



Asian Journal of Chemistry; Vol. 28, No. 9 (2016), 1972-1984

ASIAN JOURNAL OF CHEMISTRY

<http://dx.doi.org/10.14233/ajchem.2016.19858>



Correlation Between Boiling Temperature and Viscosity Arrhenius Activation Energy in N,N-Dimethylformamide + 2-Propanol Mixtures at 303.15 to 323.15 K

H. SALHI¹, N.A. AL-OMAIR^{2,*}, A.A. AL-ARFAJ², M.A. ALKHALDI², N.O. ALZAMEL², K.Y. ALQAHTANI² and N. OUERFELLI²

¹Université de Tunis El Manar, Laboratoire de Biophysique et Technologies Médicales, LR13ES07, Institut Supérieur des Technologies Médicales de Tunis, 9 Avenue Dr. Zouhaier Essafi, 1006 Tunis, Tunisia

²University of Dammam, Department of Chemistry, College of Science, P.O. Box 1982, Dammam 31441, Saudi Arabia

*Corresponding author: E-mail: nalomair@uod.edu.sa

Received: 20 January 2016;

Accepted: 10 April 2016;

Published online: 1 June 2016;

AJC-17926

Excess properties determined from literature of experimental density and viscosity values in N,N-dimethylformamide + 2-propanol mixtures over the temperature range from 303.15 to 323.15 K can conduct to test some correlation equations as well as their corresponding derivative properties. Investigation on the enthalpy of activation of viscous flow (ΔH^*) and the Arrhenius activation energy (E_a) shows very close values. Here we can define new thermodynamic functions such as the molar partial activation energies E_{a1} and E_{a2} for N,N-dimethylformamide and 2-propanol, respectively and which can reveal their individual contribution separately. Causal correlation between the two viscosity Arrhenius parameters in the whole compositions range shows existence of distinct interaction behaviours delimited by particular compositions in N,N-dimethylformamide. The correlation between viscosity Arrhenius parameters shows the interesting new concept of Arrhenius temperature which is closely in relation to the temperature of vapourization in the vapour-liquid equilibrium and the limiting corresponding partial molar thermodynamic functions can permit to predict reliable values of the boiling temperature of pure liquid components.

Keywords: Viscosity, Binary liquid mixture, Boiling temperature, Arrhenius activation energy, Arrhenius temperature.

INTRODUCTION

We are committed in a research program of our laboratories on application of the results of transport and thermodynamic properties of some binary liquid systems [1-5] in recently suggested correlation equations.

Majority of the studied mixtures are non-ideal and indicate individual behaviour and the interpretation of non-ideality is an interesting area especially when is argument with new concepts of universal Herráez exponent, Belda parameters, friccohesity and reduced Redlich-Kister excess functions [1-38]. Theory of solution is still far from sufficient to account non-idealities in terms of the properties of the molecules constituting the solution [23-29]. The knowledge of the main factors engaged in the non-ideality of binary liquid mixtures is essential for a better interpreting and understanding of viscosities deviation and excess molar volumes and its derived properties. Amide-alcohol mixtures are of practical importance. N,N-dimethylformamide (DMF) to some extent is associated by means of dipole-dipole interactions. Large structural effects are absent due to the lack of hydrogen bonds. Therefore, it acts as an aprotic protophilic solvent of fairly

high dielectric constant ($\epsilon = 36.71$) of molecules with a large dipole moment ($\mu = 3.8$ D) at 298.15 K [1-5]. A 2-propanol (2-Prop) molecule can interact with a DMF molecule by virtue of better hydrogen bond acceptor ability of its oxygen atom, resulting in structural and packing effects in the light of the most critical interface of frictional and cohesive forces depicted by friccohesity [23-29].

Recently and through the new concepts of the universal Herráez exponent, reduced Redlich-Kister functions and Belda parameters [30-38], we have initiated a comprehensive research programme to get more information about the internal liquid structure of the binary liquid systems of most promising solvents that have a great biological importance found in the literature [1-22]. Considering the values given by the literature and expanded by some interpolations for mathematical derivations needed, here it is extended to study the dynamic viscosity and the corresponding Arrhenius behaviour along with a new parameter designated as viscosity Arrhenius temperature (T_A), in N,N-dimethylformamide (DMF) + 2-propanol (2-Prop) binary liquid mixtures at temperatures from 303.15 to 323.15 K [23-29].

More, the close variation with molar composition between the enthalpy of activation of viscous flow (ΔH^*) and the molar activation energy leads us to supposing that (E_a) is a thermodynamic function for which partial molar activation energies have been determined to reveal individual interaction's contributions of each pure liquid component within the binary mixture for each molar fraction and the new introduced parameter designated as viscosity current Arrhenius temperature (T_{Ai}) related to each liquid component (i) can conduct to predict in a good estimation the value of the boiling point of the pure liquid components constituting the treated binary liquid mixture [15,16,39-45].

The enthalpy of activation of viscous flow (ΔH^*), Arrhenius activation energy (E_a) and cohesive forces do hold a most intimate relationship because the viscosity Arrhenius activation energy which is kinetic in nature and represent the amount of the energy derived from potential energy depicted by the cohesive forces. Thus the cohesive forces characterizes the surface tension so for the better explanation of the surface tension along with shear viscosity measurements are of thermodynamic meaning interfaced by friccohesity [23-29]. In addition, correlation between temperature and viscosity Arrhenius parameters through the temperature of vapourization further is highly affected by the surface tension, the enthalpy of vapourization and the friccohesity [23-29].

Temperature dependence of liquid viscosity

Viscosity Arrhenius behaviour: Given the small number of points furnished by the literature [1-5] and the need for mathematical handlings of derivation, we have fitted in polynomial of fifth order with least-squares optimization method the afforded ten data points [1-5] against molar composition (x_1) of liquid DMF at the five temperatures 303.15, 308.15, 313.15, 318.15 and 323.15 K. Using the determined polynomials and interpolation methods, we have added nineteen calculated points (x_1) uniformly distributed throughout the whole range of molar composition and then determined the corresponding dynamic viscosity (Table-1 and Fig. 1). The goodness of this polynomial's technique of interpolation [$\eta = a_0 \cdot x_1 + a_1 \cdot x_1^2 + \dots + a_5 \cdot x_1^5$] for the five used temperatures indicates a correlation of non-linear regression better than $R = 0.99999$. It's found that the relationship between viscosity and temperature can be adjusted with an Arrhenius type-equation as follows:

$$\eta = A_s \cdot e^{\frac{E_a}{RT}} \quad (1)$$

where R , E_a and A_s are, respectively, the perfect gas constant, the viscosity Arrhenius activation energy and the pre-exponential (or entropic) factor of Arrhenius type-equation for the binary liquid mixture. Eqn. 1 can be re-expressed in the natural logarithmic form:

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

The plot of the natural logarithm of dynamic viscosity $\ln(\eta)$ versus the reciprocal of absolute temperature ($1/T$) for DMF (1) + 2-propanol (2) binary liquid system in the whole range of molar composition (x_1) is as good as linear (Fig. 2) and the viscosity Arrhenius parameters E_a and A_s are consequently

TABLE-1
CALCULATED SHEAR VISCOSITIES (η , 10^{-3} Pa.s) BY INTERPOLATION TECHNIQUE FOR {DMF (1) + 2-PROPANOL (2)} MIXTURES AGAINST THE MOLE FRACTION (x_1) OF DMF AT 303.15, 308.15, 313.15, 318.15 AND 323.15 K

x_1	η (10^{-3} Pa.s)				
	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
0.0000	17.907	15.523	13.560	11.833	10.473
0.02020	16.904	14.751	12.911	11.362	10.058
0.04040	16.006	14.053	12.328	10.932	9.6826
0.07071	14.834	13.135	11.563	10.354	9.1883
0.13131	13.018	11.688	10.367	9.4155	8.4084
0.16162	12.324	11.124	9.9066	9.0394	8.1049
0.23232	11.114	10.118	9.0979	8.3555	7.5671
0.27273	10.613	9.6932	8.7629	8.0633	7.3425
0.33333	10.039	9.1984	8.3797	7.7259	7.0848
0.36364	9.8091	8.9987	8.2269	7.5927	6.9825
0.44444	9.3111	8.5694	7.8994	7.3175	6.7664
0.50505	9.0060	8.3122	7.6993	7.1608	6.6382
0.53535	8.8672	8.1974	7.6075	7.0918	6.5806
0.56566	8.7359	8.0899	7.5195	7.0267	6.5262
0.65657	8.3839	7.8064	7.2754	6.8453	6.3779
0.74747	8.1059	7.5834	7.0689	6.6788	6.2535
0.84848	7.9042	7.4201	6.9138	6.5324	6.1580
0.92929	7.8154	7.3546	6.8704	6.4844	6.1281
0.95960	7.7897	7.3414	6.8755	6.4928	6.1294
0.97980	7.7716	7.3346	6.8854	6.5088	6.1343
1.00000	7.7508	7.3284	6.9003	6.5344	6.1423

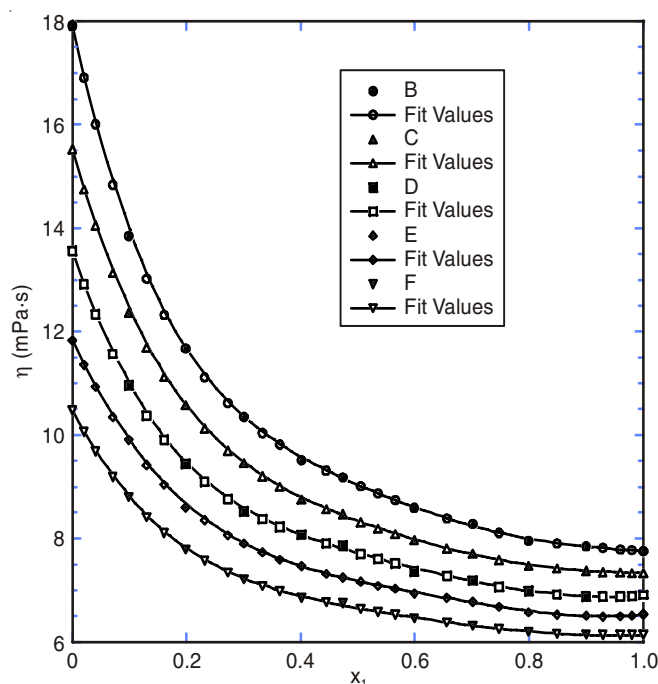


Fig. 1. Shear viscosity (η) for the system of DMF (1) + 2-propanol (2) mixtures versus the mole fraction x_1 of DMF at the temperatures: (●) and (○): 303.15 K; (▲) and (△): 308.15 K; (■) and (□): 313.15 K; (◆) and (◇): 318.15 K; (▼) and (▽): 323.15 K. Full symbols: literature data¹ and empty symbols: interpolated data

independent of temperature over the treated temperature range (from 303.15 to 323.15) K. Utilizing both graphical and fitting by least-squares techniques, the slope value of the straight line is equable to the ratio: E_a/R and the intercept to the ordinate value is equal to the entropic factor $\ln(A_s)$ either for the pure

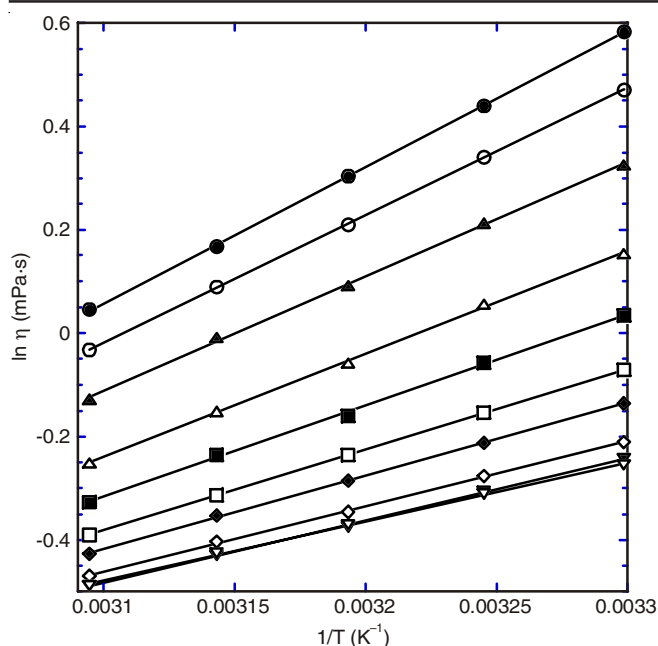


Fig. 2. Logarithm of shear viscosity $\ln(\eta)$ for the system of DMF (1) + 2-propanol (2) mixtures *versus* the reciprocal absolute temperature at some fixed mole fractions x_1 in the range of temperature (303.15 to 323.15 K). (●): $x_1 = 0.000$; (○): $x_1 = 0.0404$; (▲): $x_1 = 0.0995$; (△): $x_1 = 0.1992$; (■): $x_1 = 0.03011$; (□): $x_1 = 0.4444$; (◆): $x_1 = 0.5657$; (◇): $x_1 = 0.7475$; (▼): $x_1 = 0.8995$ and (▽): $x_1 = 1.00$

liquid components ($x_1 = 0$ or $x_1 = 1$) or for their corresponding liquid mixtures ($x_1 \neq 0$).

Case of pure components: We have added an additional reliable parameter such as the viscosity Arrhenius temperature (T_A) for each pure fluid obeying to Arrhenius-type equation *i.e.* more than the two popular Arrhenius parameters such as the pre-exponential factor (A_s) and the viscosity Arrhenius

activation energy (E_a). This viscosity Arrhenius temperature (T_A) is deduced from the intercept to abscissa axis ($1/T_A$) or determined from the following equation:

$$T_A = -\frac{E_a}{R \cdot \ln A_s} \quad (3)$$

Table-2 recapitulates some viscosity Arrhenius parameters of some pure solvents studied in previous works [15-21, 30,34,36,39-45] and Fig. 3 shows mutual causal correlation between the viscosity parameters of Arrhenius. It is well noticed attractive causal correlation which can allow helping the theoretical development of Arrhenius empirical equation and also think about restricting the number of parameters into the utilized or programmed model. So, the linear least square fit yields the following equations: ($Y = 47.759 + 6.093X$) for $T_A = f(E_a)$ and: ($Y = 65.447 + 2.735X$) for $(-\ln A_s) = f(E_a)$ with a correlation coefficients values are: $R = 0.9828$ and $R = 0.9599$, respectively. Due to the small number of experimental data points used in this statistical analysis, we can confirm that there is a net causal correlation between the viscosity Arrhenius parameters which can be enhanced in future when we consider a large number of experimental data set for numerous binary liquid solvents.

Case of binary mixtures: The calculated values for each molar composition (x_1) of $E_a(x_1)$ and of $\ln A_s(x_1)$ are given in Table-3 and are plotted *versus* the mole composition of DMF (1) in Figs. 4 and 5 respectively.

Likewise, for each mole composition x_1 of liquid DMF, the values of $\ln A_s(x_1)$ permitted us to determinate the pre-exponential factor values (A_s) in mPa·s [$A_s(x_1) = 10^6 \exp(\ln(A_s))$] which is equivalent to the shear viscosity at infinite temperature ($A_s = \eta_\infty$) is presented in Table-3 and are plotted *versus* mole fraction of liquid DMF (1) in Fig. 6.

TABLE-2
VISCOSITY ARRHENIUS PARAMETERS OF SOME PURE SOLVENTS CALCULATED BY COUPLE OF PURE LIQUIDS OF SOME BINARY MIXTURES PRESENTED AT EARLIER WORKS (EQNS. 3 AND 4)

No.	Pure liquid	Ref.	T_A (K)	E_a (kJ mol ⁻¹)	$\ln A_s$ (Pa·s)
1	N,N-Dimethylacetamide		107.50	9.7533	-10.912
2	2-Ethoxyethanol	[15]	149.87	15.803	-12.682
3	N,N-Dimethylacetamide		110.37	10.166	-11.078
4	Water	[16]	140.43	15.510	-13.284
5	1,4-Dioxane		128.86	12.660	-11.816
6	Water	[17]	142.42	15.920	-13.444
7	N,N-Dimethylacetamide		107.89	9.8844	-11.019
8	Formamide	[44]	157.98	16.405	-12.489
9	N,N-Dimethylacetamide		109.72	10.849	-11.892
10	2-Methoxyethanol	[40]	127.87	12.941	-12.172
11	N,N-Dimethylacetamide		107.36	9.7260	-10.896
12	N,N-Dimethylformamide	[42]	101.00	9.0530	-10.780
13	Isobutyric acid		119.41	11.120	-11.200
14	Water	[41]	141.46	15.741	-13.383
15	1,4-Dioxane		128.26	12.640	-11.853
16	Water	[36]	143.35	16.100	-13.508
17	N,N-Dimethylformamide		104.40	9.4802	-10.921
18	Methanol	[39]	111.03	11.018	-11.935
19	N,N-Dimethylacetamide		109.72	10.849	-11.892
20	Methanol	[43]	127.87	12.941	-12.172
21	N,N-Dimethylformamide		104.38	9.4768	-10.919
22	2-Propanol	Present work	175.63	21.959	-15.037

TABLE-3
ENTROPIC FACTOR OF ARRHENIUS (A_s , 10^{-6} Pa·s),
ARRHENIUS ACTIVATION ENERGY (E_a , kJ mol^{-1}) AND
ENTROPY AND ENTHALPY OF ACTIVATION OF VISCOUS
FLOW (ΔS^* , $\text{J K}^{-1} \text{mol}^{-1}$) AND (ΔH^* , kJ mol^{-1}) (EQNS. 19-21)
FOR {DMF (1) AND 2-PROPANOL (2)} MIXTURES AGAINST
THE MOLE FRACTION (x_1) OF DMF OVER THE
TEMPERATURE RANGE (303.15 to 323.15) K

x_1	A_s (10^{-6} Pa·s)	E_a (kJ mol^{-1})	ΔS^* ($\text{J K}^{-1} \text{mol}^{-1}$)	ΔH^* (kJ mol^{-1})
0.00000	0.29466	21.959	1.5483	21.015
0.02020	0.38009	21.172	-0.5193	20.243
0.04040	0.47593	20.470	-2.3729	19.545
0.07071	0.65289	19.482	-4.9872	18.562
0.09950	0.94891	18.369	-7.9555	17.491
0.13131	1.1347	17.763	-9.5467	16.853
0.16162	1.4350	17.034	-11.481	16.128
0.19920	1.8049	16.208	-12.674	15.627
0.23232	2.2494	15.640	-15.178	14.745
0.27273	2.7648	15.003	-16.871	14.115
0.30110	3.1023	14.643	-17.829	13.753
0.33333	3.5965	14.199	-19.026	13.319
0.36364	4.0457	13.843	-19.989	12.968
0.40090	4.9306	13.268	-21.572	12.413
0.44444	5.4144	12.975	-22.375	12.112
0.47370	6.2730	12.569	-23.571	11.714
0.50505	6.6589	12.369	-24.071	11.514
0.53535	7.3592	12.078	-24.891	11.226
0.56566	8.1040	11.797	-25.683	10.949
0.59870	8.7658	11.551	-26.331	10.707
0.65657	10.457	11.051	-27.778	10.213
0.70110	10.726	10.954	-27.995	10.118
0.74747	12.458	10.524	-29.222	9.6942
0.79910	13.661	10.248	-29.991	9.4197
0.84848	13.745	10.213	-30.041	9.3868
0.89950	14.716	10.021	-30.061	9.1975
0.92929	14.925	9.9782	-30.742	9.1512
0.95960	15.904	9.8111	-31.280	8.9829
0.97980	16.911	9.6523	-31.798	8.8227
1.00000	18.104	9.4768	-32.376	8.6447

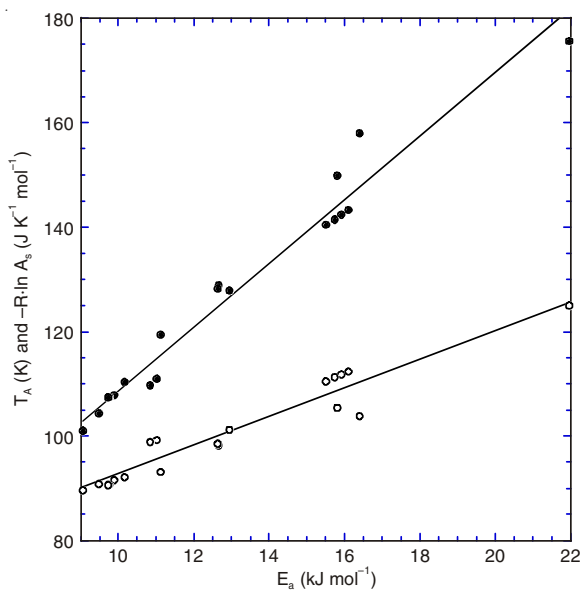


Fig. 3. Correlation between the Arrhenius activation energy E_a (kJ mol^{-1}) and (%): the Arrhenius temperature T_A (K) or (%): the logarithm of the entropic factor of Arrhenius $-R \ln(A_s/\text{Pa}\cdot\text{s})$ ($\text{J mol}^{-1} \text{K}^{-1}$) for some pure solvents determined by couple of components from some binary liquid mixtures studied at previous works (eqn. 3) [15-17,39-44]. (—): linear least square fit

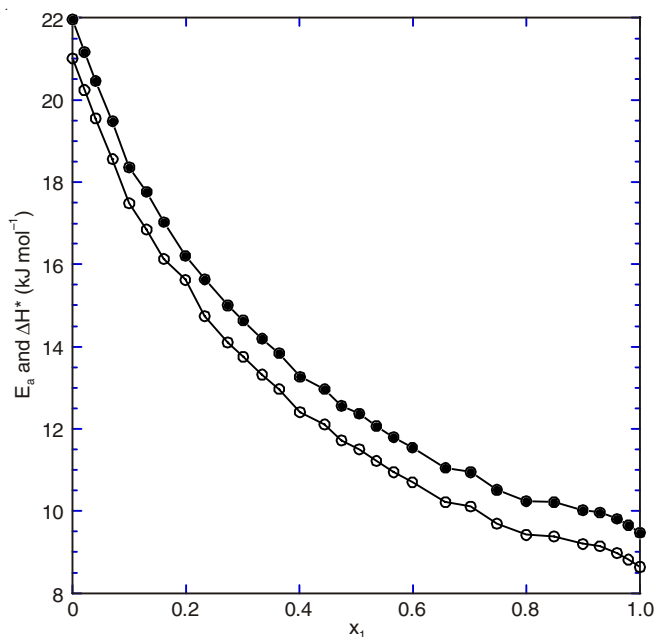


Fig. 4. Arrhenius activation energy E_a and enthalpy of activation of viscous flow ΔH^* for DMF (1) and 2-propanol (2) mixtures versus the mole fraction x_1 of N,N-dimethylformamide calculated over the temperature range (303.15 to 323.15) K; (●): E_a (kJ mol^{-1}); (○): ΔH^* (kJ mol^{-1})

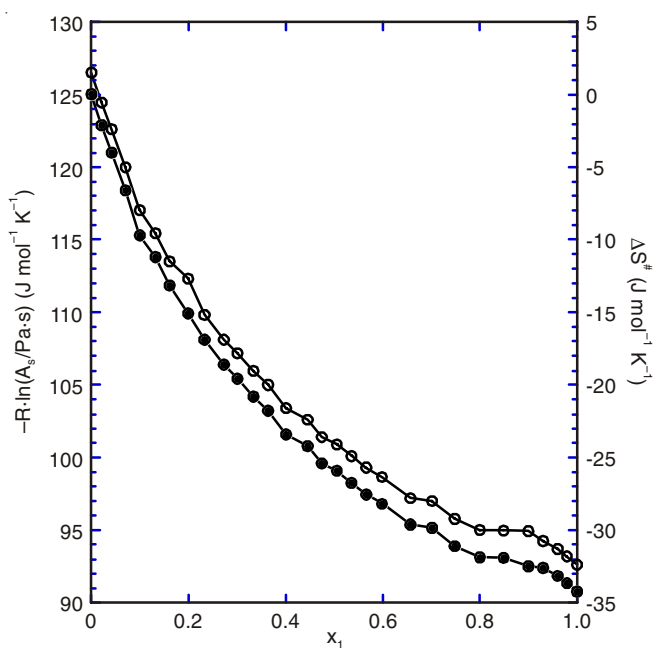


Fig. 5. Logarithm of the entropic factor of Arrhenius $-R \ln(A_s)$ and entropy of activation of viscous flow ΔS^* for DMF (1) and 2-propanol (2) mixtures versus the mole fraction x_1 of N,N-dimethylformamide calculated over the temperature range (303.15 to 323.15) K; (●) $-R \ln(A_s/\text{Pa}\cdot\text{s})$ ($\text{J K}^{-1} \text{mol}^{-1}$); (○): ΔS^* ($\text{J K}^{-1} \text{mol}^{-1}$)

From the moment that the A_s values are narrowly correlated to the viscosity of the same chemical system in vapour-state at the normal boiling point and at the same pressure [15-22], we observe that the great A_s -value of liquid DMF, presumes that the viscosity of DMF at vapour-state is roughly greater sixty times than of vapour 2-propanol and can also suppose that the 2-propanol molecules bonding are more disordered and random in vapour phase.

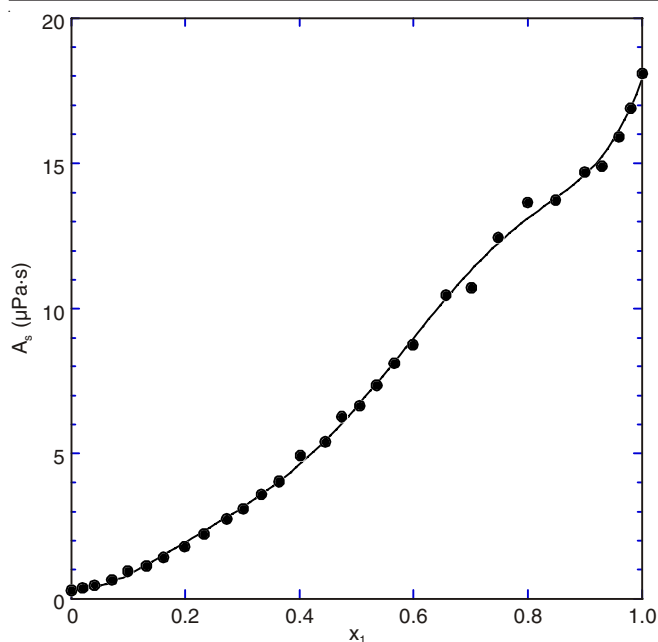


Fig. 6. Viscosity at infinite temperature (η_{∞} or A_{∞}) in $\mu\text{Pa}\cdot\text{s}$ for N,N-dimethylformamide (1) + 2-propanol (2) mixtures versus the mole fraction x_1 of N,N-dimethylformamide calculated over the temperature range (303.15 to 323.15) K

In this context, the variation of the molar Arrhenius activation energy E_a against molar composition (x_1) can show eventual change in the complex liquid structure or clusters formed in binary liquid systems under temperature effect and/or mixture molar composition [15-22]. When the molar Arrhenius activation energy E_a for all range of molar compositions in the present liquid system is plotted in Fig. 4, it is found that there is only an even decrease in molar activation energy E_a with the mole composition of DMF (x_1). Also, there is no observable change of curvature (Fig. 5).

Monotonous variation of the logarithm of the viscosity Arrhenius entropic factor $-R \ln(A_{\infty})$ and of the molar activation energy E_a , supposes that there is a gradually change of solvent's liquid structure when we insert one liquid component into other in the binary mixture. These verifications suggest that the clustering liquid structure in present binary system is monitored by the same mechanism as simple associating liquid systems, which should in turn aid in the regulation of dispersion of these molecules [15-38,39-45].

Whereas, the decrease of $E_a(x_1)$ values with the mole composition of DMF (x_1) is absolutely monotonous, without any extremum, the negative values of excess molar activation energy E_a^E shown in the curve of Fig. 7 imply that it is an indication of a cluster formation of that may occur. There is an absolute minimum at molar fraction ($x_1 = 0.33$), this can be interpreted by supposing complex formation between liquid DMF and 2-propanol molecules, corresponding to: (1×DMF:2×2-propanol).

Moreover, the utilization of the Herráez exponent P_{ij} can give information to interaction at very low concentration of one liquid component in the other one. Hence, Herráez *et al.* [32,33] suggest a new correlation equation (eqns. 4 and 7) which presents a correcting polynomial (eqns. 5 and 8) as an exponential-acting upon the molar composition of one of the mixture's liquid components.

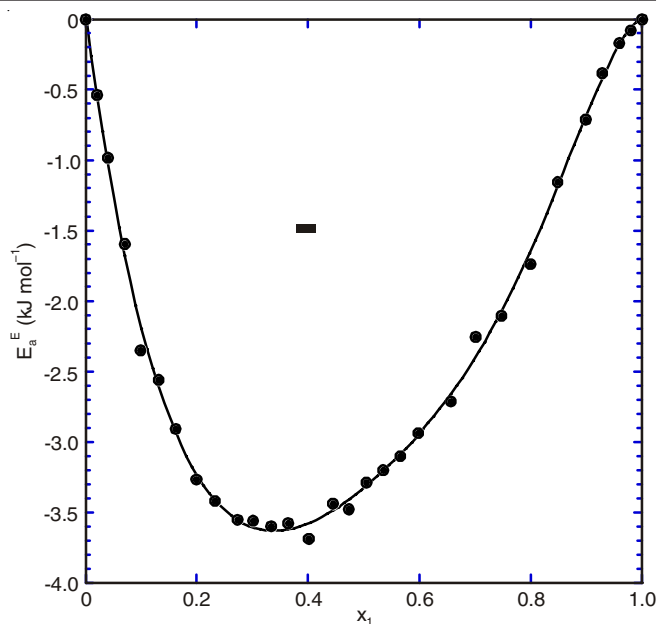


Fig. 7. Variation of the excess molar activation energy E_a^E for DMF (1) + 2-propanol (2) mixtures against mole fraction x_1 in DMF calculated over the temperature range (303.15 to 323.15) K

It is noticed that the dynamic viscosity deviations estimated with this equation generally gives satisfactory results for many studied liquid mixtures manifesting monotonous variation in dynamic viscosity values with molar composition, but the equation records low performance when the distribution exhibits an extremum (maximum or minimum) [32,33]. Hence, the following expression was proposed:

$$\eta(x_1) = \eta_2 + (\eta_1 - \eta_2) \cdot x_1^{P_{12,T}(x_1)} \quad (4)$$

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

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

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

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

where η_1 and η_2 are the shear viscosity of pure liquid components DMF (1) and 2-propanol (2), respectively and $\eta_{\text{exp},T}(x_1)$ the shear viscosity of binary liquid mixture at molar composition x_1 and temperature T for [$x_1 = 0, 1$].

On the other side or face of the equation and when it is mathematically possible, we can rewrite the Herráez model as follows:

$$\eta(x_2) = \eta_1 + (\eta_2 - \eta_1) \cdot x_2^{P_{21,T}(x_2)} \quad (7)$$

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

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

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

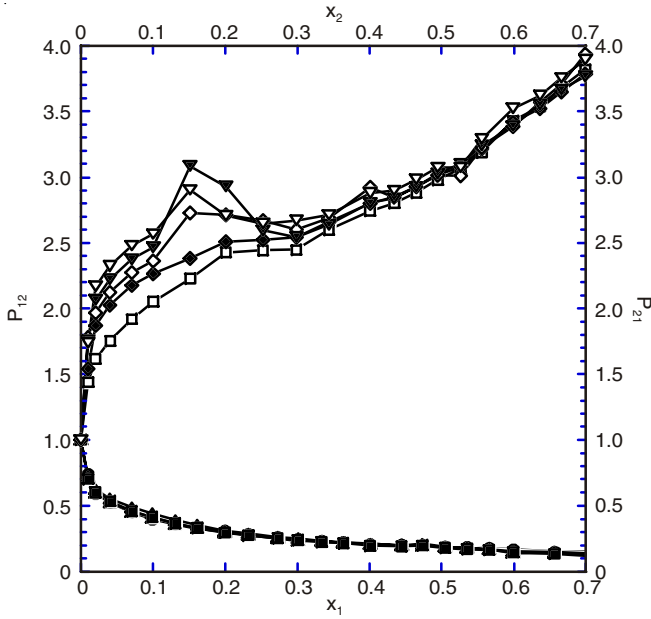


Fig. 8. Variation of the experimental Herráez exponent $P_{12,exp,T}(x_1)$ (eqn. 5) for DMF (1) + 2-propanol (2) mixtures against mole fraction x_1 in DMF at the temperatures (●): 303.15 K; (○): 308.15 K; (▲): 313.15 K; (△): 318.15 K; (■): 323.15 K; and variation of $P_{21,exp,T}(x_2)$ (Eq. 8) for DMF (1) + 2-propanol (2) mixtures against mole fraction x_2 in 2-propanol at the temperatures, (□): 303.15 K; (◆): 308.15 K; (◇): 313.15 K; (▼): 318.15 K; (▽): 323.15 K

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

where η_1 and η_2 are the shear viscosity of pure liquid components DMF (1) and 2-propanol (2), respectively and $\eta_{exp,T}(x_2)$ the shear viscosity of mixture at temperature T and molar fraction x_2 for $[x_2 = 0, 1]$.

Nevertheless, at infinite dilution ($x_i \rightarrow 0^+$), it is noticed that the $P_{exp,T}(x_i)$ values tend to a single point ($P_{exp,T}(0) = 1.0$) independent of temperature (Fig. 8) showing a fixed constant value of $B_{0,T}$ or $B'_{0,T}$ corresponding to the first monomial of $P_{ij,T}(x_i)$ of Herráez polynomial in eqns. 5 and 8. It points out that the solute-solute or ion-ion interaction is missing at very high dilution of liquids DMF or of 2-propanol in the two regions. The same results were observed in our earlier works [34-38] investigating viscosity in 1,4-dioxane + water and isobutyric acid + water binary liquid mixtures.

It is concluded that B_0 coefficient is considered as a universal exponent describing the type of interaction preponderant at infinite dilution.

In the case of low concentrated solution of liquid 2-propanol (2) in DMF (1), we can write the viscosity as a new limiting asymptotic expansion:

$$\eta = \eta_1(1 + b_1x_2^{1/2} + b_2x_2 + \dots) \quad (10)$$

So, in the basic of the theory of extended conformal solution (ECS) [46,47], the $Q_{exp,T}(x_1=1)$ is the regular term of viscosity and denoted η_{21} [38,46-49]. Thus, we can deduce the value of b_2 coefficient for a non-electrolyte binary liquid solution as given by Nakagawa [48] as follows:

$$b_2 = [(\eta_2 - \eta_1) + \eta_{21}]/\eta_1 \quad (11)$$

where the subscripts (1) and (2) denote liquids (DMF) and (2-propanol) respectively and η_{21} is the real reduced (R-K) function $Q_{exp,h,T}(x_1=1)$ for viscosity [15-22], which is expressed by the ratio of (eqn. 12) representing in general the experimental reduced R-K excess quantities $Q_{Y,exp,T}(x_1)$:

$$Q_{Y,exp,T}(x_1) = Y^E/(x_1(1-x_1)) \quad (12)$$

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

The b_2 coefficient may be separated in two parts: the first coefficient B_{id} which is based on the contribution of ideal liquid mixture (*i.e.* term in parenthesis in eqn. 11) and the second coefficient B_n is based on the neat interaction between the solute (liquid 2-propanol) and the solvent (DMF) [48,49].

However, we can add that in the case of solution of non-electrolyte when the parameter of Falkenhagen [50] (solute-solute interaction) vanish small or is null (a_i or $b_i = 0$) and considering the eqn. 10 we can re-express the eqns. 6 and 9 in another limiting asymptotic expansion at low concentration solutions of liquid 2-propanol (2) in DMF (1) or the reverse and then we obtain:

$$P_{12,exp,T}(x_1) = 1 + \frac{\ln\left(\frac{\eta_2}{\eta_1 - \eta_2} - a_2\right) + o(x_1)}{\ln x_1} \quad (13)$$

$$\text{or } P_{21,exp,T}(x_2) = 1 + \frac{\ln\left(\frac{\eta_1}{\eta_2 - \eta_1} - b_2\right) + o(x_2)}{\ln x_2} \quad (14)$$

from which we can conclude that: ($\lim_{x_i \rightarrow 0^+} P_{ij,exp,T}(x_i) = 1$) and at very low concentration, only the interaction solute-solvent is reigning. Notice that the universal exponent B_0 of the polynomial of Herráez tends to the exponent value of the first present term of eqn. 9 or of similar limiting asymptotic expansion.

Regarding the fact that the reduced Redlich-Kister (RK) excess properties $Q_{Y,exp,T}(x_1)$ [15-22] in binary liquid mixtures, reveal some information on the deviation to linearity (or ideality) and from the relationship [23-29] between the surface tension (γ), the viscosity (η) and the friccohesity (σ), we can conclude that the interpretation and discussion, only of the reduced Redlich-Kister related to the viscosity $Q_{exp,h,T}(x_1=1)$ [15-22] is poor because it implicitly not consider all different types of interaction's forces (frictional forces, cohesive forces, ...). Then, we must explicit these different manifestations of forces from the friccohesity (σ) and the surface tension (γ) [23-29]. Writing eqn. 12 for the three quantities separately (surface tension, viscosity and friccohesity ($\sigma = \eta/\gamma$), we can find out the interesting relationships expressed by the eqns. (15-18) which demonstrate that the discussion should not be limited only to the viscosity-property but as well it must takes into account the surface tension and friccohesity.

$$Q_{exp,h,T}(x_1) = x_1 \cdot q_1 + x_2 \cdot q_2 + x_1 x_2 \cdot q_{12} \quad (15)$$

$$q_1 = \sigma_1 \cdot Q_{exp,g,T}(x_1) + \gamma_1 \cdot Q_{exp,s,T}(x_1) - \Delta\sigma \cdot \Delta\gamma \quad (16)$$

$$q_2 = \sigma_2 \cdot Q_{exp,g,T}(x_1) + \gamma_2 \cdot Q_{exp,s,T}(x_1) - \Delta\sigma \cdot \Delta\gamma \quad (17)$$

$$q_{12} = Q_{exp,g,T}(x_1) \cdot Q_{exp,s,T}(x_1) \quad (18)$$

where $(\Delta\sigma = \sigma_2 - \sigma_1)$ and $(\Delta\gamma = \gamma_2 - \gamma_1)$ are the gap between the quantity values of the pure liquid components (2) and (1) respectively. In addition, graphical depiction of these functions *versus* molar composition (x_1) can then be a new interesting basis for discussion and interpretation.

Enthalpy and entropy of activation of viscous flow: In case of the liquid state we can add that the theory of absolute reaction rate of Eyring and John [51] and Ali *et al.* [52] relates free energy (ΔG^*) of activation of viscous flow with kinematic viscosity:

$$\Delta G^*(x_1, T, P) = RT \cdot \ln \left(\frac{\eta(x_1, T, P) \cdot V(x_1, T, P)}{h N_A} \right) \quad (19)$$

where η , h , R , N_A and V are the shear viscosity of binary liquid mixture, the Plank's constant, the perfect gas constant, the Avogadro's number and the molar volume of mixture (eqn. 21), respectively and:

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (20)$$

$$V = \frac{x_1 M_1 + (1 - x_1) M_2}{\rho} \quad (21)$$

where ρ is the density of binary liquid mixture, M_1 and M_2 are the molar weight of the pure liquid components of DMF and 2-propanol, respectively.

By considering that the viscosity activation parameters ΔH^* and ΔS^* [52,53] are independent of temperature, we obtained, for each molar composition of liquid binary mixture (x_1, x_2), these parameters when the quantity: $R \ln(\eta \cdot V / (h \cdot N_A))$ is plotted as a function of $1/T$. Using both graphical and linear least-square fit method, the slope value is equal to ΔH^* and the intercept on the ordinate value is equal to $-\Delta S^*$. The eqn. 20 was used to calculate the viscosity activation parameters ΔH^* and ΔS^* . Indeed, the plot of $R \ln(\eta \cdot V / (h \cdot N_A))$ as a function of the reciprocal of absolute temperature ($1/T$) is as good as linear and the enthalpy (ΔH^*) and the entropy (ΔS^*) of activation of viscous flow become practically independent of temperature in the whole studied range of temperature (from 303.15 to 323.15) K. Different values of the enthalpy (ΔH^*) and entropy (ΔS^*) of activation of viscous flow are shown in Table-3 and are plotted *versus* the mole fraction of liquid DMF (1) in Figs. 4 and 5 respectively.

Correlation between Arrhenius parameters: In general, investigation of Arrhenius parameters [E_a and $\ln(A_s)$] leads us to bring to light eventual existing distinct behaviours which are distinctly shown when the causal correlation between order and disorder is schematized [15-22] through the viscosity Arrhenius activation energy E_a *versus* the logarithm of the viscosity entropic factor of Arrhenius $-\ln(A_s)$ (Fig. 9).

Fig. 4 shows that there is an even decrease of E_a with the mole composition of DMF (x_1) without any maxima present in the curve. There is also no observable change of curvature found when the viscosity activation energy E_a is plotted with the viscosity Arrhenius entropic factor $\ln A_s$ in Fig. 9.

Monotonous variation of the viscosity activation energy E_a , suggests that there is a gradually change of solvent's liquid structure when we insert one liquid component into other in the binary mixture.

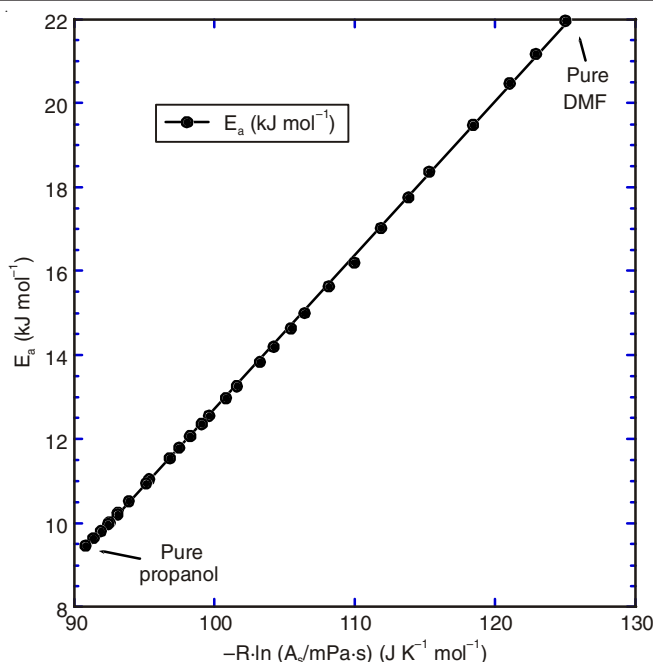


Fig. 9 Correlation between the Arrhenius activation energy E_a (kJ mol^{-1}) of viscosity and the logarithm of the entropic factor of Arrhenius $-\ln(A_s/\text{Pa}\cdot\text{s})$ ($\text{J K}^{-1} \text{mol}^{-1}$) for N,N-dimethylformamide (1) + 2-2-propanol (2) mixtures in the temperature range (303.15 to 323.15) K (●): experimental data points; (—): linear least square fit of eqn. 2

The similar feature is observed in the binary liquid mixture of N,N-dimethylacetamide + N,N-dimethylformamide [21]. In present case, a pseudo-linear behaviour is observed where there is a progressive liquid structure change [3,38]. It is noted that the progressive formation of cluster or complex (DMF: 3×2-propanol) is studied by ^1H NMR spectroscopy [6] while the second molar fraction ($x_1 = 0.865$) corresponds to the highly dilution of 2-propanol in DMF which the interpretation of the molecular liquid structure is based on "Neighborhood Model Approach" [6,23-29,54] whereas at initial insertion of liquid 2-propanol molecule into pure DMF, creates preferentially the stable cluster (1×2-propanol:32×DMF) where one liquid 2-propanol molecule is surrounded by 8 liquid DMF molecules roughly without greatly modifying the liquid structure of pure DMF [44].

Overall, the viscosity Arrhenius activation energy $E_a(x_1)$ increases *versus* the logarithm of the viscosity Arrhenius entropic factor $-\ln(A_s)$ [15-22]. Moreover, we can consider roughly the linear behaviour which is also observed for some other treated binary liquid mixtures such as water with 1,4-dioxane, isobutyric acid or N,N-dimethylacetamide [2,6,20], *etc.*

We can add that for each binary liquid mixture; even in the case of the existing of distinct domains with different behaviours in Fig. 9, it is noticed that all different branches' curves in this figure show roughly the same slope value of their quasi-straight line for which we can express the following standardized semi-empirical equation as follows:

$$-\frac{E_a}{R} = T_A \cdot \ln(A_s) + B \quad (22)$$

where B is a constant in relationship to the viscosity of the liquid binary system at boiling point and which is equal to the

intercept on the ordinate when $\ln A_s$ is mathematically null; while the slope value T_A characterizes each binary liquid system and it is physically equivalent to a temperature for which we suggest Arrhenius temperature as a name for the corresponding binary liquid system [2,6,15-22,44].

The T_A -values for all the studied liquid binary systems are near the boiling points (T_{bi}) of the corresponding two pure liquid components. In case of the DMF-2-propanol liquid mixtures, the T_A value which deduced from least squares linear regression (Fig. 9) is equal to 365.1 K with correlation factor value $R = 0.99987$, while the boiling point of liquids DMF and 2-propanol are 426.15 K and 355.15 K respectively. It is concluded that Arrhenius temperature T_A is narrowly related to the mean value of the temperature function of the isobaric vapour liquid equilibrium ($T-x$) of the system DMF-2-propanol at the same pressure.

In future, we will try to show that the viscosity Arrhenius temperature T_A is narrowly correlated to the mean value of the temperature function $T(x_1)$ versus molar fraction(x_1) in the interval [0,1] for the binary liquid-vapour diagram at constant pressure and which can be expressed as follows:

$$\int_0^1 T(x_1, P) dx_1 \sim T_A(P) \quad (23)$$

and the viscosity Arrhenius temperature T_A is roughly the average height of the graph of temperature-molar fraction ($T-x_1$) of the corresponding phase diagram at constant atmospheric pressure of the treated binary mixture. Alike and depending on whether the T_A -value is framed, undervalued or overvalued by one of the boiling temperature T_{bi} , we can predict the graph-type of the temperature-molar fraction ($T-x_1$) diagram (azeotropic or regular with low or high boiling temperature).

Thermodynamic features

Correlations with the enthalpy of activation of viscous flow: Examination of the enthalpy (ΔH^*) of activation of viscous flow determined from the Gibbs energy (ΔG^*) and those of the E_a values (Fig. 4, Table-3), shows that the ΔH^* and E_a values have similar variation and are very narrowly

related. So, it is suggested that the difference between the enthalpy (ΔH^*) of activation of viscous flow and those of E_a values (Table-4), can be expressed as an increment δH^* which it varies linearly as follow [15-17,53] (Fig. 10):

$$\Delta H^* = E_a - \delta H^* \quad (24)$$

$$\text{and} \quad \delta H^* = x_1 \cdot \delta H^*_{1} + x_2 \cdot \delta H^*_{2} \quad (25)$$

where $\delta H^*_{1} = 0.8264 \text{ kJ mol}^{-1}$ and $\delta H^*_{2} = 0.9384 \text{ kJ mol}^{-1}$ are the enthalpy increments related to the pure liquid solvents DMF (1) and 2-propanol (2), respectively (Fig. 4). Also, the entropy (ΔS^*) of activation of viscous flow is narrowly correlated (Fig. 5) with the viscosity Arrhenius entropic factor ($-R \cdot \ln A_s$) and their difference can be explicated by an entropy increment (δS^*) as:

$$\Delta S^* = -R \cdot \ln A_s + \delta S^* \quad (26)$$

$$\text{and} \quad \delta S^* = x_1 \cdot \delta S^*_{1} + x_2 \cdot \delta S^*_{2} + x_1 \cdot x_2 \cdot \delta S^*_{12} \quad (27)$$

where $\delta S^*_{1} = 123.15 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\delta S^*_{2} = 123.47 \text{ J K}^{-1} \text{ mol}^{-1}$ are the entropy increments related to the pure liquid solvents DMF (1) and 2-propanol (2) respectively and $\delta S^*_{12} = -0.5198 \text{ J K}^{-1} \text{ mol}^{-1}$ is the interaction increment (Fig. 5).

Otherwise, it is noticed that there is a practically linear dependence between the enthalpy of activation of viscous flow (ΔH^*) and the viscosity Arrhenius activation energy E_a and, between the entropy of activation of viscous flow ΔS^* and the logarithm of the entropic factor of Arrhenius $-R \cdot \ln(A_s)$ (Fig. 10). The two straight lines $Y = f(X)$ related to the linear least square fit can be expressed as follows: ($Y = 123.4 + 1.0103X$) for $-R \cdot \ln(A_s) = f(\Delta S^*)$ and ($Y = 0.76138 + 1.0073X$) for $E_a = f(\Delta H^*)$; with the same correlation coefficient value $R = 0.99988$. In the same context, the two dimensionless slopes values are narrowly to the unit and deviate from the unit to about 1.03 and 0.73 % respectively, due to the average thermal expansion and the volume effect in the studied temperature range.

Partial molar activation energy: Taking into consideration the quasi-linear dependence between the enthalpy of activation of viscous flow ΔH^* and the viscosity Arrhenius activation

TABLE-4
PARTIAL MOLAR PROPERTIES RELATIVE TO THE LOGARITHM OF THE ENTROPIC FACTOR OF ARRHENIUS $-R \cdot \ln(A_s/Pa \cdot s)$ (J K⁻¹ mol⁻¹) AND THE ACTIVATION ENERGIES E_{a_i} (kJ mol⁻¹) FOR {N,N-DIMETHYLFORMAMIDE (1) + 2-PROPANOL (2)} MIXTURES AGAINST THE MOLE FRACTION (x_1) OF DMF AT 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)	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)
0.00000	22.016	-20.711	125.16	10.753	0.47370	20.553	-1.4126	121.26	62.831
0.02020	21.996	-18.766	125.11	16.111	0.50505	20.417	-0.70434	120.90	64.670
0.04040	21.958	-16.935	125.01	21.136	0.53535	20.281	-0.04690	120.55	66.369
0.07071	21.905	-15.215	124.86	25.843	0.56566	20.145	0.56282	120.20	67.936
0.09950	21.837	-13.600	124.67	30.249	0.59870	20.011	1.1279	119.86	69.381
0.13131	21.756	-12.084	124.45	34.369	0.65657	19.878	1.6511	119.52	70.712
0.16162	21.664	-10.664	124.21	38.218	0.70110	19.748	2.1353	119.19	71.937
0.19920	21.563	-9.3330	123.93	41.809	0.74747	19.620	2.5831	118.87	73.064
0.23232	21.454	-8.0880	123.64	45.157	0.79910	19.495	2.9971	118.56	74.100
0.27273	21.337	-6.9240	123.33	48.275	0.84848	19.372	3.3795	118.25	75.053
0.30110	21.215	-5.8367	123.00	51.175	0.89950	19.253	3.7329	117.96	75.928
0.33333	21.088	-4.8221	122.66	53.870	0.92929	19.137	4.0592	117.67	76.733
0.36364	20.958	-3.8762	122.32	56.373	0.95960	19.024	4.3606	117.39	77.472
0.40090	20.825	-2.9951	121.97	58.693	0.97980	18.914	4.6391	117.12	78.153
0.44444	20.690	-2.1751	121.61	60.842	1.00000	18.807	4.8964	116.86	78.780

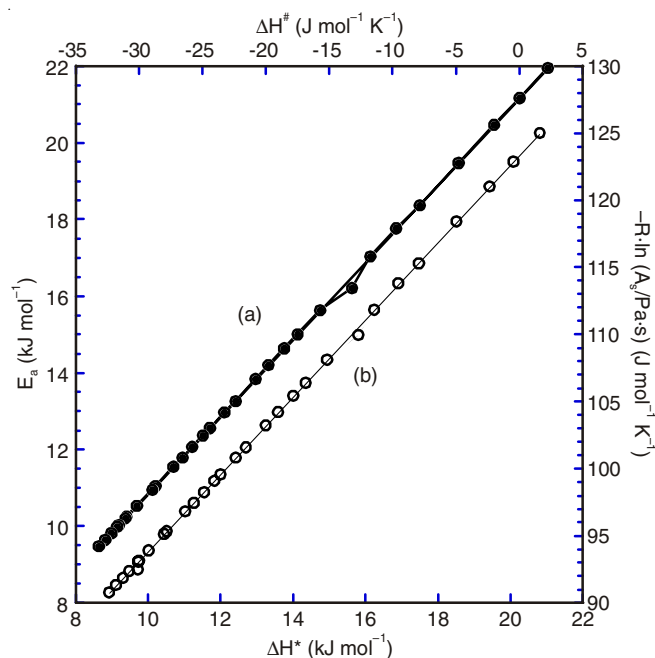


Fig. 10. Correlation between: (a) Arrhenius activation energy E_a (kJ mol⁻¹) of viscosity and the enthalpy of activation of viscous flow ΔH^* (kJ mol⁻¹) for DMF (1) and 2-propanol (2) mixtures calculated over the temperature range (303.15 to 323.15) K (●): experimental data points; (—): linear least square fit. (b) the logarithm of the entropic factor of Arrhenius $-R \cdot \ln(A_s/Pa \cdot s)$ (J K⁻¹ mol⁻¹) and entropy of activation of viscous flow ΔS^* (J K⁻¹ mol⁻¹) for DMF (1) and 2-propanol (2) mixtures calculated over the temperature range (303.15 to 323.15) K (○): experimental data points; (—): linear least square fit

energy E_a and, between the entropy of activation of viscous flow ΔS^* and the logarithm of the entropic factor of Arrhenius $-R \cdot \ln(A_s)$, mentioned in the precedent section, we can roughly suppose that the activation energy $E_a(x_1)$ is a thermodynamic state function and then we can explicit the partial molar properties Y_1 and Y_2 for DMF (1) and 2-propanol (2), respectively using the following equations:

$$Y_1(x_1, T, P) = Y(x_1, T, P) + (1 - x_1) \cdot \left(\frac{\partial Y(x_1, T, P)}{\partial x_1} \right)_{T,P} \quad (28)$$

$$Y_2(x_1, T, P) = Y(x_1, T, P) - x_1 \cdot \left(\frac{\partial Y(x_1, T, P)}{\partial x_1} \right)_{T,P} \quad (29)$$

where Y_i represents the molar partial property relative to Arrhenius entropic factor $-R \cdot \ln(A_{si})$ or the molar partial activation energy E_{a1} and E_{a2} . This action is useful because the molar partial activation energy $E_{ai}(x_1)$ -values reveal eventual individual contribution of each pure liquid component (i) and preferential phenomena in competition of each fixed composition of binary mixture (x_1, x_2).

Values of molar partial properties $E_{a1}(x_1)$, $E_{a2}(x_1)$, $-R \cdot \ln(A_{s1})$ and $-R \cdot \ln(A_{s2})$ are presented in Table-4 and $E_{a1}(x_1)$ and $E_a(x_1)$, depicted in Fig. 11 versus mole fraction (x_1) in DMF.

The molar partial activation energy $E_{a1}(x_1)$ of liquid DMF monotonously increases from a negative value (about -20 kJ mol⁻¹) to attain a local maximum (about 9.6 kJ mol⁻¹) at ($x_1 = 0.863$), then decreases very lightly to reach a local minimum

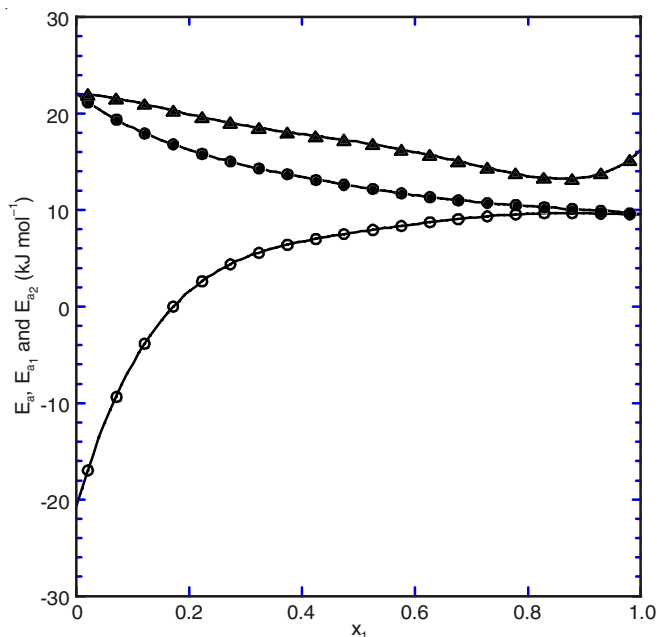


Fig. 11. Arrhenius activation energy E_a (kJ mol⁻¹) and partial molar activation energies of viscosity (eqns. 28 and 29) E_{ai} (kJ mol⁻¹) for {N,N-dimethylformamide (1) + 2-propanol (2)} mixtures as a function of the mole fraction of N,N-dimethylformamide (x_1) over the temperature range (303.15 to 323.15) K; (●) $E_a(x_1)$; (○) $E_{a1}(x_1)$ and (▲) $E_{a2}(x_1)$

to reach the corresponding value of pure liquid DMF (around 9.2 kJ mol⁻¹). This behaviour supposes that at very high dilution, the adding of DMF liquid on 2-propanol one favours the formation of hetero-association through multiple hydrogen bonding between the polar groups of unlike molecules until the molar fraction $x_1 \approx 0.863 = 7/8$ (7×DMF:8×2-propanol) where there is a weak changing of 2-propanol liquid structure [1-14].

Otherwise, the molar partial activation energy of 2-propanol $E_{a2}(x_1)$ varies in similarly (Fig. 11) in the second face (*i.e.* against molar fraction x_2 of 2-propanol), except it attains a local minimum at very high dilution of 2-propanol in DMF at ($x_1 = 0.863$).

So, in the frame of laminar flow, the introduced molecules of liquid DMF in the 2-propanol-rich region, find high facility to become integrated into the layers' of liquid 2-propanol molecules. Alike, the introduced molecules of liquid 2-propanol in the DMF-rich region, find high difficulty to become integrated into the layers' of liquid DMF molecules, in the frame of laminar flow.

This symmetrical behaviour at very high dilution can be confirmed by the specific values of Herráez exponent. In addition, the universal exponent B_0 of Herráez equation [32,33] at infinite dilution investigated before (Fig. 8), shows that $B_{0,T}$ takes the unit-value in the two cases of the liquid DMF in 2-propanol and the liquid 2-propanol in DMF. Hence, we can confirm that at very high dilution the solute-solute interaction is absent in the two cases of liquid DMF in 2-propanol and liquid 2-propanol in DMF.

More, the distinct shape variation of $E_{ai}(x_1)$ -values (Fig. 11) conducts us to eliminate the mole composition x_1 as a variable and to plot the correlation between the two molar partial activation energies $E_{a1}(x_1)$ and $E_{a2}(x_1)$ (Fig. 12) and we can affirm that the individual contribution of liquids 2-propanol

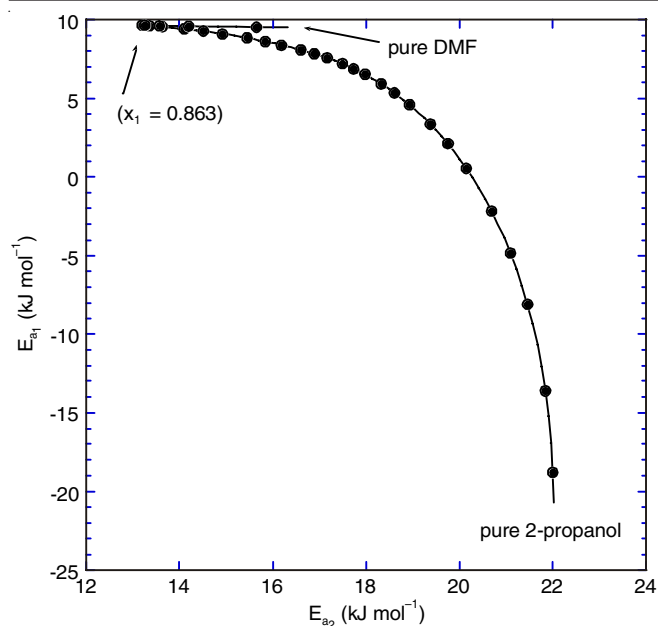


Fig. 12. Correlation between the partial molar Arrhenius activation energies $E_{a1}(x_1)$ and $E_{a2}(x_1)$ for {N,N-dimethylformamide (1) + 2-propanol (2)} mixtures over the temperature range (303.15 to 323.15) K

and DMF in the molar activation energy indicates clearly the domains delimitation of 2-propanol solvation in liquid DMF and inversely ($x_1 \approx 0.863$) which corresponds roughly to a cluster (7×DMF:8×2-propanol) around which, the transition from one liquid structure to another is abrupt.

However, if we abandon the approximation of eqn. 22 that the viscosity Arrhenius temperature (T_A) is no longer a constant over the full range of molar fractions, we can redefine it as viscosity Arrhenius' current temperatures (T_{cAi}) by the derivative of the molar partial Arrhenius activation energy $E_{ai}(x_i)$ with respect to the molar partial property corresponding to the logarithm of Arrhenius entropic factor $-R \cdot \ln(A_{si})$ at selected molar composition (x_i) and at constant pressure:

$$T_{Ai} = \left(\frac{\partial(E_{ai})}{\partial(-R \cdot \ln A_{si})} \right)_P \quad (30)$$

The form of eqn. 30 is justified from the fact of the similarity of behaviour of the two molar Arrhenius parameters [$E_{ai}(x_i)$ and $-R \cdot \ln(A_{si})$] with the molar enthalpy (ΔH^*) and molar entropy (ΔS^*) of activation of viscous flow respectively (Figs. 4 and 5, eqns. 2,20,24-29). Indeed, considering the molar Gibbs free energy expression (eqn. 20) and molar partial derivatives functions of Maxwell equations, we can account that eqn. 30 is equivalent to the following expression at constant pressure.

$$[(\partial\Delta H^*/\partial\Delta S^*)_P = T] \quad (31)$$

The T_{cAi} -values are equal to slope value of the tangent line (Fig. 13) at a given point of curve (*i.e.* at given molar fraction x_i of mixture). As an application of this feature, we obtain very interesting finding especially near the two limits of molar fraction range. Then, we obtain as viscosity Arrhenius' current temperatures (T_{cAi}) from the slopes values of the two curves shown in Fig. 13-curve (a) such as: in the case of the very high concentration of one pure liquid component (i) we

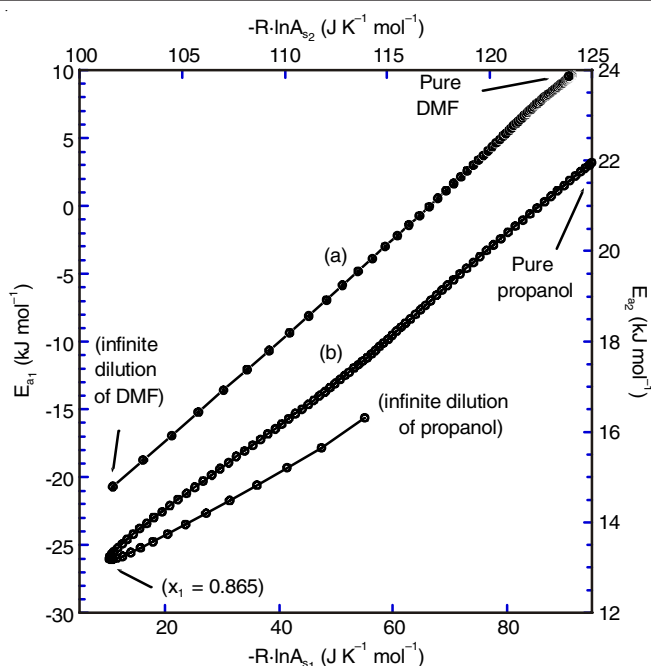


Fig. 13. Correlation between: (a) the partial molar quantities relative to the activation energies E_{a1} (kJ mol^{-1}) and the logarithm of the entropic factors of Arrhenius $-R \cdot \ln(A_{s1}/\text{Pa}\cdot\text{s})$ ($\text{J K}^{-1} \text{mol}^{-1}$); (b) the partial molar quantities relative to the activation energies E_{a2} (kJ mol^{-1}) and the logarithm of the entropic factors of Arrhenius $-R \cdot \ln(A_{s2}/\text{Pa}\cdot\text{s})$ ($\text{J K}^{-1} \text{mol}^{-1}$) related to 2-propanol in {N,N-dimethylformamide (1) + 2-propanol (2)} mixtures over the temperature range (303.15 to 323.15)

discover that $T_{cA1}(x_1 \approx 1) = 398.3 \text{ K} \approx T_{b1}$ for the Fig. 13 (i = 1), $T_{cA2}(x_2 \approx 1) = 367.6 \text{ K} \approx T_{b2}$ for the Fig. 13-curve (b) (i = 2), while in the case of very high dilution of the pure component (i) in the second one (j), we locate that $T_{cA1}(x_1 \approx 0) = 366.4 \text{ K} < T_{b1}$ for the first curve and, $T_{cA2}(x_2 \approx 0) = 293.7 \text{ K} < T_{b2}$ for the second curve.

With this ascertainment, we can estimate the boiling temperature of the two pure liquid components at constant pressure through investigation of the dependence of viscosity on temperature in the corresponding liquid phase. More, this very interesting verification is also confirmed from other studied binary liquid mixtures such as water with N,N-dimethylacetamide (DMA) or 1,4-dioxane and N,N-dimethylacetamide with 2-ethoxyethanol (EOE) or formamide (FA) [15-17,44] (Table-5).

Considering the accuracy of experimental data and the corresponding errors obtained in calculations, we can affirm that the viscosity Arrhenius' current temperature at very high concentration of one pure component (T_{cAi}) at ($x_i \approx 1$), is near to its corresponding boiling point while in other cases, the viscosity Arrhenius' current temperatures (T_{cAi}) at ($x_i \neq 1$) is in strong causal correlation with the temperature of vapourization of the liquid-vapour equilibrium of the corresponding binary liquid mixture at constant pressure. We can then assert these observations as follows:

$$\lim_{x_i \rightarrow 1} \left(\frac{\frac{\partial E_{ai}(x_i)}{\partial x_i}}{\frac{\partial \ln A_{si}(x_i)}{\partial x_i}} \right)_P \approx -R \cdot T_{bi} \quad (32)$$

TABLE 5
COMPARISON BETWEEN THE BOILING TEMPERATURE (T_{bi} , K) AND THE CURRENT ARRHENIUS TEMPERATURE (T_{Ai} , K) FOR ($x_i \approx 1$) CORRESPONDING TO THE PURE COMPONENT (i) IN SOME BINARY MIXTURES

Component 1	Component 2	Ref.	T_{Ai} (K)	T_{bi} (K)	T_{A2} (K)	T_{b2} (K)
DMA	EOE	[15]	440.0	438.45	410.0	408.15
DMA	Water	[16]	456.1	438.45	378.5	373.15
Dioxane	Water	[17]	378.6	374.25	380.5	373.15
DMF	Met	[39]	394.5	426.15	316.3	337.85
DMA	MOE	[40]	361.5	438.15	332.3	397.65
IBA	Water	[41]	433.1	428.15	362.9	373.15
DMA	DMF	[42]	330.6	438.15	329.1	426.15
DMA	Met	[43]	418.7	438.15	319.4	337.85
DMA	FA	[44]	429.1	438.15	479.6	483.65
DMF	2-Propanol	Present work	398.3	426.15	367.6	355.15

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

Correlation between the viscosity Arrhenius' current temperatures (T_{cAi})/K at ($x_i \approx 1$) for the pure liquid component (i) and the corresponding boiling points T_{bi} /K calculated by couple of pure solvents from some binary systems studied at earlier works (eqns. 30 or 32) [15-21,30,34,36] is shown in Fig. 14 and presented in Table-5. It is observed that the straight line related to the fit of linear least square method. ($Y = -3.9852 + 0.98329X$); with a correlation coefficient value $R = 0.96881$, is approximately parallel to the straight line of the first bisector ($Y = +X$). Where $X = T_{bi}$ and $Y = T_{cAi}$. Indeed, the slope value is equal to 0.98329 which deviates from the unit to about 1.2 % and the absolute value related to the intercept to the ordinate (3.99) is less than the value of the standard deviation ($\sigma = 31.64$) of the set of boiling points utilized in this correlation study (where T_{bi} are a mean value equal to 407.51 K). So as to compare the statistical values of the distribution of the 20 obtained viscosity Arrhenius' current temperatures (T_{Ai} /K) of pure solvents and the corresponding boiling temperatures (T_b /K) we can write that $T_{Ai}/K = (385.84 \pm 21.19)$ and $T_{bi}/K = (407.51 \pm 17.81)$ i.e. with an overlap of 17.32 K where there is a net intersection between their confidence intervals (CI).

Furthermore, a new proposed Hajkacem-Ouerfelli model [55,56] suggests peculiar causal correlation and good agreement between the two Arrhenius parameters ($\ln A_s$ and E_a) for moderate and low viscous pure liquids (eqn. 33) which have not very low values of the pre-experimental factor ($\ln(A_s/\text{Pa}\cdot\text{s}) > -17$, i.e. $A_s > 42 \text{ nPa}\cdot\text{s}$) and not very high values of the activation energy ($E_a < 30 \text{ kJ mol}^{-1}$).

$$E_a = \lambda \cdot R \times (-\ln A_s)^{\alpha_0} \quad (33)$$

where R is the constant of perfect gas, $\alpha_0 = 2.933$ and $1 \approx 1 \text{ K}$.

We notice that this model can be also utilized for the two Arrhenius parameters of several binary liquid systems with a reliable agreement. Further, this equation would be very helpful in several branches of the physical and chemical sciences. More, it will be very useful for engineering experimental data and will permit to predict one non-existent parameter when the second one is available (eqn. 33 or eqn. 34), or can be further more estimated by some theories proposed in the literature [51].

$$\ln A_s = -\left(\frac{E_a}{\lambda R}\right)^{\frac{1}{\alpha_0}} \quad (34)$$

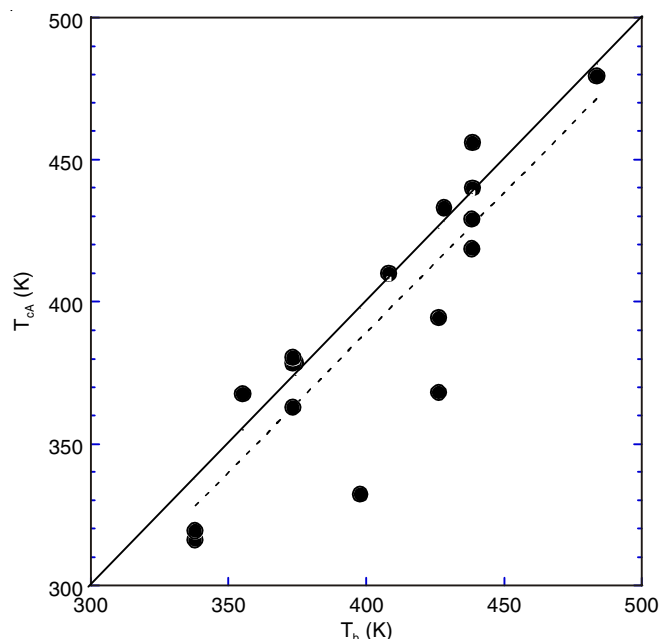


Fig. 14. Correlation between the current Arrhenius temperatures (T_{Ai}) (K) for ($x_i \approx 1$) for the pure component (i) and the corresponding boiling temperature T_{bi} (K) determined by couple of components from some binary liquid mixtures studied at previous works (eqn. 3) [15-17,39-44]; (—) the first bisector ($Y = +X$) in the present axis system and (---) linear least square fit

It is noticed that we obtain the same results with the Messaâdi-Dhouibi model (eqn. 35 or eqn. 36) [57], but for more extended domain of validation ($5 < E_a < 60 \text{ kJ mol}^{-1}$) and ($-25 < \ln(A_s/\text{Pa}\cdot\text{s}) < -9$).

$$\ln(A_s) = \frac{-E_a}{RT_0 \cdot \left(1 - e^{-\frac{E_a}{\alpha_0 RT_0}}\right)} \quad (35)$$

$$E_a = -\frac{RT_0 \cdot [\ln(A_s) + \alpha_0]}{\left(1 - e^{-\frac{RT_0 \cdot \ln(A_s)}{\gamma_0}}\right)} \quad (36)$$

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

In addition, considering the causal correlation shown in Fig. 14 and eqn. 33, it is suggested that the direct correlation

between the boiling temperature and the activation energy expressed by the following equation:

$$T_b = -\frac{E_a}{68 - 4.05 \times E_a^{0.34}} \quad (37)$$

However, due to the restriction of the validity domain of eqns. 33 and 34 ($E_a < 30 \text{ kJ mol}^{-1}$) this equation fails for fluids with high or low viscosity especially for low boiling temperature ($T_b < T_{b, \text{Water}}$).

Likewise, when we consider the eqn. 34 instead of eqn. 33, we can deduce the following expression:

$$T_b = \frac{(-\ln A_s)^{2.933}}{8.2 + \ln A_s} \quad (38)$$

Also, we note the same precedent conclusion due to the restriction domain on the logarithm of the entropic factor ($\ln(A_s/\text{Pa}\cdot\text{s}) > -17$). Fig. 15 is showing the comparison between the experimental and the calculated boiling temperatures through the two eqns. 37 and 38, we can conclude that there are three classes of causal correlations. In fact, we observe that two different points' forms don't match. It is concluded that the two Arrhenius parameters are in causal correlation with the boiling temperature, but with other physicochemical properties implicitly for which there are some ones are common for the two parameters while others are in connection only for one parameter (E_a) or ($\ln A_s$). To remedy this observation, we will try to propose in next works, an expression both explicit, the two Arrhenius parameters alternatively in the denominator and in the numerator.

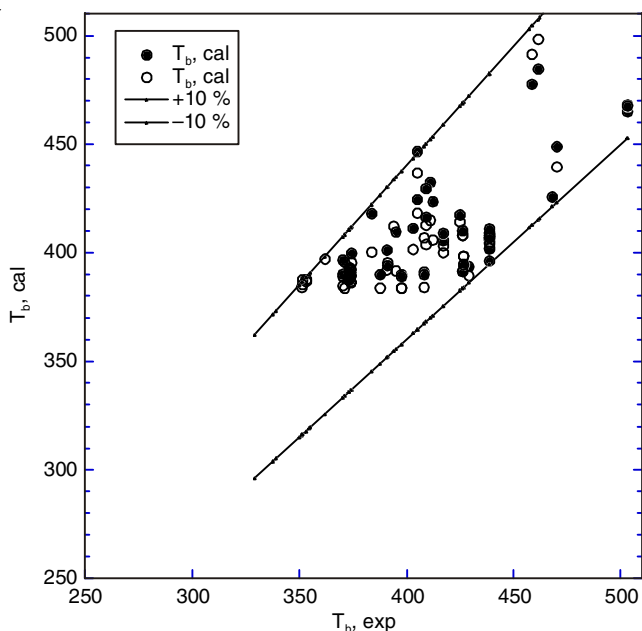


Fig. 15. Correlation between the experimental boiling temperature $T_{b, \text{exp}}$ (K) and the calculated boiling temperature ($T_{b, \text{cal}}$) (K) for some pure liquids studied at previous work [55]; (○) from eqn. 37 and (●) from eqn. 38; (—) around the first bisector ($Y = +X \pm 10\% \times X$) in the present axis system

Conclusions

Based on the same experimental data of densities and shear viscosities of DMF + 2-propanol binary liquid mixtures at five

temperatures (303.15 to 323.15) K and under atmospheric pressure, some original theoretical and semi-empirical approaches have been taken into consideration, for improving investigations of the dependence with molar composition of the partial molar properties related to Arrhenius activation energy.

Viscosity Arrhenius parameters of pure liquid components (2-propanol and DMF) against temperature can be estimated. The correlation between the two viscosity Arrhenius parameters ($\ln(A_s)$) and (E_a) for binary liquid mixtures permits us to bring to light Arrhenius temperature which characterizes the binary mixture and can give information on the temperature of vapourization of the liquid-vapour equilibrium at constant pressure. In addition, this correlation can show the existence of distinct regions of composition with distinct behaviours.

Hence, assuming that the viscosity activation energy is a thermodynamic function, we have calculated the corresponding molar partial activation energy to reveal contributions of individual interaction about each pure liquid component within the liquid mixture at each well-known molar composition. The correlation between the molar properties relative to the logarithm of Arrhenius entropic factor and Arrhenius activation energy for DMF + 2-propanol liquid mixtures over the studied temperature range can exhibit a roughly linear behaviour *i.e.* no observation of any change in curvature. This approximately straight line behaviour supposes us to make a semi-empirical equation by introducing the new defined parameter (T_A) denoted as Arrhenius temperature that characterizes each binary liquid system. In case of the molar properties, we consider that, over the full range of composition, the viscosity Arrhenius temperature (T_A) is no longer constant, we introduce then, for each pure liquid component (i), a new physical concept of the viscosity Arrhenius' current temperature (T_{Ai}) to estimate its two limit values *i.e.*, at very high dilution and very high concentration respectively. The derived results in the treated binary liquid system shows an interesting fact that, at constant pressure, the boiling temperature (T_{bi}) of the two pure liquid components strongly depends on Arrhenius' current temperature (T_{Ai}). In addition, in consequence of this causal correlation we have suggested two original empirical equations for predicting the boiling temperature values through the viscosity Arrhenius parameters. Finally, we can affirm that with extended mathematical handlings, we will be able to bring to light some physical significances of Arrhenius parameters and it surely promote as well as ameliorates the thermodynamic theories and then to estimate some information on isobaric liquid-vapour diagram through the treatment of the viscosity as a function of composition and temperature just in the binary mixture liquid phase and due to the viscosity Arrhenius temperature with regard to the boiling points of the pure liquid components.

More, an additional treatment on the ultimate relationship between viscosity Arrhenius temperature and numerous mixtures properties can prove how this method can estimate the properties values of other not studied binary mixture. In order to tightly develop the utility of the viscosity Arrhenius temperature and establish some means for estimating such properties, more binary liquid mixtures will be treated in future to provide a protocol more clearly discussed. To our best of knowledge, there is no large physical and theoretical

basis of this new concept study or any developed predictive methods for our initial hypothesis and so we cannot able to supply more clearly our examinations. We are very much optimistic that these interesting and original experimental findings can be well welcomed by the researchers for promoting new theoretical approaches. More, in next studies, we will discuss the pressure effect on the viscosity and how the correlation can be expected with theories already available.

ACKNOWLEDGEMENTS

The authors thank the Deanship of Scientific Research of University of Dammam, Saudi Arabia, for supporting this work and funding this project [Grant number 2015151].

REFERENCES

- M.M.H. Bhuiyan and M.H. Uddin, *J. Mol. Liq.*, **138**, 139 (2008).
- J.A. Riddick, W.B. Bunger and T.K. Sakano, *Organic Solvents*, Wiley Interscience, New York, edn 4 (1986).
- A. Laesecke, *J. Mol. Liq.*, **145**, 51 (2009).
- C. Yang, Y. Sun, Y. He and P. Ma, *J. Chem. Eng. Data*, **53**, 293 (2008).
- M.H. Uddin, M.Z.H. Khan, M.H. Rahman, M.A. Shahriar and M. Abdullah-Al-Mashud, *Phys. Chem. Liq.*, **52**, 251 (2014).
- C.M.N. Kinart, *Phys. Chem. Liq.*, **27**, 115 (1994).
- R.K. Das and M.N. Roy, *Phys. Chem. Liq.*, **52**, 55 (2014).
- B. Zhang, Y. Cai, X.L. Mou, N. Lou and X. Wang, *Chem. Phys.*, **280**, 229 (2002).
- J.B. Rabor, T. Yoshidome, T. Mitsushio, K. Yoshida, B.J. Sarno and M. Higo, *Int. Res. J. Pure Appl. Chem.*, **3**, 159 (2013).
- Z. Zhang, L. Yang, Y. Xing and W. Li, *J. Chem. Eng. Data*, **58**, 357 (2013).
- J. Zielkiewicz, *J. Chem. Thermodyn.*, **27**, 415 (1995).
- P. Sivagurunathan, K. Ramachandran and K. Dharmalingam, *Main Group Chem.*, **5**, 89 (2006).
- J.P. Chao, M. Dai and Y.X. Wang, *J. Chem. Thermodyn.*, **21**, 1169 (1989).
- M. Stockhausen and H. Busch, *Phys. Chem. Liq.*, **32**, 183 (1996).
- M. Hichri, D. Das, A. Messaâdi, E.S.B.H. Hmida, N. Ouerfelli and I. Khattech, *Phys. Chem. Liq.*, **51**, 721 (2013).
- D. Das, A. Messaâdi, N. Dhouibi, N. Ouerfelli and A.H. Hamzaoui, *Phys. Chem. Liq. Phys. Chem. Liq.*, **51**, 677 (2013).
- N. Ouerfelli, Z. Barhoumi and O. Iulian, *J. Solution Chem.*, **41**, 458 (2012).
- D. Das and N. Ouerfelli, *J. Solution Chem.*, **41**, 1334 (2012).
- D. Das, A. Messaâdi, Z. Barhoumi and N. Ouerfelli, *J. Solution Chem.*, **41**, 1555 (2012).
- D. Das, Z. Barhoumi and N. Ouerfelli, *Phys. Chem. Liq.*, **50**, 346 (2012).
- D. Das, Z. Barhoumi, N. Dhouibi, M.A.M.K. Sanhoury and N. Ouerfelli, *Phys. Chem. Liq.*, **50**, 712 (2012).
- D. Das, A. Messaâdi, N. Dhouibi and N. Ouerfelli, *Phys. Chem. Liq.*, **50**, 773 (2012).
- M. Singh, *J. Biochem. Biophys. Methods*, **67**, 151 (2006).
- A. Chandra, V. Patidar, M. Singh and R.K. Kale, *J. Chem. Thermodyn.*, **65**, 18 (2013).
- M. Singh, V. Kumar and R.K. Kale, *Int. J. Therm.*, **14**, 87 (2011).
- R.K. Ameta, M. Singh and R.K. Kale, *New J. Chem.*, **37**, 1501 (2013).
- M. Singh, V. Kumar, J.S. Patel and R.K. Kale, *Int. J. Therm.*, **14**, 135 (2011).
- M. Singh, R.K. Ameta, B.S. Kitawat and R.K. Kale, *J. Mater. Sci. Chem. Eng.*, **2**, 43 (2014).
- S. Singhal, *Int. J. Chem. Tech. Appl.*, **2**, 152 (2013).
- N. Ouerfelli, A. Messaadi, E.B.H. H'mida, E. Cherif and N. Amdouni, *Phys. Chem. Liq.*, **49**, 655 (2011).
- O. Iulian and O. Ciocirlan, *Roum. Chim.*, **55**, 45 (2010).
- J.V. Herraez, R. Belda, O. Diez and M. Herráez, *J. Solution Chem.*, **37**, 233 (2008).
- N. Ouerfelli, M. Bouaziz and J.V. Herráez, *Phys. Chem. Liq.*, **51**, 55 (2013).
- N. Ouerfelli, T. Kouissi, N. Zrelli and M. Bouanz, *J. Solution Chem.*, **38**, 983 (2009).
- E. Cherif, N. Ouerfelli and M. Bouaziz, *Phys. Chem. Liq.*, **49**, 155 (2011).
- N. Ouerfelli, T. Kouissi and O. Iulian, *J. Solution Chem.*, **39**, 57 (2010).
- N. Ouerfelli, O. Iulian and M. Bouaziz, *Phys. Chem. Liq.*, **48**, 488 (2010).
- N. Ouerfelli, Z. Barhoumi, R. Besbes and N. Amdouni, *Phys. Chem. Liq.*, **49**, 777 (2011).
- Z. Trabelsi, M. Dallel, H. Salhi, D. Das, N.A. Al-Omair and N. Ouerfelli, *Phys. Chem. Liq.*, **53**, 529 (2015).
- A. Messaâdi, H. Salhi, D. Das, N.O. Alzamil, M.A. Alkhalidi, N. Ouerfelli and A.H. Hamzaoui, *Phys. Chem. Liq.*, **53**, 506 (2015).
- D. Das, H. Salhi, M. Dallel, Z. Trabelsi, A.A. Al-Arfaj and N. Ouerfelli, *J. Solution Chem.*, **44**, 54 (2015).
- N. Dhouibi, M. Dallel, D. Das, M. Bouaziz, N. Ouerfelli and A.H. Hamzaoui, *Phys. Chem. Liq.*, **53**, 275 (2015).
- H. Salhi, M. Dallel, Z. Trabelsi, N.O. Alzamil, M.A. Alkhalidi and N. Ouerfelli, *Phys. Chem. Liq.*, **53**, 117 (2015).
- M. Dallel, D. Das, E.S. Bel Hadj Hmida, N.A. Al-Omair, A.A. Al-Arfaj and N. Ouerfelli, *Phys. Chem. Liq.*, **52**, 442 (2014).
- N.A. Al-Omair, D. Das, L. Snoussi, B. Sinha, R. Pradhan, K. Acharjee, K. Saoudi and N. Ouerfelli, *Phys. Chem. Liq.*, [doi:10.1080/00319104.2016.1139707](https://doi.org/10.1080/00319104.2016.1139707).
- H.C. Longuet-Higgins, *Proc. R. Soc. Lond.*, **205**, 247 (1951).
- N. Matsubayashi and M. Nakahara, *J. Chem. Phys.*, **94**, 653 (1991).
- T. Nakagawa, *J. Mol. Liq.*, **63**, 303 (1995).
- M.E. de Ruiz Holgado, C.R. de Schaefer and E.L. Arancibia, *J. Mol. Liq.*, **79**, 257 (1999).
- H. Falkenhagen, *Theorie der Elektrolyte*, Hirzel: Leipzig (1971).
- H. Eyring and M.S. John, *Significant Liquid Structure*, Wiley: New York (1969).
- A. Ali, A.K. Nain and S. Hyder, *J. Indian Chem. Soc.*, **75**, 501 (1998).
- D.G. Leaist, K. MacEwan, A. Stefan and M. Zamari, *J. Chem. Eng. Data*, **45**, 815 (2000).
- R. Besbes, N. Ouerfelli and M. Abderabba, *Mediterr. J. Chem.*, **1**, 289 (2012).
- R.B. Haj-Kacem, N. Ouerfelli, J.V. Herráez, M. Guettari, H. Hamda and M. Dallel, *Fluid Phase Equilib.*, **383**, 11 (2014).
- R.B. Haj-Kacem, N. Ouerfelli and J.V. Herráez, *Phys. Chem. Liq.*, **53**, 776 (2015).
- A. Messaadi, N. Dhouibi, H. Hamda, F.B.M. Belgacem, Y.H. Adbelkader, N. Ouerfelli and A.H. Hamzaoui, *J. Chem.*, Article ID 163262 (2015).