Effect of Palm Kernel Oil Extraction Method on The Electrical Conductance of Nigerian Traditional Soaps in Alcohols

Moses O. Adebajo*[a], Michael S. Akanni[b] and Ray L Frost [a]

[a]School of Physical and Chemical Sciences, Queensland University of Technology, Gardens Point Campus, GPO Box 2434, Brisbane, QLD 4001, Australia.

[b]Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria.

---

* Corresponding Author. Phone: 61-7-3864-2265

Fax: 61-2-3864-1804

E-mail address: m.adebajo@qut.edu.au

ABSTRACT

Nigerian traditional soaps were prepared using two commercial samples of palm kernel oils (black and pale orange oils) that are extracted locally using two different traditional methods. The effect of the oil extraction method on the conductances of the soaps in alcohols was then investigated. The conductances of the soaps prepared from the pale orange oil are found to be higher than those prepared from the black type. The plots of Λ_c versus $\sqrt{C}$ for the methanolic solutions of the pale orange oil soaps are linear while the plots obtained for the black oil soaps are non-linear. The plots of $\log_{10}k$ versus 1/T are linear for all the soaps in methanol and for K soaps in 1-propanol while they are non-linear for Na soaps in 1-propanol. While the activation energy terms for the soaps prepared from the pale orange oil generally decrease with increase in concentration, the activation energies for the black oil soaps are less sensitive to change in concentration. These observations therefore suggest that the purity of the palm kernel oil can have a significant effect on the properties and quality of the traditional soaps and that the pale orange oil is probably purer than the black type.

Keywords: Alcoholic solutions, Arrhenius plots, electrical conductance; oil extraction method, palm kernel oil soaps.

INTRODUCTION

The Nigerian traditional soaps have been found to have intrinsic antibacterial action in addition to their excellent foaming properties and they, in fact, serve as a medium for preparing local drugs for the treatment of skin diseases (1). However, these soaps have an unattractive black colour and undesirable texture resulting from the crudeness of the local preparation method and previous analysis of the soaps have shown them to contain very high proportion of free alkali (high pH values) which may render them harmful to the skin. Thus, a series of investigations are now being undertaken on the development of the soaps for industrial and medicinal applications. The properties of the soaps are, in the first instance, being investigated in the present series of studies with a view to identifying the sources of impurities in the soaps and the effect of such impurities on their properties. The elemental composition of the soaps was first determined using thermal neutron activation analysis techniques, the results of which indicated high concentrations of potassium and sodium in the soaps (2). Our recent investigation (1) of the electrical conductivity of the solutions of the commercial soaps in alcohols have also demonstrated clearly that the purity, the texture and the foaming capability of the soaps could easily be improved by employing the purification procedures adopted in that work. In this previous study, the electrical conductances of some other soaps prepared in the laboratory from palm kernel oil were also found to be lower than those of the commercial soaps and metal ions were suggested to be the main charge carriers in solution. The conductance data were further confirmed by the viscosity data (1). It should be noted that there are two different traditional methods of extracting palm kernel oils which are normally used in the traditional soap manufacture and these two methods produce oils that probably differ remarkably in quality. This paper therefore reports the effect of the method of extraction of palm kernel oil used in the traditional soap preparation on the electrical conductivity of the soaps in alcohols.

EXPERIMENTAL PROCEDURES

Local methods of extraction of palm kernel oils

As mentioned earlier in the introduction, there are two traditional methods of extracting the palm kernel oils that are used in the manufacture of Nigerian traditional soaps. The first process involves preliminary drying and smoking of the palm kernels. The dried and smoked palm kernels are sieved and heated strongly (almost destructively) in a tray made of clay for the oil to drain from the nuts. The resulting black oil is then filtered and sold commercially as local cosmetic. The second method begins by drying palm kernels in the sun. The dried palm kernels are sieved and washed thoroughly with water. The clean palm kernels are then warmed with water or soaked in water for some days after which they are removed by filtration and then ground. The pulverised palm kernels are then mixed thoroughly with water and squeezed to obtain a solution. This solution is filtered to remove the particles of palm kernels in it. The clear filtrate is then evaporated leaving behind a pale orange oil.

Preparation of the soaps

Samples of the black and pale orange palm kernel oils which are used to prepare the soaps used in the work were purchased from the open market in Ile-Ife, Nigeria in the same conditions in which they are sold to consumers. Potassium or sodium soaps were then prepared in the laboratory by adding stoichiometric amounts of potassium or sodium hydroxide solution to the warm oil samples; the oils were assumed to contain mainly about 47 % dodecanoic (lauric) acid (3). The potassium and sodium hydroxide used were analytical reagent grade obtained from BDH Chemicals Ltd. Poole, England. The details of the preparation and purification procedures have been described elsewhere (1). The Infra Red spectra of all the purified soaps showed them to be free of water and excess acid.

Electrical conductance measurement

Conductances were measured using a dipping type conductivity cell that is made of platinum electrodes. The two electrodes of the cell are connected to the two terminals of a universal Wayne-Kerr B224 conductivity bridge operating at a frequency of 1592 Hz. The cell constant was determined between each run using 0.01 M KCl solution in a water bath thermostated at

298 K. The other details of the conductance measurement have been reported in our recent paper (1). Conductances were measured in the temperature range 283 - 318 K for different concentrations of the soaps in alcohols. The cell constant did not change by more than ± 3 % between runs and the conductivity values are thus accurate to within ± 3 % (1). The potassium chloride and alcohols used were all analytical reagent grade obtained from BDH Chemicals Ltd. Poole, England.

RESULTS AND DISCUSSION

The sodium or potassium soap molecules are considered to dissociate in solution to form charged species according to the reaction:

$$MA \rightleftharpoons M^{+} + A^{-} \qquad (1)$$

where M^+ is the metal ion and A^- is the anion of a fatty acid. It is logical to suppose that M^+, out of the two species in solution, carries the major fraction of the charge than the other more bulky anion. Assuming that the major charge carrier, M^+, moves by a simple activated process, then, as reported in our previous paper (1),

$$\log k = \log Q - \frac{\Delta H_m + \Delta H_d / 2}{2.303\ RT} \qquad (2)$$

where ΔH_m and ΔH_d are the enthalpies of activation for the movement of M^+ (ie. for conduction) and for dissociation, respectively.

$$\log Q = \log\left(\frac{NeA}{2V_m}\right) + \frac{\Delta S_m + \Delta S_d / 2}{2.303R} \qquad (3)$$

where ΔS_m and ΔS_d are the entropies of activation for the movement of M^+ and for dissociation, respectively, N is Avogadro's number, e is the charge on an electron, A is a pre-exponential factor in the relationship between the electrical mobility of M^+ and the absolute temperature and V_m is the molar volume of the pure soap. It therefore follows from equation 2 that a plot of $\log_{10}k$ against 1/T should be linear, with slope equal to $(\Delta H_m + \Delta H_d/2)/2.303R$. Such plots for the alcoholic solutions of dry recrystallised soaps prepared from the pale orange palm kernel oil are illustrated in Figures 1 to 3. Like the results obtained recently for the soaps prepared from black palm kernel oil (1), the plots are all linear for all the soaps in methanol (Figure 1) and for the K soaps in 1-propanol (Figure 2) while they are all non-linear for Na soaps in 1-propanol (Figure 3). The linearity of the plots for the soaps in methanol and for the potassium soaps in 1-propanol therefore suggests that such solutions are non-associated within the range of the concentrations studied. The non-linearity obtained for the Na soaps in 1-propanol can again be attributed to the low solubility of the soaps in this solvent as reported recently (1). It was observed that small particles of the soaps often settled down in 1-propanol with clear solution on top, especially at low temperatures. The different behaviour of the potassium soap in 1-propanol is therefore attributed to the more readily soluble nature of potassium salts.

Figures 1 to 3 also show that the specific conductance increases with both increase in temperature and concentration as observed in our earlier report (1) for the soaps prepared from the black oil. Similar observations have also been reported by several workers (4-10) for various metal soaps (alkali, alkaline earth, transition, lanthanide and actinide) in a range of non-aqueous and mixed organic solvents. The increase in conductivity with increase in temperature is due to the increased mobilities of the charge carriers at high temperatures while the increase with increase in concentration may be attributed to the ionisation of the soaps into the metal cations and fatty acid anions in dilute solutions.

The values of the activation energy, $\Delta H_m + \Delta H_d/2$ are presented in Tables 1 and 2. It is shown in these tables that the activation energy terms for the soaps prepared from the pale orange palm kernel oil generally decrease slightly with increase in concentration. On the other hand, these activation energy values for the soaps prepared from the black palm kernel oil appear to be less sensitive to increase in concentration of the soaps. The lower sensitivity of the activation energy for the conductance of the black oil soaps to change in concentration may be related to the purity of the black palm kernel oil from which it is prepared since visual observation indicates that the pale orange oil is more attractive (cleaner and probably purer) than the black oil.

One significant observation is illustrated in Figure 4 which shows that the specific conductances of the methanolic solutions of the pale orange palm kernel oil soaps are much higher than those of the black oil soaps especially at higher concentrations. It is therefore most likely that the pale orange oil is purer than the black oil as revealed by visual observation. Figure 4 also illustrates further the increase in conductance with increase in concentration.

Like in our previous publication (1), we define again the term "concentration conductance, Λ_c", as:

$$\Lambda_c = \frac{k}{C} \tag{4}$$

where k is the specific conductance in $ohm^{-1}m^{-1}$ and C is the concentration in g/L ($\equiv kgm^{-3}$) so that Λ_c is in $ohm^{-1}m^2kg^{-1}$. This term is used rather the usual molar conductance because the molecular weight of our traditional soap is unknown, being a mixture of many salts.

Another significant observation is that the plots of Λ_c against $\sqrt{C}$ are linear for the methanolic solutions of the soaps prepared from the pale orange palm kernel oil suggesting that these solutions are probably strong electrolytes. In contrast, the same plots for the methanolic solutions of the black oil soaps are non-linear (indicating that they are weak electrolytes) as reported recently (1). The plots for the 1-propanoic solutions of the pale orange oil soaps are also still non-linear as observed for the black oil soaps in our recent investigation. These observations are illustrated in Figure 5. The linear variation of the equivalent conductance with the square root of soap concentration has also been reported previously for the dilute solutions of rubidium soaps in water, methanol and other higher alcohols (11). The limiting concentration conductances, Λ_o, of the methanolic solutions of the soaps prepared from the light orange oil were determined by the usual extrapolation method and the values obtained are presented in Table 3. The limiting conductances are shown clearly in Table 3 to increase gradually with increase in temperature which is consistent with the variation of specific and concentration conductances with temperature. It is shown in Figure 5 that the concentration conductances decrease with increase in concentration and this decrease may be due to the combined effects of ionic atmosphere, solvation of ions and decrease of mobility and ionisation with formation of micelles. Similar observation has been reported recently by Topallar et al. (4,5) the pale orange oil soaps are much higher than those for the black oil soaps suggesting again the possibility of the light orange oil being purer than the black oil as already mentioned. Figure 5 reveals too that the Λ_o values for the soaps prepared from the pale orange oil are higher for K soaps than for the Na soaps in the same solvent indicating that the metal ions are the main charge carriers in solution as already reported (1) for the soaps prepared from the black oil.

It is worth mentioning that not only metal ions are involved in the purification of these soaps. The removal of other impurities such as excess water and excess acid/alkali is also involved. As mentioned in our earlier report (1), the separation and purification procedures in the modern methods by which the imported soaps are produced significantly remove excess water, glycerol and other impurities and give the soap a good texture. In contrast, these important procedures are lacking in the local manufacture of Nigerian traditional soaps. However, our earlier report (1) has shown clearly that a lot of impurities present in these traditional soaps such as the excess acid and water as well as the unattractive black colour of the soaps can be removed by employing the purification procedures employed in that work. The conductivity and viscosity data together with the results of the percentage composition of carbon and hydrogen in the soaps, the IR spectra and the foaming test in this earlier work all appear to confirm the increased purity of the soaps after purification.

The antibacterial action of Nigerian traditional soaps may be due to the proportion of the fatty acid moieties constituting the soaps. Previous analysis by Collin and Hilditch (3) of palm kernel oil from which the soaps are made showed that the oil contains mainly dodecanoic (lauric) acid (about 47 %) with relatively high proportion of the more acidic low molecular weight acids (C8 to C14 = 70.7 %) and low proportion (19.2%) of unsaturated fatty acids (Table 4). More recently, Na 2-lauroyloxypropionate has also been prepared by Pandey et al. (12) as an antibacterial soap that is highly substantive to the skin. This soap and iso-propyl laurate were found by these workers to have a high affinity of binding to pancreatic lipase while glycerol monolaurate was observed to be much less stable. The Na 2-

lauroyloxypropionate was reported by the workers to show greater activity against microflora in vitro and in some other substantivity tests than lauric acid. It should also be noted that it had been previously reported (13) that the antibacterial action of a homologous class of soaps of saturated fatty acids is a direct function of the length of the C chain, the position of the maximum effect varying with regard to the different bacteria. The investigation of the antibacterial activity of the Nigerian traditional soaps is, however, not the focus of the present study. As already mentioned, the present series of investigations is rather focused on identifying the sources of impurities in the soaps and the effects of such impurities on their properties.

REFERENCES

1. Adebajo, M. O. and M. S. Akanni, The Electrical Conductance and Viscosity of Nigerian Traditional Soaps in Alcoholic Media, *Colloids Surf., A: Physicochemical and Engineering Aspects, 194* : 97-110 (2001).
2. Akanni, M. S. and V. O. Ogugbuaja, Multielement Analysis of Nigerian Traditional (Black) Soaps, *J. Radioanal. Nucl. Chem.,* 91(2): 395-402 (1985).
3. Collin, G and T. P. Hilditch, The Component Glycerides of Coconut and Palm Kernel Fats, *J. Soc. Chem. Ind. Trans., 47* : 261-269 (1928).
4. Topallar, H. and Y. Bayrak, Thermodynamics of the Dissociation of Chromium Soap Solutions in Benzene-Dimethyl Formamide, *Turk. J. Chem., 23* : 31-39 (1999).
5. Topallar, H. Y. Bayrak and M. Isçan, Thermodynamics of Dissociation and Micellization of Sodium, Calcium, Aluminium and Tin Stearates in Mixed Organic Solvents, *J. Am. Oil Chem. Soc., 74* : 793-796 (1997).
6. Upadhyaya, S. K. and P. S. Sharma, Effect of Temperature on Micellization and Thermodynamics of Dissociation and Association of Copper Soaps in Benzene-Methanol Mixture, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor., Anal. Chem., 34* : 220-223 (1995).
7. Kumar, A., Physicochemical Characteristics of Cerium (III) Caprylate, *Phys. Chem. Liq., 28* : 57-62 (1994).

8. Kumar, A., Conductivity, Molar Volume and Rheology of Uranyl Soap, *Phys. Chem. Liq., 28* : 251-260 (1994).
9. Upadhyaya, S. K., Conductometric, Viscometric and Acoustical Studies on Gadolinium Caprylate and Caprate in Non-aqueous Medium, *Phys. Chem. Liq., 27* : 11-24 (1994).
10. Mehrotra, K. N., S. P. Sharma and A. Kumar, A Study of the Physicochemical Characteristics of Strontium Palmitate, *J. Indian Chem. Soc., 70* : 19-23 (1993).
11. Mehrotra, K. N., S. P. S. Saroha and M. Jain, Conductometric Investigations of Rubidium Soaps in Water and Alkanols, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor., Anal. Chem., 32* : 819-821 (1993).
12. Pandey, N. K., C. V. Natraj, G. P. Kalle, M. E. N. Nambudiry, Antibaterial properties of soap containing some fatty acids, *International Journal of Cosmetic Science,* 7(1): 9-14 (1985).
13. Klarmann, E., Antibacterial Properties of Soaps, *Soap,* 9(12): 23-7, 107-9, 111, 113,115 (1933).

Table 1. Activation energy for conductance of Na soaps in methanol in the temperature range 283 - 318 K

Concentration (g/L)	Activation energy term, $\Delta H_m + \Delta H_d/2$ (kJ/mol)	
	Soap prepared from black oil	Soap prepared from pale orange oil
1.0	10.60	9.60
3.0	9.39	9.34
5.0	9.63	8.98
8.0	9.50	8.74
10.0	9.17	8.83

Table 2. Activation energy for conductance of K soaps in 1-propanol in the temperature range 283 - 318 K

Concentration (g/L)	Activation energy term, $\Delta H_m + \Delta H_d/2$ (kJ/mol)	
	Soap prepared from black oil	Soap prepared from pale orange oil
1.0	12.52	13.51
3.0	10.17	10.92
5.0	10.98	10.67
8.0	10.00	9.84
10.0	11.20	9.64

Table 3. Limiting concentration conductances, Λ_o, of methanolic solutions of sodium soaps prepared from light orange palm kernel oil at different temperatures

Temperature (K)	$\Lambda_o \infty 10^4$ ($\Omega^{-1}m^2kg^{-1}$)
283	1.09
290	1.19
298	1.35
303	1.48
308	1.54
313	1.60
318	1.71

Table 4. Fatty acid composition of palm kernel oil (3)

Fatty Acids	Percentage of fatty acids
Saturated acids	
Hexanoic (Caproic) acid	Trace
Octanoic (Caprylic) acid	2.7
Decanoic (Capric) acid	7.0
Dodecaoic (Lauric) acid	46.9
Tetradecanoic (Myristic) acid	14.1
Hexadecanoic (Palmitic) acid	8.8
Octadecanoic (Stearic) acid	1.3
Tetracosanoic (Lignoceric) acid	-
Unsaturated acids	
cis-9-Octadecenoic (Oleic) acid	18.5
cis,cis-9,12-Octadecadienoic (Linoleic) acid	0.7

Figure Captions

Figure 1. Plots of $log_{10}k$ against 1/T for different concentrations of solutions (in methanol) of Na soap prepared from pale orange palm kernel oil.

Figure 2. Plots of $log_{10}k$ against 1/T for different concentrations of solutions (in 1-propanol) of K soap prepared from pale orange palm kernel oil.

Figure 3. Plots of $log_{10}k$ against 1/T for different concentrations of solutions (in 1-propanol) of Na soap prepared from pale orange palm kernel oil.

Figure 4. Plots of specific conductance, k, against concentration at 298 K for methanolic solutions of Na soap prepared from (1) pale orange palm kernel oil; (2) black palm kernel oil.

Figure 5. Plots of Λ_c against $\sqrt{C}$ at 318 K for: (1) methanolic solution of Na soap prepared from the pale orange palm kernel oil; (2) methanolic solution of Na soap prepared from the black palm kernel oil; (3) 1-propanolic solution of K soap prepared from the pale orange oil; (4) 1-propanolic solution of Na soap prepared from the pale orange oil.

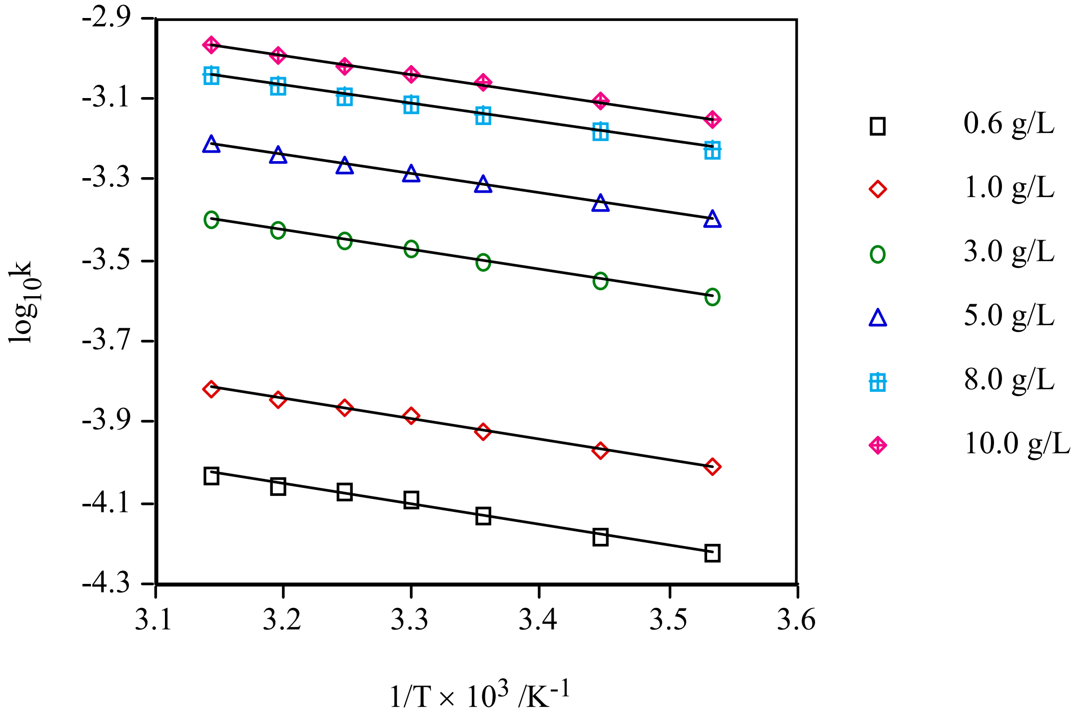
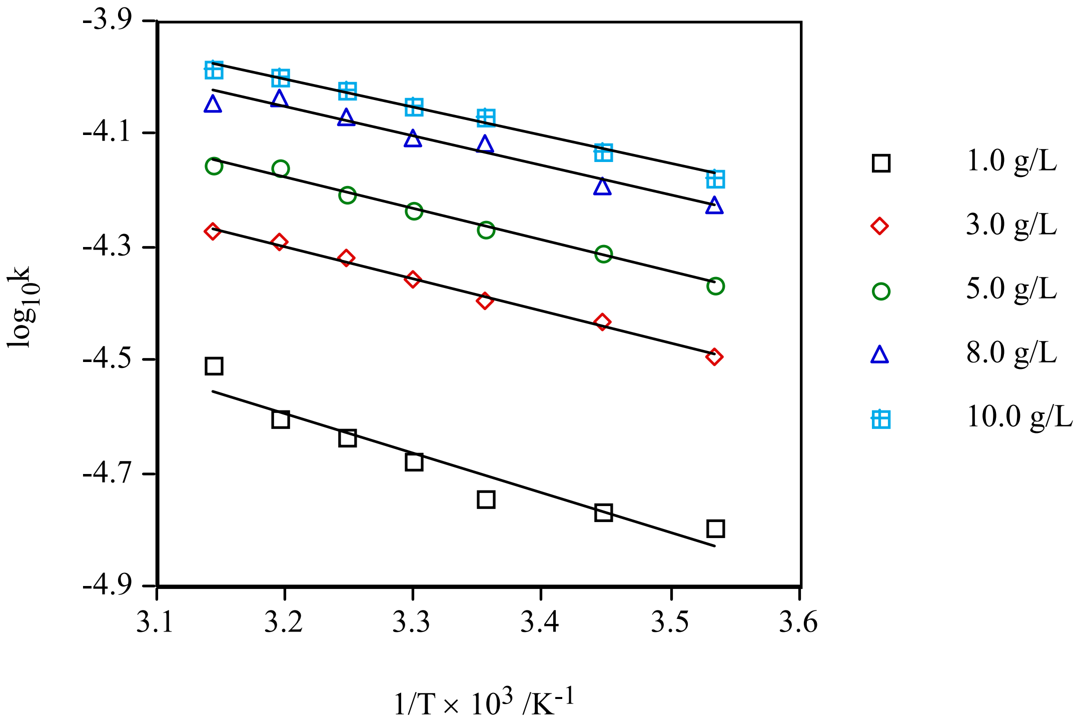

-2.9
-3.1
-3.3
-3.5
-3.7
-3.9
-4.1
-4.3
log10k
3.1
3.2
3.3
3.4
3.5
3.6
1/T × 10^3 /K^-1
0.6 g/L
1.0 g/L
3.0 g/L
5.0 g/L
8.0 g/L
10.0 g/L

Figure 1



-3.9
-4.1
-4.3
-4.5
-4.7
-4.9
log10k
3.1
3.2
3.3
3.4
3.5
3.6
1/T × 10^3 /K^-1
1.0 g/L
3.0 g/L
5.0 g/L
8.0 g/L
10.0 g/L

Figure 2

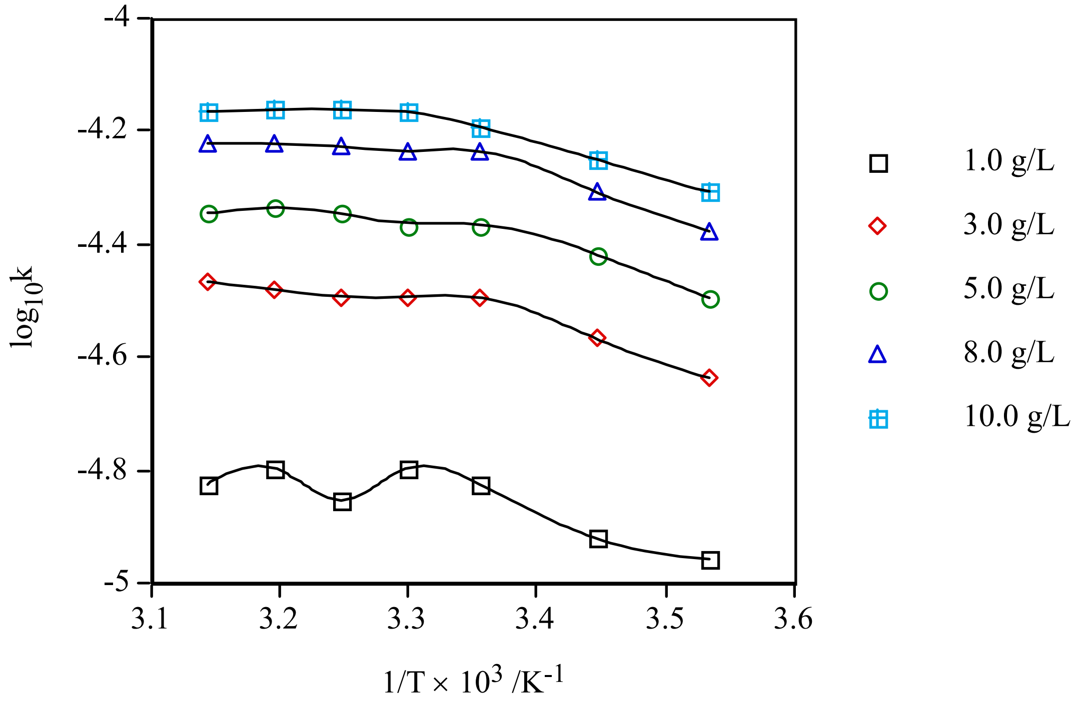

-4
-4.2
-4.4
-4.6
-4.8
-5
log10k
3.1
3.2
3.3
3.4
3.5
3.6
1/T × 10^3 /K^-1
1.0 g/L
3.0 g/L
5.0 g/L
8.0 g/L
10.0 g/L

Figure 3

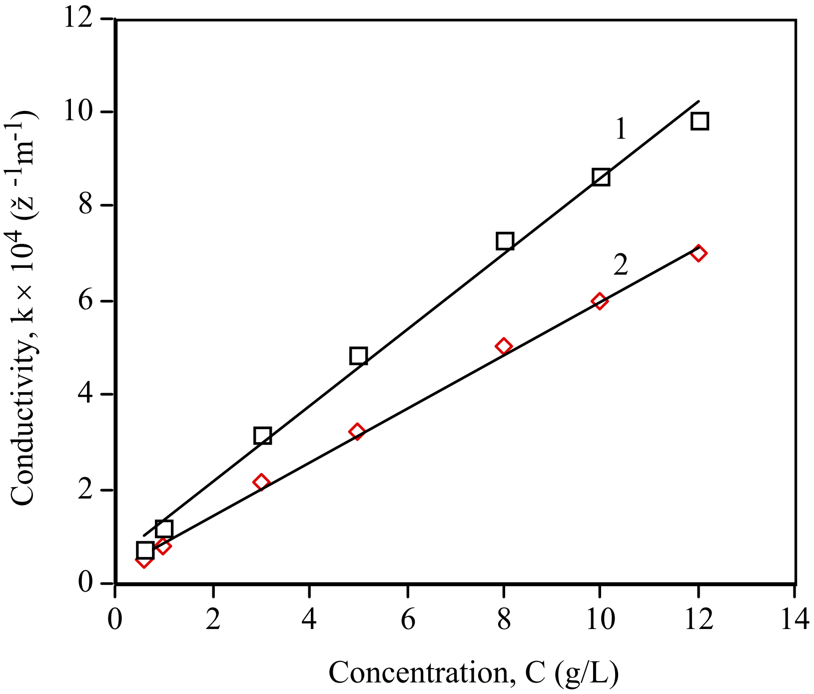
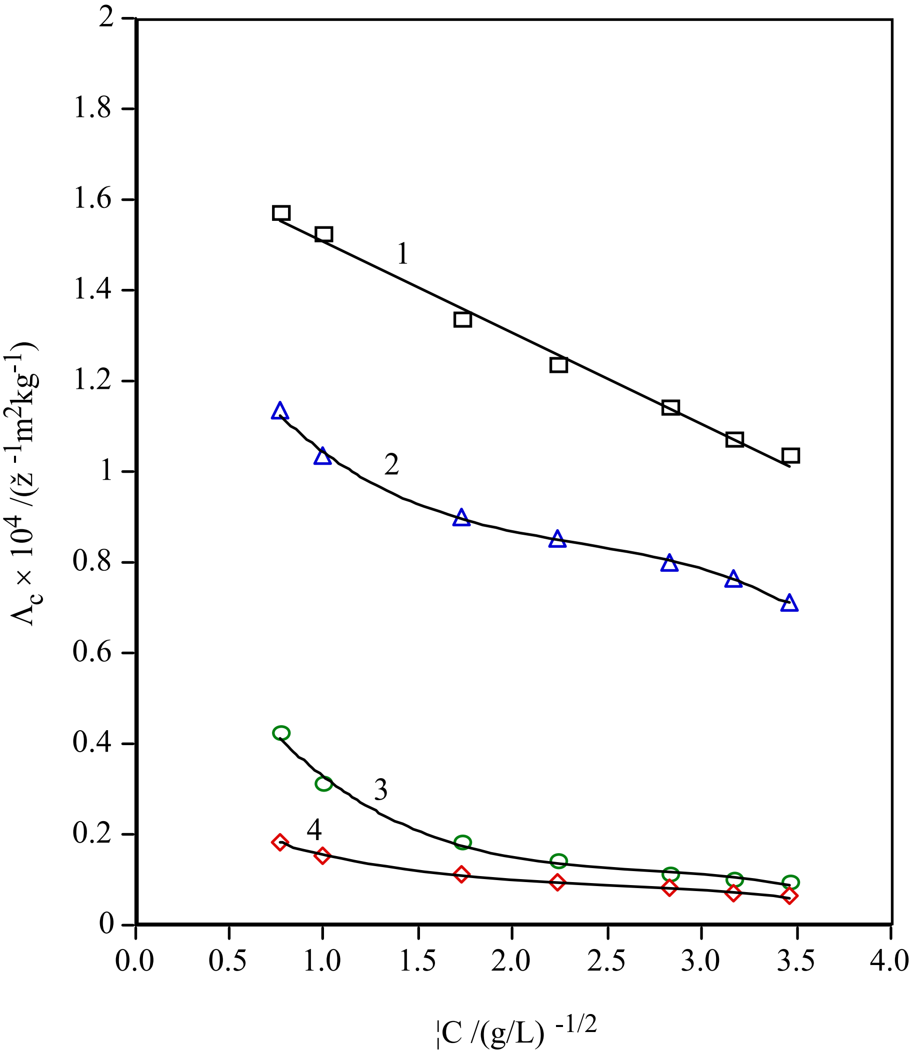


Figure 4



2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
1
2
3
4
$\Lambda_c \times 10^4$ /(ž $^{-1}$m^{2}kg^{-1})
¦C /(g/L) $^{-1/2}$

Figure 5