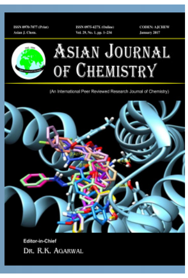
Asian Journal of Chemistry; Vol. 29, No. 9 (2017), 2038-2050
ASIAN JOURNAL OF CHEMISTRY
https://doi.org/10.14233/ajchem.2017.20764



A Novel Approach of Partial Derivatives to Estimate the Normal Boiling Temperature *via* Viscosity Arrhenius Behaviour in N,N-Dimethylformamide + Ethanol Fluid Systems

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Received: 5 May 2017; *Accepted*: 31 May 2017; *Published online*: 15 July 2017; AJC-18489

The experimental values of absolute viscosity in N,N-dimethylformamide + ethanol binary fluid mixtures (from 303.15 to 323.15 K) can induce us to investigate different correlation expressions as well as their derivative quantities. Investigation of the molar enthalpy of viscous flow (ΔH*) and the viscosity activation energy (Ea) reveals close values and similar variation against composition, here we can justify the notion of partial activation energies Ea_1 and Ea_2 for pure components along with their separately individual contributions. Correlation between the two Arrhenius parameters in the whole range of compositions shows the existence of different interaction behaviours, delimited by peculiar compositions. It is also noticed that the ratio between the two parameters leads to the Arrhenius temperature which is in causal correlation with the temperature of vapourization in the liquid-vapour isobaric diagram and the limiting partial properties can permit us to predict values of the boiling temperatures of the pure fluid components.

Keywords: Binary fluid mixture, Viscosity, Activation energy, Arrhenius temperature, Boiling point.

INTRODUCTION

We are engaged in a research program of experimental data on thermodynamic and transport properties of binary mixtures [1-5] in lately suggested correlation equations.

Generally, the mixtures have non-ideal characters and show specific behaviour for which the interpretation of the non-ideality is an interesting topic, especially with new concepts like Herráez exponent, friccohesity, Belda coefficients and reduced Redlich-Kister excess properties [1-43]. Theory of solutions is still far from sufficient to well treat non-idealities for liquid solution, in terms of properties of the constituent molecules [28-34]. The knowledge of the principal factors engaged in the non-ideality of fluid mixtures is important for a better understanding of excess viscosities and volumes and its derived functions. Regarding the practical importance of amide-alcohol solutions, N,N-dimethylformamide (DMF), in a certain manner is associated through of dipole-dipole interactions. Substantial structural effects are missing due to the lack of hydrogen bonding. Thus it acts as a protophilic aprotic solvent of large dipole moment (μ = 3.80 D) of molecules with a fairly high dielectric constant (ε = 36.71) at 298.15 K [1-5]. An ethanol molecule can interact with a N,N-dimethylformamide molecule in accordance with the better hydrogen bonding acceptor ability of its oxygen atom, resulting in packing and structural effects in the light of the critical interface of cohesive and frictional forces represented by friccohesity [28-34].

By means of the novel concepts of the universal exponent of Herráez, reduced Redlich-Kister (RK) properties and Belda coefficients [35-43], we have launched a perceivable research program to obtain more information about the internal structure of the mixtures of most of the organic solvents that have a high importance in biology as cited in the literature [1-27]. In view of the data given from the literature and augmented by some interpolation operations for derivations needed, it is extended to examine the viscosity Arrhenius-type behaviour along with a new coefficients nominated as Arrhenius temperature (T_A), in ethanol + N,N-dimethylformamide binary fluid mixtures from 303.1 to 323.15 K [28-34].

Furthermore, the close dependence on composition, between the molar enthalpy of viscous flow (ΔH*) and the viscosity activation energy (E_a) guided to considering that (E_a) is approximately a thermodynamic state function for which partial quantities have been determined to arise individual interaction's contributions of each pure solvent within the fluid mixture for each mole composition and the new given parameter nominated as the current Arrhenius temperature (T_{Ai}) related to each pure solvent (i) can provide in a reliable estimation of the boiling point value of the two pure solvents constituting the studied binary fluid mixture [20,21,44-50].

In addition, the cohesive forces, the activation energy (E_a) and the molar enthalpy of viscous flow ΔH^* do retain a most implicit relationship because the activation energy is kinetic in nature and represents the energy amount derived from potential energy depicted by the cohesive forces. Consequently, as mentioned in the literature that the cohesive forces characterizes the surface tension so for well clarification of the surface tension along with absolute viscosity measurements are of thermodynamic significance interfaced by the friccohesity [28-34]. Furthermore, correlation between the Arrhenius parameters and the temperature, by means of the temperature of vapourization is greatly affected by the friccohesity, the molar enthalpy of vapourization and the surface tension [28-34].

RESULTS AND DISCUSSION

Temperature-dependence of liquid shear viscosity

Arrhenius behaviour: The small number of experimental data are available the literature [1-5] and the necessity for of mathematical derivations manipulations, we have fitted with non-linear least-squares methods in fifth order polynomial with the help of available experimental data points [1-5] *versus* molar composition (x_1) of DMF at the five temperatures (303.15, 308.15, 313.15, 318.15 and 323.15) K. Using the expression of the optimal polynomials, we have added 18 interpolated points (x_1) evenly distributed throughout the full domain of composition (x_1) of DMF and then determinate the corresponding shear viscosity values (Table-1 and Fig. 1).

TABLE-1
CALCULATED DYNAMIC VISCOSITIES (η)/(10^{-3} Pa.s) BY INTERPOLATION METHOD FOR {DMF (1) AND EtOH (2)} SYSTEMS AGAINST THE MOLE COMPOSITION (x_1) of DMF AT THE TEMPERATURES (303.15, 308.15, 313.15, 318.15 AND 323.15) K

x_1	η (10^{-3} Pa·s)				
	303.15K	308.15K	313.15K	318.15K	323.15K
0.00000	1.08570	0.97325	0.87974	0.79953	0.72810
0.02020	1.11440	0.99894	0.90242	0.82014	0.74803
0.04040	1.12810	1.01170	0.91425	0.83160	0.75820
0.06061	1.13060	1.01480	0.91790	0.83545	0.76225
0.08081	1.12500	1.01090	0.91558	0.83453	0.75967
0.15152	1.07260	0.96959	0.88305	0.81068	0.73816
0.25253	0.98718	0.90237	0.82697	0.76498	0.70083
0.35354	0.92784	0.85730	0.78819	0.73138	0.67343
0.45455	0.88570	0.82571	0.76157	0.70900	0.65635
0.54545	0.85291	0.80044	0.74149	0.69344	0.64553
0.56566	0.84616	0.79512	0.73739	0.69032	0.64337
0.64646	0.82234	0.77580	0.72271	0.67893	0.63495
0.74747	0.80127	0.75678	0.70806	0.66648	0.62445
0.84848	0.78564	0.73950	0.69374	0.65427	0.61459
0.92929	0.77358	0.72664	0.68314	0.64666	0.60992
0.94949	0.77173	0.72535	0.68231	0.64638	0.60993
0.96970	0.77131	0.72603	0.68328	0.64747	0.61073
1.00000	0.77528	0.73298	0.69007	0.65302	0.61396

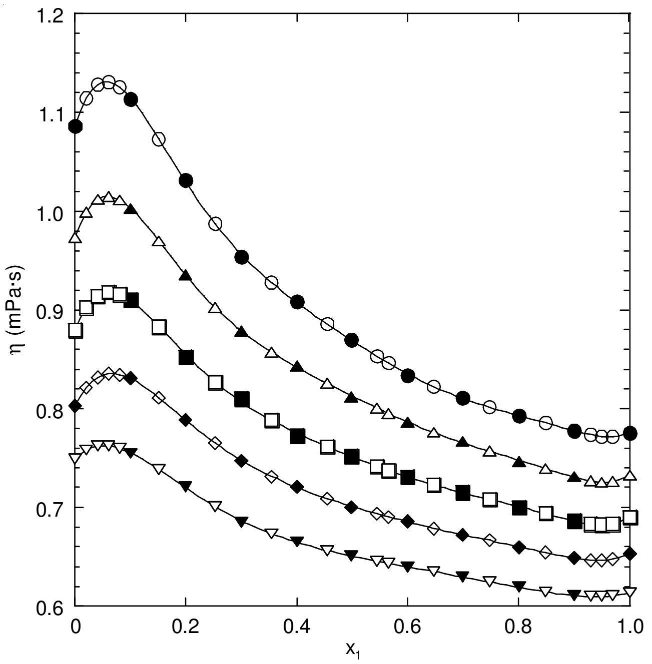

Fig. 1. Dynamic viscosity (η) for {DMF (1) and EtOH (2)} systems *versus* the mole composition x_1 of DMF at the temperatures: (●) and (○): 303.15 K; (▲) and (△): 308.15 K; (■) and (□): 313.15 K ; (◆) and (◇): 318.15 K; (▼) and (▽): 323.15 K. full symbols: literature data and empty symbols: interpolated data

The quality of this polynomial's method [$\eta = a_0 \cdot x_1 + a_1 \cdot x_1^2 + \ldots + a_5 \cdot x_1^5$] for the five studied temperatures shows a non-linear correlation regression better than R = 0.99995. It is observed that the relationship between the dynamic viscosity (η) and the absolute temperature (T) can be well adjusted with the Arrhenius type-equation as follows:

$$\eta = As \cdot e^{\frac{Ea}{RT}} \tag{1}$$

where R, E_a and A_s are, respectively, the perfect gas constant, the activation energy and the pre-exponential factor related to the liquid mixture. eqn. 1 can be expressed in the logarithmic form:

$$\ln(\eta) = \ln(A_s) + \frac{E_a}{R}\left(\frac{1}{T}\right) \tag{2}$$

The plot of the logarithm of dynamic viscosity ln (h/Pa·s) with the reciprocal of temperature (1/T) for DMF (1) + EtOH (2) binary fluid system in the full range of composition (x_1) is as good as linear (Fig. 2) and the two parameters E_a and A_s are thus practically independent over the full studied temperature range (from 303.15 to 323.15) K. Using both linear least-squares fitting and graphical methods, the intercept to the ordinate is equal to ln (A_s) and the slope of the straight line is equal to E_a/R either for the pure components ($x_1 = 0$ or $x_1 = 1$) and for their corresponding fluid mixtures ($x_i \neq 0$).

Case of pure components: For phenomenological discussion of the causal correlation, we have proposed an extra endogenous variable such as the viscosity Arrhenius temperature (T_A) where the reciprocal value is determined by the intercept to abscissa axis ($1/T_A$) or using the following equation:

$$T_A = -\frac{E_a}{R \cdot \ln A_s} \tag{3}$$

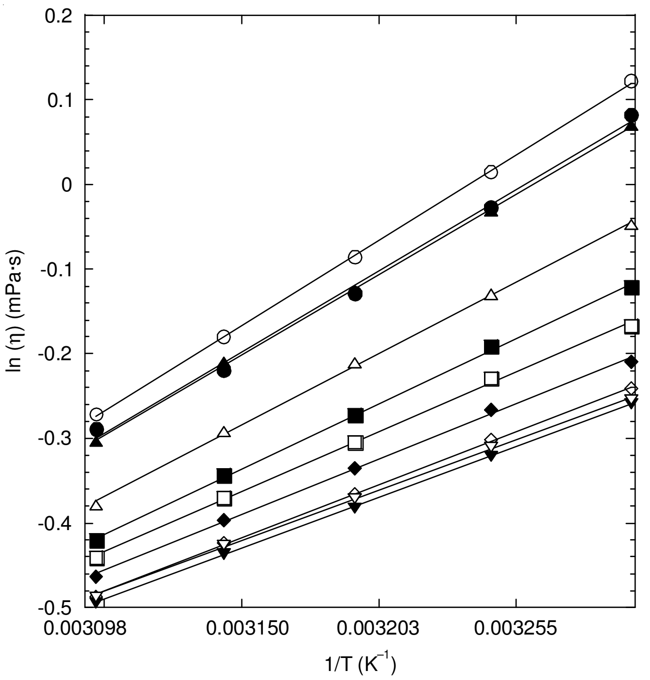

Fig. 2. Logarithm of dynamic viscosity ln (η) for {DMF (1) and EtOH (2)} systems *versus* the reciprocal temperature at some fixed mole compositions x_1 in the domain of temperatures (303.15 to 318.15 K). (●): x_1 = 0.000; (○): x_1 = 0.0606; (▲): x_1 = 0.1515; (△): x_1 = 0.3003; (■): x_1 = 0.4546; (□): x_1 = 0.5657; (◆): x_1 = 0.6988; (◇): x_1 = 0.8485; (▼): x_1 = 0.9495 and (▽): x_1 = 1.000

Table-2 summarizes the viscosity Arrhenius parameters of some solvents studied in previous works [21-26,35,39,41,44-50] and Fig. 3 indicates mutual correlation between the parameters (E_a, ln A_s and T_A) of Arrhenius.

TABLE-2
ARRHENIUS PARAMETERS OF SOME SOLVENTS DETERMINED BY PAIR OF COMPONENTS FROM SOME BINARY MIXTURES STUDIED EARLIER (EQNS. 3 AND 4)

No.	Solvent	Ref.	E_a (kJ mol^{-1})	ln (A_s/Pa·s)	T_A (K)
1	N,N-dimethylacetamide	[20]	9.7533	-10.912	107.50
2	2-Dthoxyethanol		15.803	-12.682	149.87
3	N,N-Dimethylacetamide	[21]	10.166	-11.078	110.37
4	Water		15.510	-13.284	140.43
5	1,4-Dioxane	[22]	12.660	-11.816	128.86
6	Water		15.920	-13.444	142.42
7	N,N-Dimethylacetamide	[49]	9.8844	-11.019	107.89
8	Formamide		16.405	-12.489	157.98
9	N,N-Dimethylacetamide	[45]	10.849	-11.892	109.72
10	2-Methoxyethanol		12.941	-12.172	127.87
11	N,N-Dimethylacetamide	[47]	9.7260	-10.896	107.36
12	N,N-Dimethylformamide		9.0530	-10.780	101.00
13	*iso*-Butyric acid	[46]	11.120	-11.200	119.41
14	Water		15.741	-13.383	141.46
15	1,4-Dioxane	[41]	12.640	-11.853	128.26
16	Water		16.100	-13.508	143.35
17	N,N-Dimethylformamide	[44]	9.4802	-10.921	104.40
18	Methanol		11.018	-11.935	111.03
19	N,N-Dimethylacetamide	[48]	10.849	-11.892	109.72
20	Methanol		12.941	-12.172	127.87
21	N,N-Dimethylformamide	[a]	9.4793	-10.920	104.41
22	Ethanol		16.227	-13.266	147.12

[a] Present work

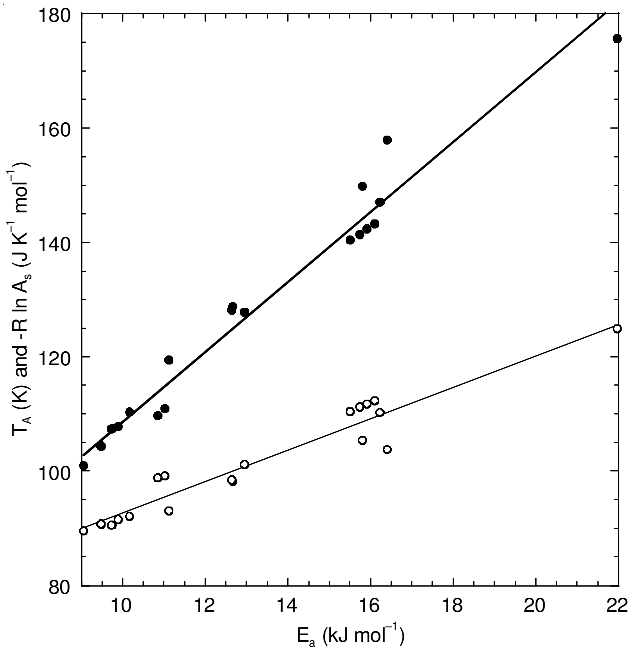

Fig. 3. Causal correlation between the activation energy E_a (kJ mol^{-1}) and (●): the viscosity Arrhenius temperature T_A (K) or (○): the natural logarithm of the entropic factor of Arrhenius –R ln (A_s/Pa·s)/(J mol^{-1} K^{-1}) for some pure fluids determined by couple of solvents from some binary fluids mixtures studied at earlier works (eqn. 3) [Ref. 20-22,41,44-49]. (—): linear least square fit

It is noticed that a helpful causal correlation which can improve the theoretical development of the semi-empirical Arrhenius-type equation and also to think about the diminution of the parameters number into the programmed or utilized model. Linear least square fit gives the following equations: ($Y = 47.462 + 6.115X$) for $T_A = f(E_a)$ and ($Y = 65.262 + 2.749X$) for ($-R \ln A_s) = f(E_a)$ with R-square equal to 0.9844 and 0.9636, respectively. Though the few experimental data points used in this statistical analysis, we can confirm that there is a clear causal correlation between the two Arrhenius parameters which can be enhanced later when we consider a great number of data set for diverse pure fluid systems.

Case of binary mixtures: For each molar composition (x_1), calculated values of $E_a(x_1)$ and ln $A_s(x_1)$ are presented in Table-3 and are depicted *versus* the mole fraction of DMF (1) in Figs. 4 and 5, respectively.

Furthermore, for each mole composition x_1 of DMF, the values of ln $A_s(x_1)$ lead us to determinate the (A_s)-values in μPa·s, of the pre-exponential factor [*i.e.* $A_s(x_1) = \exp(\ln (A_s))$] which is equal to a absolute viscosity at infinite value of temperature ($A_s = \eta_\infty$) is showed in Table-3 and are plotted *versus* mole composition of DMF (1) in Fig. 6.

The A_s-values are very close to the shear viscosity of the same system in its vapour-phase at the same pressure and at the normal boiling temperature [20-27]. Thus the high A_s-value of DMF, imply that the shear viscosity of DMF at vapour phase is nearly about ten times than of EtOH and it is also concluded that EtOH molecules bounding are more random and disordered in vapour state.

In the same context, the variation of the activation energy E_a *versus* the molar composition (x_1) can give evidence of eventual change or modification in the complex structure or clusters

TABLE-3
ACTIVATION ENERGY, E_a (kJ mol^{-1}), PRE-EXPONENTIAL FACTOR OF ARRHENIUS, A_s (10^{-6} Pa·s) AND MOLAR ENTHALPY AND MOLAR ENTROPY OF ACTIVATION OF VISCOUS FLOW, ΔH* (kJ mol^{-1}) AND ΔS*/(J K^{-1} mol^{-1}) FOR {DMF (1) AND EtOH (2)} SYSTEMS *versus* OF THE MOLE COMPOSITION (x_1) OF DMF IN THE ABSOLUTE TEMPERATURE DOMAIN (303.15 to 323.15) K

x_1	E_a (kJ mol^{-1})	A_s (10^{-6} Pa·s)	ΔS* (J K^{-1} mol^{-1})	ΔH* (kJ mol^{-1})
0.000000	16.227	1.7327	4.6915	15.322
0.020202	16.207	1.7911	4.5183	15.303
0.040404	16.146	1.8580	4.3172	15.241
0.060606	16.019	1.9586	3.9840	15.115
0.080808	15.921	2.0272	3.8027	15.017
0.10060	15.745	2.1534	3.3972	14.840
0.15152	15.093	2.6860	1.8325	14.192
0.19910	14.453	3.3259	0.31307	13.558
0.25253	13.854	4.0498	-1.0454	12.960
0.30030	13.420	4.6616	-1.9540	12.534
0.35354	13.027	5.2955	-2.7338	12.145
0.39990	12.703	5.8982	-3.3837	11.825
0.45455	12.242	6.9127	-4.4017	11.373
0.49910	11.846	7.9403	-5.2998	10.986
0.54545	11.410	9.2670	-6.3417	10.552
0.56566	11.225	9.8933	-6.7750	10.369
0.59960	10.884	11.174	-7.6113	10.029
0.64646	10.593	12.351	-8.1755	9.7476
0.69880	10.396	13.179	-8.4466	9.5494
0.74747	10.189	14.131	-8.7352	9.3518
0.80100	10.051	14.738	-8.7699	9.2234
0.84848	9.9932	14.937	-8.6343	9.1629
0.90070	9.8069	15.891	-8.8447	8.9823
0.92929	9.6456	16.838	9.1779	8.8180
0.94949	9.5458	17.480	-9.3756	8.7175
0.96970	9.4718	18.000	-9.5051	8.6437
1.00000	9.4793	18.088	-9.3754	8.6501

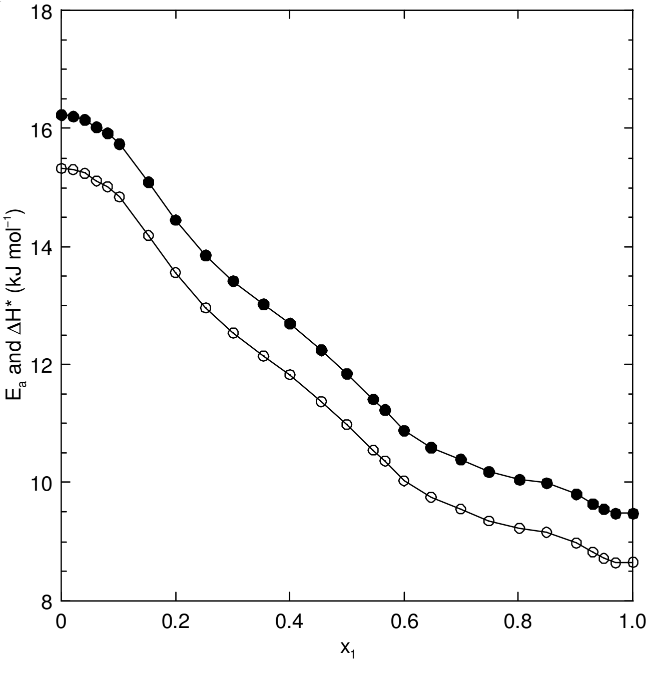

Fig. 4. Activation energy E_a and molar enthalpy of activation of viscous flow ΔH* for {DMF (1) and EtOH (2)} systems against the mole composition x_1 of DMF over the absolute temperature domain (303.15 to 323.15) K, (●): E_a/kJ·mol^{-1}; (○): ΔH* (kJ mol^{-1})

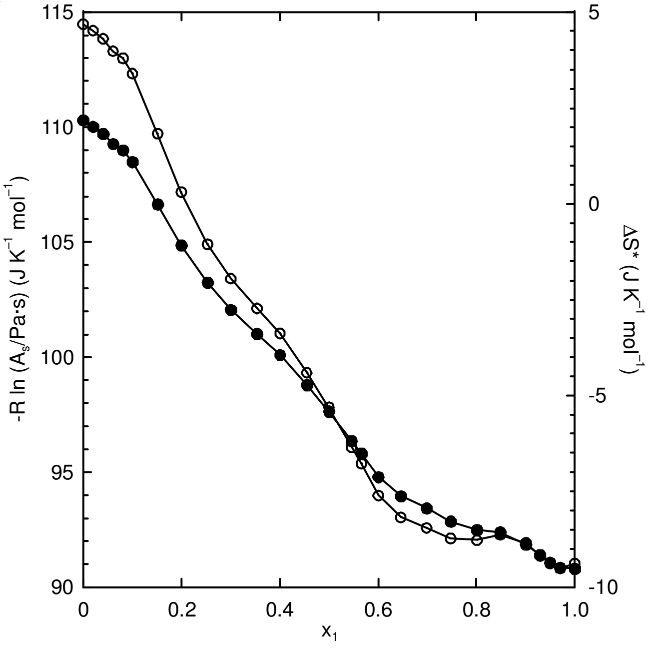

Fig. 5. Arrhenius entropic factor of –R ln (A_s) and molar entropy of activation of viscous flow ΔS* for {DMF (1) and EtOH (2)} systems against the mole composition x_1 of DMF over the temperature range (298.15 to 323.15) K. (●) –R ln(A_s/Pa·s) (J K^{-1} mol^{-1}); (○): ΔS* (J K^{-1} mol^{-1})

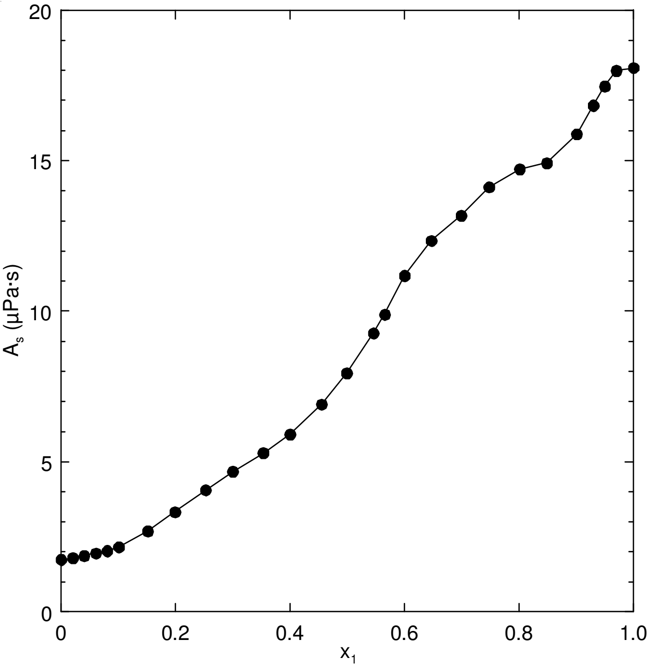

Fig. 6. Pre-exponential factor (η_∞ or A_s) in mPa·s for {DMF (1) and EtOH (2)} systems against the mole composition x_1 of DMF in the temperature range (303.15 to 323.15) K

formed in binary fluid systems under effect of temperature and/or mixture composition [20-27]. When the activation energy E_a for the full mole compositions in the studied fluid system is depicted in Fig. 4. It is found that there is only an monotonous decrease in activation energy E_a with the mole fraction of DMF (x_1). Also, there is no observable clear change of curvature detected in Fig. 5.

Monotonous dependence of the activation energy E_a and of the entropic factor of Arrhenius –R ln (A_s), suggests that there is a progressively change of solvent's structure when we progressively introduce one pure component into other in the fluid mixture. These observations imply that the clustering structure in present studied system is controlled by the same mechanism as simple associating systems, which should in turn aid in the control of dispersion of these molecules [20-50].

While, the decrease of $E_a(x_1)$ with the composition of DMF (x_1) is strictly monotonous, without any extremum, the excess activation energy [$E_a^E = E_a(x_1) - x_1 \cdot E_a(1) - (1 - x_1) \cdot E_a(0)$] plotted *versus* the composition of DMF (1) in Fig. 7 supposes that it is an indication of a cluster formation that may occur at high dilution of DMF in EtOH.

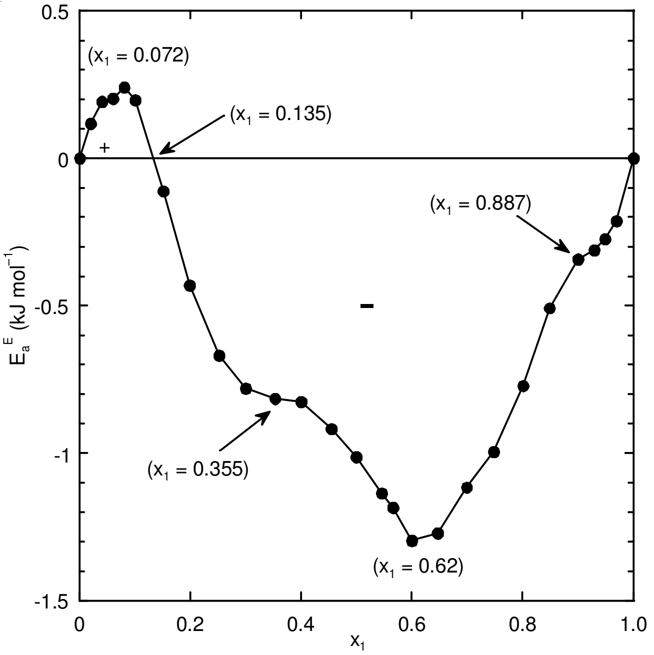

Fig. 7. Variation of the excess activation energy E_a^E for DMF (1) + EtOH (2) mixtures *versus* mole composition x_1 in DMF calculated over the absolute temperature domain (303.15 to 323.15) K

The change of sign in the excess molar activation energy can be explained by a change of the nature of structure between molecules. We observe then, a maximum at ($x_1 = 0.072$) and a minimum at ($x_1 = 0.62$), which can be interpreted by assuming complex formation between DMF and EtOH molecules, corresponding approximately to: ($x_1 = 0.072$, 1DMF:13 EtOH and for $x_1 = 0.62$, 8DMF:13EtOH).

Moreover, investigations of Herráez universal exponent P_{ij} can give indication to the present nature of interaction at very high dilution of one component in the other one. Herráez *et al.* [37,38] suggested correlation empirical equation (eqns. 4 or 7) which introduces a correcting polynomial (eqns. 5 and 8) as an exponential-acting upon the molar composition of one of the mixture's liquid pure components.

It revealed that the deviations of absolute viscosity determined with the Herráez equation generally lead to reliable results for several studied fluid mixtures showing strictly monotonous variation in dynamic viscosity values with molar fraction, but the model records inferior performance when distribution exhibits an extremum [37,38]. Then, the following expression was proposed:

$$\eta(x_1) = \eta_2 + (\eta_1 - \eta_2)\cdot x_1^{P12,T(x1)} \quad (4)$$

where $P_{12,T}(x_1)$ is a polynomial in a power with an (n)-order and (n+1) adjustable parameters $B_{p,T}$:

$$P_{12,T}(x_1) = \sum\nolimits_{p=0}^{p=n} B_{p,T} \cdot x_1^p \quad (5)$$

Thus, the Herráez $P_{12,T}(x_1)$ polynomials (eqn. 5) can be examined graphically and experimentally (Fig. 8) using eqn. 6.

$$P_{12,\exp,T}(x_1) = \frac{\ln\left(\dfrac{\eta_{\exp,T}(x_1) - \eta_2}{\eta_1 - \eta_2}\right)}{\ln x_1} \quad (6)$$

where η_1 and η_2 are the absolute viscosity of pure liquid components DMF (1) and EtOH (2), respectively and $\eta_{\exp,T}(x_1)$ the absolute viscosity of fluid mixture at the DMF mole fraction x_1 and temperature T for [x_1 = 0,1].

On the other face of the model (*i.e.* η *versus* x_2) and when it is mathematically acceptable we can express the absolute viscosity of mixture as follows:

$$\eta(x_2) = \eta_1 + (\eta_2 - \eta_1)\cdot x_2^{P21,T(x2)} \quad (7)$$

where $P_{21,T}(x_2)$ is a polynomial in a power with an (n)-order and (n + 1) adjustable parameters $B'_{p,T}$:

$$P_{21,T}(x_2) = \sum\nolimits_{p=0}^{p=n} B'_{p,T} \cdot x_2^p \quad (8)$$

Evenly, the Herráez $P_{21,T}(x_2)$ polynomials (eqn. 8) can also be examined graphically and experimentally (Fig. 8) using eqn. 9.

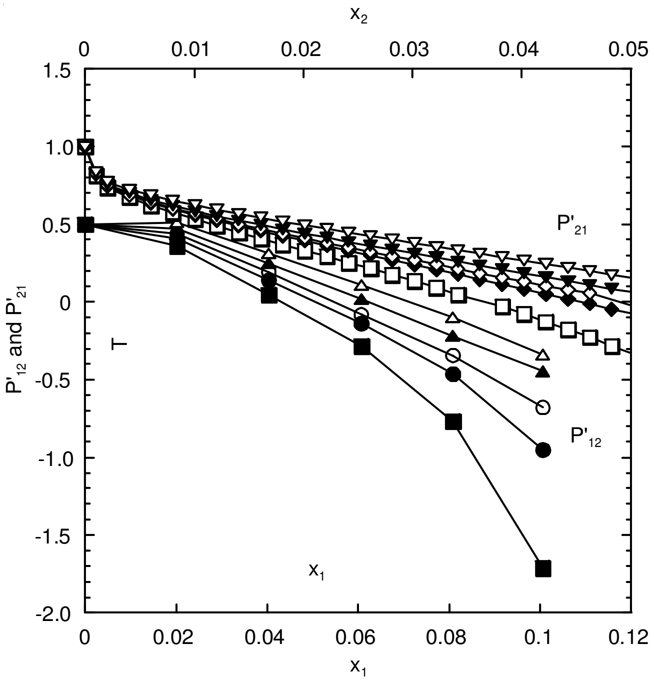

Fig. 8. Experimental Herráez exponents $P'_{12,\exp,T}(x_1)$ (eqn. 5) for {DMF (1) and EtOH (2)} systems *versus* DMF mole fraction x_1 at the temperatures, (●): 303.15 K; (○): 308.15 K; (▲): 313.15 K; (△): 318.15 K; (■): 323.15 K and variation of $P'_{21,\exp,T}(x_2)$ (eqn. 8) for {DMF (1) and EtOH (2)} systems *versus* EtOHmole fraction x_2 at the temperatures, (□): 303.15 K; (◆): 308.15 K; (◇): 313.15 K; (▼): 318.15 K; (▽): 323.15 K

$$P_{21,\exp,T}(x_2) = \frac{\ln\left(\dfrac{\eta_{\exp,T}(x_2) - \eta_1}{\eta_2 - \eta_1}\right)}{\ln x_2} \qquad (9)$$

where η_1 and η_2 are the absolute viscosity of pure liquid components DMF (1) and EtOH (2), respectively and $\eta_{\exp,T}$ (x_2) the absolute viscosity of fluid mixture at the EtOH molar fraction x_2 and absolute temperature T for $[x_2 = 0.1]$.

Although, at infinite dilution $(x_i \to 0^+)$, it is observed that the $P_{\exp,T}$ (x_i) values tend to a unique point $[P_{\exp,T}(0) = 1.0]$ independent of temperature (Fig. 8) given then a fixed value of $B_{0,T}$ or $B'_{0,T}$ constant corresponding to the first monomial of $P_{ij,T}(x_i)$ in eqns. 5 or 8. It shows that the ion-ion or solute-solute interaction is absent at very high dilution of DMF or of EtOH in the two limiting rich regions. Same suggestion is reported in previous works [39-43] studying absolute viscosity in 1,4-dioxane and isobutyric acid liquid mixtures with water. It is concluded that the first coefficient B_0 is considered as a universal exponent characterizing the nature of present or dominant interaction at infinite dilution.

So, in case of very high diluted solution of DMF (1) in EtOH (2), we can express the limiting asymptotic expansion as follows:

$$\eta = \eta_2(1 + a_1x_1^{1/2} + a_2x_1 + a_3x_1^{3/2} + \cdots) \qquad (10)$$

Likewise, in the reverse case of very high diluted solution of EtOH (2) in DMF (1), we can express the limiting asymptotic expansion as follows:

$$\eta = \eta_1(1 + b_1x_2^{1/2} + b_2x_2 + \cdots) \qquad (11)$$

Moreover, in the basic of the extended conformal solution (ECS) theory [51-54], the reduced Redlich-Kister (R-K) term $Q_{\exp,T}$ $(x_1 = 1)$ is the regular absolute viscosity term (eqn. 12) and denoted as η_{21} [43,51-54]. Therefore, it's possible to deduce the value of b_2 coefficient for a nonelectrolyte binary solution as given by Nakagawa [52] as follows:

$$b_2 = [(\eta_2 - \eta_1) + \eta_{21}]/\eta_1 \qquad (12)$$

where the subscripts (1) and (2) denote (DMF) and (EtOH), respectively and η_{21} is equal to the famous reduced (R-K) function $Q_{\exp,h,T}$ $(x_1 = 1)$ as defined in previous works [22-27], which is expression by the ratio of (eqn. 13) representing the experimental reduced R-K excess quantities $Q_{Y,\exp,T}(x_1)$,

$$Q_{Y,\exp,T}(x_1) = Y^E/(x_1(1 - x_1)) \qquad (13)$$

where Y^E denotes the property deviation or the excess property.

Moreover, the values of reduced (R-K) functions $Q_{Y,T}$ (x_i) at infinite dilution represent values of the equivalent of the excess partial molar physicochemical properties at infinite dilution $(x_1 \to 0^+)$ [55], which can be also determined from the adjustable parameters using eqns. 14 and 15:

$$Q_{\eta,T}(x_1 = 0) = (\eta_1 - \eta_2)\cdot[1 + (\partial\ln(\eta - \eta_2)/\partial x_1)_{T,x1=0}] \qquad (14)$$

and

$$Q_{\eta,T}(x_1 = 1) = (\eta_1 - \eta_2)\cdot[1 - (\partial\ln(\eta - \eta_2)/\partial x_1)_{T,x1=1}] \qquad (15)$$

The b_2 coefficient (eqn. 12) may be divided in the two parts: the first B_{id} which is based on the contribution of ideal fluid mixture (term in parenthesis in eqn. 12) and the second B_n coefficient is based on the net interaction between the solvent such as (DMF) and the solute such as (EtOH) [53,54].

Considering the eqns.4 to 6 and the limiting expansion of eqn. 10 we can express the experimental Herráez polynomial $P_{12,T}(x_1)$ in a first order limiting expansion at very high dilution of DMF in EtOH:

$$P_{12,\exp,T}(x_1) = ½ + \frac{\ln\left(\dfrac{\eta_2}{\eta_1 - \eta_2}\cdot a_1\right) + \dfrac{a_2}{a_1}\cdot x_1^{½}}{\ln x_1} \qquad (16)$$

We can easily justify the limit value of $P_{12,T}(x_1)$ at infinite dilution of DMF as:

$$(\lim_{x_1 \to 0^+} P_{12,T}(x_1) = ½)$$

and thus it is concluded that the first monomial of $P_{12,T}(x_1)$ is a constant value independent of temperature and equal to 0.5 for the absolute viscosity h (*i.e.* $B_{n,0,T} = 0.5$) of this fluid mixture-type. We add that the 0.5-value of the Herráez universal exponent B_0 leads us to assert the presence of the $(a_1x_1^{1/2})$-term in eqn. 10 which justifies the abrupt changes in slope observed at low mole composition (x_1) in Fig. 8. In fact, values of the experimental reduced RK related to the absolute viscosity deviation $Q_{h,T}(x_1)$ (eqn. 13) must diverge at the boundary when $(x_1 \to 0^+)$) due to divergence of values of the derivative function in eqn. 14.

Hence, we can notice that in the case of nonelectrolyte solution when the parameter of Falkenhagen [56] (solute-solute interaction) is null or vanish small $(b_1 = 0)$ and considering the eqns. 7 and 9, we can re-express the eqn. 11 in a new limiting asymptotic expansion at very high dilution solution of EtOH (2) in DMF (1) or the reverse. Thereby, we obtain then the following expression:

$$P_{21,\exp,T}(x_2) = 1 + \frac{\ln\left(\dfrac{\eta_1}{\eta_2 - \eta_1}b_2\right) + o(x_2)}{\ln x_2} \qquad (17)$$

from which we can obtain the following limit:

$$(\lim_{x_i \to 0^+} P_{\exp,T}(x_i) = 1)$$

and at high dilution, only the interaction solute-solvent is existent or dominant. Notice that the Herráez universal exponent B_0 of the polynomial tends to the power value of the existent term of eqn. 10.

Starting from the fact that the reduced RK excess quantities $Q_{Y,\exp,T}(x_1)$ [20-27] in binary fluid mixtures, gives evidence of some information on the deviation to linearity (or ideality) and from the relationship [28-33] between the surface tension (γ), the absolute viscosity (η) and the friccohesity (σ), we can remark that the discussion only on the RK reduced quantities related to the absolute viscosity $Q_{\exp,h,T}(x_1=1)$ [20-27] is insufficient because it implicitly consider different natures of interaction's forces (cohesive and frictional forces, *etc.*). Then, we must explicit these different manifestations of forces from the surface tension (γ) and the friccohesity (σ) [28-33]. Applying eqn. 13 separately on the three properties [friccohesity, absolute viscosity and surface tension $(\sigma = \eta/\gamma)$], we can obtain the interesting following relationships (eqns. 18-21) which demonstrates that the discussion and interpretation must not be restricted only to the property of absolute viscosity but also it must take in consideration the surface tension and friccohesity.

$$Q_{exp,\eta,T}(x_1) = x_1 \cdot q_1 + x_2 \cdot q_2 + x_1 x_2 \cdot q_{12} \quad (18)$$

$$q_1 = \sigma_1 \cdot Q_{exp,g,T}(x_1) + \gamma_1 \cdot Q_{exp,\sigma,T}(x_1) - \Delta\sigma . \Delta\gamma \quad (19)$$

$$q_2 = \sigma_2 \cdot Q_{exp,g,T}(x_1) + \gamma_2 \cdot Q_{exp,\sigma,T}(x_1) - \Delta\sigma . \Delta\gamma \quad (20)$$

$$q_{12} = Q_{exp,\gamma,T}(x_1) \cdot Q_{exp,\sigma,T}(x_1) \quad (21)$$

where ($\Delta\sigma = \sigma_2 - \sigma_1$) and ($\Delta\gamma = \gamma_2 - \gamma_1$) are the difference between the property values of the pure components EtOH (2) and DMF (1), respectively. We can add that the graphical representation of these properties *versus* the composition (x_1) can also be an original interesting basis for discussion and interpretation.

Molar enthalpy and molar entropy of activation of viscous flow: It is noticed that in the case of liquid phase we can mention that the absolute reaction rate theory of Eyring *et al.* [57] and Ali *et al.* [58] relates the Gibbs free energy (ΔG^*) of activation of viscous flow to the kinematic viscosity as follows:

$$\Delta G^*(x_1, T, P) = RT \cdot \ln\left(\frac{\eta(x_1, T, P) \cdot V(x_1, T, P)}{hN_A}\right) \quad (22)$$

where η, h, R, N_A and V are the dynamic viscosity of binary fluid mixture, Plank's constant, ideal gas constant, Avogadro's number and molar volume of fluid mixture at molar composition (x_1) (eqn. 24), respectively and:

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (23)$$

$$V = \frac{x_1 M_1 + (1 - x_1) M_2}{\rho} \quad (24)$$

where ρ is the density of binary fluid mixture, M_1 and M_2 are the molar mass of the pure fluid component of DMF and EtOH, respectively and, ΔH^* and $\rho\Delta S^*$ are the molar enthalpy and molar entropy of activation of viscous flow, respectively.

By assuming that the two parameters of activation of viscous flow ΔH^* and ΔS^* [58,59] are practically independent of temperature, we obtained, for each composition of fluid mixture (x_1, x_2) these parameters values when $R.\ln[\eta \cdot V/(h \cdot N_A)]$ is plotted against 1/T. Using both least-square fit and graphical method, the intercept on the ordinate is equal to $-\Delta S^*$ and the slope is equal to ΔH^*. We can use eqn. 23 to determine these parameters $\Delta H^*$and ΔS^*. In fact, the plot of $R.\ln[\eta \cdot V/(h \cdot N_A)]$ *versus* the reciprocal of temperature (1/T) is practically linear for the studied mixture and the molar enthalpy (ΔH^*) and the molar entropy (ΔS^*) become independent of temperature over the range of temperature (303.15 to 323.15) K. Values of the molar enthalpy (ΔH^*) and molar entropy (ΔS^*) are given in Table-3 and are plotted *versus* the composition of DMF (1) in Figs. 4 and 5, respectively.

Correlation between Arrhenius parameters: Generally, investigation of the parameters of Arrhenius [E_a and $\ln(A_s)$] leads us to spotlight eventual present distinct behaviours which are distinctly shown when the correlation between order and disorder is schematized [20-27] through the activation energy E_a of absolute viscosity *versus* the entropic factor of Arrhenius – R $\ln(A_s)$ (Fig. 9).

Fig. 4 shows that there is continuous decrease of the activation energy (E_a) with the composition of DMA (x_1) without any present extremum in the curve. There is also no clearly observable change of curvature found when the activation energy (E_a) is plotted with the entropic factor ln A_s in Fig. 9. Monotonous variation of the activation energy (E_a), implies that there is a little by little, change of the structure of liquid solvent when we introduce one component into the other into the liquid mixture.

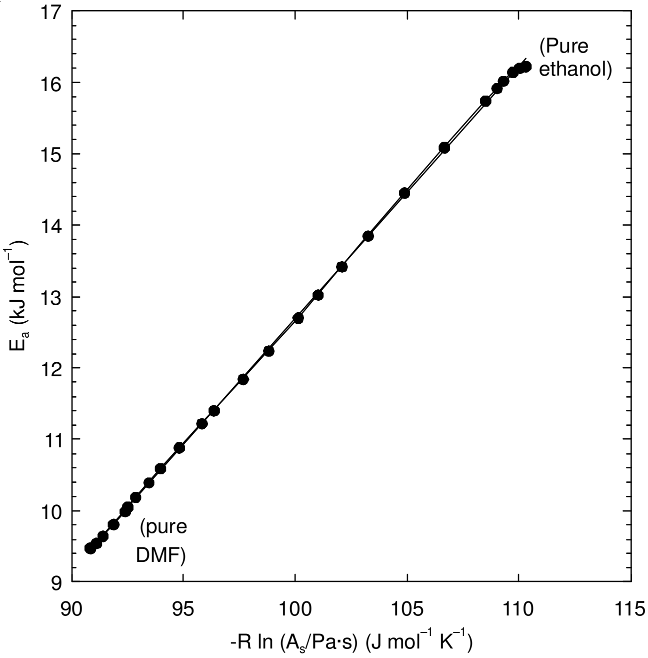

Fig. 9. Correlation between the activation energy E_a (kJ mol^{-1}) and the entropic factor of Arrhenius – $R \cdot \ln(A_s/Pa \cdot s)/(J \cdot K^{-1} \cdot mol^{-1})$for {DMF (1) and EtOH (2)} systems in the absolute temperature domain (303.15 to 323.15) K. (•): experimental data points; (—): non linear least square fit

The analogous behaviour is observed in the binary system of DMA + N,N-dimethylformamide [26]. In our case, we observe a quasi-linear behaviour limited by a very feeble curvature at very diluted region of DMF in EtOH which is characterized by the molar fraction ($x_1 = 0.059 \approx 1/17$) where there is a change of structure and brings to light more distinct structures [3,43]. We add that for the precedent particular molar fraction the interpretation of the molecular liquid structure can be based on "Neighborhood Model Approach" [6,28-43,60] whereas the beginning introduction of DMF molecules into pure EtOH liquid, preferentially creates the stable cluster (1DMF:16EtOH) where one DMF molecule is surrounded by 16EtOH molecules roughly without notably modification the structure of pure EtOH [49].

In general, the activation energy $E_a(x_1)$ increases against the entropic factor $- R \cdot \ln(A_s)$ [20-27]. In addition, we can consider roughly the linear behaviour which is also noticed for some other studied binary liquid mixtures like water with 1,4-dioxane or isobutyric acid or DMA, *etc.* [2,6,20-22,25,44-50].

We can add that for each fluid mixture; even in the case of the existing of different domains with distinct behaviours in Fig. 9, we observe that all different branches of curves in this figure indicate approximately the same slope value of their quasi-straight line for which we can write the following standardized equation:

$$-\frac{E_a}{R} = T_A \cdot \ln(A_s) + B \quad (25)$$

where B is a constant related to the absolute viscosity of the fluid mixture at boiling temperature and which is equal to the intercept on the ordinate when the value of ln A_s is theoretically zero; while the slope T_A specifies each binary fluid system and it is worth to an absolute temperature for which we propose the viscosity Arrhenius temperature as a name for the related treated binary fluid mixture [2,6,20-27,49].

It is also noted that the T_A–values for all the treated fluid systems are not far from the boiling points (T_{bi}) of the corresponding constituting pure fluid components. In the case of the DMF-EtOH fluid mixtures, the T_A value which deduced from linear least square (Fig. 9) is equable to 353.2 K with a correlation factor R = 0.99991, while the boiling temperature of DMF and EtOH are 426.15 K and 335.15 K, respectively. It is concluded that the Arrhenius temperature T_A is in close relationship to the average value of the temperature's function $T(x_1)$ in all the composition range of the liquid-vapour equilibrium (T–x) of the system DMF-EtOH at the same studied constant pressure.

We can add that our future plan will to indicate that the Arrhenius temperature T_A is in close causal correlation with the average value of the temperature function $T(x_1)$ *versus* molar composition (x_1) in the interval [0,1] for the isobaric liquid-vapour diagram and which can be expressed as follows:

$$\int_0^1 T(x_1,P)dx_1 \sim T_A(P) \qquad (26)$$

and the Arrhenius temperature T_A is roughly the average height of the temperature-composition graph ($T–x_1$) of the corresponding isobaric phase diagram at the same studied pressure of the treated binary system. Also, depending on weather the T_A–value is overvalued, undervalued or framed by one of the boiling temperature T_{bi} of one pure fluid component, we can estimate roughly the graph-type of the temperature-composition ($T–x_1$) phase diagram (regular or azeotropic with low or high boiling temperature).

Thermodynamic characters

Correlations with molar enthalpy of activation of viscous flow: Examination of the E_a-values and those of the molar enthalpy (ΔH^*) (Table-3, Fig. 4) shows that the E_a and ΔH^* values have similar behaviour and are very close. So, we can express the difference between E_a-values and those of the molar enthalpy (ΔH^*) (Table-3) with an increment δH^* which it is expressed as follows [20-27,58]:

$$\Delta H^* = E_a – \delta H^* \qquad (27)$$

where:

$$\delta H^* = x_1 \cdot \delta H^*_1 + x_2 \cdot \delta H^*_2 + x_1 \cdot x_2 \cdot \delta H^*_{12} \qquad (28)$$

and where $\delta H^*_1 = 0.8209$ kJ mol^{-1} and $\delta H^*_2 = 0.9117$ kJ mol^{-1} are the molar enthalpy increments related to the pure fluid components DMF (1) and EtOH (2), respectively and $\delta H^*_{12} = – 0.1038$ J mol^{-1} is a term of interaction increment (Fig. 4). Similarly, we can add that the molar entropy (ΔS^*) is closely correlated (Fig. 5) with the entropic factor ($–R \cdot \ln A_s$) for which its difference can be expressed by the increment of molar entropy (δS^*) as follows:

$$\Delta S^* = –R \cdot \ln A_s – \delta S^* \qquad (29)$$

where:

$$\delta S^* = x_1 \cdot \delta S^*_1 + x_2 \cdot \delta S^*_2 + x_1 \cdot x_2 \cdot \delta S^*_{12} \qquad (30)$$

where $\delta S^*_1 = 100.16$ J K^{-1} mol^{-1} and $\delta S^*_2 = 105.61$ J K^{-1} mol^{-1} are molar entropy increments related to the pure fluid components DMF (1) and EtOH (2), respectively and $\delta S^*_{12} = 0.2376$ J K^{-1} mol^{-1} is a term of interaction increment (Fig. 5).

Otherwise, we can remark that there is a quasi-linear dependence between E_a and ΔH^* and also between $–R \cdot \ln(A_s)$ and ΔS^* (Fig. 10).

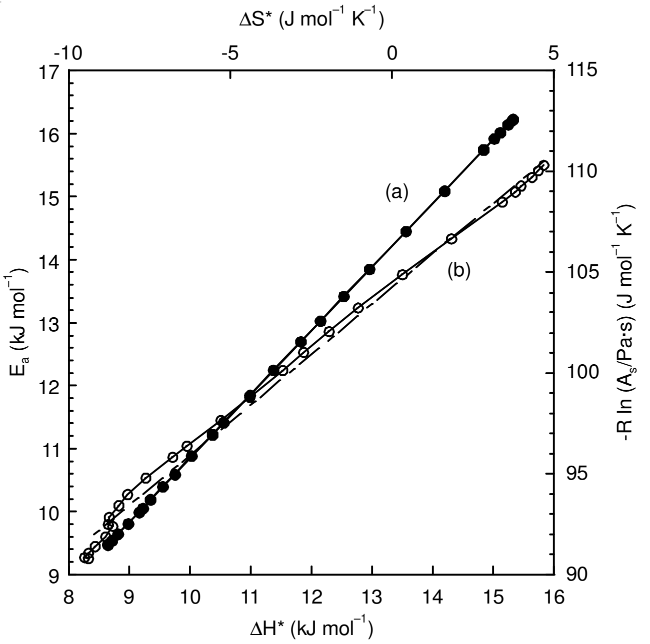

Fig. 10. Correlation between: (a): the activation energy E_a (kJ mol^{-1}) and the molar enthalpy ΔH^* (kJ mol^{-1}) for DMF (1) and EtOH (2) systems calculated over the absolute temperature domain (303.15 to 323.15) K. (•): experimental data points; (—): linear least square fit. (b): the entropic factor of Arrhenius $–R \cdot \ln(A_s/Pa \cdot s)$ (J K^{-1} mol^{-1}) and the molar entropy ΔS^* (J K^{-1} mol^{-1}) for DMF (1) and EtOH (2) systems calculated over the absolute temperature domain (303.15 to 323.15) K. (o): experimental data points; (—): linear least square fit

We observe that the straight lines Y = f(X) representing the linear regression can be expressed as follows: (Y = 0.72489 + 1.0122X) for $E_a = f(\Delta H^*)$ and (Y = 104.25 + 1.3318X) for $–R \cdot \ln(A_s) = f(\Delta S^*)$; an R-coefficients value as: R = 0.99999 and R = 0.99767, respectively. So, the two dimensionless slops are close to the unit with a deviation about 1.2 and 33.2 %, respectively, due to the average thermal expansion and the volume effect at atmospheric pressure and in the treated range of temperature.

Partial molar activation energy: In view of the quasi-linear behaviour between ΔH^* and the E_a and also, between ΔS^* and $–R \cdot \ln(A_s)$, presented earlier, we can consider roughly that $E_a(x_1)$ can be considered approximately a classical thermodynamic state function and we can then talk about the corresponding partial molar properties Y_1 and Y_2 for DMF (1) and EtOH (2), respectively through the derivative thermodynamic following equations:

$$Y_1(x_1,T,P) = Y(x_1,T,P) + (1 - x_1) \cdot \left(\frac{\partial Y(x_1,T,P)}{\partial x_1} \right)_{T,P} \qquad (31)$$

$$Y_2(x_1,T,P) = Y(x_1,T,P) + x_1 \cdot \left(\frac{\partial Y(x_1,T,P)}{\partial x_1} \right)_{T,P} \qquad (32)$$

where Y_i indicates the partial molar property related to the activation energy E_{ai} or to the entropic factor $-R \cdot \ln(A_{si})$ and (i) is equal to 1 or 2 and related to DMF (1) and EtOH (2), respectively.

This thermodynamic handling is interesting because the partial activation energy $E_{ai}(x_1)$-values reveal eventual individual contribution of each pure fluid component (i) and preferential phenomena in concurrence with each given binary fluid mixture composition (x_1, x_2).

Values of different partial molar quantities $E_{a1}(x_1)$, $E_{a2}(x_1)$, $-R \cdot \ln(A_{s1})$ and $-R \cdot \ln(A_{s2})$ are given in Table-4 and $E_{a1}(x_1)$ and $E_{a2}(x_1)$ with $E_a(x_1)$, plotted in Fig. 11 *versus* mole composition (x_1) in DMF.

TABLE-4
PARTIAL MOLAR QUANTITIES RELATIVE TO THE ACTIVATION ENERGIES, E_{ai} (kJ mol^{-1}) AND THE ENTROPIC FACTOR $-R \cdot \ln(A_{si}/Pa \cdot s)$ (J K^{-1} mol^{-1}) FOR {DMF (1) AND EtOH (2)} SYSTEMS AGAINST OF THE MOLE COMPOSITION OF DMF (x_1) OVER THE ABSOLUTE TEMPERATURE DOMAIN (303.15 TO 323.15) K

x_1	E_{a1} (kJ mol^{-1})	E_{a2} (kJ mol^{-1})	$-R \cdot \ln A_{s1}$ (J K^{-1} mol^{-1})	$-R \cdot \ln A_{s2}$ (J K^{-1} mol^{-1})
0.000000	16.269	16.227	92.834	110.30
0.020202	16.051	16.211	92.906	110.38
0.040404	12.010	16.320	92.007	110.46
0.060606	9.0492	16.469	90.581	110.49
0.080808	7.0236	16.704	88.263	110.82
0.10060	5.6718	16.872	84.207	111.21
0.15152	4.5721	16.972	77.233	111.91
0.19910	4.8903	16.830	80.924	110.83
0.25253	6.2369	16.427	84.607	109.53
0.30030	7.4021	16.002	86.206	108.88
0.35354	8.1657	15.686	86.332	109.04
0.39990	8.2741	15.654	85.675	109.73
0.45455	7.8104	15.935	84.754	110.49
0.49910	7.2517	16.425	84.548	110.69
0.54545	7.1031	16.578	84.994	109.99
0.56566	7.2403	16.413	85.410	109.36
0.59960	7.5351	15.898	86.190	107.70
0.64646	8.6872	14.079	87.928	105.01
0.69880	9.1796	13.220	89.886	101.65
0.74747	9.3476	12.678	90.883	98.667
0.80100	9.5819	11.937	91.321	97.242
0.84848	9.6007	12.191	91.326	98.333
0.90070	9.3253	14.175	90.857	101.08
0.92929	9.2595	14.720	90.562	102.30
0.94949	9.2769	14.602	90.474	102.47
0.96970	9.3800	12.410	90.502	101.54
1.00000	9.4793	9.0693	90.796	96.691

It is observed that the partial molar quantity $E_{a1}(x_1)$ related to DMF regularly decreases from a maximum (about 16 kJ mol^{-1}) to tend to a local minimum (about 4.5 kJ mol^{-1}) at (x_1 = 0.16), then increases lightly to attain a local maximum (about 8.1 kJ mol^{-1}) at (x_1 = 0.40) and decreases lightly to tend once again to a local minimum (about 7.2 kJ mol^{-1}) at (x_1 = 0.55), then increases to reach the value of pure DMF (around 9.28 kJ mol^{-1}). This behaviour supposes that at high dilution of DMF, the introduction of DMF into EtOH promotes the hetero-association formation through multiple hydrogen bounds between the polar groups of unlike molecules till the molar fraction x_1 ≈ 016 = 1/6 (1DMF:5EtOH) where there is a beginning of structure changing of EtOH [1-14].

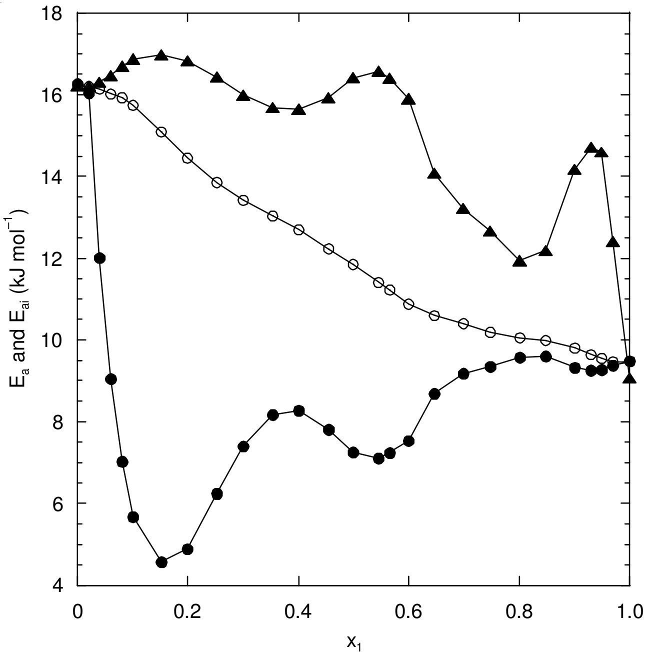

Fig. 11. Activation energy E_a (kJ mol^{-1}) and related partial activation energies (eqns. 5 and 6) E_{ai} (kJ mol^{-1}) for {DMF (1) and EtOH (2)} systems *versus* of the mole composition of DMF (x_1) over the absolute temperature domain (303.15 to 323.15) K. (○): $E_a(x_1)$; (●): $E_{a1}(x_1)$ and (▲): $E_{a2}(x_1)$

Otherwise, the partial molar activation energy of EtOH $E_{a2}(x_1)$ varies in a reverse manner (Fig. 11) in the second sense of abscissa axis (*i.e.* against molar composition x_2 of EtOH), except it tends to a local maximum at high dilution of EtOH in DMF at (x_1 = 0.93 ≈ 15/16).

Then, the introduction of molecules of DMF (1) in the EtOH-rich domain, meet easiness to become integrated into the layers' of EtOH molecules. Likewise, the introduction of molecules of EtOH (2) in the DMF-rich domain, meet hardness to become integrated into the layers' of DMF molecules.

This asymmetrical behaviour at very low concentration can be proved by the Herráez exponent value. Hence, we remember that the exponent B_0 of Herráez equation [37,38] at infinite dilution (Fig. 8) indicates that $B_{0,T}$ whatever the temperature, take a half unit-value in the case of the DMF in EtOH while it take a unit-value the EtOH in DMF (eqns. 16 and 17). Then, we can conclude that in case of the high dilution of DMF in EtOH, the solute-solvent interaction is absent while the solute-solute interaction is absent in the case of high dilution of EtOH in DMF.

Moreover, the distinct shapes of variation of $E_{ai}(x_1)$-values (Fig. 11) conducts us to remove the mole composition x_1 as an explicit variable and to plot mutual correlation between the two partial activation energies $E_{a1}(x_1)$ and $E_{a2}(x_1)$ (Fig. 12).

It is observed that the individual contribution of DMF (1) and EtOH (2) on the activation energy indicates distinctly the delimitation of regions of EtOH solvation in DMF and the transition from one structure to another is brusque. The change in the coefficient of temperature of dielectric constant

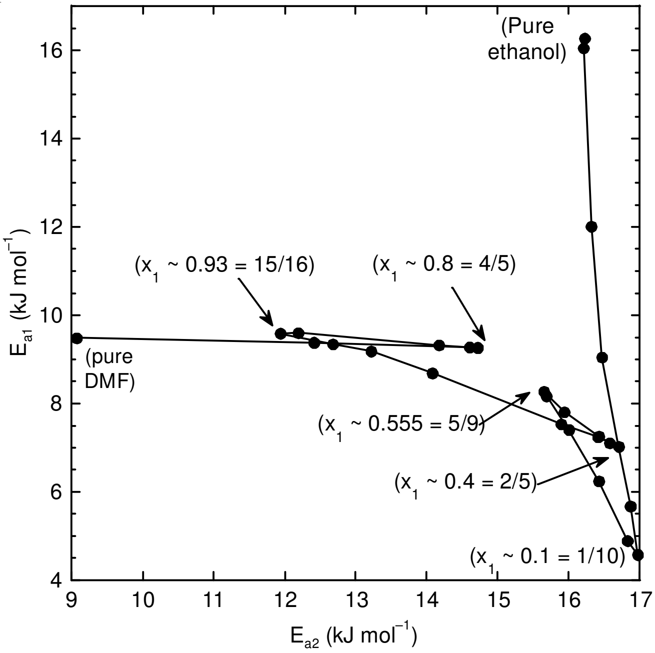

Fig. 12. Correlation between the partial molar activation energies $Ea_1(x_1)$ and $Ea_2(x_1)$ for {DMF (1) and EtOH (2)} systems over the absolute temperature domain (303.15 to 323.15) K

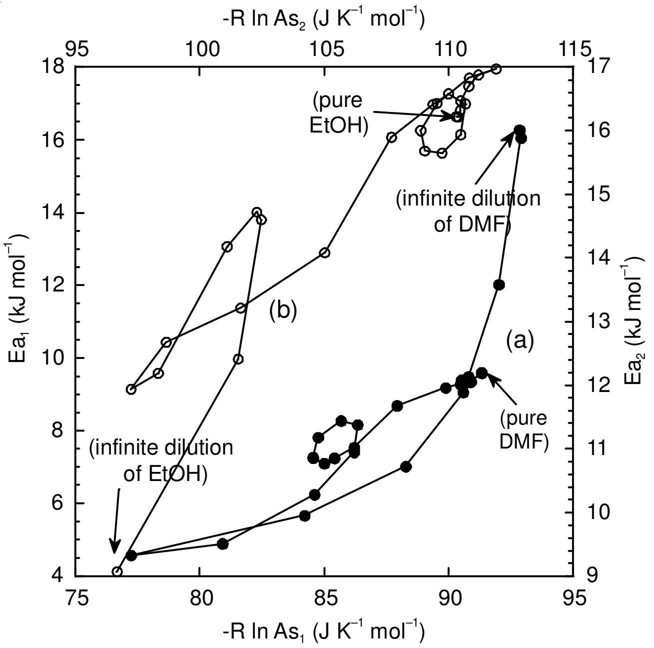

Fig. 13. Correlation between the partial quantities relative to the activation energies E_{ai}/(kJ mol^{-1}) and the logarithm of the entropic factors –R·ln (As_i/Pa·s) (J K^{-1} mol^{-1}) related to, curve a, (%): DMF (i = 1) and curve b, (%): EtOH (i = 2) in{DMF (1) and EtOH (2)} mixtures *versus* the mole compositionof DMF (x_1) over the absolute temperature domain (303.15 to 323.15) K

drawn *versus* composition for the DMF-EtOH fluid mixtures, at 298.15 K is observed [3].

Nonetheless, if we abandon the supposition of eqn. 25 that the viscosity Arrhenius temperature (T_A) varies slightly over the full domain of molar composition, we can redefine it as new variable denoted Arrhenius' current temperatures (T_{cAi}) by deriving partial activation energy $Ea_i(x_1)$ with respect to the partial quantity corresponding to the entropic factor –R·ln(As_i) at given molar composition (x_1) and at constant pressure:

$$T_{Ai} = \left(\frac{\partial(E_{ai})}{\partial(-R\cdot\ln A_{si}}\right) \qquad (33)$$

The form of eqn. 33 is justified from thermodynamic character and the behaviour's likeness of the two Arrhenius parameters [E_{ai} (x_1) and –R·ln(A_{si})] with the molar enthalpy (ΔH^*) and molar entropy (ΔS^*) (Figs. 4 and 5, eqns. 2,23,27-32). Considering the Gibbs free energy (ΔG^*) expressed by (eqn. 23) and the partial derivatives quantities of Maxwell equations, we can envisage that the eqn. 33 it physically analogous to the following expression at constant pressure.

$$\left(\frac{\partial(\Delta H^*)}{\partial(\Delta S^*)}\right)_P = T \qquad (34)$$

The T_{cAi}-values are determined by the tangent line slope (Fig. 13) at a given point in the curve (*i.e.* at given mixture mole composition x_1).

So, we obtain interesting results especially in the neighbors of the two limits of the mole fraction domain. Then, we obtain some values of Arrhenius' current temperatures (T_{cAi}) from the slopes of the two curves given in Fig. 13 such as: in the case of very high concentration of one pure component (i) we obtain that T_{cA1} ($x_1 \approx 1$) = 405.2 K ≈ T_{b1} from the Fig. 13 curve a (i = 1) and T_{cA2} ($x_2 \approx 1$) = 385.1 K ≈ T_{b2} from the Fig. 13-curve b (i =2). Whereas in the case of very high dilution of the pure component (i) in the second one (j), we obtain that T_{cA1} ($x_1 \approx 0$) = 659.2 K > T_{b1} from the curve a and T_{cA2} ($x_2 \approx 0$) = 340.8 K > T_{b2} from the curve b.

Regarding this finding, we can estimate the boiling temperatures of the two pure liquid components at the constant studied pressure through investigation of the dependence between absolute viscosity and absolute temperature in the corresponding liquid phase mixture. We can add that this finding is also roughly checked from other treated binary liquid mixtures constituted by the following components such as: water, N,N-dimethylacetamide (DMA), 1,4-dioxane, DMF, formamide (FA), 2-methoxyethanol (MOE), 2-ethoxyethanol (EOE) and isobutyric acid (IBA) [20-22,49] (Table-5).

Taking in consideration the accuracy of experimental data and the errors in calculations, we can decide that the Arrhenius' current temperature (T_{cAi}) at ($x_i \approx 1$) is very close to its corresponding boiling point while in the other cases, (T_{cAi}) at ($x_i \approx 1$) is in causal correlation with the temperature of vapourization of the liquid-vapour equilibrium, at constant pressure, of the corresponding binary fluid mixture.

We can then affirm these observances as follows:

$$\lim_{x_i \to 1}\left(\frac{\dfrac{\partial E_{ai}(x_i)}{\partial x_i}}{\dfrac{\partial \ln A_{si}(x_i)}{\partial x_i}}\right)_P \approx -R\cdot T_{bi} \qquad (35)$$

and, we can then, estimate a value of the boiling temperature (T_{bi}) of the pure liquid component (*i*) with a reliable approximation.

TABLE-5
COMPARISON BETWEEN THE CURRENT ARRHENIUS TEMPERATURE (T_{Ai}, K) for ($x_i \approx 1$) AND THE CORRESPONDING BOILING POINT (T_{bi}, K) OF THE PURE LIQUID COMPONENT (i) IN SOME BINARY SYSTEMS

1	2	Ref.	T_{A1} (K)	T_{b1} (K)	T_{A2} (K)	T_{b2} (K)
DMA	EOE	[20]	440.0	438.45	410.0	408.15
DMA	Water	[21]	456.1	438.45	378.5	373.15
Dioxane	Water	[22]	378.6	374.25	380.5	373.15
DMF	Met	[34]	394.5	426.15	316.3	337.85
DMA	MOE	[45]	361.5	438.15	332.3	397.65
IBA	Water	[46]	433.1	428.15	362.9	373.15
DMA	DMF	[47]	330.6	438.15	329.1	426.15
DMA	Met	[48]	418.7	438.15	319.4	337.85
DMA	FA	[49]	429.1	438.15	479.6	483.65
DMF	Ethanol	[a]	398.3	426.15	367.6	351.52

[a] Present work

Causal correlation between the limiting Arrhenius' current temperatures (T_{cAi})/K at ($x_i \approx 1$) for the pure component (i) and the corresponding boiling temperature T_{bi}/K established by couple of solvents from various binary liquid systems studied at earlier works (eqns. 33 or 35) [20-27,35,39,41] is plotted in Fig. 14 and presented in the Table-5.

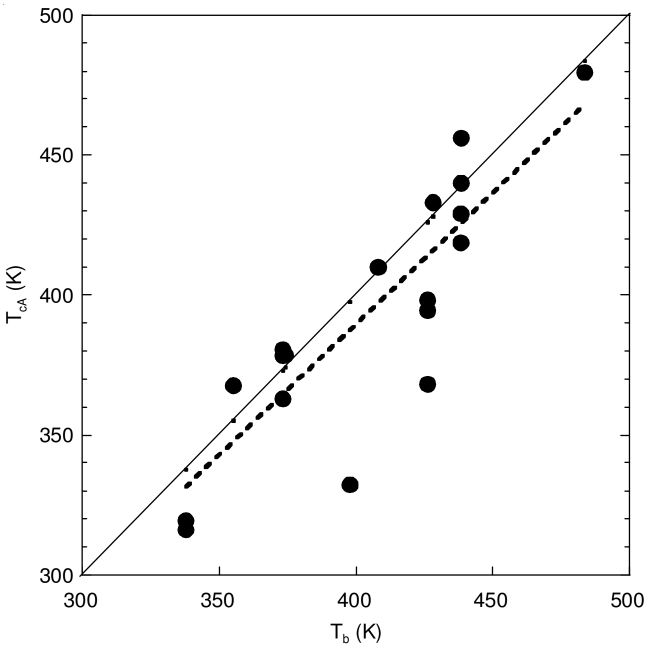

Fig. 14. Correlation between the current Arrhenius temperatures (T_{Ai})/K for ($x_i \approx 1$) for the pure solvent (*i*) and the corresponding normal boiling temperature T_{bi}/K determined by couple of components from some binary mixtures studied at earlier works (eqn. 3) [20-27,44-49]. (—): the first bisector (Y = +X) in the present axis system and (---): linear least square fit

We can see that the straight line depicting the linear regression (Y = 15.515 + 0.93547X); with a correlation coefficient R = 0.85982 is close to the straight line corresponding to the bisector (Y = +X), where X = T_{bi} and Y = T_{cAi}. In effect, the straight line slope is equable to 0.93547 which deviates from the unit to about 6.4 % for which the intercept to the ordinate has an absolute value (15.515) and it is less than the standard deviation (σ = 29.37) related to the set of boiling points handled in this correlation (where T_{bi}–values have a mean value equal to 418.23 K). In order to compare statistically the distribution of the 20 obtained Arrhenius' current temperatures (T_{Ai}/K) of some pure solvents and the corresponding boiling points(T_b/K) (Table-5), we obtain: T_{Ai}/K = (387.84 ± 21.07) and T_{bi}/K = (402.35 ± 17.93) *i.e.* with an overlap of 24.49 K where there is a reliable intersection between their corresponding confidence intervals (CI).

Moreover, a new suggested Hajkacem-Ouerfelli empirical equation (eqns. 36 and 37) [61,62] presents interesting causal correlation with reliable agreement between the viscosity Arrhenius parameters (E_a and ln A_s) for moderate and low viscous fluids (eqn. 36) which haven't very high values of activation energy (E_a < 30 kJ mol^{-1}) and alsohaven't very low values of pre-exponential factor (A_s > 42 nPa·s, *i.e.* ln(As/Pa·s) > –17).

$$E_a = \lambda \cdot R \times (-\ln A_s)^{\alpha_0} \tag{36}$$

where R is the universal gas constant, $l \approx 1$ K and $\alpha_0 = 2.933$.

It is noticed that this empirical equation can be also used for the two Arrhenius parameters related to some binary fluid systems with a reliable approximation. In addition, this equation should be useful in various disciplines of the applied chemical sciences. More, it will be fruitful for chemical and physical engineering experimental data and it will allow to evaluate one non-available parameter when the second one is available (eqn. 36 or eqn. 37), or it can be evermore estimated by theories proposed in the literature [59].

$$\ln A_s = -\left(\frac{E_a}{\lambda R}\right)^{\frac{1}{\alpha_0}} \tag{37}$$

We obtain the same results with the suggested Messaâdi empirical model (eqn. 38 or 39) [63], but for more extended validation domain (5 < E_a < 60 kJ mol^{-1}) and (– 25 < ln(A_s/Pa·s) < – 9).

$$\ln (A_s) = \frac{-E_a}{RT_0[1 - e^{-\frac{E_a}{\alpha_0 RT_0}}]} \tag{38}$$

$$E_a = -\frac{RT_0[\ln(A_s) + \alpha_0]}{[1 - e^{\frac{RT_0 \ln(A_s)}{\gamma_0}}]} \tag{39}$$

where R is the rare gas constant, (T_0) is the limiting Arrhenius temperature ($T_A < T_0 = 330.03 \pm 4.36$) K and, ($\alpha_0 = 9.894 \pm 0.536$) and ($\gamma_0 = 44.86 \pm 1.91$) 10^3 are two dimensionless adjustable constants.

Moreover, considering the correlation presented in Fig. 14 and eqn. 36 we can propose direct correlation between the boiling point (T_b) and the Arrhenius activation energy E_a expressed by the following empirical expression:

$$T_b(E_a) = -\frac{E_a}{68 - 4.05 \times E_a^{0.34}} \tag{40}$$

However, due to the restriction of the domain of validity of eqns. 36 and 37 (6 < Ea < 30 kJ mol^{-1}), this empirical equation fails for fluids with high or low absolute viscosity especially for those with low boiling point ($T_b < T_{b,Water}$). Also, when we explore the eqn. 37 instead of eqn. 36, we can obtain another empirical expression:

$$T_b(\ln A_s) = \frac{(-\ln A_s)^{2.933}}{8.2+\ln A_s} \tag{41}$$

Likewise, we note the same conclusion due to the restriction of the domain on the logarithm of the entropic factor to ($-17 < \ln(As/Pa{\cdot}s) < -10$). However, when we examine Fig. 15 presenting the comparison between the experimental and the calculated boiling points by means of the two eqns. 40 and 41, we can conclude that there are two classes of causal correlations. In effect, we observe that the two different points' shapes don't match. It is concluded that the boiling point is in causal correlation with the two viscosity Arrhenius parameters, but also implicitly in correlation with other chemical and physical properties for which there are some properties are common for the two Arrhenius parameters while others properties are in relationship for only a single parameter (E_a) or ($\ln A_s$). To rectify this issue, we will try to propose in future statistical investigations, an expression both explicit, the two Arrhenius parameters T_b (E_a, $\ln A_s$) alternatively one in the numerator and the second in the denominator.

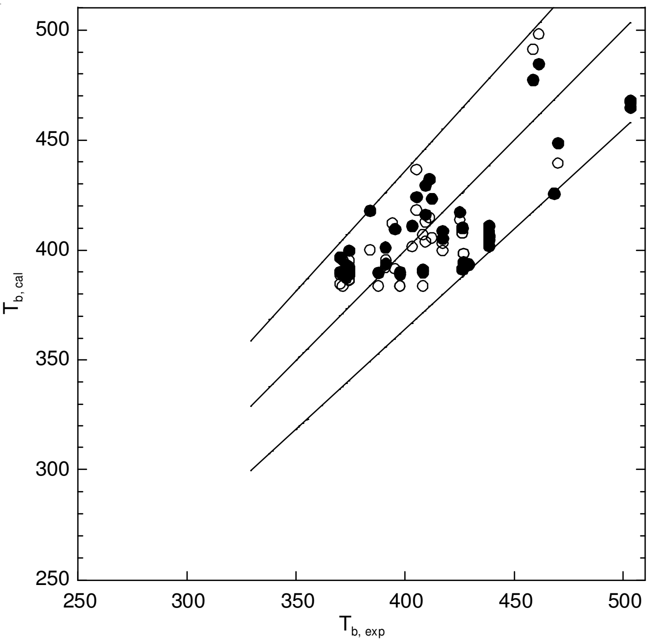

Fig. 15. Correlation between the experimental normal boiling points $T_{b,exp}$/K and the calculated boiling points ($T_{b,cal}$)/K for some pure solvents studied at earlier work [Ref. 61]; (•): from eqn. 17 and (o): from eqn. 18). (—): around the first bisector (Y = +X and Y = (1 ± 9 %) × X) in the present axis system

Conclusion

Based on the same experimental data of densities and absolute viscosities of (DMF + EtOH) binary fluid mixtures at atmospheric pressure and at five absolute temperatures from 303.15 to 323.15 K [1-5], some new approaches have been presented, for enhancing investigations of variation of Arrhenius parameters and the corresponding partial molar quantities against molar fraction composition.

Causal correlation between the absolute viscosity parameters (E_a) and [$\ln(A_s)$] for binary fluid mixtures permits us to bring to light the Arrhenius temperature characterizing the treated binary fluid mixture and providing information on the temperature of vapourization of the isobaric liquid-vapour diagram. Likewise, this correlation can give evidence of the existence of different domains of composition with distinct behaviours or liquid structures.

Therefore, assuming that the viscosity activation energy is a classical thermodynamic state function, we have determined the partial molar activation energy to release individual interaction's contributions of each pure fluid component within the mixture for each well-defined mole fraction. Causal correlation between the molar quantities relative to the viscosity activation energies and the entropic factors for DMF + EtOH fluid mixtures over the studied absolute temperature interval can give an approximately linear behaviour *i.e.* no observable net change in curvature. This observed quasi-straight line supposes us to express a semi-empirical equation by introducing a new parameter T_A denoted as Arrhenius temperature that characterizes each studied binary fluid system. In the treatment of partial molar quantities, we consider that the Arrhenius temperature (T_A) varies slightly over the full range of molar compositions, we introduced then a new notion of the Arrhenius' current temperature (T_{Ai}) for each pure liquid solvent (i) and determinate its value at the two limits *i.e.*, at very high concentration and very high dilution, respectively. The results derived in the studied binary fluid system gives an interesting finding that the isobaric boiling point (T_{bi}) of the pure fluid components strongly depends upon the Arrhenius' current temperature (T_{Ai}). Finally, we can ascertain that with more mathematical manipulations, we will be able to bring to light some physical significances of the Arrhenius parameters which can definitely develop as well as improve thermodynamic theories and also permit to estimate the boiling temperatures of the pure fluid components and to predict some information on liquid-vapour equilibrium, through the study of the absolute viscosity against absolute temperature and composition only in the liquid state of binary fluid mixture.

In addition, a supplemental treatment on the eventual relationship between the viscosity Arrhenius temperature and the properties of various binary fluid mixtures can demonstrate how the method predicts the properties values of other non-investigated fluid mixtures. In order to firmly establish the utility of the viscosity Arrhenius temperature and develop a means for predicting such quantities, more fluid mixtures will be treated in future works to give a more clear discussed protocol. To our best of knowledge, there is no stronger physical and theoretical basis of this study or any other developed predictive techniques for our presented assumptions and so we cannot able to provide more clearly our verifications. It is hoped that these interesting and original experimental findings can be well received by theoretical workers for expanding new theoretical approaches. Furthermore, in future investigations, we will also address the pressure effect on the absolute viscosity and how causal correlation can be deduced in connection with theories already available.

ACKNOWLEDGEMENTS

The authors thank the Deanship of Scientific Research in Imam Abdulrahman Bin Faisal University, Formerly. University of Dammam, Saudi Arabia, for supporting this work and funding this research project [Grant No. 2015014].

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