

## Refractive Index and Density of Urea dissolved in Ammonium phosphate's Solution at Different Temperature

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### Abstract

Densities ( $\rho$ ) and Refractive Indices  $n$  of Urea dissolved in aqueous solutions of Ammonium phosphate's at 298.15, 303.15 and 308.15 K<sup>0</sup>. From these experimental data apparent molar volume ( $\Phi_v^0$ ), limiting partial molar volume ( $\Phi_v^0$ ) and molar refraction  $R_m$  have been calculated we develop an expression we called it limited apparent molar refractivity ( $R_m^0$ ) that we found it is give the same indication of ( $\Phi_v^0$ ) about solute-solvent interactions. The results are interpreted from the point of view of solute – solvent and solute – solute interactions in these systems. The results also show that the solvated Urea has the property of breaking structure of liquid water with increasing temperature with this range this result agree with meaning of ( $R_m^0$ ) derivatives with respect to the temperature.

### Introduction

Aqueous urea solutions have been of long-standing interest due to their peculiar physical properties. For example, urea increases the solubility of hydrocarbons in water<sup>[1]</sup>.

It has been suggested that urea increases the aqueous solubility of non polar compounds by destroying the highly structured network of solvent molecules that characterize the water medium<sup>[2]</sup>.

The properties of water and urea in aqueous solutions have been extensively studied there exists a large variation in their behavior in physical and chemical properties of urea in liquid phase especially in aqueous solutions. There have been conflicting reports, considerable debate, and controversies which are still prevalent about the peculiar behavior of urea in aqueous solutions and its varying hydrogen-bonding properties exhibited in the solvents. Urea, which strongly interacts with the solvent, is still an area of considerable challenge for the chemists. Two such mechanisms were proposed to explain the role of urea in water: one mechanism depicts that urea acts as a structure breaker by breaking the water structure, whereas the other mechanism envisages that urea displaces some water molecules around a hydrophobic group and changes the solvation properties<sup>[3]</sup>.

A large numbers of researchers reported that urea acts as a net structure breakers for water. On the other hand, another researcher reported that urea enhances water structure. The later view has been supported by our

recent studies. The structure making or breaking property of urea in aqueous solution was found to be a temperature – dependent property. It will be interesting to see what happens when some water structure making and breaking salts are add in water + urea solution systems to substantiate the former studies<sup>[4]</sup>.

Urea is produced in natural course from ammonia and carbon dioxide by metabolic reactions, known as the urea cycle, in all living beings and excreted from the body so as to avoid the toxic effects of ammonia. Water solution of urea also shows very exceptional, specific properties. These solutions can change the structure of proteins, increase the solubility of hydrophobic species such as hydrocarbons, and prevent micelle formation. This makes urea very interesting for researchers in the field of biochemistry<sup>[5]</sup>.

The electrolytes possessing different charge and size of the ions may affect water and water + urea solution structure differently. This may be reflected in the apparent molar volume and viscosity coefficient data. This type of study on simple system sometimes provides very useful information regarding the structure for more complex system<sup>[4]</sup>.

The behavior of urea in solution is a very important topic in biological and environmental studies because of its involvement as a waste product in our daily life. The interactions of sparingly soluble solutes in aqueous solutions of urea are of contemporary interest at both the theoretical

and practical level. Weak nonbonding interactions are important in many biological processes, and among these interactions occurring in aqueous solutions, the hydrophobic interactions are the most important driving force found in all biological processes<sup>[1]</sup>.

## Experimental Section

### Materials:

Urea (99%), BDH chemicals Ltd Poole England, Ammonium phosphate Dibasic BDH chemicals London, distilled water.

The solvent solution was prepared by the dissolving (10 gm) of Ammonium phosphate  $(\text{NH}_4)_2\text{HPO}_4$  Dibasic in distilled water to give one liter of solution. This solution used to prepare a series of ten concentrations of urea.

The molalities of the solutions were calculated from molar concentration (C) ( $\text{mol.L}^{-1}$ ) using eq.(1)<sup>[4]</sup>.

$$m = \frac{1000C}{1000\rho - CM} \dots\dots\dots (1)$$

Where the (M) ( $\text{gm.mol}^{-1}$ ) is the molecular weight of urea.

### Refractive Index Measurements:

Refractive indices were determined with respect to the sodium D line. An Abbe refractometer (ATAGO type 3) was used. It was connected with the same Hetrofrig constant-temperature bath used for the density measurements. Calibration of the instrument

was performed with double-distilled water. Precision is estimated to be better than  $2 \times 10^{-4}$ .

### Densities Measurements:

Densities were measured by using 50 ml pycnometer equipped with internal thermometer its accuracy ( $0.01 \text{ K}^{-1}$ ), the side arm of the pycnometer has a cup that capable of isolating accurate volume of solution at definite temperature and preventing the loss of weight that caused by evaporation. The volumes of the pycnometer were calibrated with deionized and doubly distilled water at (298.15, 303.15, 308.15)  $\text{K}^0$ . The densities of urea solution were determined from the weight of the solution in the pycnometer after reaching thermal equilibrium in the water bath at the studied temperatures, divided by the volume of pycnometer.

Weight measurements were carried out by using Sartorius BL 210s Germany with an accuracy of ( $10^{-4} \text{ gm}$ ).

Temperature was controlled using a scott-Gerate CT1150 thermostat with a precision ( $\pm 0.01 \text{ K}^0$ ).

## Results and Discussion

The practical data of densities and refractive index of urea dissolved in ammonium phosphate solution at (298.15, 303.15 and 308.15  $\text{K}^0$ ) were listed in Table (1).

**Table (1)**  
**Values of densities (d), Refractive index ( $\eta$ ) of urea aqueous solution dissolved in Ammonium phosphate at (298.15, 303.15 and 308.15)  $\text{K}^0$ .**

298.15 $\text{K}^0$			303.15 $\text{K}^0$			308.15 $\text{K}^0$		
m(mol/kg)	d(gm/cm <sup>3</sup> )	$\eta$	m(mol/kg)	d(gm/cm <sup>3</sup> )	$\eta$	m(mol/kg)	d(gm/cm <sup>3</sup> )	$\eta$
0	0.9991	1.342	0	0.9962	1.3415	0	0.9941	1.3411
0.0084	0.9993	1.345	0.0085	0.9965	1.3445	0.0085	0.9944	1.344
0.0169	0.9995	1.3451	0.0169	0.9967	1.3446	0.0169	0.9948	1.3441
0.0253	0.9997	1.3452	0.0254	0.9969	1.3447	0.0254	0.9951	1.34421
0.0337	0.9999	1.34532	0.0338	0.9971	1.3448	0.0339	0.9954	1.3443
0.0422	1.0001	1.34544	0.0423	0.9973	1.3449	0.0424	0.9956	1.34442
0.0506	1.0003	1.34553	0.0508	0.9974	1.345	0.0509	0.9959	1.34452
0.0591	1.0004	1.34564	0.0593	0.9976	1.3451	0.0594	0.9961	1.34461
0.0676	1.0006	1.34574	0.0678	0.9977	1.34522	0.0679	0.9963	1.34472
0.076	1.0008	1.34588	0.0763	0.9979	1.34531	0.0764	0.9965	1.34482
0.0845	1.001	1.346	0.0848	0.9981	1.3454	0.0849	0.9966	1.34493

These data show increasing of density and refractive index values with increasing urea concentration in the solution, to estimate the nature of solute -solvent and solute -solute interactions of this system more deeply we calculate the apparent molar volume (cm<sup>3</sup>/mole) by using the equation(2)<sup>[6,7]</sup>:

$$f_v = \frac{M}{\rho} - \frac{1000(\rho - \rho_0)}{m\rho_0\rho} \dots\dots\dots(2)$$

Where (m) is the molal concentration of urea in (mole/kg) units (M) molecular weight of urea in (gm/mole), (ρ, ρ<sub>0</sub>) is the densities of solution and solvent respectively in (gm/cm<sup>3</sup>) units then we plot (f<sub>v</sub>) values vs. (m) according to the equation(3):<sup>[6]</sup>

$$\Phi_v = \Phi_v^0 + S_v m \dots\dots\dots(3)$$

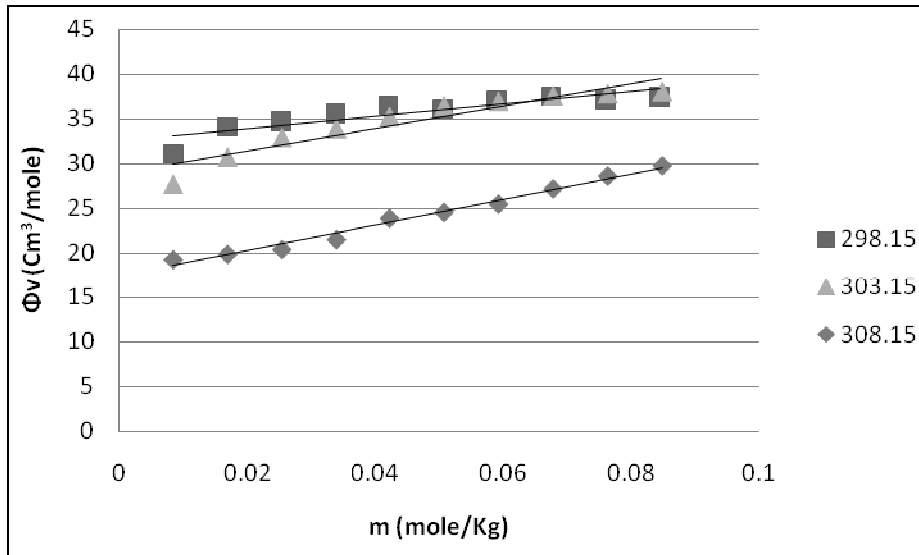


Fig.(1) f<sub>v</sub> of urea dissolved in ammonium phosphate solution at (298.15, 303.15 and 308.15) K<sup>0</sup>.

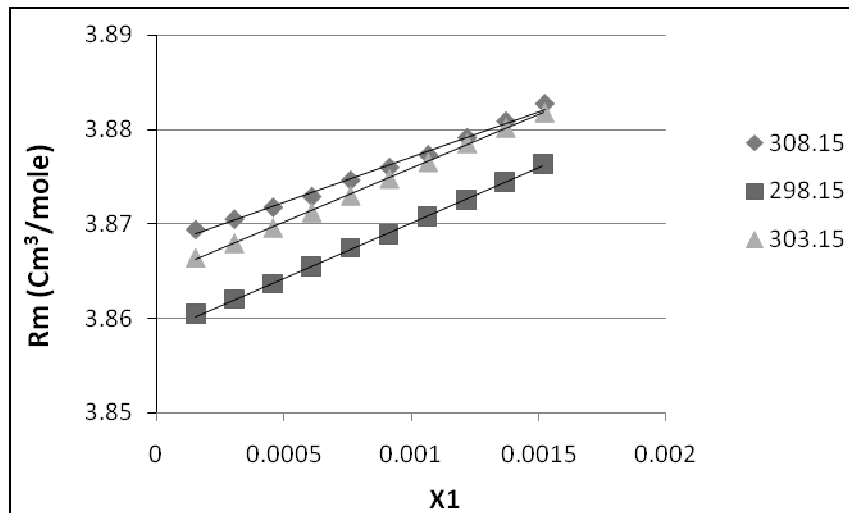
(Φ<sub>v</sub><sup>0</sup>) is the limited apparent molar volume (Cm<sup>3</sup>/mole), it is a measure for solute – solvent interactions and is equal to the partial molar volume of solute at infinite dilution,<sup>[6]</sup> (S<sub>v</sub>) is a constant can give an indication about solute-solute interactions, its unit is (kg.cm<sup>3</sup>.mole<sup>-2</sup>)<sup>[7]</sup>. The values of (Φ<sub>v</sub><sup>0</sup>) and (S<sub>v</sub>) with its correlation coefficient are listed in Table (2) both values were obtained by least squares fitting of (Φ<sub>v</sub>) to equation (3).

From Table (2) we observe decrease of (Φ<sub>v</sub><sup>0</sup>) value with increase temperature and they were largely positive suggesting strong solute-solvent interaction and this interaction decreased by increasing temperature, (S<sub>v</sub>) values are found to be positive indicate strong solute–solute interaction, by increasing temperature (S<sub>v</sub>) increases which show that the interactions become more strong.

Also by employing Lorentz-Lorenz equation we predict molar refraction values which has the expression (4)<sup>[8,9]</sup>:

$$Rm = \frac{\eta^2 - 1}{\eta^2 + 2} \left[ \frac{x_1 M_1 + x_2 M_2 + x_3 M_3}{\rho_{mix}} \right] \dots\dots\dots(4)$$

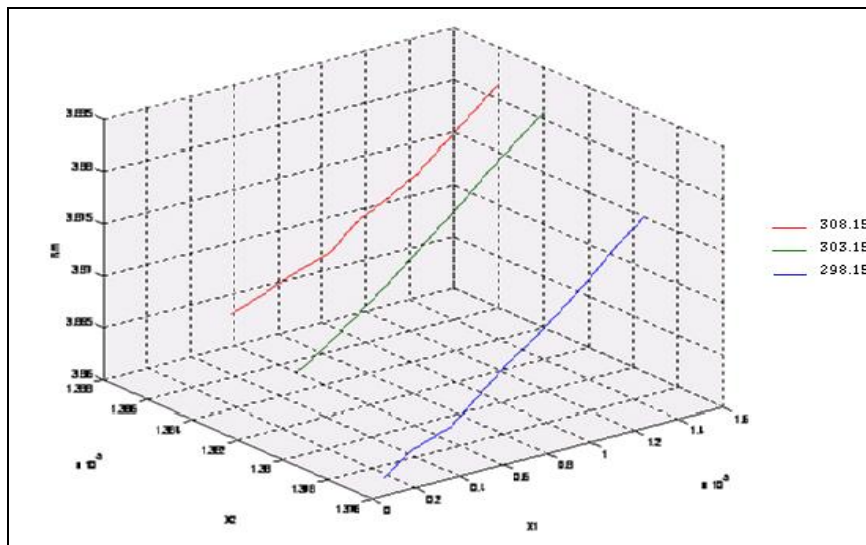
where (Rm) is the molar refraction of the mixture in (cm<sup>3</sup>/mole) units, (x<sub>1</sub>, x<sub>2</sub>, x<sub>3</sub>) are the mole fractions of urea, ammonium phosphate and water respectively, (η) is the refractive index then we plot Rm values vs. mole fraction of urea solutions as shown in Fig.(2) these data are treated by least square method which show a good agreement with linear model according to the correlation coefficient values that listed in Table (2).



**Fig.(2) Plot of  $R_m$  vs. mole fraction of urea ( $X_1$ ) at (298.15, 303.15 and 308.15  $K^0$ ).**

In spite of this linear response of  $R_m$  with urea concentration we try to take a global view about varying of  $R_m$  values with remaining dissolved other constituents of solution the cause of this further investigation is that we take a constant molar concentration of ammonium phosphate solution as solvent but this concentration actually is varying with

variation of the densities of solution that caused by increasing of urea concentration or by increasing temperature for this reason we plot a three dimensional curve showing the variation of  $R_m$  values with both mole fraction of urea and mole fraction of ammonium phosphate solution as shown in Fig.(3).



**Fig.(3) Shows the refractive index and  $x_1$  of urea dissolved solution and  $x_2$  of Ammonium phosphate.**

Fig.(3) show that  $R_m$  still respond with a good linearity with varying mole fraction of urea in spite of the small changes of the mole fraction of ammonium phosphate that due to the variation of density of the solution this over all linearity suggests an increase in overall polarizability of all the ternary systems under study with increasing amount of urea in the mixtures<sup>[10, 11]</sup>.

From Fig.(2) we calculate the relation  $\lim_{x_1 \rightarrow 0} \frac{\partial R_m}{\partial x_1}$  that we expect has a equivalent meaning of the apparent molar volume of urea at infinite dilution so we called it a limited apparent molar refractivity and denote it by a symbol ( $R_m^0$ ) this proposition is suggested for the first time in this work by returning to the basic principles of solution thermodynamics

and molar refraction of mixtures, the mathematical basis of this suggestion is shown in the appendix that combined with this paper and values of ( $R_m^0$ ) were listed in Table (2).

The values of limited apparent molar refractivity show a high positive value which means a strong solute-solvent interaction and

this interaction become weaker with increasing temperature as indicated by decrease of limited apparent molar refractivity that shown in the table, this result is in agreement with results that we obtained from apparent molar volume calculations.

**Table (2)**  
*Shows values of  $f_v^0$ ,  $S_v$  with its correlation coefficient and  $r_1$ , limited apparent refracted and  $r_2$ .*

$T(K^0)$	$\Phi_v^0$ ( $cm^3/mole$ )	$S_v$ ( $kg\ cm^3\ mole^{-2}$ )	$r_1$	$R_m^0$ ( $cm^3/mole$ )	$r_2$
298.15	32.54076	70.06324	0.885	11.700	0.999
303.15	28.86864	127.1721	0.941	11.360	0.999
308.15	17.37782	145.2069	0.992	9.633	0.996

The temperature dependence of ( $\Phi_v^0$ ) follows the equation (5) :<sup>[12]</sup>

$$\Phi_v^0 = \alpha + \beta T + \gamma T^2 \dots\dots\dots(5)$$

Values of coefficients ( $\alpha$ ), ( $\beta$ ) and ( $\gamma$ ) have been calculated and are listed with first and second derivatives in Table (3), first derivative called partial molar expansibility which is a measure to structure-forming, structure – breaking tendency to solute molecules on long range order of solvent molecules from Table (3) we observe the structure breaking tendency of the urea increases with increasing temperature.

Helper<sup>[13]</sup> has proposed a method by which qualitative information on hydration of solutes can be obtained from thermal expansion of aqueous solution by the following relation:

$$\left(\frac{\partial c_p^0}{\partial P}\right)_T = -T\left(\frac{\partial^2 \Phi_v^0}{\partial T^2}\right)_P \dots\dots\dots(6)$$

According to this the left hand side of the above equation should be positive for structure – breaking solutes, and therefore, structure – breaking solutes posses negative values of

$$\left[\frac{\partial^2 \Phi_v^0}{\partial T^2}\right]_P$$

on the other hand, positive values of

$$\left[\frac{\partial^2 \Phi_v^0}{\partial T^2}\right]_P$$

should be associated with structure –

making solutes.

Also as a consequence of the connection between limited apparent molar volume and molar refractivity through limited apparent refractivity we expected the thermal change of ( $R_m^0$ ) is also related to the thermal variation of ( $\Phi_v^0$ ) with same manner and their meaning is similar, up to this we drive the expressions  $\partial R_m^0 / \partial T$  and  $\partial^2 R_m^0 / \partial T^2$  from the equation:

$$R_m^0 = \alpha' + \beta' T + \gamma' T^2 \dots\dots\dots(7)$$

Where ( $\alpha'$ ), ( $\beta'$ ) and ( $\gamma'$ ) are coefficients similar to that exist in equation (5) values of ( $\Phi_v^0$ ) and ( $R_m^0$ ) and their derivatives with temperature are listed in Table (3).

**Table (3)**  
Shows the  $\Phi_v^0$  values with its derivatives and  $R_m^0$  with its derivatives at (298.15, 303.15 and 308.15).

$T$ ( $K^0$ )	$\Phi_v^0$ ( $cm^3.mole^{-1}$ )	$\partial\Phi_v^0/\partial T$ ( $cm^3.mole^{-1}k^{-1}$ )	$\partial^2\Phi_v^0/\partial T^2$ ( $cm^3.mole^{-1}k^{-2}$ )	$(R_m^0)$ ( $cm^3.mole^{-1}$ )	$\partial R_m^0/\partial T$ ( $cm^3.mole^{-1}$ )	$\partial^2 R_m^0/\partial T^2$ ( $cm^3.mole^{-1}k^{-2}$ )
298.15	32.54	0.217	-0.312	11.700	0.920	-0.054
303.15	28.87	-1.343	-0.312	11.360	0.650	-0.054
308.15	17.38	-2.903	-0.312	9.633	0.380	-0.054

The values of Table (3) shows that the negative values of the second derivative of ( $\Phi_v^0$ ) and the decreased value of its first derivative means that urea behave as structure – breaking effect in the liquid ammonium phosphate solution<sup>[13]</sup> also the ( $R_m^0$ ) first and second derivatives show the same behavior which support our proposition of about the validity of using ( $R_m^0$ ) and its thermal derivatives to give the same meaning of ( $\Phi_v^0$ ) and its thermal derivatives.

**Appendix:**

**Physical Origin of ( $R_m^0$ )<sup>[14,15,16]</sup>**

We start from Lorentz-Lorenz equation<sup>(8,9)</sup>:

$$R_m = \frac{\eta^2 - 1}{\eta^2 + 2} \left[ \frac{\sum x_i M_i}{\rho_{mix}} \right] \dots\dots\dots (i)$$

$$x_i = \frac{n_i}{\sum n_i}$$

where  $n_i$  is the number of moles of species (i) with the substitute this execration in equation (i) we get eq. (ii)

$$R_m = \frac{\eta^2 - 1}{\eta^2 + 2} \left[ \frac{\sum n_i M_i}{\rho_{mix} \sum n_i} \right] \dots\dots\dots (ii)$$

$$\sum n_i M_i = \sum W_i = W_{mix}$$

The product of  $n_i$ ,  $M_i$  equal to  $W_i$  which is the weight of i species by summing  $W_i$  over all species we get the total weight of the solution. This is clearly exists in eq. (iii).

$$R_m = \frac{\eta^2 - 1}{\eta^2 + 2} \left[ \frac{W_{mix}}{\rho_{mix} \sum n_i} \right]$$

But  $V_{mix} = \frac{W_{mix}}{\rho_{mix}}$  and substitute in eq. (iii)

$$R_m = \frac{\eta^2 - 1}{\eta^2 + 2} \left[ \frac{V_{mix}}{\sum n_i} \right] \dots\dots\dots (iv)$$

The total volume of the solution is equal to the sum of partial molar volume of the constituent product by its number of moles as :

$$V_{mix} = \sum \bar{V}_i n_i$$

and substitute in eq. (iv) we get the eq. (v)

$$R_m = \frac{\eta^2 - 1}{\eta^2 + 2} \left[ \frac{\sum \bar{V}_i n_i}{\sum n_i} \right] \dots\dots\dots (v)$$

By returning to the  $x_i = \frac{n_i}{\sum n_i}$ , we get eq. (vi)

$$R_m = \frac{\eta^2 - 1}{\eta^2 + 2} \left[ \sum \bar{V}_i x_i \right] \dots\dots\dots (vi)$$

By defection eq. (vi) with respect to the mole fraction of constitution as (vii).

$$\frac{\partial R_m}{\partial x_i} = \frac{\eta^2 - 1}{\eta^2 + 2} \bar{V}_i \dots\dots\dots (vii)$$

At infinity dilution the  $v_i$  of the constituent i become equal to the limit partial molar volume and also its equal to the limiting apparent molar volume<sup>(6)</sup>.

Some expect the limit of the relation (vii) at xi approach zero is related to  $\phi_v^0$  as eq.(viii).

$$\lim_{x_i \rightarrow 0} \frac{\partial R_m}{\partial x_i} = \frac{\eta^2 - 1}{\eta^2 + 2} \bar{V}_i^0 = \frac{\eta^2 - 1}{\eta^2 + 2} \Phi_v^0 \dots\dots\dots (viii)$$



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اطلقنا عليها الانكسار المولاري الظاهري المحدد ( $R_{m}^0$ ) والتي وجدنا بانها تعطي نفس الدلالة التي يعطيها الحجم الظاهري المحدد وخاصة حول تداخلات (مذاب- مذيب) ومن ثم تم استعراض النتائج من زاوية التداخلات الجزيئية من نوع مذيب-مذاب او مذاب- مذاب في هذا النظام كما ان اليوريا تسلك كعامل مهدم لتركيب الماء السائل مع زيادة درجة الحرارة وهو ما يتوافق مع نتيجة كون مشتقات ( $R_{m}^0$ ) المستحدثة بالنسبة لدرجة الحرارة تشير الى هذا التأثير المهدم ايضا.

## الخلاصة

في هذه الدراسة تم الحصول على النتائج التجريبية لكثافة ( $\rho$ ) ومعامل انكسار  $\eta$  اليوريا الذائبة في المحاليل المائية لفوسفات الامونيوم في الدرجات الحرارية 298.15, 303.15 و 308.15 درجة مطلقاً. من هذه النتائج تم حساب الحجم المولاري الظاهري ( $\Phi_{v}$ ) و الحجم المولاري المحدد ( $\Phi_{v}^0$ ) وقيم الانكسار المولاري كذلك فقد استحدثنا كمية