Journal of Applied Solution Chemistry and Modeling, **2015**, *4*, **173-177** **173**

Thermodynamic Investigation of $NaClO_3$ Solubility in the Mixed Solvent Medium and the Related Ion – Pair Formation at Different Temperatures

Mehran Aghaie* and Roshanak Kishani

Faculty of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran

Abstract: Using the evaporating method, the solubility of sodium chlorate was determined in the various mixed solvents (water + ethanol + propanol) at various temperatures. The results showed that the solubility of $NaClO_3$ decreases with increasing the mass percent of ethanol and propanol. On the other hand, the solubility of $NaClO_3$ increases with increasing the temperature .In addition, the equilibrium constant of ion pair formation, $K_{IP,}$ for the reaction

$Na^+_{(aq)} + ClO_3^-{}_{(aq)} \rightarrow Na^+ClO_3^-{}_{(\text{Ion Pair})}$ was estimated upon Fuoss contact ion pair model and then, the values of ion-pair concentrations were determined by using the extended Debye-Hückel model and iteration calculations in various mixed solvents and various temperatures . Finally the value of thermodynamic solubility product constant, $K_{sp(th)}$, and the values of $\Delta H^o, \Delta S^\circ$ and ΔG° of ion-pair formation were estimated in the mixed solvent media.

Keywords: Mixed solvent, The extended Debye-Hückel model, Ion- pair, Thermodynamic function.

INTRODUCTION

As we know, ion association has an important role in chemical, biological and agricultural systems like colloids, proteins, soils, corrosion and lithium batteries. So, the ion association has been investigated widely experimentally and theoretically [1-14]. When two ions of opposite charges approach enough each others an ion-pair species may be formed due to the coulombic attraction. Ion triplet and ion cluster also may be formed in the concentrated ionic solutions under the appropriate conditions. The formation of ion-pair, ion-triplet and … is due to the balance between the electrostatic interaction of involved ions and their thermal agitation. So, increasing the electrolyte concentration or decreasing the dielectric constant and the variation of temperature affect the extend of ion association and the results can be used in controlling corrosion, or improving electrolysis process and other applications [15-31]. Fuoss and Kerress [18, 19] predicted the ion pair, and ion triplet formation by conductivity measurements. Bjerrum [15], Moller and Guggenheim [16, 17] concluded that ion pair formation is important and the Debye-Hückel model isn't sufficient rigorous to explain the behavior of ions in the electrolytic solutions. In general, we refer to the Debye –Huckel theory, when we want to evaluate the approximate behavior of ions in the dilute electrolytic solutions. The final results of the theory can be summarized as follows:

$$\log \gamma_{\pm} = AZ_+Z_-\sqrt{I_m} \tag{1}$$

for dilute solutions, and

$$\log \gamma_{\pm} = \frac{Az_+z_-\sqrt{I_m}}{1+aB\sqrt{I_m}} \tag{2}$$

for fairly dilute solutions. B and A are constants that depend on the dielectric constant, D and temperature, T

$$B = \sqrt{(2000F^2/\varepsilon_\circ DRT)}, A = N_A Be^2 / 8\pi\varepsilon_\circ DRT \ln(10) \tag{3}$$

where, N_A is Avogadro constant, F is Faraday constant, R is universal gas constant.

One of the basic assumptions of Debye-Hückel theory is that, the electrolyte is completely dissociated at all concentrations without any ion-pair, ion-triplet or ion-cluster formation. Neglecting the ion-pair formation or other ion associations is an important shortcoming of the Debye-Hückel theory. Bjerrum [15], Guggenheim [16, 17] and Fuoss [18, 19, 32] have pointed out the existence of ion-association phenomenon in eletrolytic solutions. Indeed, in the solution of a strong electrolyte, such as BA(an ionic compound), a fraction of ions participate in ion-association phenomenon, for example, the following equilibrium takes place in the electrolytic solution in order to form B^+A^- ion pair

$$B^+ + A^- \rightarrow IP \tag{4}$$

where IP refers to the B^+A^- ion –pair. The constant of this ion-pair formation is written as:

---

*Address correspondence to this author at the Faculty of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran; Tel: 021-22977862-3; Fax: 02122977853; E-mail: marmin20042000@yahoo.com, m_aghaie@iau-tnb.ac.ir

E-ISSN: 1929-5030/15

Table 1: Solubilities, s, of $NaClO_3$ in the Mixed Solvent (Propanol 10%, ethanol 30%, Water 60%) at Various Temperatures

$t/^0C$	Sample 1 g/in10 mL	Sample 2 g/in10 mL	Sample 3 g/in10 mL	Sample 4 g/in10 mL	Average g/in10 mL	$s/(molL^{-1})$
0	1.375	1.371	1.373	1.374	1.373±0.002	1.29
10	1.790	1.722	1.790	1.826	1.78±0.02	1.67
25	3.080	2.796	3.190	2.890	3.0±0.15	2.8
30	3.301	3.350	3.189	3.206	3.26±0.06	3.0

*g in10 mL denotes the amount of $NaClO_3$ in grams per10mL of saturated solution at given temperature.

Table 2: Solubilities of $NaClO_3$ in the Mixed Solvent (Propanol 30%, Ethanol 40%, Water 30%) at Various Temperatures

$t/^0C$	Sample 1 g/in10 mL	Sample 2 g/in10 mL	Sample 3 g/in10 mL	sample 4 g/in10 mL	Average g/in10 mL	$s/(molL^{-1})$
0	0.027	0.028	0.027	0.030	0.028±0.01	0.026
10	0.0725	0.0724	0.0724	0.0722	0.0724±0.01	0.068
25	0.15	0.2	0.2	0.15	0.18±0.02	0.168
30	0.446	0.431	0.433	0.504	0.45±0.02	0.430

*g in10 mL denotes the amount of $NaClO_3$ in grams per 10mL of saturated solution at given temperature.

$$K_{IP} = \frac{a_{IP}}{a_+ a_-} = \frac{[IP]\gamma_{IP}}{[B][A]\gamma_\pm^2} \tag{5}$$

If θ is the fraction of ion pairs, then we have

$$K_{IP} = K_{IP} = \left(\frac{\theta}{(1-\theta)^2[BA]_\circ}\right)\frac{\gamma_{IP}}{\gamma_\pm^2} \tag{6}$$

Once, having the value of θ, then it may calculate γ_{IP} and $\gamma_\pm$ from the modified Debye-Huckel formula as follow:

$$\log\gamma_\pm = \frac{AZ_+Z_-\sqrt{(1-\theta)I_m}}{1+Ba\sqrt{(1-\theta)I_m}} \tag{7}$$

and ultimately calculate the value of K_{IP} (eq.6).

On the other hand, the Fuoss model of contact ion-pair formation is a suitable approach for estimating the constant, K_{IP}, for the equilibrium (4) [32]

$$K_{IP} = 2.52\times 10^{21} e^{1.674Z^2/DaT} \tag{8}$$

EXPERIMENTAL

$NaClO_3$, Ethanol and Propanol were purchased from Merck Company with high purity and were used without further purification. The solubility of $NaClO_3$ in the mixed solvent (propanol 10%, ethanol 30%, water 60%) and (propanol 30%, ethanol 40%, water 30%) were determined by evaporating method at various temperatures (0,10,25,30 $^\circ C$) and the results are given in Tables **1** and **2**.

Estimation of Dielectric Constant of the Mixed Solvent

The dielectric constants of the mixed solvents, D were estimated by the following equation:

$$D_{(mix)} = D_w X_w + D_e X_e + D_p X_p \tag{9}$$

The results are summarized in Table **3**.

Table 3: The Dielectric Constants of the Mixed Solvent (Propanol+Ethanol +Water)

Composition	D_{mix}
(propanol 10%, ethanol 30%, water 60%)	67.747
(propanol 30%,ethanol 40%, water 30%)	53.545

DISCUSSION

Ion-pair constants for Na^+ ClO_3^- ion pair formation were estimated upon equation (8) at different temperature and the results are given in Tables **4** and **5**.

Table 4: The Values of K_{IP} in the Mixed Solvents (Propanol 10%, Ethanol 30%, Water 60%) at Different Temperatures

T/K	273	283	298	303
K_{IP}	1.551	1.431	1.282	1.239

Table 5: The values of K_{IP} in the Mixed Solvents (Propanol 30%, Ethanol 40%, Water 30%) at Different Temperatures

T/K	273	283	298	303
K_{IP}	2.824	2.552	2.221	2.127

$$Na^{+}_{(aq)} + ClO_3{}^{-}_{(aq)} \rightarrow Na\ {}^{+}ClO3\ {}^{-}_{(ion\ pair)}$$

The constant of equilibrium (4) may be rewritten as follow:

$$K_{IP} = x\gamma_{IP}/(s\text{-}x)^2\ \gamma_\pm^2 \qquad (10)$$

Or

$$K_{IP}\gamma_\pm^2\ x^2 - x(2\ K_{IP}\ s\gamma_\pm^2 + \gamma_{IP}\ ) + K_{IP}\gamma_\pm^2\ s^2 = 0 \qquad (11)$$

where x represents the molarity of ion-pair in equilibrium (4).

Solving this equation, one can obtain the values of x at various temperatures. Once, the values of x were calculated, then calculating the concentration of free cations and free anions participating in the equilibrium $BA_{(s)} \leftrightarrow B^{+}_{(so\ln)} + A^{-}_{(so\ln)}$ is quite straightforward

$$[B^+]_{free} = s\text{-}x\ ,[A^-]_{free} = s\text{-}x \qquad (12)$$

Using $[B^+]_{free}$ and $[A^-]_{free}$ and estimating $\gamma_\pm$ upon equation(2), we can calculate the values of thermodynamic solubility product, $K_{sp(th)}$ of the following equilibrium in the considered mixed solvent and desired temperature as follow :

$$NaClO_{3(s)} \leftrightarrow Na^{+}_{(so\ln)} + ClO^{-}_{3(so\ln)} \qquad (13)$$

$$K_{sp(th)} = [B^+]_{free}\ [A^-]_{free}\ \gamma_\pm^2\ = (s-x)^2\ \gamma_\pm^2 \qquad (14)$$

In order to calculate the value of $K_{sp(th)}$, we need the value of $\gamma_\pm$. This can be obtained upon eq. (2). The constants A and B in equation (2) respect to the mixed solvents were estimated as follow [24-33]:

$$B=0.328/(D'/D)^{1/2}\ ,\ A=0.509(d'/d)^{1/2}/(D'/D)^{3/2} \qquad (15)$$

where d',d,D' and D represent density of the mixed solvent and water and

dielectric constant of the mixed solvent and water respectively [24-27, 29, 33].

The results of our calculations respect to x, $\gamma_\pm$, K_{IP} and $K_{sp(th)}$ are given in

Tables **6** and **7**. ^{2}

The variation of ln $K_{sp(th)}$ *vs.* 1/T was ploted in Figure **1**. According to the Van 't Hoff equation

$$\ln K = -\ \Delta H^\circ/RT + \Delta S^\circ/R \qquad (16)$$

The slope of the plot is equal to - $\Delta H^\circ/R$ and the intercept is equal to $\Delta S^\circ/R$. In addition the value of ΔG° at a given temperature T, is:

$$\Delta G^\circ = -RT\ln K_{sp(th)} \qquad (17)$$

The calculated values of ΔG°, ΔH° and ΔS° of dissolution of $NaClO_3$ in the mixed solvents at $25^\circ C$ are summarized in Tables **8** and **9**.

Table 6: The Values of x, K_{IP}, $\gamma_\pm$ and $K_{sp(th)}$ in the Mixed Solvent (Propanol 10%, Ethanol 30%, Water 60%) at Various Temperatures

T/K	s/molL^{-1}	x/ molL^{-1}	$\gamma_\pm$	K_{IP}	$K_{sp(th)} = (s\text{-}x)^2\gamma_\pm^2$
273	1.290	0.4116	0.586	1.551	0.2649
283	1.670	0.5669	0.570	1.431	0.3953
298	2.808	1.1033	0.544	1.282	0.8599
303	3.000	1.1872	0.540	1.239	0.9582

Table 7: The Values of x, K_{IP}, $\gamma_\pm$ and $K_{sp(th)}$ in the Mixed Solvent (Propanol 30%, Ethanol 40%, Water 30%) at Various Temperatures

T/K	s/molL^{-1}	x/ molL^{-1}	$\gamma_\pm$	K_{IP}	$K_{sp(th)} = (s\text{-}x)^2\gamma_\pm^2$
273	0.026	0.0011	0.794	2.824	0.0003
283	0.068	0.0052	0.720	2.552	0.0020
298	0.168	0.0215	0.674	2.221	0.0097
303	0.430	0.0842	0.574	2.127	0.0393

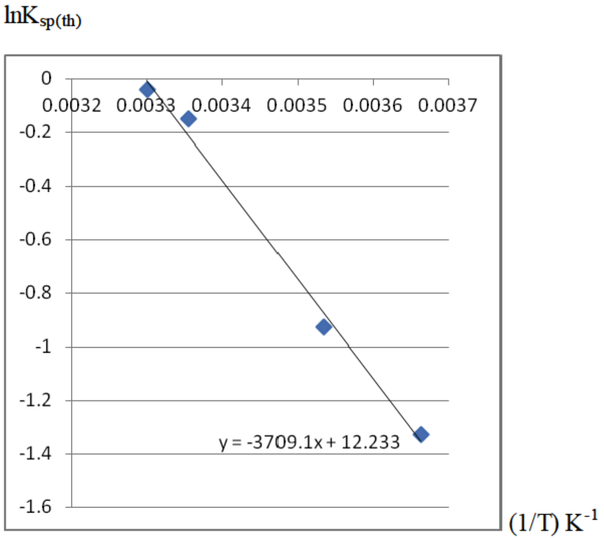

Figure 1: The plot of $\ln K_{sp(th)}$ versus 1/T respect to the mixed solvent (propanol 10%, ethanol 30%, water 60%).

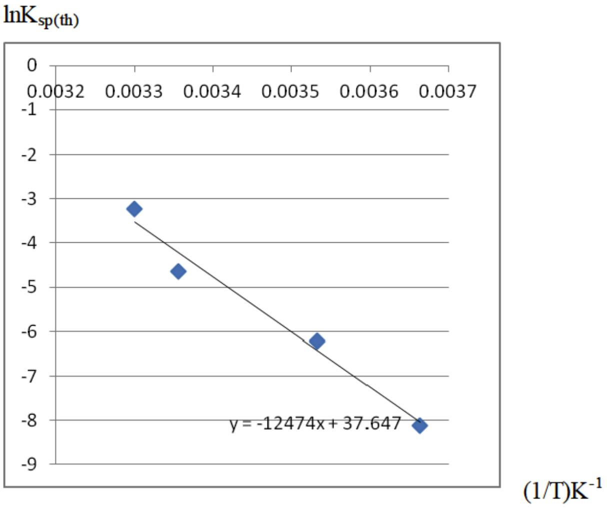

Figure 2: The plot of $\ln K_{sp(th)}$versus 1/T respect to the mixed solvent (propanol 30%, ethanol 40%, water 30%).

Table 8: The Calculated Values of ΔG°, ΔH° and ΔS° Related to the Dissolving $NaClO_3$ in the Mixed Solvent (Propanol 10%, Ethanol 30%, Water 60%) at 298 K

$\Delta G^{\circ}/kJmol^{-1}$	$\Delta H^{\circ}/kJmol^{-1}$	$\Delta S^{\circ}/kJmol^{-1}K^{-1}$
0.44	30.84	0.102

Table 9: The Calculated Values of ΔG°, ΔH° and ΔS° Related to the Dissolving $NaClO_3$ in the Mixed Solvent (Propanol 30%, Ethanol 40%, Water 30%) at 298 K

$\Delta G^{\circ}/kJmol^{-1}$	$\Delta H^{\circ}/kJmol^{-1}$	$\Delta S^{\circ}/kJmol^{-1}K^{-1}$
11.32	103.70	0.31

CONCLUSION

The experimental results showed that the solubility of $NaClO_3$ in the mixed solvent (water+ethanol+propanol) increases by increasing of temperature. On the other hand, the solubility of $NaClO_3$ in the mixed solvent was decreased by increasing the percentages of ethanol and propanol. The formation constant of ion pair was estimated by fuoss model at various temperatures. On the basis of the estimated K_{IP} the concentration of free ions in the considered mixed solvent was calculated .Then by using the estimated values of free ion concentration and estimated $\gamma_{\pm}$, we were enable to calculate the values of $K_{sp(th)}$ at various mixed solvent and at various temperatures. Finally we could evaluate the values of ΔG°, ΔH° and ΔS° relating to the dissolving of $NaClO_3$ in the mixed solvents. During the ion-pair formation, the number of solvated free ions decreases and this leads to an increase in entropy, so, the entropy change, ΔS°, related to ion-pair formation may be positive in spite of formation one species, IP, from two opposite ions B^+ and A^-.We expect that the formation of $Na^+ClO_3^-$ ion-pair should be more favorable at lower temperatures and lower dielectric constants (if the concentration of electrolytic solution is constant).

REFERENCES

[1] Danil NAF, Tanco Lioso MAL, Salomon M, NG Joec Y. Thermodynamic, structural, and conductance studies of lithium coron and electrolytes relevant to lithium battery technology. J Phys Chem 1994; 98: 11796-802. http://dx.doi.org/10.1021/j100096a027

[2] Rey R, Guardia E. Dynamical Aspects of the Na^+ - Cl^- Ion pair Association in water. J Phys Chem 1992; 96: 4712-4718. http://dx.doi.org/10.1021/j100190a104

[3] Henderson D, Sokolowski S, Trokhymehuk A. Association in a Lennard-Jones fluid from a second-order percus-yevik aquation. Physical Reviw 1995; 2(3): 3260-3262.

[4] Muhuri PK, Das B, Hazra DK. Ionic association of some Lithium salts in 1,2-Dimethoxyethane. A Raman spectroscopic and conductivity study. J Phy Chem B 1997; 101: 3329-3332. http://dx.doi.org/10.1021/jp963747d

[5] Wasylkiewcs S. Ion association in aqueos solution of Electrolytes.II. Mathematical Modl for sulphates of Bivalent Metals. Fluid Phase Equilibria 1990; 57: 277-296. http://dx.doi.org/10.1016/0378-3812(90)85127-V

[6] Almeda MA.DE, Fatima MDE, IHA NYM, Osorio VKL. The Ion-pair Association constant of oxalate with fac-tris (2-Aminomethyl pyridine) cobalt (III). Polyhedron 1996; 15(24): 4579-4584.

[7] One K, Honda H. Proton NMR chemical shift Induced by Ionic Association an a poly (ethylene oxid) chain. Macronolecales 1992; 25(23): 6368-6369. http://dx.doi.org/10.1021/ma00049a038

[8] Wang J, Hamet ADJ. Integral equation theory for association liquids: Dimer and trimer concentration for model 1-3 electrolytes. J Chem Phys 1994; 100(5): 3767-3774. http://dx.doi.org/10.1063/1.466364

[9] Chialv Ariel A, Gruszkiewicz Miroslaw S, Cole, David R. Ion – Pair Association in ultrasupercritical Aqueous Environments. J Chem Eng Data 2010; 55: 1828-1836. http://dx.doi.org/10.1021/je900788r

[10] Wright MR, Patterson ILLJ, Harris KDM. Non – Ideality and Ion – Association in Aqueous Electrolyte Solution Overview and a Simple Experimental Approach. J Chem Educ 1998; 75930: 352-357. http://dx.doi.org/10.1021/ed075p352

[11] Davies CW. Ion Association; London: Butterworths 1962.

[12] Kazuko Y, Maski S, Toshitaka F. Molecular dynamic simulation on ion – pair association of NaCl from ambient to supercritical water. Fluid Phase Equilibria 2010; 297: 227-235. http://dx.doi.org/10.1016/j.fluid.2010.05.012

[13] Yokoyama H, Yamatera HA. Theory of Ion Association as a complement of the Debye – Huckle Theory. Bull Chem Soc Jpn 1975; 48: 1770-1776. http://dx.doi.org/10.1246/bcsj.48.1770

[14] Tsierkezos Nikos G, Philippopoulos Athanassios L. Studies of ion solvation and ion association of n-tetrabutylammonium hexafluorophosphate and n-tetrabutylammonium tetraphenylborate in various solvents. Fluid Phase Equilibria 2009; 277: 20-28. http://dx.doi.org/10.1016/j.fluid.2008.11.004

[15] Bjerrum N. Ionic Association,I.Influence of ionic association on the activity of ions at moderate degrees of association. Mat Fys Medd K Dan Vidensk, Selsk 1926; 7: 1-48.

[16] Guggenheim EA. Ion Distribution in Dilute Aqueous Solution of single Binary Electrolytes. Discuss Faraday Soc 1957; 53-65. http://dx.doi.org/10.1039/df9572400053

[17] Guggenhim EA, Turgeon JC. Specific interaction of ions. Trans Faraday Soc 1960; 56: 747-761.

[18] Fuoss RM, Kraus CA. Properties of electrolytic solutions (IV) the conductance minimum the formation of triple ion due to the action of columb force. J Am Chem Soc 1933; 55: 2387. http://dx.doi.org/10.1021/ja01333a026

[19] Fuoss RM, Kraus CA. Properties of electrolytic solutions (III) the dissociation constant. J Am Chem Soc 1933; 55: 1019. http://dx.doi.org/10.1021/ja01330a023

[20] Dang LX. Temperature dependence of interaction of an ion pair in water: A Molecular dynamics study. J Chem Phys 1992; 97(3): 1919-1921. http://dx.doi.org/10.1063/1.463128

[21] Fuoss RM. Ionic Association, III.The Equilibrium Between Ion – Pairs and Free Ions. J Am Soc 1958; 80: 5059-5061.

[22] Cote JF, Deshoyers JE, Justice JC. Application of the Bjrrum Association in water and Acetonitrile. Journal of Solution Chemistry 1996; 25(2): 113-134. http://dx.doi.org/10.1007/BF00972684

[23] Alia JM, Edwards HGM. Ion solvation and ion association in lithium trifluromethanesulfonate solutions. Vibrational Spectroscopy 2000; 24: 185-200. http://dx.doi.org/10.1016/S0924-2031(00)00073-4

[24] Aghaie M, Shahamat Z. Thermodynamic study of solutbility product constant of $K_2Cr_2O_7$ in aqueous solution and related ion – pair format ion at 25°C. J Chemical Engineering Data 2013; 58: 383-387. http://dx.doi.org/10.1021/je301134x

[25] Aghaie M, Jalili T. The investigation of ionic association in the CdF_2 solution with the mixed solvent (water +ethanol +propanol) at 25. J Physical Theoretical Chemistry 2013; 9(4): 263-268.

[26] Aghaie M, Moradian S. Thermodynamics of ion association in the sarutaded solution of the mixed solvent(methanol+water) and ion pairing at 25C. J Physical Theoretical Chemistry 2012; 9(1): 135.

[27] Aghaie M, Ghafourian S. Solubility Product of K_2SO_4 in a Mixed Solvent Medium and Ion – Pair Formation. J Chemical Engineering Data 2010; 55: 1867-1870. http://dx.doi.org/10.1021/je9008816

[28] Aghaie M, Najafi Z. Solubility Product study of CdF_2 in a Mixed Solvent Medium and Related Ion - Pair Formation at 25˚C. J Phys Theor Chem IAU Iran 2012; 8: 231-234.

[29] Aghaie M, Aghaie H, Ebrahimi A. Thermodynamics of the solubility of Barium Nitrate in the mixed solvent Ethanol + Water and Related Ion – Association. J Mol Liq 2007; 135: 72-74. http://dx.doi.org/10.1016/j.molliq.2006.10.005

[30] Aghaie M, Samaie E. Non – Ideality and Ion – pairing in Saturated Aqueous Solution of Sodium Fluoride at 25˚C. J Mol Liq 2006; 126: 72-74. http://dx.doi.org/10.1016/j.molliq.2005.09.007

[31] Sohrabi B, Aghaie M, Aliabadi A. Investigation of Ion – Pairing Phenomenon in BaF_2 Aqueous Solution: Experimental and Theoretical Studies. J Fluorine Chemistry 2010; 7496: 1-7.

[32] Fuoss RM, Distribution of Ions in Electrolytic Solutions. Trans Faraday Soc 1934; 30: 967-980. http://dx.doi.org/10.1039/tf9343000967

[33] Aghaie M, Broojeni BS. Non – Ideality and Ion – pairing in Saturated Aqueous Solution of Lithium Carbonate at 25˚C. J Phys Theor Chem IAU Iran 2007; 3: 249-253.

Received on 20-10-2015 Accepted on 09-11-2015 Published on 18-12-2015

DOI: http://dx.doi.org/10.6000/1929-5030.2015.04.04.2