

The effect of solute concentration on activation energy change of a solution and the determination of solute concentration in the solution

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ABSTRACT

Time of flow, reduced time ratios, viscosity coefficients, reduced viscosity ratios, change in activation energies of distilled water, powdered Dano milk-water mixtures and Glucose-water mixtures, were determined through a simple constructed capillary viscometer. It was observed that activation energy change increases linearly with increase in solute concentration in a solvent. Simple techniques were developed that can determine solute concentration in a solvent at 308 K, by placing the value of the reduced time ratio $(t_2/t_1)_T$ on the calibrated curve to get the corresponding solute concentration. An equation was then developed for the solute concentration, C_s in solvent which takes care of the temperature fluctuations slightly around the calibration

temperature, 308 K, as $C_s = \frac{K_B T \ln\{(\mu_2/\mu_1)_T \exp(T/T_{cal})\} - D}{S}$, where $(\mu_2/\mu_1)_T$ is the reduced

viscosity ratio, T_{cal} is the calibration temperature, T is the temperature at which $(\mu_2/\mu_1)_T$ is determined, k_B is the Boltzmann constant. ($S = 0.1773$, $D = 0.294$ for glucose, $S = 0.1764$, $D = 0.437$ for Dano milk, $S = 0.09016$, $D = 0.0$ for methanol, and $S = 0.0909$, $D = 0.0$ for ethanol). This equation has been tested on some powdered glucose-water mixtures and found to be effective.

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I. INTRODUCTION

In laminar flow, a molecule to go ahead must squeeze past pushing aside the neighboring molecules. To achieve this, the molecule flowing ahead must acquire a definite amount of energy which may be called activation energy, E_a . Then, with Boltzmann factor, the number of molecules having such energy will be proportional to $\exp(-E_a/k_B T)$, (Shiekh *et al*, 2002). The rate of flow and hence fluidity would depend on this number, and the viscosity is given by

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

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. This is the energy barrier that must be surmounted in order for a molecule to squeeze by its neighbors. The activation energy of the original pure liquid should change when a solute molecule is added to it since the addition may change the bond strength of the given liquid or the solvent molecule as the solute molecule tends to occupy the neighboring positions. The change obviously will depend on the type and the concentration of the solute molecule. Thus, from Eq.(1), the viscosity, μ , is expected to be affected significantly by addition of solute molecules to original solvent.

Fig 1 Design of the simple



Viscometer

Plate I Photograph of the Constructed Viscometer

The densities (ρ) of the solutes and the various mixtures, the time of flow (t) of the mixtures, viscosity coefficients (μ) and the change in activation energy (ΔE_a), were determined and recorded in Tables (1 and 2) under average temperature of 308 K. The densities were determined by measuring the mass (m) of a given volume (v) of the mixture and using the relation, $\rho = m/v$. Time t was measured by a digital stop-watch (sport timer) with accuracy of ± 0.01 s. For determination of unknown water concentration in an alcohol sample we prepared different solutions containing different amounts of water in a fixed volume (300 cc) of ethanol or methanol.

III. RESULTS AND DISCUSSION

Results

Three readings for the time of flow, t_2 were recorded for glucose-water mixtures, Dano milk-water mixtures, pure methanol, pure ethanol, distilled water as well as for all the water-alcohol mixtures in Tables (1 to 2). For distilled water the average of three such readings was recorded to be $t_1 = 1544.03 \pm 0.01$ seconds. The temperature during the experiments was recorded at 308 K. To determine the viscosity coefficient of a given liquid mixture, we need the absolute value of μ_1 of water at 308 K is found to be 7.22 millipoise from Hand book of Physical Constants. (1 millipoise = $10^{-4} \text{kgm}^{-1}\text{s}^{-1}$ (10 poise = 1 Pa.s. = $1 \text{kgm}^{-1}\text{s}^{-1}$) (Cutnell and Johnson, 1995). Using these values of μ_1 , ρ_1 , ρ_2 and t_2/t_1 from Tables (1 to 2), the viscosity coefficient μ_2 of the glucose-water mixtures, Dano milk-water mixtures and water-alcohol mixtures are then calculated using the equation,

$$\mu_2 = \frac{\mu_1 \rho_2 t_2}{\rho_1 t_1} \quad (3)$$

(De and Dikko, 2013) and the values are also given in Tables (1 to 2).

Table 1

Variation of densities, viscosity coefficients, and activation energy changes of the solution mixtures of various amount of glucose added to 300 cc of distilled water at 308 K

S N	Vol.of distilled water (cc) ±0.05	Mass of glucose added (g)	Conc. of glucose in sol.ρ ₂ (g/cc)	Density of the sol. ρ ₂ (g/cc) ±0.005	Time of flow, t ₂ (sec) ±0.01	Reduced time ratio t ₂ /t ₁ ±0.0001	Viscosity μ ₂ of the sol. (10 ⁻⁴ Pa.sec) ±0.01	ΔE _a (meV) ±0.001
1	300	3	1	1.004	1549.04	1.0032	7.35	0.474
2	300	6	2	1.007	1555.13	1.0071	7.40	0.654
3	300	9	3	1.011	1560.12	1.0103	7.46	0.868
4	300	12	4	1.014	1566.03	1.0142	7.51	1.046
5	300	15	5	1.018	1571.12	1.0174	7.56	1'222
6	300	18	6	1.021	1576.08	1.0207	7.61	1.397
7	300	21	7	1.025	1582.11	1.0245	7.67	1.606
8	300	24	8	1.029	1587.07	1.0278	7.72	1.778
9	300	27	9	1.031	1592.14	1.0310	7.76	1.916
10	300	30	10	1.034	1598.13	1.0349	7.81	2.086
11	300	33	11	1.038	1503.09	1.0381	7.87	2.289
12	300	36	12	1.041	1609.06	1.0420	7.92	2.458
13	300	59	13	1.044	1614.06	1.0453	7.97	2.625
14	300	42	14	1.047	1619.15	1.0485	8.01	2.758
15	300	45	15	1.050	1625.05	1.0524	8.07	2.956

Density of glucose = 1.51 g / cc, t_w = 1544.03 sec, T = 308 K, μ_w = 7.22 (10⁻⁴Pa.sec)

Table 2
Variation of densities, viscosity coefficients and activation energy changes of solution mixtures of various amounts of powdered dano milk added to 300 cc of distilled water at 308 K

S/N	Vol. of distilled water (cc) ± 0.5	Mass Of Dano milk added(g)	Conc. of D/Milk (g/cc)	Density of the sol. ρ_2 (g/cc) ± 0.005	Time of flow t (sec) ± 0.01	Reduced time ratio t_2/t_1 ± 0.00001	Viscosity μ_2 of the sol. (10^{-4} Pa.sec) ± 0.001	ΔE_a (meV) ± 0.001
1	300	3	1	1.005	1551.04	1.0045	7.390	0.618
2	300	6	2	1.008	1557.12	1.0084	7.442	0.797
3	300	9	3	1.012	1562.03	1.0116	7.474	0.904
4	300	12	4	1.015	1568.31	1.0155	7.525	1.081
5	300	15	5	1.019	1574.04	1.0194	7.583	1.292
6	300	18	6	1.022	1579.06	1.0226	7.630	1.467
7	300	21	7	1.026	1585.14	1.0265	7.689	1.640
8	300	24	8	1.029	1591.21	1.0304	7.740	1.847
9	300	27	9	1.032	1597.06	1.0343	7.792	2.018
10	300	30	10	1.035	1603.13	1.0382	7.844	2.188
11	300	33	11	1.039	1609.12	1.0421	7.940	2.525
12	300	36	12	1.042	1614.05	1.0453	7.951	2.558
13	300	39	13	1.045	1620.02	1.0492	8.004	2.725
14	300	42	14	1.048	1626.14	1.0531	8.057	2.890
15	300	45	15	1.051	1636.01	1.0556	8.110	3.087

$$P_2 = (\rho_D \times v_D + \rho_w \times v_w) / v_2, t_w = 1544.03 \text{ sec. } \rho_D = 1.55 \text{ g/cc, } T = 308 \text{ K, } \mu_w = 7.22 \times 10^{-4} \text{ Pa.sec}$$

IV. DISCUSSION

For both glucose and Dano milk water mixtures, (Tables 1 and 2), the viscosity coefficients and change in activation energies slightly increase with increase in mass per volume concentration. As the concentration increases from 1 g/cc to 15 g/cc, (Fig 1), the viscosity coefficient of glucose-water mixture increases from 7.35 to 8.07 (10^{-4} Pa.sec), while that of Dano milk-water mixture increases from 7.39 to 8.11 (10^{-4} Pa.sec) at room temperature. The Dano milk-water mixtures viscosity is slightly higher than that of glucose-water mixtures.

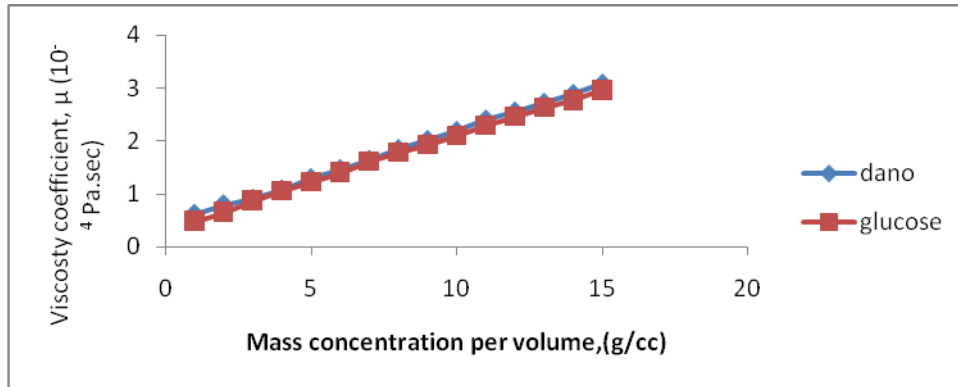


Fig 1 Variation of viscosity with mass per volume conc. for glucose and dano milk,

Similarly, the change in activation energy of glucose-water mixture, (Fig 2), increases from 0.474 meV to 2.956 meV, while that of Dano milk-water mixture increases from 0.618 meV to 3.087 meV. The slightly higher values of viscosity and change in activation energy of Dano milk than that of glucose could be due to the fact that Dano milk is denser than glucose, (Abdollah et al, 2010)

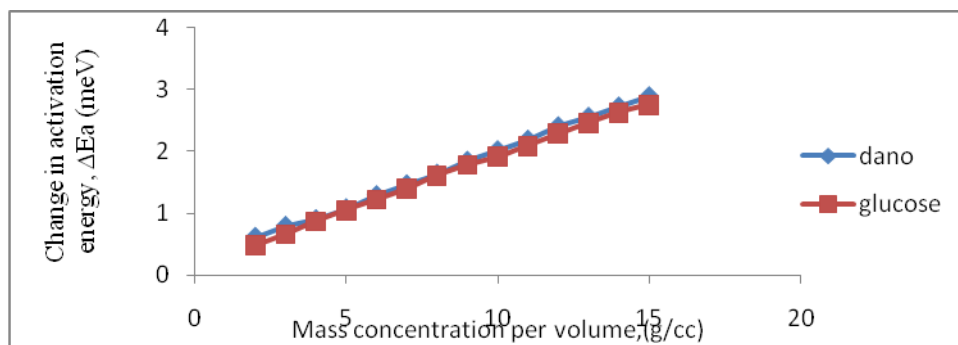


Fig 2 Variations of change in activation energy with mass per volume concentration of glucose and Dano milk in water,

The reduced time ratios for both glucose and Dano milk water mixtures (Fig 3) increase with increase in concentration (g/cc) of glucose or Dano milk. It can be observed that the reduced time ratio for Dano milk-water mixture at a particular concentration is always slightly higher than that of glucose-water mixture at the same concentration.

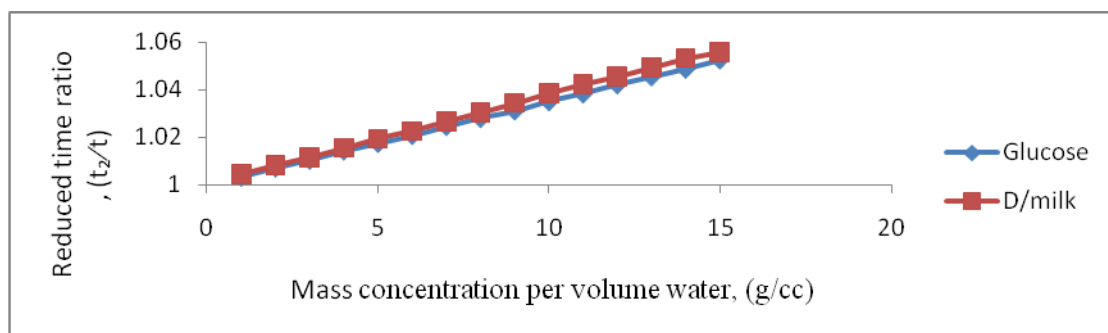


Fig 3 Variation of reduced time ratio with mass per volume concentration of Dano milk and glucose in water

Determination of Solute Concentration in Water

First, we determine t_2 for the sample mixture with unknown miscible solute concentration and t_1 for pure distilled water employing the procedure described above and then take the ratio (t_2/t_1) . Assuming that the type of the miscible solute is known, say glucose. Then looking at the calibration curve we see that when the concentration of glucose in water changes from 1 to 15 g/cc the reduced time ratio (t_2/t_1) changes from 1.0032 to 1.0524 (Table 1). It can be seen from Table (2) that (t_2/t_1) the corresponding changes for Dano milk are from 1.0045 to 1.0556. Then (t_2/t_1) for the sample with unknown miscible solute concentration can be placed on Fig (3) corresponding to the type of solution, to give us the concentration of solute. The same techniques apply to alcohol-water mixtures.

Second, the relationship between the changes of activation energy and solute concentration as seen in Fig (2) is linear and can be expressed as $\Delta E_a = SC_s + D$. Using equation (1) we get the solute concentration as

$$C_s = \frac{K_B T_{cal} \ln(\mu_2/\mu_1)_{T_{cal}} - D}{S} \quad (4)$$

where T_{cal} is calibration temperature, 308 K, S is the slope and D is the intercept on the ΔE_a axis. ($S = 0.1773$, $D = 0.294$ for glucose and $S = 0.1764$, $D = 0.437$ for Dano milk. When there is slight temperature fluctuation of not more than $\pm 2K$, then $(\mu_2/\mu_1)_{T_{cal}}$ in (4) is substituted using the equation

$$\left(\frac{\mu_2}{\mu_1}\right)_{T_{cal}} = \left(\frac{\mu_2}{\mu_1}\right)_T \exp(T/T_{cal}) \quad (\text{De and Dikko, 2012}), \text{ then}$$

$$C_s = \frac{K_B T \ln\{(\mu_2/\mu_1)_T \exp(T/T_{cal})\} - D}{S} \quad (5)$$

Where K_B is the Boltzmann constant and T is the absolute temperature at which $(\mu_2/\mu_1)_T$ is determined.

V. CONCLUSION

Activation energy change increases linearly with increase in solute concentration in a solvent. The solute concentration in a solvent can be determined via the simple techniques and equations developed. This study shows that the new technique can be used to determine unknown concentration of one-component solute like sugar, salt, acid alkali, etc in water (as solvent) with fairly good accuracy and in a short time.

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