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Activation energy of controlled carboxymethyl cellulose size in dilute solution: conductivity measurements

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ABSTRACT

In this research, the conductivity (κ) of carboxymethyl cellulose (CMC) solutions of different concentrations and chains length was studied at various temperatures. κ was found to increase with increasing concentration, temperature, and decreasing the chain length of CMC. The activation energy (E_κ) of the different solutions was estimated according to the Andrade equation, E_κ was increased with increasing concentration and decreasing the chain length of CMC. The results indicated that solute – solute contact is decreased and the solute-solvent interaction is increased in CMC solutions with increasing temperature and decreasing chain dimensions of CMC.

Introduction

In the Eyring (Eyring, 1936) sense, the effect of temperature on the transport properties, like viscosity and conductivity, is of fundamental importance to the structure and behaviour of polymers in dilute solutions since activation energy and internal energy of activation as well as cohesive energy and solubility values are based on such properties (Eyring, 1936; Glasstone et al., 1941). Thus, changes in the transport properties such as conductivity and related parameters at different temperatures are expected; in which the quantity of activation energy is the energy barrier that must be overcome before the process can occur. According to the Andrade (Andrade et al., 1930) equation, it was suggested that the logarithm of the transport processes is to a good approximation a linear function of *1/T*.

Carboxymethyl cellulose (CMC) is a linear water-soluble cellulose derivative with good mechanical and electrical properties (Zhivkov 2013). It deserves special attention due to its numerous advantages. Broniarz-Press et al. studied the thermal conductivity of CMC sodium salt aqueous solutions (Broniarz-Press et al., 2007). Other researchers worked on the development of CMC products using oxidation (Li et al., 2014) and ion doping (Ahmad and Isa, 2016). Kwak and Johnston measured the equivalent conductivity of aqueous solutions of different salts of CMC at 25ºC (Kwak and Johnston, 1975).

The objective of this research is to measure the conductivity of CMC, with different chain lengths, in dilute aqueous solutions. Also, the Andrade (Andrade et al., 1930) equation (Arrheniuse–like equation) is used to study the effect of CMC chain lengths, and concentration on the conductivity behaviour and activation energy of CMC in dilute aqueous solution.

Experimental

2.1 *Materials and Preparation*

The powder material of carboxymethyl cellulose (CMC) was supplied from Jowfe Oil Technology (JOT), Benghazi, Libya. The mother solution of CMC in deionized water (1.00 mg.cm^{-3} concentration) was prepared and the solution was divided into two equal volumes. One was used as a non-degraded solution (highly viscous sample with long chains, labelled as L-

CMC). The second solution was photodegraded by UV-irradiation, the technique of the irradiation is described in our previous work (El Ashhab et al., 2006). The degraded solution (low viscous sample with short chains) was labelled as S-CMC. Two series of different concentrations (*C* ranged 0.50 - 1.00 mg.cm^{-3}) were prepared for both L-CMC and S-CMC.

2.2 *Conductivity measurements*

Conductivities (κ in S.cm^{-1}) of the CMC aqueous solutions were measured at different temperatures in the range of 20- 60 °C using the conductivity meter of digital CMD 650 (cell constant = 1 cm^{-1}), manufactured by MPA Linton, Cambridge, UK. Moreover, the conductivity of CMC with medium chain length (moderate viscous) was estimated as an average of the conductivities of long chains and short chains (labelled as M-CMC).

2.3 *Activation energy estimation from conductivity measurements*

The activation energies of CMC solutions were estimated according to the following form of Andrade Eq. (Andrade et al., 1930),

$$\kappa = A_{\kappa} e^{-\frac{E_{\kappa}}{RT}} \qquad (1)$$

where A_κ is the Arrhenius – type pre-exponential factor, E_κ is the activation energy at different temperatures (*T*), and *R* is the gas constant (8.314 J K^{-1} mol^{-1}).
Taking the natural log of each side of Eq. (1) to obtain linear formula:

$$\ln \kappa = \ln A_{\kappa} - \frac{E_{\kappa}}{RT} \qquad (2)$$

Results and discussion

Figure 1(a-c) shows κ of different *C* of CMC solutions determined at various *T* for different chains length. It is clearly shown that κ is increased with increasing the *C*, and the relationship between κ and increasing *C* is linear. This could be explained based on the behaviour of polymers in dilute solutions. The CMC chains are separated and exist individuals. The behaviour of κ with respect to *T* can be interpreted in terms of polymer mobility. At lower *T* the mobility of CMC is slow due to the higher viscosity (Huggins et al., 1942), which results to lower κ. The CMC chains gain kinetic energy and the restrictive forces decrease with increasing *T*. Thus, accounting for more space is available for the CMC chains to move around easily and higher κ. These observations remain almost unchanged with changing the CMC chains length, however, the κ is increased with decreasing the length as shown in Figure 1(b and c).

The linear decreases of the conductivity logarithm (*ln* κ) with increasing reciprocal temperature (*1/T*) values for CMC conductivity measurements in water is shown in Figure 2 (a-c). According to equation (2), the A_κ values are obtained from the intercept and E_κ is calculated by multiplying the slope by *R*, the values are listed in Table (1). Figures 3 and 4 show E_κ and A_κ of CMC, with different chains length, in dilute solutions versus the *C*, respectively. The results show typical increases of A_κ and E_κ with increasing the *C* and decreasing CMC chains length in the dilute solutions, it was a trend similar to that observed for κ versus *C*. The observation could be due to the reduction in the potential energy barrier according to Eyring sense (Eyring, 1936).

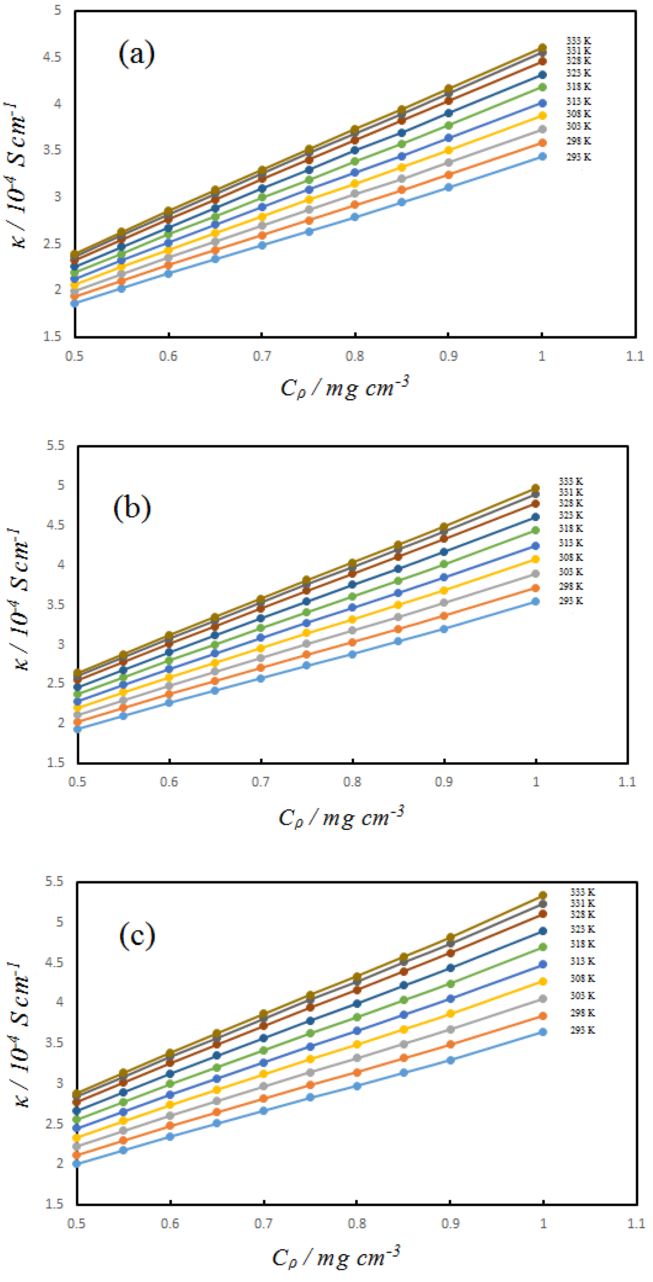

Fig. 1. The conductivity of carboxymethyl cellulose solutions of various concentrations at different temperatures (a) L-CMC, (b) M-CMC, and (c) S-CMC.

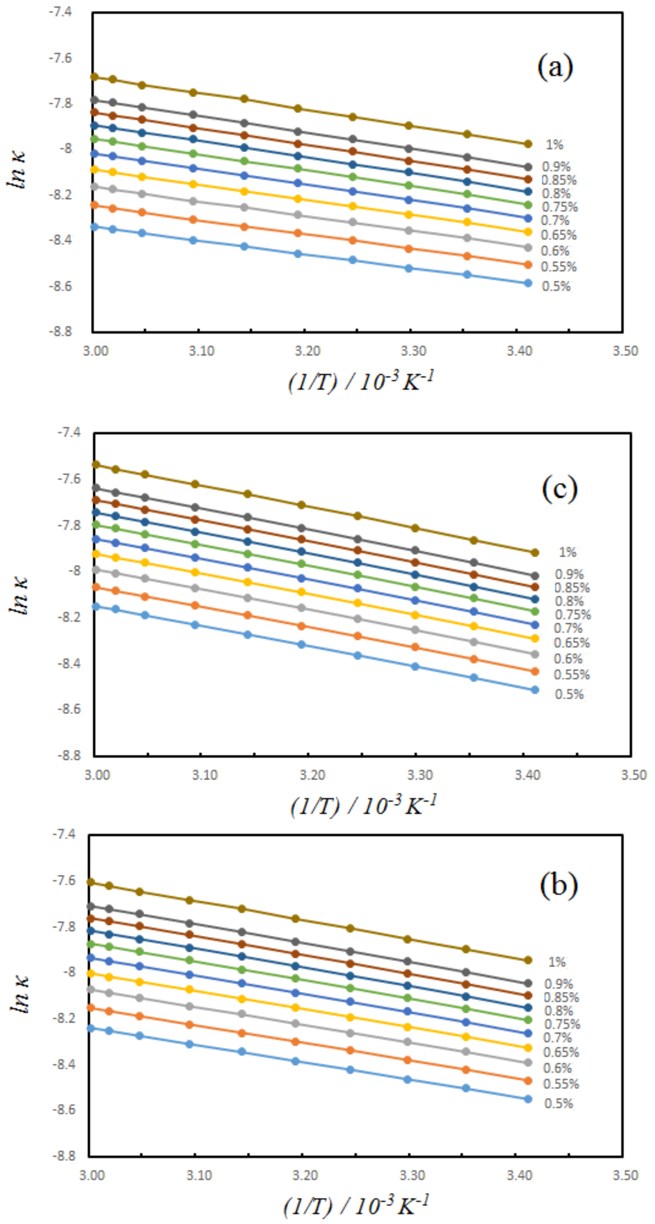

Fig. 2. The Andrade plots of various concentrations of carboxymethyl cellulose solution (a) L-CMC, (b) M-CMC, and (c) S-CMC.

Table 1. The values of Arrhenius pre-exponential factors and activation energy of carboxymethyl cellulose in dilute solutions

Concentration of CMC / mg cm-3	A_κ / 10^{-4} S cm^{-1}			E_κ / kJ mol^{-1}		
	L-CMC	M-CMC	S-CMC	L-CMC	M-CMC	S-CMC
0.50	14.68	25.43	41.28	5.02	6.27	7.36
0.55	17.16	28.66	45.17	5.20	6.36	7.38
0.60	19.65	32.03	49.48	5.34	6.45	7.42
0.65	22.46	35.59	53.70	5.51	6.54	7.46
0.70	25.60	39.53	58.37	5.67	6.64	7.51
0.75	28.43	43.25	63.06	5.78	6.72	7.56
0.80	31.38	47.00	67.67	5.89	6.79	7.60
0.85	33.42	50.15	72.40	5.91	6.82	7.64
0.90	35.59	53.23	76.67	5.94	6.84	7.66
1.00	39.54	59.23	85.46	5.95	6.86	7.68

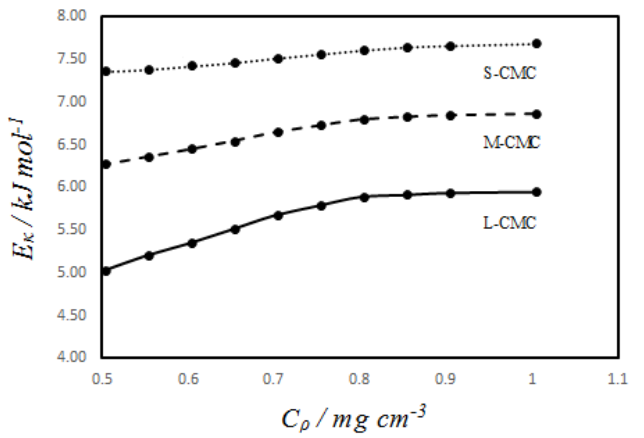

Fig.3. Activation energies of the carboxymethyl cellulose conductivity in dilute solutions vs. the concentrations.

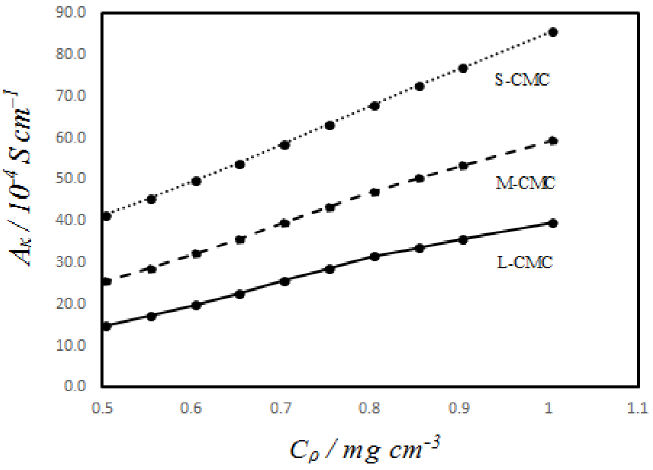

Fig. 4. The Arrhenius pre-exponential factors of the carboxymethyl cellulose in dilute solutions vs. the concentrations.

Conclusions

The conductivity of CMC, with different chains length, in dilute solution was measured for various concentrations at different temperatures. Moreover, the activation energy of the CMC was calculated. It was concluded that the values of conductivity and conductivity activation energy increase with increasing the concentration and decreasing CMC chains length.

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