International Journal of Chemical Engineering and Analytical Science
Vol. 1, No. 2, 2016, pp. 66-70
http://www.aiscience.org/journal/ijceas

The Use of Citric Acid from Citrus Fruits as Substitute for Weak Electrolyte in Conductance Measurement

Nene Pearl Eluchie*

Biotechnology and Energy Research, Ministry of Science and Technology, Umuahia, Nigeria

Abstract

This paper reports the effect of solvation of the species of citrus fruits in water on its conductivity behaviour as a function of concentration. The specific conductance was measured in two fold dilutions for five different observations and the evaluated equivalent conductance data were analysed by Kraus- Bray conductivity models. Limiting molar conductance (conductance at infinite dilution (λm^{∞}), and dissociation constant (Kc) were evaluated for their solvent composition. The limiting molar conductance's (λm∞) were found to decrease with addition of co-solvent (Orange, Grape, Lime, Lemon and Tangerine) to water due to increased solvent-solvent interaction. The Kc values decreased with increase in dilution in all the composition of solvent. This computed values have been used to discuss qualitatively, the suitability of citrus fruits with water in conductance measurement.

Keywords

Specific Conductance, Citric Acid, Citrus Fruits, Limiting Molar Conductivity, Electrolyte

Received: June 21, 2016 / Accepted: July 22, 2016 / Published online: August 16, 2016

1. Introduction

One of the points of the millennium development goals is the provision of job opportunities, eradication of poverty and creation of wealth. These goals have been discussed elsewhere [1]. This can only be realized when our vast bio-diversity is exploited to the fullest to provide economic activities, wealth creation and employment to the rural and urban areas. Nigeria is a country that is blessed with abundant human and natural resources including natural vegetation. But in spite of the economic trees that abound in the country, little or nothing has been done at processing them into primary products for the sustenance of the manufacturing sector [2]. One economic tree that has not been fully exploited for economic gains is the citrus trees (orange, grape, lime, lemon, and tangerine) and other related trees.

The citrus tree botanically called citrus simensis for orange, citrus limonium for lemon, citrus auransifolin for lime, citrus grandis for grape and citrus reticulate for tangerine are one of the most versatile and ecologically friendly tree of the tropical region that is widely distributed in most parts of the world including Nigeria. The citrus tree is known to contain (2 hydroxyl propane 1, 2, 3 tricarboxylic acids, ($C_6H_8O_7$) a hydroxyl tricarboxylic acid [3] that is naturally concentrated in fruits. It is an important intermediate in carbohydrate metabolism (Citric acid cycle or Krebs cycle) [3]. It is mainly used as a food additive to provide acidity and sour taste to food and beverages. It can be used as plasticizer in the manufacture of soft drinks and candies [4].

The most abundant part of the fruit is the juice which has found a wide range of applications in the chemical industry such as pharmaceuticals, food and beverages etc. studies on electrical conductivity of an electrolyte in solution give many

* Corresponding author
E-mail address: nellypearl21@yahoo.com, nellypearl21@gmail.com

important qualitative insights into the properties of electrolyte solution [5, 6]. In this investigation, the choice of citric acid from citrus fruit is not incidental. The acid plays an important role in biological and industrial processes; an accurate knowledge of its thermodynamic and transport properties is of considerable interest. Aqueous citric acid can be considered as model system for weak unsymmetrical 1:3 electrolyte which are characterised by overlapping dissociation equillibra. In this present investigation, electric conductance of dilute solutions of (Acetic acid CH_3COOH), Lime, Lemon, Grape, Orange and Tangerine were measured.

Conductivity measurements are widely used in industry. Some important applications have been discussed elsewhere [7, 8] to include Water Treatment: Raw water as it comes from lakes; river or the tap is rarely suitable for industrial use. The water contains contaminants, largely ionic that if not removed will cause scales and corrosion in plants equipment, particularly in heat exchangers, cooling towers and boilers. Conductivity is also used to monitor the build-up of dissolved ionic solids in evaporating cooling water systems and in boilers. When the conductivity gets too high, indicating a potentially harmful accumulation of solids, a quantity of water is drained out of the system and replaced with water having lower conductivity. Leak detection: Water used to cooling in heat exchangers and surface condensers usually contains large amounts of dissolved ionic solids. Leakage of cooling water into the process liquid can result in potentially harmful contamination. Measuring conductivity in the outlet of a heat exchanger or in the condenser hot well is an easy way of detecting leaks. Clean in place: in the pharmaceutical, food and beverage industries, piping and vessels are periodically cleaned and sanitized in a procedure called clean-in-place (CIP). Conductivity is used to monitor both the concentration of the CIP solution, typically sodium hydroxide and the completeness of the rinse. Interface detection: If two liquids have appreciably different conductivity, a conductivity sensor can detect the interface between them. Interface detection is important in a variety of industries including chemical processing and food beverage manufacturing. Desalination: Drinking water desalination plants, both thermal (evaporative) and membrane (reverse osmosis) make extensive use of conductivity to monitor how completely dissolved ionic solids are being removed from the brackish raw water.

Literature has shown some work on conductivity of citric acid in aqueous solution at different temperature [9]. Literature also reveals the fact that there is little work [10] on the conductometric behaviour of citric acid in solution. But no report is found on variation of conductance with concentration of citrus fruits even though several electrolytes have been studied in a good number of conductance measurements [11]. The purpose of this present study is to evaluate citric acid from various citrus fruits and to clarify concerns on the suitability of citric acid from citrus fruits as a weak electrolyte in ionic conductance and to examine the relative strength of citric acid from citrus fruits with those of acetic acid in conductance measurement.

2. Materials and Methods

Locally available citrus fruits (orange, grape, lime, lemon, and tangerine) were directly used without further purification. Triply distilled water of specific conductivity 0.9 MS/CM was used. 0.1M acetic acid (CH_3COOH) electrolyte were purified as reported [12] and specific conductivity after two fold dilution taken for five successive observations for each solution. Citrus juices were extracted from their fruits and specific conductivity taken after two fold dilution. The concentration was evaluated from their pH values. Conductance measurements were made with a non-digital direct reading conductivity meter (micron conductivity meter (model CN 140, Elico make) and a calibrated [13] conductivity cell (1.0MS/CM). All the measurements were made in a thermostat maintained at a desired temperature 25°C ± 0.01°C. The instrument was standardised elsewhere [14].

3. Results and Discussion

3.1. Limiting Molar Conductance

Solutions of citrus fruits in water (in terms of volume of 5ml) were subjected to conductometric study. The specific conductance (k) of salt solution was directly read from the instrument. The specific conductance was used in the determination of the molar conductance of citric acid for all the cases of solvent at 298k using the relation

$$\lambda m = \frac{1000 \ x \ K}{C} \quad (1)$$

Where C is concentration in molar and k is specific conductance (MS cm-1).

As it is known, citric acid a weak electrolyte will not follow Onsager's condition. This weak electrolyte is expected to dissociates according to equation

$$C_6H_8O_7 \leftrightharpoons C_6H_5O_7^- + 3H^+ \quad (2)$$

Previous work [15, 16] has tried Kraus Bray conductivity equation related to 3:1 electrolyte and 2:1 electrolyte and the plots were found to be nonlinear. Therefore, the equation relating to 1:1 electrolyte was tried and the related plot of 1/ λm versus λmC (based on the following equations was und to be linear. The linearity is an indication of Kc increasing as concentration decreases or dilution increases. The analysis was done with this equation.

$$\frac{1}{\lambda} = \frac{1}{\lambda m\infty} + \frac{\lambda mC}{\lambda m\infty 2Kc} \quad (3)$$

Where K_c is the dissociation constant, C is the concentration in mol/dm^3; λm is the molar conductance in $\Omega^{-1}M^2Mol^{-1}$and λ_m^{∞} is the molar conductance at infinite dilution. The slope $1/K_c\lambda_m^{\infty 2}$ and intercept $1/\lambda_m^{\infty}$ of the plot figure 1 and 2 gave λ_m^{∞} and K_c values. These are shown in Table 1 and Table 2. The limiting molar conductance (λ_m^{∞}) varies from one solvent to another and also it increases with decrease in concentration or increase in dilution as expected. The decrease in concentration brings about the decreased thermal energy and less breaking of weak bonds leading to decrease in mobility and hence, decreased conductivity.

Table 1. Experimental values of molar conductance for citrus fruit and acetic acid from Kraus bray model in various compositions of water at 298k.

	Acetic acid					**Orange**				
Concentration	0.1	0.05	0.033	0.025	0.02	1.8e-5	$9.0e^{-6}$	$6.^{0e-6}$	$4.5e^{-6}$	$3.6e^{-6}$
Conductivity	3.0	1.4	1	0.8	0.6	1.1	0.7	0.4	0.2	0.1
Molar Conductance (λm)	3000	2800	30303.03	320000	300000	$6e^{+07}$	$8e^{+07}$	$7e^{+07}$	$4e^{+07}$	$3e^{+07}$
1/λ∞	$3.3e^{-4}$	$3.6e^{-4}$	$3.3e^{-5}$	$3.1e^{-6}$	$3.3e^{-6}$	$1.6e^{-8}$	$1.3e^{-8}$	$1.5e^{-8}$	$2.25e^{-8}$	$3.68e^{-8}$
	Grape					Lime				
Concentration	$3.9e^{-4}$	$1.9e^{-5}$	$1.32e^{-7}$	$9.9e^{-6}$	$7.9e^{-6}$	$1.9e^{-4}$	$9.8e^{-5}$	$6.5e^{-5}$	$4.86e^{-6}$	$3.9e^{-5}$
Conductivity	1.20	0.9	0.5	0.3	0.1	2.2	1.7	1.4	1.2	1.0
Molar Conductance (λm)	$3e^{+07}$	$5e^{+07}$	$4e^{+07}$	$3e^{+07}$	$1e^{+07}$	$1e^{+07}$	$2e^{+07}$	$2e^{+07}$	$2e^{+07}$	$3e^{+07}$
1/λ∞	$3.3e^{-9}$	$2.2e^{-8}$	$2.65e^{-8}$	$3.32e^{-8}$	$7.96e^{-8}$	$8.7e^{-8}$	$4.7e^{-8}$	$4.6e^{-8}$	$4.06e^{-8}$	$3.9e^{-8}$
	Lemon					Tangerine				
Concentration	$1.8e^{-4}$	$8.9e^{-5}$	$5.9e^{-5}$	$4.5e^{-5}$	$3.7e^{-5}$	$3.1e^{-5}$	$1.1e\text{-}^{5}$	$1.0e^{-5}$	$0.9e^{-6}$	0.3e-6
Conductivity	1.1	0.9	0.5	0.4	0.3	2.1	1.6	1.3	1.1	1.0
Molar Conductance (λm)	$6e^{+07}$	$1e^{+07}$	$8e^{+06}$	$9e^{+06}$	$8e^{+06}$	$1e^{+08}$	$2e^{+07}$	$1e^{+08}$	$1e^{+08}$	$2e^{+08}$
1/λ∞	$1.6e^{-7}$	$1.4e^{-7}$	$1.1e^{-7}$	$1.11e^{-7}$	$1.19e^{-7}$	$9.9e^{-8}$	$4.7e^{-9}$	$8.1e^{-9}$	$7.18e^{-9}$	$6.32e^{-9}$

From [15, 16] the concentrations in this work are higher than those reported in this study and from Kraus bray conductivity model, (equation 3) the dissociation constant reported in this work vary from one citrus fruit to another.

From [17] the measured conductance of citric acid as a function of concentration is given as

$$\lambda = \alpha_1\lambda_1 + 2\,\alpha_2\lambda_2 + 3\alpha_3\lambda_3 + 4\,\alpha_4\lambda_4 + 5\alpha_5\lambda_5 \quad (4)$$

Where α_1- α_5 are given in the works of [18]. Considering this equation, it is assumed that the contributions coming from the electrolyte constituent are additive Table 3. Formally in the limit of infinite dilution ($\alpha_1 - \alpha_5$) tends to unity.

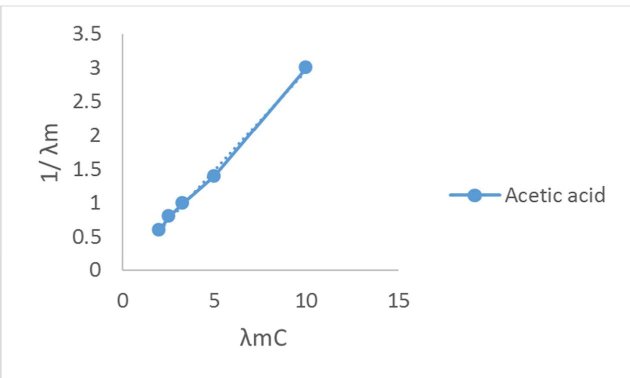

Figure 1. Plot of 1/λm versus λmc for acetic acid.

It can also be said that the addition of co-solvent (citrus fruit) to water result in a competition for hydrogen bonding with water by cation and co-solvent by anion and as a result some water molecules are removed from solvation shell of cation or anion. Because of this, the effective ionic size increases, this held limiting conductance to decrease as seen in plot below. Figure 2. As can be seen, the citrates behave like strong, completely dissociated electrolytes and citric acid is a Partially dissociated weak electrolyte. The results obtained included in figure 1 and 2 cover the more concentrated solutions of citric solutions of citric acid and acetic acid (c ≥ 0.018 moldm^{-3}. Both data sets yield a common curve.

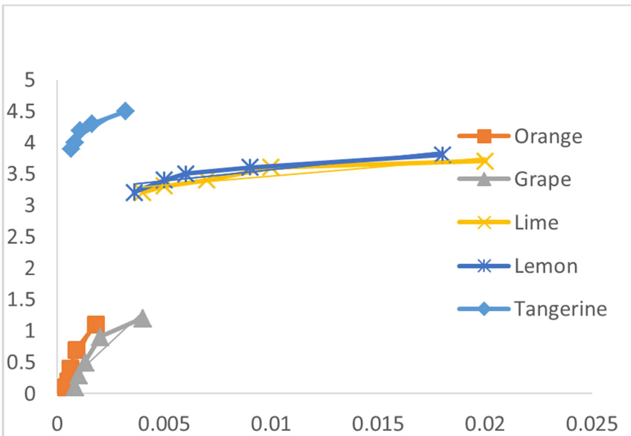

Figure 2. Plot of 1/λm versus λmc for Citrus fruit.

3.2. Dissociation Constant

The dissociation constants were evaluated respectively from the linear plot of Kraus bray at various composition of water at 298k (Table 2). The variations of kc with concentration indicate the acidity of the system with lemon and lime greater than others. With decreasing acid concentration, the contribution of λ from secondary and tertiary steps of dissociation becomes less important and the problem reduces to the case of weak monobasic acid. In the works of [18] the degree of dissociation of primary step is given by

$$\alpha_1 = \lambda/\lambda^* \quad (5)$$

Where λ* is the conductance of completely dissociated acid (to the primary dissociation step only). λ* can be calculated from

$$\lambda^* = \lambda(CH_3COOH) - \lambda(Mecl) + \lambda c(Mecit) \quad (6)$$

Table 2. Experimental values of dissociation constant Kc for citrus fruits and acetic acid from Kraus bray model in various composition of water at 298K.

	5ml	10ml	15ml	20ml	25ml
Acetic acid	0.0047	0.0062	0.0071	0.0074	0.0079
Orange	0.0295	0.0301	0.0314	0.0317	0.0321
Grape	0.0082	0.0104	0.0108	0.0112	0.0116
Lime	1.5859	1.573	1.577	1.581	1.583
Lemon	1.6022	1.6041	1.6045	1.6049	1.6051
Tangerine	1.1346	1.1357	1.1359	1.1363	1.1365

Table 3. Conductance's of completely dissociated citrus fruit λ* = λ (Mecit) and degree of primary dissociation (step α_1-α_5) at 298.15k.

λ*A	λ*B	λ*C	λ*D	λ*E
386.14	385.12	412.68	423.11	387.13
384.02	383.05	411.68	423.11	285.13
383.11	382.28	410.49	420.19	384.28
382.83	381.17	409.36	419.52	383.11
381.17	380.43	408.18	418.27	382.59
α_1 A	α_2 B	α_3 C	α_4 D	α_5 E
0.8011	0.9053	0.9821	0.9873	0.8521
0.7154	0.7076	0.7893	0.7420	0.6442
0.6420	0.6413	0.6421	0.6518	0.5708
0.5666	0.5422	0.5090	0.5697	0.4387
0.4820	0.4697	0.4720	0.4659	0.3877

Where A= Orange, B = Grape, C = Lime, D = Lemon, E = Tangerine

Concentration (c), Conductivity (Ms/cm), Molar Conductance λm ($\Omega^{-1}m^2mol^{-1}$), Limiting Molar Conductance 1/λm∞

4. Conclusion

Among the citrus studied, citric acid is found to be more concentrated in lime and lemon. This conforms to the result of [19] that among fruits, citric acid is more concentrated in Lime and lemon. It is an indication that both would yield a higher output when integrated as an electrolyte in conductance measurement. Obviously, it can be inferred that citrus fruit can be substituted as a weak electrolyte in conductance measurement as the result are in reasonable agreement when taking into account that the differentiation of experimental data is always associated with loss of precision.

Acknowledgements

I appreciate the encouragement from Dr. Abia A. A. for his contributions during the experimental planning and to all those working at quality control laboratory, Abia state water board for the chemical analysis.

References

[1] Godswill O. 2006. Resources for science, mathematics and technology, (STM) Education in the context of education reforms in Nigeria. Proceedings of the 47th Annual Conference. Science Teachers Association of Nigeria. ISBN: 978-37639-7-0, pp. 3-7.

[2] Okonkwo E. M., Ladan Z., Agbaji S. A., Varanasi S., 2008. Neem Tree: A blue PRINT FOR POVERTY ERADICATION. "CHEMISTRY IN NIGERIA. vol. 3 NO. 2 PP6-11.

[3] Http// en.wikipediaorg/wiki/citric acid.

[4] Raj. K. Bawal. 1990. A textbook of organic chemistry, 2nd edn. Wiley western limited, New Delhi, PP. 447.

[5] Chatterji A., B. 2006. J Chem. Eng. Data.

[6] Kasha H. K, P. J. Pradhan, 2006. J Chem. Physics, 125.

[7] David M. G., 2006. A comprehensive look at conductivity measurement in steam and power generation waters. Mettle-Toledo Thornton, Inc. Bedford, MA IWC -06-29.

[8] Gurdeep R., K. Sham. 2011. Instrumental methods of chemical analysis. Annand, Himalaya publishing house, pp. no 2 482-496.

[9] Hayskens P. L., 1978. Lanm beau yon .phys chem.82, 17.

[10] Levien. B. J. 1955. J. Phys Chem, 55,640.

[11] Light T., S. Light., A. Bevilacqua, K. Morasch. 2005. The fundamental conductivity and resistivity of water, Electrochemical and solid state letters, 8(1) E 16-19.

[12] Perin D. D., W. L. F. Armarego, D. R Perin. 1996. Purification of laboratory chemicals, Pergamum press, New York. pp. 192.

[13] Gray D. 2005. Measurement of organics in power plant make up water treatment, power plant chemistry, 7 (12).

[14] Gray D. 2004. pH and Co_2 Determination based on power plant conductivity measurements, international water conference paper Iwc-04-43, pihsburgh, PA.

[15] J. Ishwara Bhatt and M. N Manjunatha 2011. Studies on the effect of dielectric constant on the solvation behaviour of citric acid as a function of temperature. Scholars research library, Archives of applied Science research, 2011, 3 (5): 362-380.

[16] J. Ishtar Bhatt and M. N Manjunatha 2010. Conductometric studies on the solvation behaviour of citric acid in water + ethanol mixture + methanol and water at different temperatures. Indian journal of chemical technology. Vol 17. P. 462-467.

[17] Apelblat A., Barthes J., and Naturforsch Z., 1992. Conductance studies on aqueous citric acid. 47a, 493-498.

[18] Maclnnes D. A and Shedlovsky T. 1932. J. Amer. Chem.soc. 54.1441.

[19] Muller M., K. Irkens., Rubinstein. 1996. on the mechanism of hyper acidification in lemon: comparism of the vacuolar H (+) – ATPase activities of fruits and epicotyls. J. Biol Chem. 271: 1916.