

PRELIMINARY STUDIES ON THE ELECTRICAL CONDUCTANCE AND THE VISCOSITY OF SOME NIGERIAN TRADITIONAL SOAPS IN AQUEOUS SOLUTION

B F Adeosun , T T Akande, P A Oyewusi and S A Akinyele*

Science Technology Department, Federal Polytechnic, PMB 5351, Ado-Ekiti, Ekiti State, Nigeria

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The viscosity and electrical conductance of some Nigerian traditional soaps and their separate mixtures with sodium chloride and calcium chloride have been examined. The activation energies of viscous flow and of electrical conductance were evaluated from viscous and conductance data respectively. Results on viscous flow suggest structural similarities between the soaps examined. The halides used enhanced the electrical conductance of the soaps in solution and hence the halides can be used to dope the conducting ability of the soaps. The soap solution thus doped could be used industrially as electrolyte, an economic use to which the soaps has not been put hitherto.

Key words: Viscosity, Electrical conductance, Electrolyte, Traditional soap, Activation energy.

Introduction

Metal carboxylates are of two distinct classes. One class is water soluble while the other is water insoluble but hydrocarbon soluble. The physical and chemical properties of the hydrocarbon soluble metal carboxylates in the solid state have been studied extensively (Spegt and Skoulios 1964). The electrical conductivity of molten metal carboxylates (hydrocarbon soluble class) has been thoroughly investigated (Adeosun 1976; Ekwenfe 1975). The temperature dependence of electrical conductivities of even chain-length lead and zinc carboxylates (C_6-C_{18}) was studied by Adeosun and Ellis (1979). Their results revealed that the plots of specific conductivity versus inverse absolute temperature show linearity for zinc but curvature for lead. Several workers have also shown interest in the examination of the solubility of these hydrocarbon metal carboxylates in organic solvents (Akanni *et al* 1984; Everett 1972; Jain *et al* 1979). The viscosity of the hydrocarbon soluble metal carboxylates has been investigated in the molten state (Daruz *et al* 1969; Ubbelohde 1973; Ekpe and Sime 1976). The chain length dependence of the viscosity of molten lead and zinc n-alkanoates with even chain lengths from hexanoate to octadecanoate has been reported (Ekpe and Sime 1976). Results show lead carboxylates to be more viscous than the corresponding zinc carboxylates and that within each homologous series of carboxylates viscosity increased chain length.

The other class of metal carboxylates which is water soluble has however received less attention. They are micro-crystalline solids when anhydrous. When heated they melt into isotropic liquids (Ubbelohde 1973) after undergoing several phase

changes. This class of metal carboxylates are sub-divided into hard and soft soaps. The hard soaps are composed chiefly of sodium soaps while the soft ones are mostly those of potassium. Some Nigerian traditional soaps have been analyzed (Bedeiko 1971; Akanni and Ogungbuaja 1985) and found to be predominantly potassium soaps and therefore are soft water soluble soaps. The Nigerian traditional soaps are mainly used for domestic washing. Their use for this purpose is not even impressive as they face severe competition from modern soaps and detergents. It is therefore of interest to study the physical properties of these soaps with a view to examine other economic uses to which they could be put. It has been suggested that new areas of usage could be opened up for metal carboxylates if their electrolytic properties could be enhanced. We have therefore studied the viscosity, and the electrical conductance of some Nigerian traditional soaps. The effect of some halides on the electrical conductance of the soaps has also been studied.

Experimental

Source of soaps. The Nigerian traditional soaps produced in Oyo, Ilara-Mokin (South western Nigeria) and in Ajase (Central Nigeria) were purchased at the Local market in Akure, Nigeria. "Key" soap manufactured by Lever Brothers Nigeria Limited was purchased at the Erekesan market, Ado-Ekiti, Nigeria.

Preparation of soap solution for viscosity and conductivity measurements. 10.0g of each soap was weighed into a clean flask containing 5 cm³ distilled water where a smooth slurry of each was made. The slurry was made up to 50cm³ with distilled water and transferred completely into a litre coni-

*Author for correspondence

cal flask, made up to 500 cm³ with distilled water, shaken vigorously until a homogenous solution was obtained and made up to one litre with distilled water in the process. The bulk solution (0.038 M) was used in preparing solutions shown in Table 1 for viscosity measurement and in Table 2 for electrical conductivity measurements. 1.0g sodium chloride was dissolved and made up to one litre (0.017M) and 1.0g of calcium chloride was dissolved and made up to 1 litre with distilled water (0.009 M).

Viscosity measurement. After the determination of the cell constant of an Ostwald viscometer with glycerol, the viscosities of the solutions as contained in Table 1 were determined at 40, 50, 60, 70 and 80°C. The temperature of the bath was maintained constant at ±2°C during measurements. The densities of the solutions were determined using a specific gravity bottle.

Conductance measurement. After the determination of the cell constant with a solution of 0.01D (KCl) whose k at 25°C is known to be 1.4087×10^{-3} siemen (Janz *et al* 1968), the cell was washed with distilled water and acetone and dried. The cell was then filled with the appropriate solution (Table 2) and the conductance at the appropriate temperatures determined.

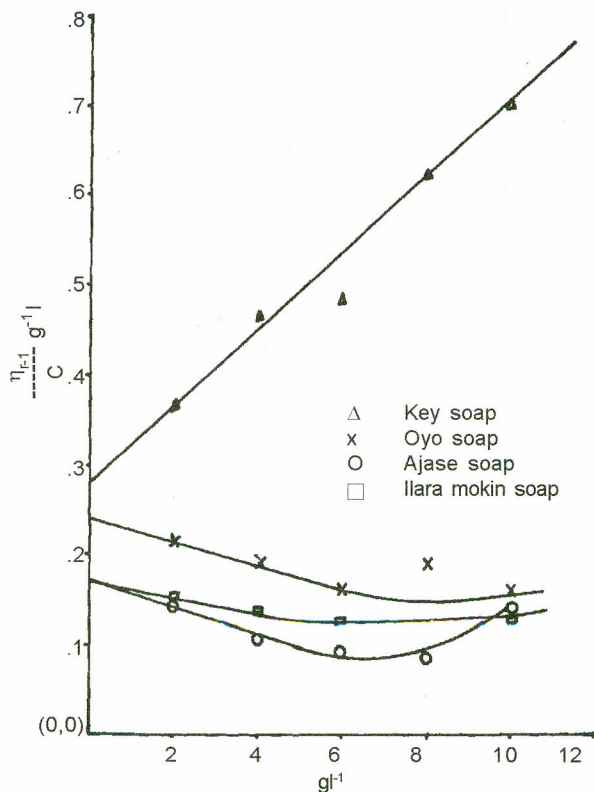


Fig 1. Plot of reduced viscosity versus concentration of soap in aqueous solution for the soaps under examination.

Table 1

Soap solution for viscosity measurement

Soap solution (cm ³)	10	8	6	4	2	6
Distilled water (cm ³)	0	2	4	6	8	10

Results and Discussion

The reduced viscosities of the local soaps in aqueous solution increased as the concentration was decreased. This is the characteristic behaviour of poly-electrolyte solutions (Basu and Gupta 1952). The plots of reduced viscosity versus concentration (Fig 1) show similarity to those of some poly-electrolytes studies by Jefferies *et al* (1982). It appears the local soaps contain some other metal ions in minute quantities apart from the potassium ion that forms the bulk of the soaps. This is consistent with the observation made on some local soaps which were found to contain Ca²⁺ and Na⁺ in minor quantities in addition to K⁺ which is the major cation in the soaps (Bedeiko 1971; Akanni and Ogubaja 1985). For the 'key' soap (modern soap) which contains only Na⁺ the reduced viscosity increased with decreased concentration. This contradicts the observation of Basu and Gupta (1952) and Jefferies *et al* (1982) for poly-electrolytes. The result appears to confirm that the key soap form a single electrolyte in solution containing essentially a single metal ion (Na⁺). The plot of reduced viscosity versus concentration of key soap in solution shows linearity (Fig 1), similar to those obtained by

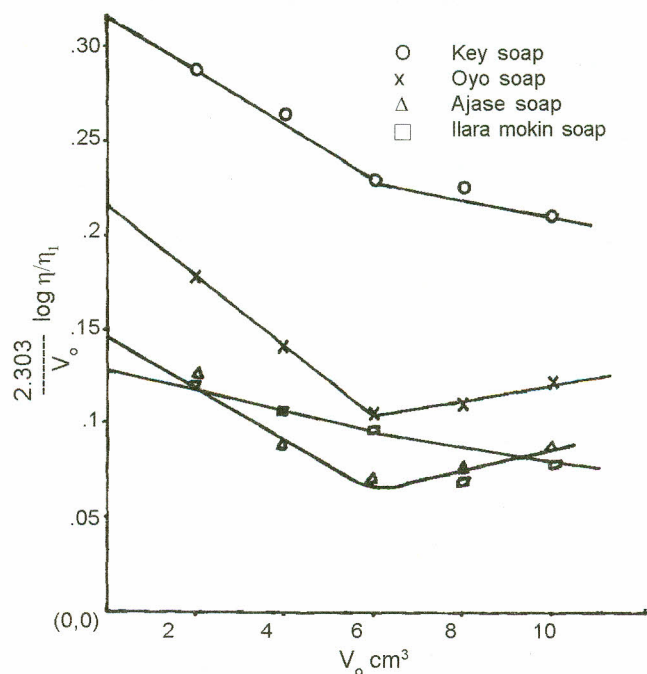


Fig 2. Plot of $\frac{2.303}{V_0} \log \eta/\eta_1$ versus V_0 of the soaps examined.

Jefferies *et al* (1982) for simple sodium and calcium electrolytes. The value of viscosity increased with increased concentration. This trend has been observed for some other electrolytes in solution (Jefferies *et al* 1982). The plots of $2.303/V_0 \log \eta/\eta_0$ versus V_0 show linearity at low concentration region (Fig 2)

from where the intrinsic viscosity (η) of each soap was evaluated as contained in Table 3. The values follow the decreasing order; key soap, Oyo soap, Ajase soap and Ilara soap. The relative molecular masses of the soaps follow the same trend (Table 3). The results suggest, that the carboxylate

Table 2
Solution for conductivity measurement

Soap/additive System	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
Soap solution (cm ³)	10	8	6	4	2	0	10	10	10	10	10	10	10	10	10	10
Sodium chloride Solution (cm ³)							1	2	3	4	5					
Calcium chloride solution (cm ³)												1	2	3	4	5
Distilled water (cm ³)	0	2	4	6	8	10										
Molarity of Soap	0.038	0.030	0.023	0.015	0.008		0.035	0.032	0.029	0.027	0.025	0.035	0.023	0.029	0.007	0.025
NaCl							0.017	0.0016	0.0028	0.039	0.0049	0.0057				
CaCl ₂							0.009					0.0008	0.0015	0.0021	0.0026	0.0030
In soap/salt mixture																
Molar ratio																
Soap							21.88	11.43	7.44	551	4.39					
NaCl																
Soap							43.75	21.33	13.81	10.39	8.33					
CaCl ₂																

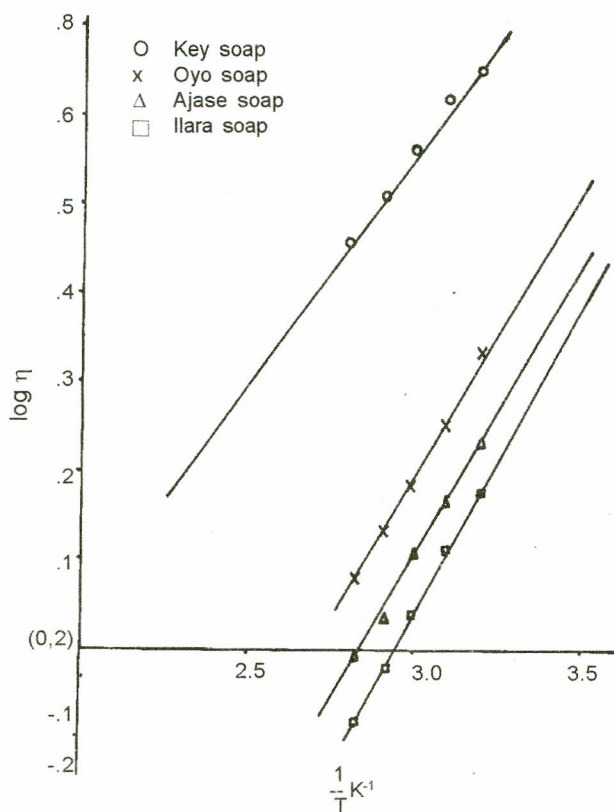


Fig 3. Plot of $\log \eta$ versus inverse absolute temperature of the soaps examined.

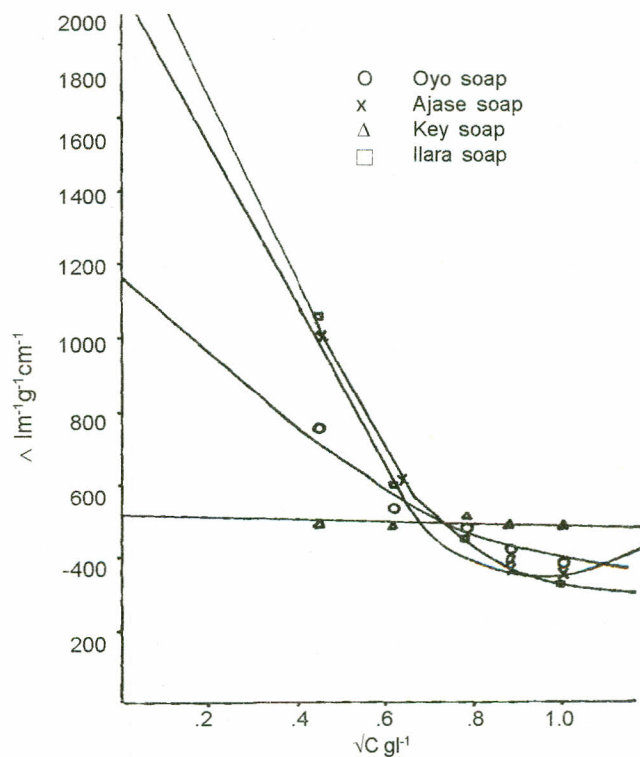


Fig 4. Plot of equivalent conductance versus square root of concentration of the soaps examined.

Table 3
Enthalpy of activation and molecular parameters of the soaps examined in aqueous solution

Soap system	Intrinsic Viscosity [η]	Relative molecular mass $\times 10^4$	Activation energy of viscous flow ΔE /mol
Key	0.320	1.65	12.35
Oyo	0.225	1.03	12.79
Ajase	0.146	0.59	12.85
Ilara	0.122	0.46	12.20

moiety of the sodium soap contains longer chain than for the potassium soaps under examination. The relative molecular masses of the local soaps are not expected to differ significantly as observed -- range (0.46 - 1.65) 10^4 average (0.69 $\times 10^4$) as they are expected to contain the same carboxylate moiety since they are prepared from the same raw materials. The variation might be due to the presence of excess carboxylic acid not neutralized during soap preparation as there is no specification to the actual concentration of the ash solution base used.

It is observed that viscosity values decreased with increased temperature. This trend has been observed for organic liquids (Barrow 1966). Tabor (1969) has suggested that the observed behaviour is as a result of thermal fluctuations which weakens intermolecular forces between the molecules of the liquids. The plots of $\log \eta$ versus inverse absolute temperature are linear for all soaps (Fig 3). Table 3 contains evaluated activation energy of viscous flow ΔE of the systems. The values of ΔE does not vary significantly. This is expected as the soaps are prepared from the same raw materials. The trend of enthalpy of activation gives a measure of the soap's relative structural complexity. The comparativeness of the enthalpy of activation values of the soaps therefore suggests structural similarities of the soaps.

The equivalent conductance increased with decreased concentration of soap in aqueous solution. This result tallies with those of Kahtrauseh (MacInnes 1939) on electrolytes in solution. The plots of equivalent conductances versus square root of concentration (Fig 4) are similar to those of some electrolytes studied by Kohlrausch (Barrow 1966). It is clear from this figure that key soap solution whose plot is essentially linear could be classed as a strong electrolyte relative to all the traditional soaps in solution. The degree of dissociation of key soap at any particular concentration is higher than for any of the traditional soaps. The degree of dissociation follows the trend key soap, Oyo soap, Ajase soap and Ilara soap in a decreasing order. The electrical conductance values decreased with decreased concentration and the soaps follow

the decreasing trend; key soap, Oo soap, Ajase soap and Ilara soap in conductivity which tallies with the degree of dissociation trend at any particular concentration.

The mean activity coefficients of the soaps over the concentration range used are shown in Table 4. Activity coefficient of the traditional soaps decreased with increased concentra-

Table 4
Mean activity coefficients of the soap solutions at room temperature

Concentration (g/l)	Key	Oyo	Ajase	Ilara
1.0	0.522	0.076	0.108	0.142
0.8	0.501	0.071	0.104	0.152
0.6	0.478	0.76	0.121	0.161
0.4	0.422	0.79	0.127	0.183
0.2	0.354	0.088	0.129	0.266

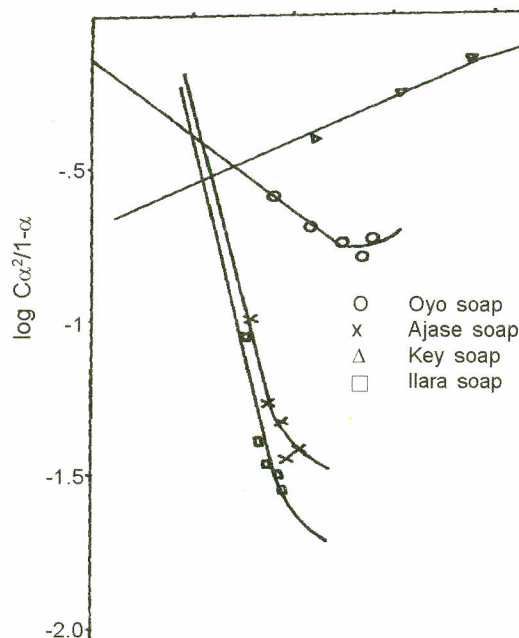


Fig 5. Plot of $\log Ca^2/1-\alpha$ versus \sqrt{Ca} for the soaps examined.

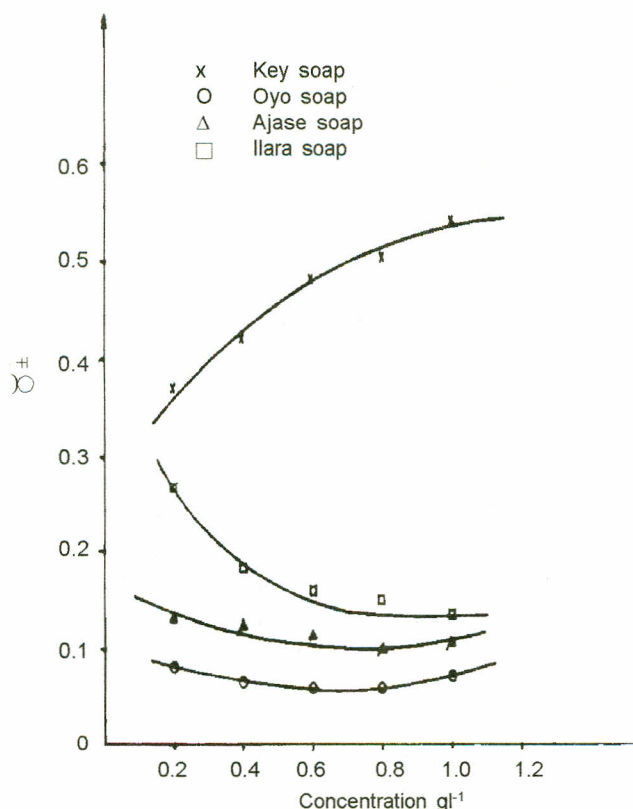


Fig 6. Plot of mean activity coefficient versus concentration of the soaps examined.

tion. This agrees with the trend observed for some electrolytes studied by Harned and Owen (1958) and Conway (1962). Plots of $\log C\alpha^2/1-\alpha$ versus $\sqrt{c\alpha}$ show curvature for the soaps (Fig 5). Such curvature has been observed for some electrolytes (Barrow 1966). At low concentration the plots show linearity similar to that obtained for acetic acid (Barrow 1966) in perfect agreement with the Debye-Huckel theory. The magnitude of γ_{\pm} for the local soaps follows the decreasing trend Ilara soap, Ajase and Oyo in contrast to the degree of dissociation trend. It has been realized that electrostatic interactions are responsible for the non-ideality which produces activity coefficient different from unity (Barrow 1966). Ion pairs and ion triplets or other species enhance electrostatic interactions which will necessarily lower the free energies of the ions and produce a value of γ_{\pm} considerably less than unity. This result suggests that the traditional soaps in solution form non-ideal solution and that the ideality of the soap solutions follows the γ_{\pm} trend.

The plot of γ_{\pm} versus concentration for the soaps (Fig 6) also show curvature similar to those obtained for some electrolytes (Hammett 1952, Barrow 1966). A quantitative explanation for data such as those in Fig 6 is as yet non-existent (Barrow 1966).

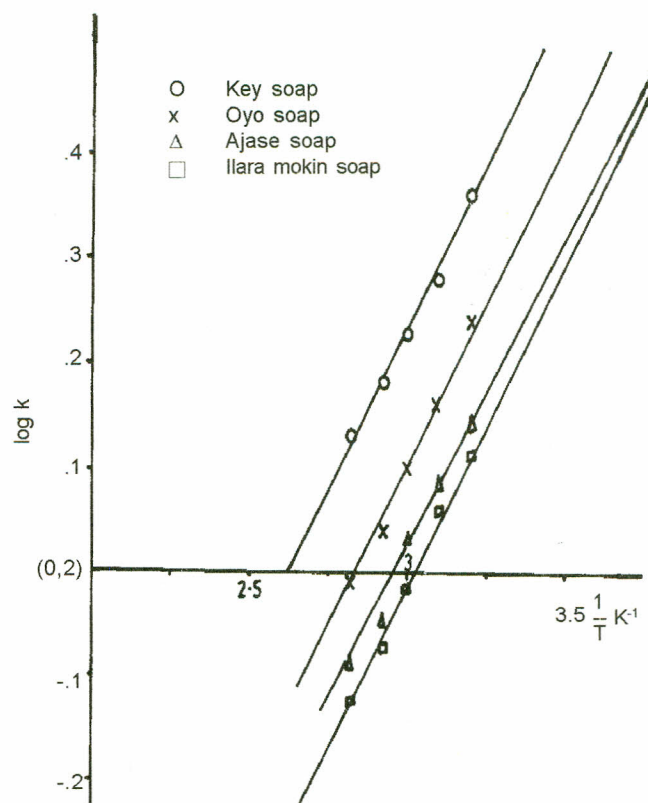


Fig 7. Plot of $\log k$ versus inverse absolute temperature of the soaps examined.

Table 5 contains enthalpy of activation for conductance for the soap/additive systems as evaluated by least square method. Generally, the value decreased with increased additive concentration. Plots of $\log k$ versus inverse absolute temperature (Fig 7) show linearity for all systems. The conductance values of the soap/additive systems were found to increase with temperature. This behaviour is similar to that observed for pure metal carboxylates and their binary mixtures in the molten state (Ekwenife *et al* 1975). The actual conductance were found to increase with increase in the composition of additives like the molten system lead dodecanoate/lead actate (Adeosun 1979). The conductance at any temperature increased with increase in the composition of additives.

Conclusion

Result on viscous flow shows that the local soaps examined are essentially the same structurally and form aqueous poly-electrolyte solutions. The electrical conductance of the soaps was enhanced by the halide additives. This connotes that the halides have the capability to dope the electrical conductance of the soaps examined. The soaps thus doped could be used industrially as electrolytes, an economic use to which the soaps has not been put hitherto.

Table 5
Enthalpy of activation for conductance of soap/additive systems examined

Soap/additive Systems	Concentration (M)										
	A	G	H	I	J	K	L	M	N	O	P
Ilara soap solution	0.038	0.035	0.032	0.029	0.27	0.025	0.035	0.032	0.029	0.027	0.25
Sodium chloride solution		0.002	0.003	0.004	0.005	0.006					
Calcium chloride solution							0.0008	0.0015	0.0021	0.0026	0.0030
Eenthalpy of activation for conductance $-\Delta H^*$ KJ mol.	-24.49	-22.42	-15.75	-26.59	-44.43	Large and negative	-34.12	-34.08	-25.14	-36.43	-35.49

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