $j1$  | $j2$  | $j3$  | σ(%)        | MAAD% |
|--------------|-------|------|------|------|--------------|-------|
| ACN + MEA    | 679.903 | -403.437 | -1321.527 | -1232.844 | 10.531 | 4.759 |
| ACN + MEEA   | 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 |

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

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

Here, $y_{cal}$ and $y_{exp}$ refer to calculated and experimental $\rho$, $\eta$, and $\nu$. $n$ 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%, as computed as follows:

$$\text{AAD}% = \frac{100}{n} \sum \left( \frac{|y_{exp} - y_{cal}|}{y_{exp}} \right)$$ \hspace{1cm} (26)

Here, $y_{cal}$ and $y_{exp}$ refer to calculated and experimental $\rho$, $\eta$, or $\nu$ 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, $\sigma %$, 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 $\eta$ for binary non-aqueous systems, (i) ACN + MEA, (ii) ACN + MMEA and (iii) ACN + MEEA were measured in the range, $0 \leq x_2 \leq 1$, at 5 different temperatures between 303.15 and 323.15 K. From experimental data of $\eta$ deviations in viscosities ($\Delta \eta$) were calculated. To get the relevant coefficients ($\alpha_i / A_i$) and $\sigma$, $\eta$ was correlated to 5-parameter polynomials, whereas, $\Delta \eta$ was fitted to the Redlich-Kister type equations. $\Delta G_f^\eta$ and $\Delta G_f^{IE}$ of activation for viscous flow for the studied systems for different molar ratios at different temperatures are also derived. The experimental $\eta$ 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, $\eta$ vs. $x_2$ varied very closely, but with the increasing amount of alkanolamines, $\eta$ lines separated widely. The order of increasing $\eta$ 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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