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Published online: 28 Oct 2014.

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Notion of viscosity Arrhenius temperature for *N,N*-dimethylacetamide with *N,N*-dimethylformamide binary mixtures and its pure components

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Excess properties calculated from the experimental values of densities and viscosities have been presented in the previous work. These experimental values can also lead us to test different correlation equations as well as their corresponding relative functions. Inspection of the Arrhenius activation energy Ea and the enthalpy of activation of viscous flow ΔH^* found very close values, here we can define partial molar activation energy Ea_1 and Ea_2 for *N,N*-dimethylacetamide and methanol respectively along with their individual contribution separately. Correlation between the two Arrhenius parameters of viscosity in all compositions shows existence of distinct behaviours separated by particular mole fractions of *N,N*-dimethylacetamide. In addition, the correlation between Arrhenius parameters reveals interesting Arrhenius temperature which is closely related to the vaporisation temperature in the liquid vapour equilibrium and the limiting corresponding partial molar properties that can permit us to estimate the boiling points of the pure components.

Keywords: binary liquid mixture; viscosity; Arrhenius activation energy; Arrhenius temperature; boiling temperature

1. Introduction

Many research works have been done to study the physicochemical properties of binary liquid mixtures using a restrict number of models and to derive some investigation and characterisation of molecular interactions. In the same way, some models attempt to correlate viscosity of various compositions in liquid mixtures at different temperatures to release eventual interactions, structures' change and peculiar behaviours. This paper is one more contribution in the series of our comprehensive research program to introduce a new parameter that characterises the binary solvent system.[1–6] Taking into account the published data in our previous works,[7,8] here it is extended to introduce a new study the viscosity and Arrhenius behaviour along with this new parameter designated as Arrhenius temperature in *N,N*-dimethylacetamide (DMA) + *N,N*-dimethylformamide (DMF) binary mixtures between 298.15 K and 318.15 K to get more information about the internal

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structures of this system. In addition, assuming that the activation energy is a thermo-dynamic quantity, partial molar activation energies have been determined to release individual interaction's contributions of each pure component within the mixture for each composition.

2. Temperature dependence of liquid viscosity

2.1. *Viscosity results*

For each temperature 23 sets of mixtures covering the entire mole fraction range were prepared for density and viscosity (with repetition) for the present binary system. Dynamic viscosity (η) and density (ρ) of (DMA + DMF) mixtures at different compositions and temperatures were reported earlier from 298.15 to 318.15 K.[1,2]

We observe a practically linear behaviour when either of the viscosity (η) or of the logarithm of viscosity $\ln(\eta)$ *v.s* composition (Equations 1 and 2) was drawn with a good linear regression coefficient R with an average for the three temperatures as: $R(\eta) = 0.999962$ and $R(\ln\eta) = 0.999925$.

$$\eta_T(x_1) = x_1\eta_{1,T} + x_2\eta_{2,T} \tag{1}$$

$$\ln\eta_T(x_1) = x_1\ln\eta_{1,T} + x_2\ln\eta_{2,T} \tag{2}$$

where $\eta_{1,T}$ and $\eta_{2,T}$ are the viscosities at the temperature T of the pure DMA (1) and DMF (2) respectively.

The variation of the experimental values of the logarithm of viscosity in mPa·s with the mole fraction of DMA are given in Figure 1. It shows that $\ln\eta(x_1)$ increases with increase in mole fraction (x_1) of DMA for each fixed temperature without any peculiarity. The quasi-linearity of the plotted curves in Figure 1 shows that the molecular interaction is weak and the mixture's nature is very much similar to the ideal solution. We can add that the Grunberg–Nissan (GN) parameter G_{12} has small values where the binary liquid mixtures using GN model [9] could be determined by the Equation (3):

$$\ln\eta = x_1\ln\eta_1 + x_2\ln\eta_2 + x_1x_2G_{12} \tag{3}$$

where G_{12} is an interaction parameter proportional to the interchange energy and the indexes 1 and 2 correspond to the pure components DMA (1) and DMF (2) respectively. Also, we can note that the deviation from the ideality of the logarithm of viscosity $\Delta\ln(\eta)$ which has a very small average value (about 0.0011) is mathematically in relationship to the GN parameter G_{12} and is equal to the relative viscosity deviation ($\Delta\eta/\eta$):

$$\Delta\ln(\eta) = x_1x_2G_{12} = \Delta\eta/\eta \tag{4}$$

which is also related to the experimental-relative reduced Redlich–Kister excess properties $Q_{rel,\eta,T}(x_1)$ for the ratio $= Q_{\eta,T}(x_1)/\eta$ of viscosity deviation reported earlier.[8] This interaction parameter G_{12} can be defined on the basis of the group contribution models. [10,11] We note that the investigation of the variation of GN parameter against the composition can give evidence of specific interaction and eventual change in the complex varieties or clusters formed in binary liquid mixtures under temperature effect and/or mixture composition.[12] In the present system it has been found earlier that the
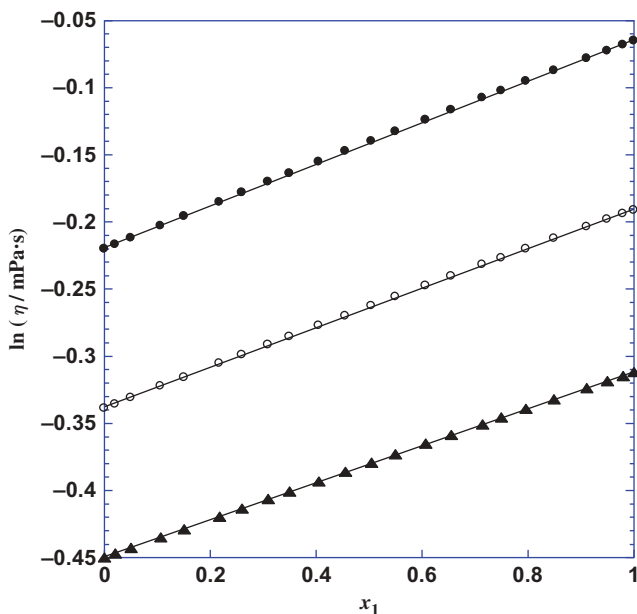
Figure 1. Logarithm of shear viscosity $\ln(\eta)$ for the system of {DMA (1) and DMF (2)} mixtures *v. s* the mole fraction x_1 of DMA at the temperatures: (●): 298.15 K; (○):308.15 K and (▲): 318.15 K.

interchange energy values G_{12} of GN are very feeble suggesting that the solvent–solvent interaction is weak.[8] In the earlier paper [7] the curves of (V^E) and ($\Delta\eta$) *v.s* mole fraction of DMA obtained for both DMA + DMF and DMA + FA (formamide) systems are found similar in nature. In the same context, Desnoyers *et al*. [13] showed that an examination of the trends of the dependence of V^E and $\Delta\eta$ on x_1 suggested that many of these systems are similar, and the differences in interactions are mostly significant in solutions very rich in one component. From the treatment of excess thermodynamic quantities for liquid mixtures proposed by Desnoyers *et al*. [13], we can conclude that the excess quantity (V^E and $\Delta\eta$) gives an overall view of the origin of the non-ideality in the mixtures but still can be quite misleading, especially for systems that show strong interactions at high dilution. Desnoyers *et al*. [13] suggested that, in agreement with the original statements of Redlich and Kister,[14] it is better to use the reduced Redlich–Kister equation that is expressed as:

$$Q_{Y,\exp,T}(x_1) = Y^E/(x_1(1-x_1)) \tag{5}$$

where Y^E denotes V^E and $\Delta\eta$ for this study. The negative deviations of $Q_{\eta,T}(x_1)$ from ideality over the whole mole fraction range without any minima or maxima predicts the presence of very weak dispersion and dipolar forces between these two aprotic solvents. [8] The moderately structured DMA seems to undergo a structure-breaking effect when mixed with DMF, similar to N-methylacetamide's behaviour to DMF.[15] Although DMA + DMF mixtures are non-electrolyte solutions, an expansion equation equivalent to the Debye–Hückel and Jones–Dole expressions [16–18] has also been adopted and used for the viscosity values of DMA + DMF non-electrolyte solution mixture and the results

reported earlier [8] showed that solute–solvent interaction parameter was same for DMA in DMF and for the reverse case. We also noticed that, at higher temperatures, there will be a competition between molecular interactions and thermal disordered movement of molecules.

2.2. *Viscosity Arrhenius behaviour*

The values of viscosity at different temperature of DMA + DMF binary system have been fitted to the Arrhenius temperature dependence equation:

$$\ln(\eta) = \ln As + Ea/RT \tag{6}$$

and using graphical and least square methods, the Arrhenius activation energy (Ea) and pre-exponential (entropic) factor (As) are thus found out and given in the Table 1 for different compositions (x_1) of DMA. Since, the As-values are closely related to the viscosity of the system in vapour phase,[3,8] we observed that the high As-value of DMF assumes that the viscosity of DMF at vapour phase is greater than of DMA and can also assume that the DMF molecules bonding are more disordered and random in vapour

Table 1. The entropy of activation of viscous $\Delta S^*/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$, the entropic factor of Arrhenius $-R \cdot \ln(As/\mathrm{Pa \cdot s})/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$ and the reduced Redlich–Kister functions relative to the Arrhenius activation energy $Q_{Ea}/\mathrm{kJ \cdot mol^{-1}}$ of viscosity and the logarithm of the Arrhenius entropic factor $Q_{\ln As}$ for {DMA (1) and DMF (2)} mixtures as a function of the mole fraction (x_1) of DMA over the temperature range (298.15–318.15) K.

| x_1	$Ea^{a}/$ $\mathrm{kJ \cdot mol^{-1}}$	$\Delta H^{*a}/$ $\mathrm{kJ \cdot mol^{-1}}$	$\Delta S^*/$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$-R \cdot \ln(As)/$ $(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$	$Q_{Ea}(x_1)/$ $\mathrm{kJ \cdot mol^{-1}}$	$Q_{\ln As}(x_1)$
0.000	9.053	8.292	−14.632	89.628	–	–
0.0200	9.070	8.310	−14.631	89.660	0.23396	−0.085316
0.0500	9.097	8.336	−14.634	89.709	0.23515	−0.085713
0.1062	9.147	8.386	−14.635	89.799	0.23535	−0.085648
0.1500	9.183	8.423	−14.641	89.862	0.23328	−0.084789
0.2171	9.237	8.478	−14.654	89.952	0.22949	−0.083202
0.2600	9.272	8.515	−14.657	90.014	0.22775	−0.082515
0.3094	9.309	8.552	−14.674	90.071	0.22512	−0.081514
0.3500	9.339	8.583	−14.690	90.117	0.22167	−0.080105
0.4050	9.379	8.625	−14.706	90.182	0.22004	−0.079524
0.4550	9.413	8.659	−14.733	90.230	0.21645	−0.078128
0.5042	9.445	8.691	−14.763	90.272	0.21461	−0.077420
0.5500	9.475	8.722	−14.787	90.314	0.21283	−0.076707
0.6071	9.512	8.761	−14.818	90.366	0.21298	−0.076845
0.6550	9.543	8.793	−14.843	90.410	0.21394	−0.077179
0.7140	9.579	8.829	−14.883	90.453	0.21615	−0.078086
0.7500	9.600	8.851	−14.906	90.481	0.21734	−0.078673
0.7968	9.624	8.876	−14.950	90.502	0.21974	−0.079550
0.8500	9.653	8.906	−14.991	90.533	0.22486	−0.081634
0.9112	9.685	8.939	−15.043	90.565	0.23770	−0.086860
0.9500	9.704	8.959	−15.080	90.580	0.24936	−0.091741
0.9800	9.717	8.973	−15.112	90.588	0.25794	−0.095269
1.0000	9.726	8.982	−15.135	90.592	–	–

^aprevious work.[8]
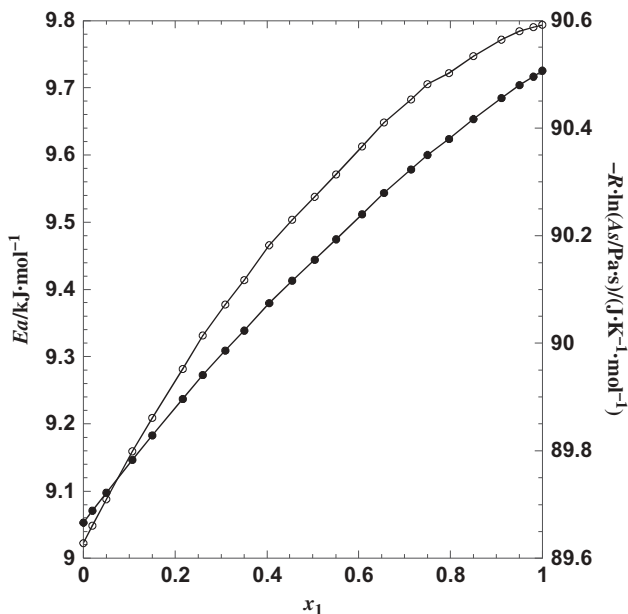
Figure 2. Variation the Arrhenius activation energy E_a (kJ·mol^{-1}) of viscosity and the logarithm of the entropic factor of Arrhenius $-R \cdot \ln(As/\text{Pa·s})/(\text{J·K}^{-1} \cdot \text{mol}^{-1})$ for {DMA (1) and DMF (2)} mixtures *v.s* the mole fraction x_1 of DMA in the temperature range (298.15–318.15) K. (●): E_a/kJ·mol^{-1}; (○): ΔH^*/kJ·mol^{-1}.

state.[8] Also, the Arrhenius activation energy is almost equal to the enthalpy of activation of viscous flow which it is much correlated with its vaporisation's enthalpy of liquid mixture. Moreover, the variation of the Arrhenius activation energy E_a (kJ·mol^{-1}) of viscosity and the logarithm of the entropic factor of Arrhenius $-R \cdot \ln(As/\text{Pa·s})/$ $(\text{J·K}^{-1} \cdot \text{mol}^{-1})$ for {DMA (1) and DMF (2)} mixtures *v.s* the mole fraction x_1 of DMA in the temperature range (298.15–318.15) K is also plotted in Figure 2. So, the quasi-linear behaviour shown in Figure 2 and the small difference between the quantities, Arrhenius activation energy E_a (kJ·mol^{-1}) and the logarithm of the entropic factor of Arrhenius $-R \cdot \ln(As)$ of the two pure components well confirms the feeble interaction manifested previously (Table 1).

In addition and similarly to Equation (6), the corresponding reduced Redlich–Kister excess quantities (Table 1) are in relationship with the GN interaction parameters [7–9] at desired temperature:

$$G_{12,T}(x_1) = Q_{\text{RK},lnAs(x_1)} + \frac{Q_{\text{RK},E_a(x_1)}}{RT} \tag{7}$$

Since as the correlation between $Ea(x_1)$ and $\ln As(x_1)$ or $Q_{\text{RK},Ea}(x_1)$ and $Q_{\text{RK},\ln As}(x_1)$ can reveal no such domains with distinct behaviours, the investigation of the interaction parameter $G_{12,\exp,T}(x_1)$ *v.s* composition at fixed temperature, can also give evidence of non-specific weak interactions between unlike components.

2.3. *Correlation between Arrhenius parameters*

2.3.1. *Pure components*

There has long been interest in the correlation of the viscosity coefficient with other, more elementary, physicochemical properties of compounds. A number of reviews [19–21] have presented relations between the viscosity and molecular weight, molar refraction, dipole moment, density molar volume along with different thermodynamic properties. The viscosity data facilitate the calculation of the thermodynamic properties that help us to predict the intermolecular interaction in the liquid mixtures. DMA is a dipolar aprotic solvent having moderately high dielectric constant and DMF is an aprotic protophilic solvent with an almost similar dielectric constant at 298.15 K.[22] The values of the main physical properties of both the solvents are given in Table 2. DMA has unique solvating properties associated with hydrogen-bonding network.[23] On the other hand, DMF also has high solvating power with respect to a lot of organic and inorganic substances and is miscible with almost all common polar and non-polar solvents. Raman and infrared spectra of liquid DMF have been recorded by Fini and Mirone,[24] X-ray diffraction [25] and NMR [26–28] study of liquid DMF indicates that there are no significant interactions; only a weak hydrogen bond interaction existed between DMF molecules.

We also add a supplementary parameter such as the Arrhenius temperature (T_A) for each pure component which has been calculated by using the equation:

$$T_A = -\frac{Ea}{R \cdot \ln(As)} \tag{8}$$

Table 3 summarises some Arrhenius parameters of the pure liquids studied in previous works.[1–8] Figures 3 and 4 show mutual correlation between the viscosity Arrhenius parameters. It is to be mentioned that this interesting causal correlation which can permit and help us to develop the above-stated empirical Arrhenius equation and also think about reducing the parameters' number into the used or programmed model. The linear least square fit gives the following equations: ($Y = -27.271-3.332X$) for $Ea = f(\ln As)$ and ($Y = -6.977 + 0.1573X$) for $Ea = f(T_A)$ with a correlation coefficients $R = 0.9657$ and $R = 0.9850$ respectively. Though the little number of data points used in this analysis statistics, we can ascertain that there is a clear causal correlation between the Arrhenius temperatures which can be improved in future when we consider a greater number of dataset for numerous liquid solvents.

Table 2. Values of the physical properties of (DMA) and (DMF) at 298.15 K. *M*: Molar mass, μ: dipolar moment, ε: dielectric constant, T_b: boiling temperature, T_f: melting point, $\Delta_{vap}H$: enthalpy of vaporisation, $\Delta_{fus}H$: enthalpy of fusion, *n*: refractive index and P_{vap} at 25°C.[22]

	M	μ	ε	T_b	T_f	$\Delta_{vap}H$	$\Delta_{fus}H$	*n*	P_{vap}
Solvent property	g.mol^{-1}	D	–	K	K	kJ.mol^{-1}	kJ.mol^{-1}	–	Pa
DMA	87.12	3.72	37.8	438.15	253.15	46.2	7.90	1.438	300
DMF	73.09	3.86	36.71	426.15	213.15	47.75	8.05	1.431	377

Table 3. Arrhenius parameters of some pure liquids studied at previous works.

| N°	Component	Abbrev.	Ref.	Ea/kJ·mol^{-1}	ln(As/Pa·s)	T_A/K
1	N,N-dimethylformamide	DMF	[4]	9.480	−10.921	104.40
2	Methanol	Met		11.018	−11.935	111.03
3	N,N-dimethylacetamide	DMA	[5]	9.884	−11.019	107.89
4	Formamide	FA		16.405	−12.489	157.98
5	N,N-dimethylacetamide	DMA	[2]	9.753	−10.912	107.50
6	2-Ethoxyethanol	EOE		15.803	−12.682	149.87
7	N,N-dimethylacetamide	DMA	[1]	10.166	−11.078	110.37
8	Water	W		15.510	−13.284	140.43
9	1,4-dioxane	Diox	[3]	12.660	−11.816	128.86
10	Water	W		15.920	−13.444	142.42
11	Isobutyric acid	IBA	[6]	11.120	−11.200	119.41
12	Water	W		15.741	−13.383	141.46
13	1,4-Dioxane	Diox	[3]	12.640	−11.853	128.26
14	Water	W		16.100	−13.508	143.35
15	N,N-dimethylacetamide	DMA	[4]	10.849	−11.892	109.72
16	Methanol	Met		12.941	−12.172	127.87
15	N,N-dimethylacetamide	DMA	[8]	9.726	−10.896	107.36
16	N,N-dimethylformamide	DMF		9.053	−10.780	101.00
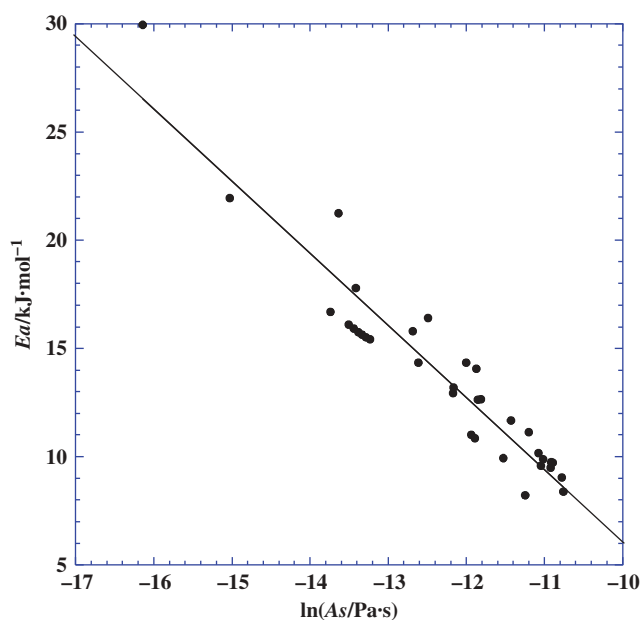
Figure 3. Correlation between the Arrhenius activation energy E_a (kJ·mol^{-1}) of viscosity and the logarithm of the entropic factor of Arrhenius ln(As/Pa·s) for {DMA (1) and DMF (2)} mixtures in the temperature range (298.15–318.15) K. (●): experimental data points; (—): linear least square fit.

2.3.2. Binary mixtures

For this studied binary mixture, considering the Redlich–Kister, reduced Redlich–Kister and relative reduced Redlich–Kister excess functions it has already been reported that the
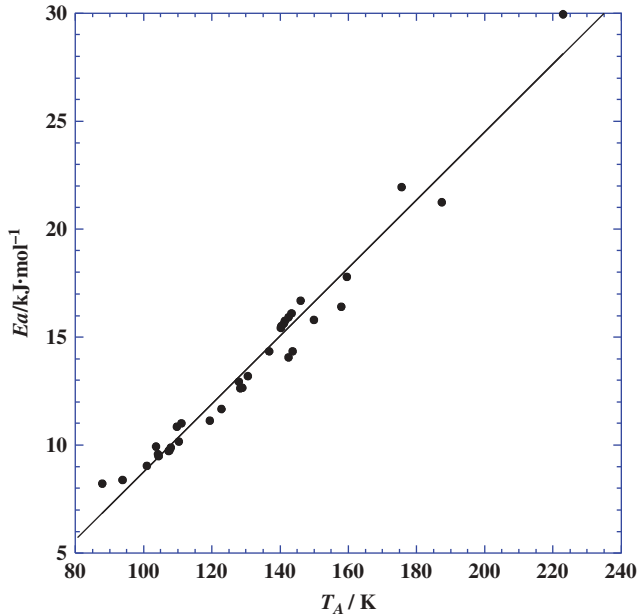
Figure 4.   Correlation between the Arrhenius activation energy E_a (kJ·mol^{-1}) of viscosity and the Arrhenius temperature T_A/K. for {DMA (1) and DMF (2)} mixtures in the temperature range (298.15–318.15) K. (●): experimental data points; (—): linear least square fit.

interaction between unlike components becomes feeble in the current system.[1,2] Correlation between the two Arrhenius parameters, Arrhenius activation energy E_a (kJ·mol^{-1}) of viscosity and the logarithm of the entropic factor of Arrhenius $-R·\ln(As/$Pa·s)/(J·K^{-1}·mol^{-1}) for {DMA (1) and DMF (2)} mixtures showed that it gave no observable change in curvature having same slope of a quasi-straight line. This inspires us to deduce the following standardised empirical equation and apply it to the present system:

$$-\frac{Ea}{R} = T_A \cdot \ln(As) + B \tag{9}$$

where B is a constant related to the viscosity of the liquid system at boiling temperature and also, it is the intercept on the ordinate when lnAs is mathematically null; while the slope T_A characterises each binary system and it is equivalent to an absolute temperature for which we suggest the viscosity Arrhenius temperature as a name for the corresponding binary system [1–6].

Noteworthy, we observe that the T_A-values for all the studied systems are of the same order of magnitude of the boiling temperatures (T_{bi}) of the corresponding constituting pure components. In the case of the DMA–DMF mixtures, the T_A value which deduced from linear regression (Figure 5) is equal to 687.3 K with correlation factor $R = 0.9955$, while the boiling temperature of DMA and DMF are 438.15 K and 426.15 K respectively; we conclude that the viscosity Arrhenius temperature T_A can be related to the average value of the temperature function of the isobaric liquid vapour equilibrium (T-x) of the system DMA–DMF at the same pressure.
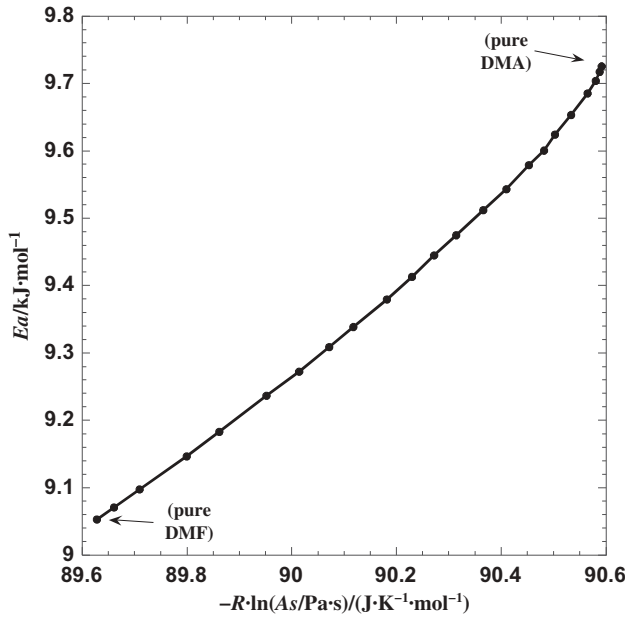
Figure 5.   Correlation between the Arrhenius activation energy E_a (kJ·mol^{-1}) of viscosity and the logarithm of the entropic factor of Arrhenius $-R \cdot \ln(As/\text{Pa·s})/(\text{J·K}^{-1} \cdot \text{mol}^{-1})$ for {DMA (1) and DMF (2)} mixtures in the temperature range (298.15–318.15) K. ($\bullet$): experimental data points; (—): non-linear least square fit.

We can add that our next program will to show the Arrhenius temperature T_A is closely correlated with the average value of the temperature function $T(x_1)$ against molar composition (x_1) in the interval [0, 1] for the isobaric binary liquid–vapour diagram and which can be expressed as:

$$\int_0^1 T(x_1) dx_1 \sim T_A \tag{10}$$

and the Arrhenius temperature T_A is approximately the average height of the graph of temperature composition $(T\text{-}x_1)$ of the corresponding isobaric phase diagram at atmospheric pressure of the studied binary liquid mixture. In the same way and depending on weather the T_A-value is framed, overvalued or undervalued by one of the boiling point T_{bi}, we can estimate the graph type of the temperature composition $(T\text{-}x_1)$ diagram (regular or azeotropic with high or low boiling point).

3.   Thermodynamic characters

3.1.   *Enthalpy and entropy of activation of viscous flow*

In case of liquid phase we can add the absolute reaction rate theory of Eyring *et al*. [29] and Ali *et al*. [30] that relates kinematic viscosity with the free energy (ΔG^*) of activation of viscous flow:

$$\Delta G^* = RT \cdot ln\left(\frac{\eta V}{hN_A}\right) \tag{11}$$

where η, h, R, N_A, ρ and M are the dynamic viscosity of binary mixture, Plank's constant, universal gas constant, Avogadro's number, density and molar mass of mixture (Equation 10) respectively and:

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{12}$$

$$M = x_1(M_1 - M_2) + M_2 \tag{13}$$

where M_1 and M_2 are the molar mass of the pure component of DMA and DMF respectively.

By assuming that the activation parameters ΔH^* and ΔS^* [30,31] are independent of temperature, we obtained, for each composition of mixture (x_1, x_2), these parameters when $ln(\eta \cdot V/(h \cdot N_A))$ is plotted against $1/T$. Using both graphical and least square fit method, the slope is equal to $\Delta H^*/R$ and the intercept on the ordinate is equal to $-\Delta S^*/R$. We can use then Equation (12) to determine the activation parameters ΔH^* and ΔS^*.

The thermodynamic activation function of viscous flow (ΔG^*) may be determined from the expression for the pre-exponential factor in the Erying relationship (the viscosity coefficient), which is a function of density and relative permittivity together with the thermal dependence of the viscosity coefficient. The exponential term in the Erying formulation is simply expressed in the form of the viscous flow activation enthalpy which determines the shape of the energy barrier to be overcome by a particle during an elementary step of the flow (Equation 12).

3.2. *Correlations with enthalpy of activation of viscous flow*

The Arrhenius activation energy *Ea* and ΔH^* of activation of viscous flow calculated in the present binary mixture are plotted in Figure 6 against mole fraction (x_1) of DMA in the temperature range (298.15–318.15) K. Inspection of the variation in the *Ea*-values and those of ΔH^* of activation of viscous flow, it states that the *Ea* and ΔH^* values are very closely related. So, we can write that the difference between *Ea*-values and those of ΔH^* of activation of viscous flow can be considered as an enthalpy increment δH^* which is expressed linearly as:

$$\Delta H^* = Ea - \delta H^* \tag{14}$$

We have also added the entropy of activation of viscous flow (ΔS^*) which is closely correlated with the difference between Arrhenius entropic factor ($lnAs$) and an entropy increment (δS^*) as [8]:

$$\Delta S^* = -R \cdot lnAs + \delta S^* \tag{15}$$

The variation in the logarithm of the entropic factor of Arrhenius $-R \cdot ln(As/\text{Pa} \cdot \text{s})/$ $(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$ *v.s* the mole fraction x_1 of DMA and entropy of activation of viscous flow $\Delta S^*/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ *v.s* the mole fraction x_1 of DMA in {DMA (1) and DMF (2)} mixtures in the temperature range (298.15–318.15) K are plotted together in Figure 7. It is found that
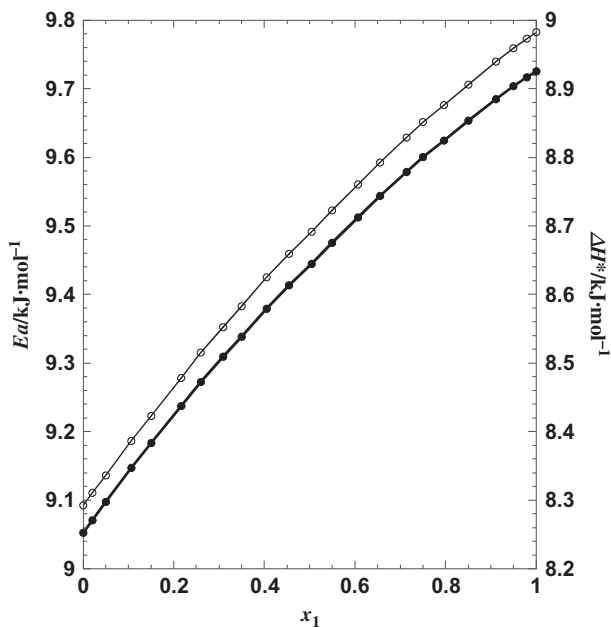
Figure 6. Arrhenius activation energy Ea and enthalpy of activation of viscous flow ΔH^* for {DMA (1) and DMF (2)} mixtures *v.s* the mole fraction x_1 DMA in the temperature range (298.15–318.15) K. (●): Ea/kJ·mol^{-1}; (○): ΔH^*/kJ·mol^{-1}.
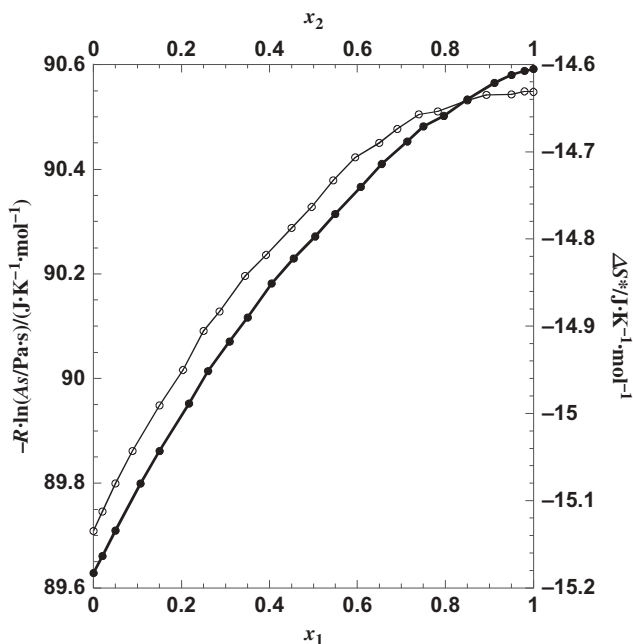

Figure 7. Logarithm of the entropic factor of Arrhenius. (●): $-R \cdot \ln(As/\text{Pa·s})/(\text{J·K}^{-1}\cdot\text{mol}^{-1})$ *v.s* the mole fraction x_1 of DMA and entropy of activation of viscous flow; (○): ΔS^*/J·K^{-1}·mol^{-1} *v.s* the mole fraction x_2 of DMF in {DMA (1) and DMF (2)} mixtures in the temperature range (298.15–318.15) K.

the change of both the values with the mole fraction gives a close resemblance to each other.

3.3. *Partial molar activation energy*

Considering the quasi-equality between the Arrhenius activation energy Ea and the enthalpy of activation of viscous flow ΔH^* and between logarithm of the entropic factor of Arrhenius $-R \cdot \ln(As)$ and the entropy of activation of viscous flow ΔS^*, mentioned in the above section, we can assume approximately that $Ea(x_1)$ is a thermodynamic function and we can define the partial molar quantities Y_1 and Y_2 for DMA (1) and EOE (2) respectively through the following equations:

$$Y_1(x_1) = Y(x_1) + (1 - x_1) \cdot \frac{\partial Y(x_1)}{\partial(x_1)} \tag{16}$$

$$Y_2(x_1) = Y(x_1) - x_1 \cdot \frac{\partial Y(x_1)}{\partial(x_1)} \tag{17}$$

where Yi represents the partial molar activation energy Ea_1 and Ea_2 or the partial molar quantity relative to the entropic factor of Arrhenius $-R \cdot \ln(As_i)$.

This action is interesting because the partial molar activation energy $Ea_i(x_1)$-values give eventual individual contribution of each pure component (i) and preferential phenomena in competition of each fixed binary mixture composition (x_1, x_2).

Values of $Ea_1(x_1)$, $Ea_2(x_1)$, $-R \cdot \ln(As_1)$ and $-R \cdot \ln(As_2)$ are reported in Table 4 and Ea_1 (x_1) and $Ea_2(x_1)$ are depicted in Figure 8 against mole fraction of DMA (x_1). The partial molar activation energy $Ea_1(x_1)$ of DMA exponentially decreases from a high value (about 9.9682 kJ·mol^{-1}) to reach a minimum (about 9.7255 kJ·mol^{-1}), on the other hand, the partial molar activation energy of DMF $Ea_2(x_1)$ varies in the opposite manner. Hence, the

Table 4. Partial molar quantities relative to the activation energies $Ea_i/(\text{kJ·mol}^{-1})$ and the logarithm of the entropic factor of Arrhenius $-R \cdot \ln(As_i/\text{Pa·s})/(\text{J·K}^{-1} \cdot \text{mol}^{-1})$ for {DMA (1) and DMF (2)} mixtures as a function of the mole fraction of DMA (x_1) over the temperature range (298.15–318.15) K.

x_1	Ea_1	Ea_2	$-R \cdot \ln As_1$	$-R \cdot \ln As_2$	x_1	Ea_1	Ea_2	$-R \cdot \ln As_1$	$-R \cdot \ln As_2$
	/kJ·mol^{-1}		/J·K^{-1}·mol^{-1}			/kJ·mol^{-1}		/J·K^{-1}·mol^{-1}	
0.0000	9.9682	9.0527	91.329	89.628	0.5500	9.7668	9.1180	90.716	89.824
0.0200	9.9567	9.0524	91.293	89.627	0.6071	9.7590	9.1302	90.693	89.860
0.0500	9.9400	9.0528	91.242	89.629	0.6550	9.7545	9.1425	90.680	89.897
0.1062	9.9109	9.0560	91.152	89.638	0.7140	9.7473	9.1573	90.659	89.940
0.1500	9.8886	9.0584	91.083	89.646	0.7500	9.7443	9.1688	90.650	89.975
0.2171	9.8580	9.0646	90.989	89.665	0.7968	9.7368	9.1821	90.627	90.015
0.2600	9.8431	9.0720	90.944	89.688	0.8500	9.7322	9.2050	90.613	90.085
0.3094	9.8247	9.0779	90.888	89.705	0.9112	9.7284	9.2396	90.601	90.193
0.3500	9.8117	9.0839	90.849	89.723	0.9500	9.7267	9.2669	90.596	90.279
0.4050	9.7983	9.0943	90.809	89.755	0.9800	9.7257	9.2913	90.592	90.356
0.4550	9.7858	9.1019	90.772	89.777	1.0000	9.7255	9.3097	90.592	90.415
0.5042	9.7744	9.1091	90.738	89.798	–	–	–	–	–

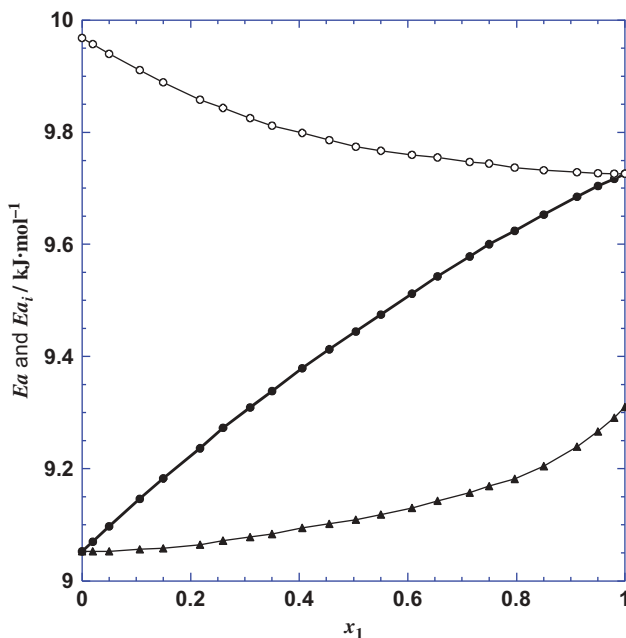Figure 8. Arrhenius activation energy Ea/(kJ·mol^{-1}) and partial molar activation energies of viscosity (Equations 5 and 6) Ea_i/(kJ·mol^{-1}) for {DMA (1) and DMF (2)} mixtures as a function of the mole fraction of DMA (x_1) over the temperature range (298.15–318.15) K. (○): $Ea(x_1)$; (●): $Ea_1(x_1)$; and (▲): $Ea_2(x_1)$.

introduced molecules of DMA in the DMF rich region find high difficulty to become integrated into the layers' of DMF molecules.

Correlation between the partial molar Arrhenius activation energies $Ea_1(x_1)$ and Ea_2 (x_1) for {DMA (1) and DMF (2)} mixtures over the temperature range (298.15–318.15) K are graphically presented in Figure 9. We can note that the mutual dependence between the two partial molar Arrhenius activation energies $Ea_1(x_1)$ and $Ea_2(x_1)$ is quadratic, a pseudo-circle with a coordinate centre ($Ea_1(x_1 = 1)$; $Ea_2(x_1 = 0)$), i.e., if we plot the correlation between the two excess partial molar Arrhenius activation energies $Ea^{ex}_1(x_1)$ and $Ea^{ex}_2(x_1)$, we will observe a pseudo quart of circle centred on the origin (0,0).

$$[Ea^{ex}_1(x_1)]^{\alpha} + [Ea^{ex}_2(x_1)]^{\alpha} = \text{constant} \qquad (18)$$

Hence, the excess thermodynamic quantities have the advantage of illustrating the sign and magnitude of their non-ideality. Correlation between the two partial molar quantities relative to the activation energies Ea_i/(kJ·mol^{-1}) and the logarithm of the entropic factors of Arrhenius $-R·\ln(As_i$/Pa·s)/(J·K^{-1}·mol^{-1}) in {DMA (1) and DMF (2)} mixtures as a function of the mole fraction of DMA (x_1) over the temperature range (298.15–318.15) K are given in Figure 10.

If we abandon the assumption that the Arrhenius temperature (T_A) is no longer a constant over the whole range of composition, we can redefine it as a Arrhenius' current temperatures (T_{cAi}) by the derivative of the partial molar Arrhenius activation energy Ea_i (x_1) with respect to the partial molar quantity corresponding to the logarithm of the entropic factor of Arrhenius $-R·\ln(As_i)$ at selected molar fraction (x_1):
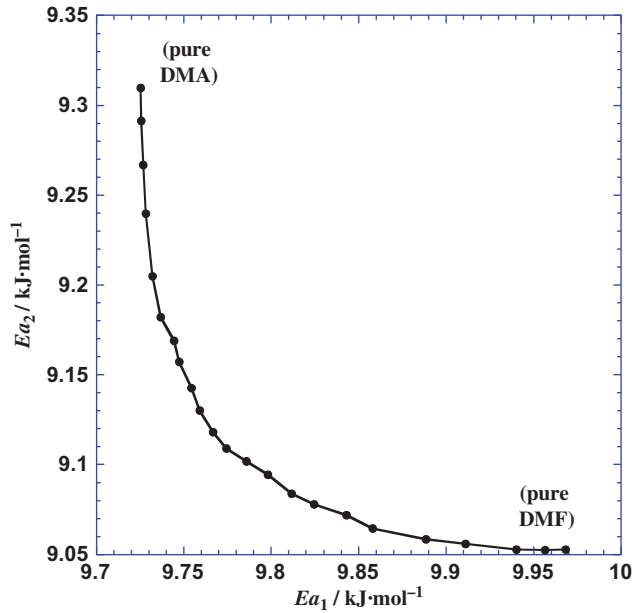
Figure 9.   Correlation between the partial molar Arrhenius activation energies $Ea_1(x_1)$ and $Ea_2(x_1)$ for {DMA (1) and DMF (2)} mixtures over the temperature range (298.15–318.15) K.
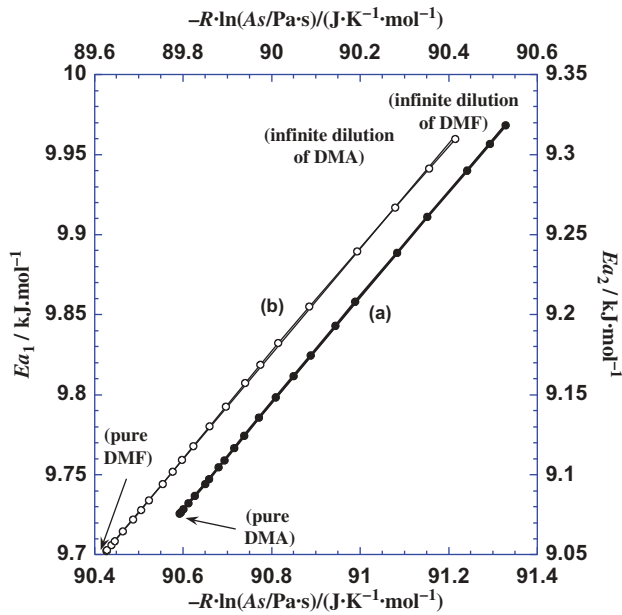
Figure 10.   Correlation between the partial molar quantities relative to the activation energies Ea_i/ (kJ·mol^{-1}) and the logarithm of the entropic factors of Arrhenius $-R\cdot\ln(As_i/\text{Pa·s})/(\text{J·K}^{-1}\cdot\text{mol}^{-1})$ related to, curve a, (●): DMA ($i = 1$) and curve b, (○): DMF ($i = 2$) in {DMA (1) and DMF (2)} mixtures as a function of the mole fraction of DMA (x_1) over the temperature range (298.15–318.15) K.

$$T_{cAi} = \partial[Ea_i]/\partial[-R \cdot \ln(As_i)] \qquad (19)$$

Note that the form of Equation (19) is justified from the fact of the behaviour's similarity of the Arrhenius parameters ($Ea_i(x_1)$ and $-R \cdot \ln(As_i)$) with ΔH^* and ΔS^* of activation of viscous flow (Figures 6 and 7, Equations 6,12,14–17). In fact, considering the Gibbs free energy expression (Equation 12) and the partial derivatives functions of Maxwell equations, we can consider that the Equation (19) is equivalent to the following equation at constant pressure.

$$[(\partial \Delta H^* / \partial \Delta S^*)_p = T] \qquad (20)$$

The experimental T_{cAi}-values are equal to the slope of the tangent line at a selected point of the curve (i.e. at selected mixture composition (x_1)). As an application of this definition, we obtain very interesting results especially in the vicinity of the two limits of composition range. So, we obtain as a Arrhenius' current temperatures (T_{cAi}) from the slopes of the two curves given in Figure 10 such as: in the case of the very high concentration of one component (i) we find that $T_{cA1}(x_1 \approx 1) = 330$ K $<$ $T_{b1} = 438.15$ K for the first curve ($i = 1$), $T_{cA2}(x_2 \approx 1) = 329$ K $< T_{b2} = 426.15$ K for the second curve ($i = 2$), while in the case of very high dilution of the component (i) in the second one (j). With this finding, we can predict the boiling point of the two pure components at constant pressure through investigation of the viscosity–temperature dependence on the corresponding liquid phase. We can add that this very interesting finding is also verified for other studied previous works [1–6] for different binary mixtures.

Correlation between the Arrhenius' current temperatures (T_{cAi})/K at ($x_i \approx 1$) for the pure component (i) and the corresponding boiling temperature T_{bi}/K determined by couple of components from some binary liquid mixtures studied at previous works (Equation 20) [1–6] is depicted in Table 5. We can observe a correlation between the current Arrhenius temperatures evaluated from the recently studied system and the boiling temperatures of some pure components, except in the present case where its behaviour is not similar to those studied systems because the two DMA and DMF are like-molecules and similar and the system is quasi-ideal where the interactions are very weak. In this only special case we note that this phenomenon does not occur.

Table 5. Comparison between the current Arrhenius temperature (T_{Ai})/K for ($x_i \approx 1$) and the corresponding boiling temperature T_{bi}/K of the pure component (i) in some binary mixtures.

Component 1	Component 2	Ref.	T_{A1}/K	T_{b1}/K	T_{A2}/K	T_{b2}/K
DMA	DMF	a	330.6	438.15	329.1	426.15
DMA	FA	[5]	429.1	438.15	479.6	483.65
DMA	EOE	[2]	440.0	438.45	410.0	408.15
DMA	Water	[1]	456.1	438.45	378.5	373.15
Dioxane	Water	[3]	378.6	374.25	380.5	373.15
IBA	Water	[6]	433.1	428.15	362.9	373.15

a: Present work.

4. Conclusion

Based on the same experimental data of dynamic viscosities and densities of DMA + DMF binary mixtures at three different temperatures from 298.15 to 318.15 K and at atmospheric pressure,[7,8] here some new theoretical approaches have been made within the framework of different correlating equations to optimise the investigations of variation of Arrhenius activation energy and derived partial molar properties against temperature. Arrhenius parameters of pure components (*N,N*-dimethylacetamide and *N, N*-dimethylformamide) are determined as a function of temperature and can be predicted. Correlation between the two Arrhenius parameters (E_a) and ($\ln(As)$) for binary mixtures permits us to reveal the viscosity Arrhenius temperature which characterises the studied binary liquid mixture and can provide information on the vaporisation temperature of the isobaric liquid vapour equilibrium.[1–3] Also, this correlation can give evidence of the existence of distinct composition regions with different behaviours.

Thus, assuming that the activation energy is a thermodynamic quantity, we have determined the partial molar activation energy to release individual interaction's contributions of each pure component within the mixture for each well-defined composition. Correlation between the molar quantities relative to the activation energies and the logarithm of the entropic factors of Arrhenius for DMA + DMF mixtures over the temperature range can give an approximately linear behaviour, i.e., no observable change in curvature. This quasi-straight line behaviour suggests us to make an empirical equation by introducing a new parameter T_A denoted as viscosity Arrhenius temperature that characterises each binary system. In the case of molar quantities, we consider that the Arrhenius temperature (T_A) is no longer a constant over the whole range of composition, and we introduce a new concept of the Arrhenius' current temperature (T_{Ai}) for each pure component (*i*) to find its value at the two extreme positions, i.e., at very high concentration and very high dilution respectively. The results derived in the studied binary system gives a new finding that the calculated Arrhenius temperatures are not very close to the boiling temperature of the pure components. This is because both the components are very like molecules and the interactions are very weak dispersion and dipolar forces between these two aprotic solvents, so the observed characters deviate from the earlier studied system of our comprehensive research program.

We conclude that an itemised investigation of the various thermodynamic properties against temperature and composition can give detailed information on eventual molecular interactions and also to predict a new parameter known as Arrhenius temperature that characterises the binary liquid mixture. In order to firmly establish the utility of the Arrhenius temperature and to develop a means for estimating such quantities, it is very much necessary that more mixtures will be studied in future to give a more clear discussed protocol.

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