

Investigations on the Effect of Temperature Change on Activation Energy and Infinite Viscosity of Some Liquids

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Abstract: Temperature change normally affects the physical properties of some liquids and their mixtures. In this paper, we investigated the effect of temperature change on viscosity, activation energy and infinite viscosity of water, alcohols and their mixtures. The viscosity and activation energy decreased with increase in temperature. The infinite viscosities of water, alcohols and their mixtures were not affected with change in temperature.

Keywords: Viscosity, Activation energy, Infinite viscosity, Temperature, Liquid, Mixture, Water, Methanol, Ethanol

1. Introduction

The effect of temperature variation on a particular liquid or liquid mixture can be studied using the Arrhenius equation [2].

$$\mu = B \exp(E_a / k_B T) \quad (1)$$

where B is a constant for a given liquid, k_B is the Boltzmann constant; T is the temperature and E_a the activation energy for viscous flow. Hence, we re-write as

$$\ln(\mu) = \frac{E_a}{K_B T} + \ln B \quad (2)$$

The activation energy, E_a can be calculated from equation (2) by plotting $\ln(\mu)$ versus $1/T$, and determining the value of the slope. If the graph is a straight line, then E_a does not change with temperature variation. However, if the graph is nearly a straight line, it shows that the variation of activation energy of that liquid with temperature is not large. The small changes can be determined by drawing a straight line tangent at lowest temperature T_1 . From the slope we get

$$\tan \theta = \frac{E_a}{K_B} \text{ at } T_1 \quad (3)$$

E_a at T_1 is the activation energy at T_1 . Then the subsequent activation energies are found from

$$\ln(\mu_1) - \ln(\mu_2) = \frac{E_{a1}}{K_B T_1} - \frac{E_{a2}}{K_B T_2} \quad (4)$$

Alternatively, E_a can also be determined by taking two consecutive points ($\ln \mu, 1/T$) on the plotted graph, then

$$\frac{\Delta(\ln \mu)}{\Delta(1/T)} = \frac{E_a}{K_B} \quad (5)$$

One can also determine the average activation energy, E_{av} of the liquid over the temperature range studied by drawing a

mean straight line or least squares fit line through these points, from the plot of $\ln(\mu)$ versus $1/T$, and from the slope of the line, the average activation energy of the liquid is determined as in equation (5).

2. Materials and Method

The most widely used mixing rules for the temperature-independent parameter, P , is given as [4],

$$A_T = \sum (P_i A_i) \quad (6)$$

where A_i is the physical property of the liquid component i , whose mole fraction in the mixture is P_i , and the excess function (A^E) for binary liquid mixtures are calculated by a formula,

$$A^E = A_{ex} - (P_1 A_1 + P_2 A_2) \quad (7)$$

where P_1 and P_2 are the mole fractions of first and second liquid components respectively, and A_{ex} is the experimental physical property.

Therefore, for viscosity coefficient, μ , equation (7) becomes

$$\mu^E = \mu_{ex} - (P_1 \mu_1 + P_2 \mu_2) \quad (8)$$

and this can be re-arranged and written as

$\mu = \mu_{ex} - \mu^E$ (9) where $\mu = (P_1 \mu_1 + P_2 \mu_2)$. Thus, from equations (8) and Eq.(1)

$$\mu_{ex} - \mu^E = B \exp\left(\frac{E_a}{K_B T}\right) \quad (10)$$

where E_a is the viscous activation energy, k_B is the Boltzmann's constant, T is the absolute temperature and B is the pre-exponential constant.

The value of B in equation (1) was approximated as the infinite-temperature viscosity (μ_∞), which is exact in the limit of infinite temperature. Hence, equation (1) can be rewritten in the following form^[6],

$$\mu = \mu_\infty \exp\left(\frac{E_a}{K_B T}\right) \quad (11)$$

and equation (11) becomes

$$\mu_{ex} - \mu^E = \mu_\infty \exp\left(\frac{E_a}{K_B T}\right) \quad (12)$$

The natural logarithmic viscosity is directly proportional to the reciprocal value of the temperature, thus,

$$\ln(\mu) = \frac{S}{T} - D \quad (13)$$

where S and D are constants and T is temperature in Kelvin (K).

Since viscosity decreases with increase in temperature, and the temperature approaches infinity, $\mu \approx \mu_\infty$, (i.e. $\mu_{ex} \approx 0$ and $\mu^E \approx 0$). Similarly, a decreasing temperature would increase the viscosity of a liquid and thus, temperature at T_{ex} would give $\mu \approx (\mu_{ex} - \mu^E)$.

With the above mentioned conditions, we can make equation (13) into the following form:

$$\mu = \mu_\infty \left(\frac{(\mu_{ex} - \mu^E)}{\mu_\infty} \right)^{(T_{ex}/T)} \quad (14)$$

Taking the natural logarithmic of equation (14), the linear regression of equation (14), is given as

$$\ln(\mu) = \ln(\mu_\infty) + \frac{T_{ex}}{T} \ln\left(\frac{\mu_{ex} - \mu^E}{\mu_\infty}\right) \quad (15)$$

The plot of $\ln(\mu)$ against $1/T$ will give a slope = $T_{ex} \ln[(\mu_{ex} - \mu^E)/\mu_\infty]$ and intercept = $\ln(\mu_\infty)$ on the $\ln(\mu)$ axis. It can be observed that the infinite viscosity can be determined from the intercept value $\ln(\mu_\infty)$ which is a constant, and the excess viscosity, μ^E can be determined from the slope of the plot of $\ln(\mu)$ versus $1/T$ from the equation (15). This indicates that the infinite viscosity is independent of temperature, unlike excess viscosity.

Comparing equations (11) and (14), we get

$$E_{ao} = K_B T_{ex} \ln\left(\frac{\mu_{ex} - \mu^E}{\mu_\infty}\right) \quad (16)$$

where E_{ao} is the activation energy constant. This is the energy required by a molecule to move from infinite temperature

down to a temperature T_{ex} . Infinite-temperature viscosity, μ_∞ indicates its internal viscosity, and is free from the influence of temperature.

A capillary temperature control viscometer constructed, (Plate II)^[2], was used to investigate the effect of temperature variation on the density, viscosity, infinite viscosity, excess viscosity and activation energy of: (a) Distilled Water, (b) Ethanol, (c) Methanol, (d) Water-ethanol mixture, (e) Water-methanol mixture, (f) Ethanol-ethanol mixture, and (g) Water-methanol-ethanol- mixture.

The viscometer was kept for 15 minutes in the thermostatically controlled water-bath to achieve constant temperature. The measurements of flow time of the solution between the two points on the viscometer were performed at least three times for each solution and the average results were noted. All liquids making up a mixture were of equal proportion by volume. The volumes of a particular mass of the liquids at different temperatures studied were noted. Then the densities of the liquids and liquid mixtures at different temperatures were calculated using the relation, density = mass/volume.^[5].

3. Results and Discussion

The viscosity coefficients of the liquids and liquid-mixtures at different temperatures were calculated using equation,^[1]

$$\mu_2 = \frac{\mu_1 \rho_2 t_2}{\rho_1 t_1} \quad (17)$$

Similarly, the corresponding activation energies at various temperatures were determined using equation (2). A graph of $\ln(\mu)$ against $1/T$ is plotted for each liquid and liquid-mixture. The interpolated value of $\ln(\mu)$ is found to be the value for $\ln B$ in equation (2), and is specific for a particular liquid or liquid-mixture. The average activation energy, E_{av} for each liquid or liquid-mixture within the temperature range studied is evaluated from the slope of least square fit line of the graphs of $\ln(\mu)$ against $1/T$.

From Fig (1), generally, density (ρ), viscosity coefficient (μ) and activation energy E_a of water, methanol and ethanol, decrease with increase in temperature. This could be due to the energy obtained to overcome the resistance to flow. Fig (1) shows that the reduction of the viscosity is greater at the initial stage of the temperature increment, and subsequent increases in the temperature during the latter part had less influence on reducing the viscosity. Ethanol has higher viscosity than distilled water and methanol (Fig 1).

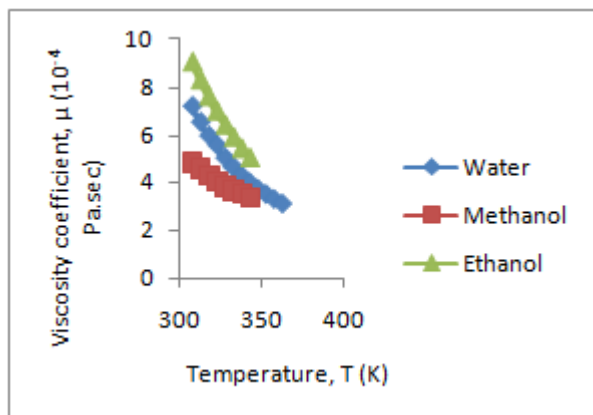


Figure 1: Variation of viscosity, of ethanol, methanol and water with temperature

As in the case of variation of viscosity coefficients of water, ethanol and ethanol with temperature, the same trend is shown in their variation of activation energies (Fig 2). Although ethanol has higher viscosity than water and methanol, but as it can be seen from Fig (2), water has higher activation energy E_a than ethanol and methanol. This most likely could be due to the stronger attractive forces between water molecules than in methanol and ethanol molecules.

The molecules in a liquid are held together much more strongly than in a gas. A force is needed to overcome the mutual attraction of the molecules so that they can be displaced relative to each other. The more strongly the molecules are held together, the smaller the flow for a given shearing stress. With increasing temperature, the random kinetic energy of the molecules helps to overcome the molecular forces and reduces the viscosity.^[3] The relationship of the activation energies of water, ethanol and methanol with temperature shows a linear trend, (Fig 2).

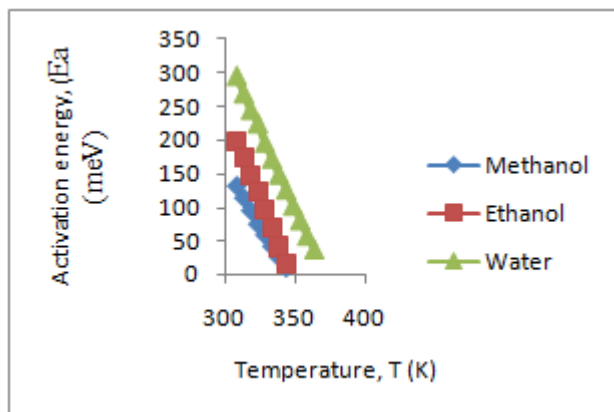


Figure 2: Variation of activation energy, E_a of water, methanol and ethanol with temperature

Fig (3) shows that, viscosity coefficient (μ) and activation energy E_a of water-alcohol mixtures, decrease with increase in temperature. It can be seen from Fig (3), that the viscosity of a mixture of ethanol, methanol and water is controlled mostly by ethanol and methanol since the temperature variation of viscosity of the mixture is the same as that of the mixture of ethanol and methanol. This feature is quite interesting and might throw light on the molecular modeling of the mixing of different molecules and formation of barrier

heights with activation energy that the molecules have to overcome in flowing motion.

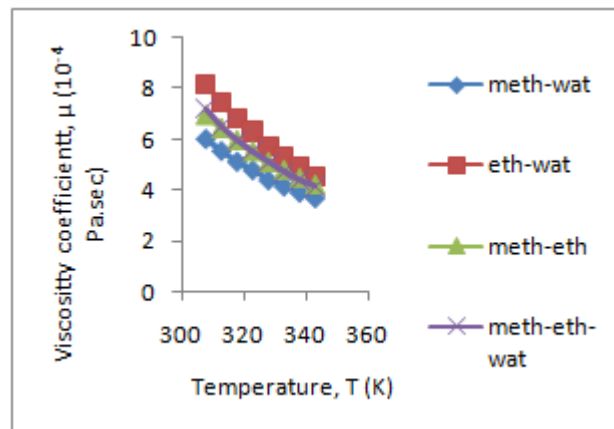


Figure 3: Variation of viscosity of water - alcohol mixtures with temperature

Fig (4) shows very close variations of activation energies of the mixtures of (a) water-methanol, (b) water-ethanol, (c) ethanol-methanol and (d) water-ethanol-methanol, more especially between the temperatures of 330 K to 343 K. The variations of activation energies of the water-alcohol mixtures have a linear trend with temperature. The ethanol-water mixture has higher activation energy than the other mixtures studied.

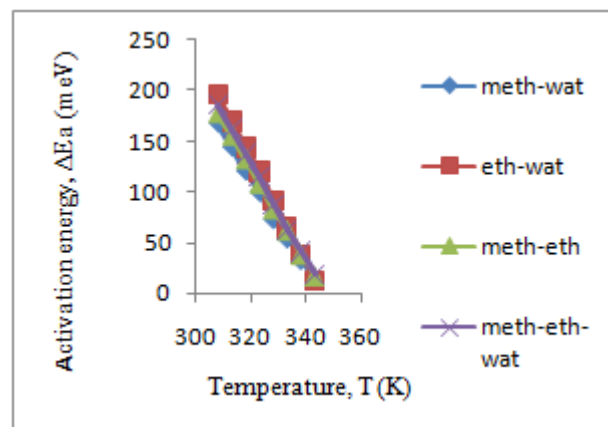


Figure 4: Variation of activation energy of water-alcohol mixtures with temperature

The average activation energy, E_{av} , activation energy constant, E_{a0} , infinite viscosity, μ_∞ , over the temperature range studied for; water, methanol, ethanol and water-alcohol mixtures, were evaluated from their graphs of the modified equations and entered in table (1)

Table 1: Average activation energies, E_{av} , infinite viscosity, μ_{∞} , activation energy constant, E_{a0} , (308 K), for liquids and liquid mixtures studied over the temperature range of 308 K to 363 K

Liquid	Average activation energy, E_{av} (meV) ± 0.01	Infinite viscosity, μ_{∞} (10^{-4} Pa.sec) ± 0.01	Activation energy, constant, E_{a0} (meV) ± 0.01
Distilled water	178.07	2.83	316.84
Pure methanol	111.56	3.26	112.62
Pure ethanol	188.13	4.06	257.28
Methanol-water	159.02	3.52	146.53
Ethanol-water	186.52	4.31	265.65
Methanol-ethanol	164.68	3.98	154.37
Methanol-ethanol-water	171.15	4.02	159.81

The results in Table (1) reveal that pure ethanol has average activation energy (188.13 meV) which is higher than that of water, methanol and alcohol-water mixtures. The values of infinite viscosity for the liquids and mixtures studied fall between 2.14×10^{-4} and 4.31×10^{-4} Pa.sec, in which ethanol-water mixture has higher value (4.31×10^{-4} Pa.sec). The infinite viscosity values obtained for alcohols and their mixtures are their internal viscosities that are independent of temperature. Sunny determined the infinite viscosities^[6] for olive, coconut and sunflower oils to be 3.28×10^{-6} , 1.63×10^{-6} and 1.27×10^{-6} Pa.sec respectively.

The activation energy constant, E_{a0} , could be evaluated via the modified equation (15). In this equation, the pre-exponential constant is well defined and has a physical interpretation as infinite temperature viscosity. The equation reveals that the infinite viscosity of a liquid or liquid-mixture is independent of temperature and concentration.

4. Conclusion

The viscosity and activation energy of water, alcohols and their mixtures decreased with increased in temperature. Change in temperature has no effect on the infinite viscosity of water, alcohols and their mixtures. Infinite viscosity is the internal viscosity of a liquid and has no temperature influence. The fact that internal (infinite) viscosity of a liquid does not change with change in temperature may have to do with the arrangement and the interaction of molecules in the liquid and liquid mixtures, which needs further investigation.

No Conflict of Interests

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