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TECHNICAL DETERMINATION OF IMPURITY CONTENT IN LIQUIDS AT SLIGHTLY FLUCTUATING TEMPERATURE AND THE ACTIVATION ENERGY CHANGE OF BINARY MIXTURE OF ALCOHOLS AT DIFFERENT TEMPERATURES

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Abstract

The method for the determination of solute content in a solvent at slightly fluctuating temperature from the calibration temperature is presented. The viscosity and activation energy change of binary mixture of ethanol and methanol at temperatures of 308 K, 313 K, 318 K, 323 K, 328 K, 333 K, 338 K and 343 K were determined The results show that both viscosity and activation energy change decrease with increase in temperature.

Keywords: Alcohol, viscosity, activation energy, mixture, temperature, technique

Introduction

As temperature increases, gas molecule velocity also increases (according to the kinetic theory of gas). This is also true for liquid and solid substances. The translational) kinetic energy of a molecule is proportional to the velocity of the molecules. Therefore, when temperature increases, KE also increases; as temperature increases, more molecules have higher KE, and thus the fraction of molecules that have high enough KE to overcome the energy barrier also increases.[1]

The fraction of molecules with energy equal to or greater than E_a is given by the exponential term $e{-}Ea/k_B\ T$ in the Arrhenius equation[2],[5]

$$\mu = B\exp\left(E_a / k_B T\right) \qquad (1)$$

μ is the viscosity, E_a is the activation energy, k_B is the Boltzmann's constant, T is temperature in Kelvin, B is frequency factor constant or also known as pre-exponential factor or Arrhenius factor. It indicates the rate of collision and the fraction of collisions with the proper orientation for the reaction to occur.

Taking the natural log of both sides of equation (5) yields the following

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

Equation (2) has the linear form y = mx + b. Graphing lnμ vs 1/T yields a straight line with a slope of $-E_a/\ k_B$ and a y-intercept of ln B.

The activation energy can also be calculated directly given two known temperatures and the viscosity at each temperature. Using Equation (2), suppose that at two different temperatures T_1 and T_2, viscosiyies μ_1 and μ_2:

$$\ln(\mu_1) = \frac{E_a}{K_B T_1} + \ln B \qquad (3) \text{ and}$$

$$\ln(\mu_2) = \frac{E_a}{K_B T_2} + \ln B \qquad (4)$$

Subtracting $\ln\mu_1$ from $\ln \mu_2$:and rearrangement:

$$\ln(\mu_{2/}\ \mu_1) = (1/T_2 - 1/T_1)Ea/k_B \qquad (5)$$

Materials and Method

The ethanol and methanol (BDH grades, 99.4% v/v) were obtained from Microbiology depaetment, Modibbo Adama University of Technology, Yola, Nigeria, without further purification. The density of the various systems at different temperatures were measured using relative measurement method and theviscosity of the mixture was measured using a constructed variable and controllable temperature viscometer.[3],[5] The selected temperature of the liquid mixture was maintained constant by circulating water from a thermostatically controlled water bath with an accuracy of ±1 K. The flow time was determined using a digital stopwatch with an accuracy of ±0.01s.

Results and Discussion

De and Dikko, (2012)[4] showed that the change in activation energy, ΔE_a arising from different concentrations of the impurity (solute) in the mixture (solution) at constant temperature can be calculated as,

$$\Delta E_a = K_B T \ln\left(\frac{\mu_2}{\mu_1}\right) \qquad (6)$$

Therefore, for the effect of temperature on the determination of unknown content of impurity in a solution or mixture using a calibrated curve at a particular temperature, T_{cal}, we may use equation (6) to obtain μ at any other temperature, *T*. Using this equation, it can easily be shown that, for small variation of *T* around the calibration temperature T_{cal}, which may not affect activation energy, E_a of the liquids and that of pure water appreciably,

$$\left(\frac{\mu_2}{\mu_1}\right)_{T_{cal}} = \left(\frac{\mu_2}{\mu_1}\right)_T \exp(T/T_{cal}) \qquad (7)$$

Substituting the value of $\frac{\mu_2}{\mu_1} = \frac{\rho_2 t_2}{\rho_1 t_1}$ in equation (7), and where not too high accuracy is required and T differs from T_{cal} by only a few degrees, $(\rho_2/\rho_1)_T$ may be reasonably assumed to be equal to $(\rho_2/\rho_1)_{cal}$ since the density of a liquid does not change significantly with small change of temperature. Then from equation (7) we get

$$\left(\frac{t_2}{t_1}\right)_{T_{cal}} = \left(\frac{t_2}{t_1}\right)_T \exp(T/T_{cal}) \qquad (8)$$

Thus, from equation (8), one can easily determine $(t_2/t_1)_{T_{cal}}$ that will correspond to the calibration curve by finding out $(t_2/t_1)_T$ experimentally and thus the unknown water concentration, C_W.

Equations (8) could be particularly useful when the calibration curve is done at a particular temperature which the experiments to measure unknown concentration is done at slightly different temperature..

Now, where the concentration of the liquid mixture is constant and the temperature changes, equation (6) becomes

$$\Delta E_a = K_B T_1 \ln\left(\frac{\mu_2}{\mu_1}\right)_{T_1} - K_B T_2 \ln\left(\frac{\mu_2}{\mu_1}\right)_{T_2} \qquad (9)$$

The experimental densities, viscosities and calculated activation energy changes at different temperatures are presented in Table 1.

Table 1

Densities, Viscosities and Activation Energy Change with Temperature for Methanol-Ethanol Mixture,

T (K) ±1	ρ (g/cm³) ±0.005	μ_2 (10^{-4}Pa.sec) ±0.01	ΔE_a (meV) ±0,01
308	0.776	6.957	115.68
313	0.761	6.442	114.19
318	0.734	5.963	112.86
323	0.712	5.516	111.53
328	0.681	5.097	110.27
333	0.653	4.788	109.03
338	0.627	4.466	107.73
343	0.604	4.208	106.46

From figure 1, the viscosity and activation energy change decreased linearly with increasing temperature**.** 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 and change in activation energy [5]

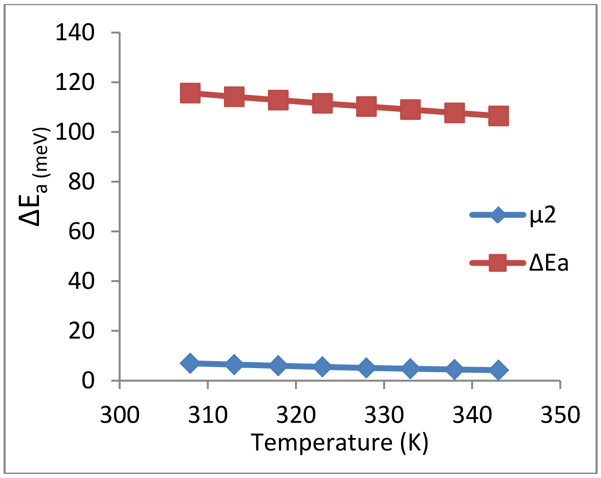

Fig 1Variation of viscosity and activation energy change with temperature

Conclusion

The technique for the determination of solute content in a solvent at slightly fluctuating temperature from the calibration temperature is developed. The viscosity and activation energy change of binary mixture of ethanol and methanol at certain temperatures were determined. The results show that both viscosity and activation energy change decrease with increase in temperature. This obviously shows that as temperature increases, the molecules of tne mixture acquire more energy and hence the less viscous and energy change they require to move to the next level.

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