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Viscosity and Density of Urea Dissolved in Ammonium phosphate's solution at different temperature.

لزوجة وكثافة اليوريا الذائبة في محلول فوسفات الامونيوم بدرجات حرارية مختلفة.

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Abstract

Densities (ρ) and viscosities (η) of urea in Ammonium phosphate solution at different temperature (298.15, 303.15and308.15) K have been measured. The results were used to determine the apparent molar volumes ($\emptyset_v$) and limiting partial molar volumes ($\emptyset_v°$), slop (S_v), Gibbs energy of activation for viscous flow of solution $\Delta G^{*}_{1,2}$ and Jones – Doles B coefficients. The results show that solvated Urea shows different types of solute – solute interactions as a result of its dissociation spatially at low concentrations. The results also show that the solvated urea has the property of breaking structure of liquid ammonium phosphate solution with increasing temperature.

الخلاصة

تضمنت هذه الدراسة قياس كثافة ولزوجة اليوريا مع فوسفات الأمونيوم في المحلول المائي بدرجات حرارية مختلفة (298.15,303.15and 308.15)مطلقة. استخدمت هذه النتائج لحساب الحجم المولالي الظاهري ϕ_V ، الحجم المولالي الظاهري المحدد$\phi_V°$،الميل S_V، طاقة كبس للانسياب اللزج للمحلول $\Delta G^{*}_{1,2}$ ومعامل جونس دول – B .حيث بينت النتائج إن اليوريا تظهر أنواع مختلفة من تداخلات مذاب – مذاب كنتيجة لتفككها عند التراكيز الواطئة، كذلك فان اليوريا تسلك كعامل مهدم لتركيب محلول فوسفات الامونيوم السائل مع زيادة درجة الحرارة .

Introduction

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. [1] 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. [2]

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.[3]

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. (4)

Urea is considered a solute class of its own, because of the possibly unique characteristics of its interactions with water. For this reason and also in liquid - state physics, much interest is directed toward the properties of urea/water system. (5)

In attempting to explain the concentration dependence of thermodynamic parameters of aqueous solution of urea, stokes has proposed an association model, in which urea molecules, according to an isodesmic reaction scheme form clusters U_{n+1} from monomers U_1.

$$U_n + U_1 \underset{K_{fn}}{\overset{K_{rn}}{\rightleftharpoons}} U_{n+1} \qquad n = 1, 2\ldots \qquad (1)$$

Frank and franks, also dealing with the thermodynamic properties of urea in solution, employed a different model. (6) Assuming water to consist of a dense non-hydrogen-bonded phase $(H_2O)_d$ and a tetrahedrally H-bonded bulky phase $(H_2O)_b$, they considered urea to mix ideally with $(H_2O)_d$ but not to interact with the bulky clusters $(H_2O)_b$. This model predicts urea to promote structure-breaking effects because of a shift, in favor of the dense phase, of the equilibrium between the dense and the bulky water. Hence, with in the framework of this model, the effect of urea in solution may be described by catalytic action in dense-bulky phase equilibrium:

$$(H_2O)_b + U \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (H_2O)_d + U \qquad (2)$$

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, (7) increase the solubility of hydrophobic species such as hydrocarbons, (8) and prevent micelle formation. This makes urea very interesting for researchers in the field of biochemistry.

Experimental section

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

The solvent solution was prepared by the dissolving (10g) of Ammonium phosphate $(NH_4)_2HPO_4$ Dibasic in (1000g) of distill water. This solution used to prepare a series of ten concentration of urea.

Densities Measurements. Densities were measured by using (50) ml pyknometers . The volumes of the pyknometers were calibrated with deionized and doubly distilled water at (298.15, 303.15and308.15) K. The densities of urea solution were determined from the weight of the solution in the pyknometer after reaching thermal equilibrium with a water bath at the studied temperatures, divided by the volume of pyknometer. Sartorius BL 210s Germany with an accuracy of (10^{-4}g) covering whole composition range of the binary mixtures.

Determination of Apparent Molar Volumes. Apparent molar volumes were determined using the measured densities of solvents and solution in eq (3).

$$\phi_V = \frac{1}{m}\left[\frac{(1000+m_1M_1+m_2M_2)}{\rho} - \frac{(1000+m_2M_2)}{\rho^o}\right] \quad (3)$$

Where ϕ_v is the apparent molar volume (Cm^3/mol), m_1 is the molality of solute (mol/kg) , m_2 is the molality of solvent , M_1 is the molar mass of the solute (g/mol) and M_2 is the molar mass of the solvent and ρo and ρ are the densities of water and solute (g/cm^3) , respectively.

The molalities of the solutions were calculated from the molarities C (mol.L^{-1}) using eq (4)

$$m = \frac{1000c}{1000\rho - C_1 M_{1wt} C_2 M_{2wt}} \quad (4)$$

were the M_1C_1 is the molecular weight and concentration of urea , M_2C_2 is the molecular weight and concentration of Ammonium phosphate .

Viscosities Measurement. Viscosities were measured with a calibrated Ubbelohde Viscometer schott gerate AVS 300 standard institution with sufficiently long efflux time to avoid kinetic energy correction. The provided calibration constants were checked with water, ethanol, and *n*-hexane. Temperatures were controlled by a thermostatic water bath fluctuating to ±0.01 K. The uncertainty of η in the present experiments was less than 2×10^{-4} *m pas*.

Results and Discussion

The measured densities and viscosities data are listed in table (1) at different molal concentrations of urea in solution 10000 *ppm* of $(NH_4)_2HPO_4$,these results shows the increase of density values with increasing of the concentration of urea solution at each specified temperature and decrease of density with increasing temperature at constant molal concentration these results are agree with general behavior of liquid solutions as soon as viscosity values obey the same normal behavior of normal liquid solutions.

Table 1. Experimental molarities, densities (ρ) and viscosities (η) of Urea dissolved in Ammonium phosphate solution in range concentration 0.09 at (298.15, 303.15and308.15) K.

m\298 mol/kg	d gm/cm^3	η *m* pas.	m\303 mol/kg	d gm/cm^3	η *m* pas.	m\308 mol/kg	d gm/cm^3	η *m* pas.
0	0.9991	0.9071	0	0.996216	0.81509	0	0.99409	0.7383
0.008427	0.999341	0.90936	0.008452	0.996486	0.81742	0.008469	0.99443	0.74071
0.01686	0.999532	0.91119	0.016908	0.996706	0.81892	0.016942	0.99476	0.74258

0.025298	0.999732	0.91309	0.025371	0.996896	0.82074	0.025417	0.995082	0.74422
0.033741	0.999913	0.91508	0.033838	0.99709	0.82261	0.033897	0.995376	0.74593
0.042191	1.000079	0.91702	0.042312	0.997252	0.82424	0.042383	0.995599	0.74744
0.050643	1.000295	0.91872	0.050792	0.997402	0.82594	0.050872	0.995868	0.74899
0.059106	1.000435	0.92061	0.059278	0.997568	0.82746	0.059366	0.996111	0.7504
0.067572	1.000601	0.92267	0.06777	0.997721	0.82933	0.067869	0.996287	0.75197
0.076041	1.000811	0.92455	0.076267	0.997891	0.83099	0.076378	0.996456	0.7547
0.084518	1.000982	0.92647	0.084769	0.998058	0.83293	0.084893	0.996624	0.75504

Apparent molar volumes (Φ_v) of the urea were shown in figure (1). The apparent molar volume is found to be dependent upon the urea concentration as well as on the temperature. We observe in figure (1) the increase of (Φ_v) with increasing concentration of urea and also increase with increasing temperature but the difference in apparent molar volume at low concentrations with temperature is larger than that in higher concentrations. This behavior may be a result of increase of ionization at low concentrations. In the mathematical treatment of value variety of (Φ_v) with concentration in polar solutions some references used linear expression as relation between (Φ_v) and concentration of solution spatially in the case of none-ionic solutes [9,12] , other used linear relation between square root of concentration (as equivalent to ionic strength of solution) and (Φ_v) for ionic solutes [13,14,15] , we have summed between the two methods to get better understanding to the interaction between solute particles with each other's and with solvent molecules .

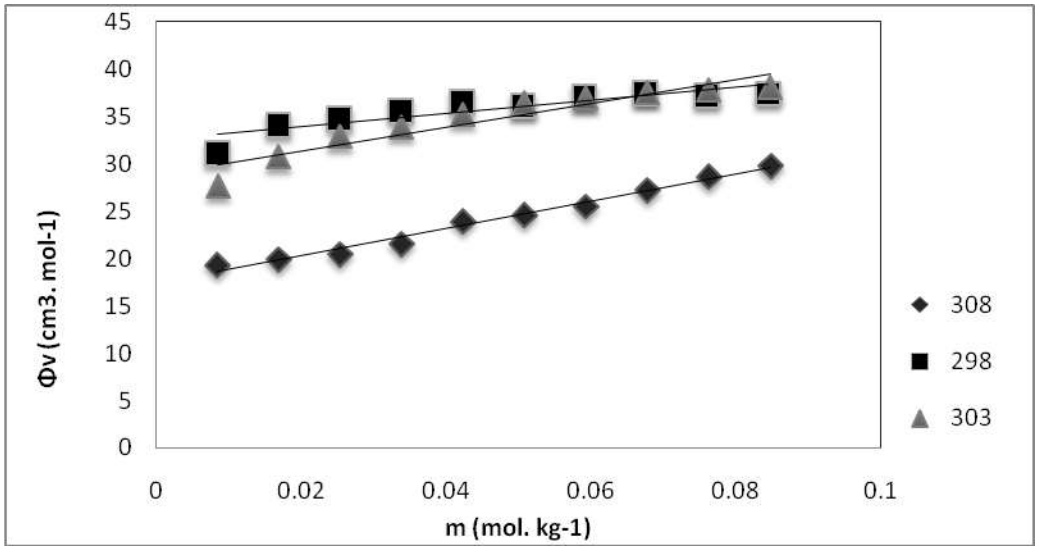


Figure (1). Plots of apparent molar volume ($Ø_v$) versus m of Urea in Ammonium phosphate solution at 298.15, 303.15 and 308.15K.

Limiting value of apparent molar volume at infinite dilution (Φ_v^0) was calculated from the relation:

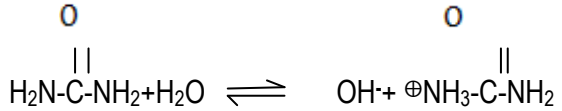
$$\phi = \phi_v{}^o + S_v\, m \qquad (5)$$

Which is equal to the partial molar volume at infinite dilution [13], (Φ_v^0) considered as a measure of solute – solvent interactions and a measure of molecular volume of solute [16], (S_v) is the experimental slop which is a parameter of solute – solute interactions [17] both values of (Φ_v^0) and (S_v) are listed in table (2) with both values were obtained by least squares fitting of (Φ_v) to equation (5).

Table (2) Limiting partial molar volume (ϕ_v^0) experimental slope (S_v) and parameters of equation (5)

T	Φ_v^0	Sv	a	b	c	d
K	cm^3mol^{-1}	$Cm^3\ Kg\ mol^{-2}$	$Cm^3\ mol^{-1}$	$Cm^3\ Kg^{1/2}\ mol^{-3/2}$	$Cm^3\ Kg\ mol^{-2}$	$Cm^3\ Kg^{3/2}\ mol^{-5/2}$
298.15	32.54076	69.35911	20.26	166.9	-584.5	739.3
303.15	28.86864	125.8904	19.72	90.94	-15.97	-274.5
308.15	17.37782	143.742	23.87	-98.85	599	-653.3

To realize the phenomena of ionization of urea which show weak base character through the reaction (I) :



(I)

We postulate the equation:

$$\Phi_v = a + bm^{1/2} + cm + dm^{3/2} \qquad (6)$$

This equation represented by plotting (Φ_v) vs. ($\sqrt{m}$) and treated it as polynomial from the third order as shown in figure (2), the numerical values of (a),(b),(c) and (d) are listed in table (2).

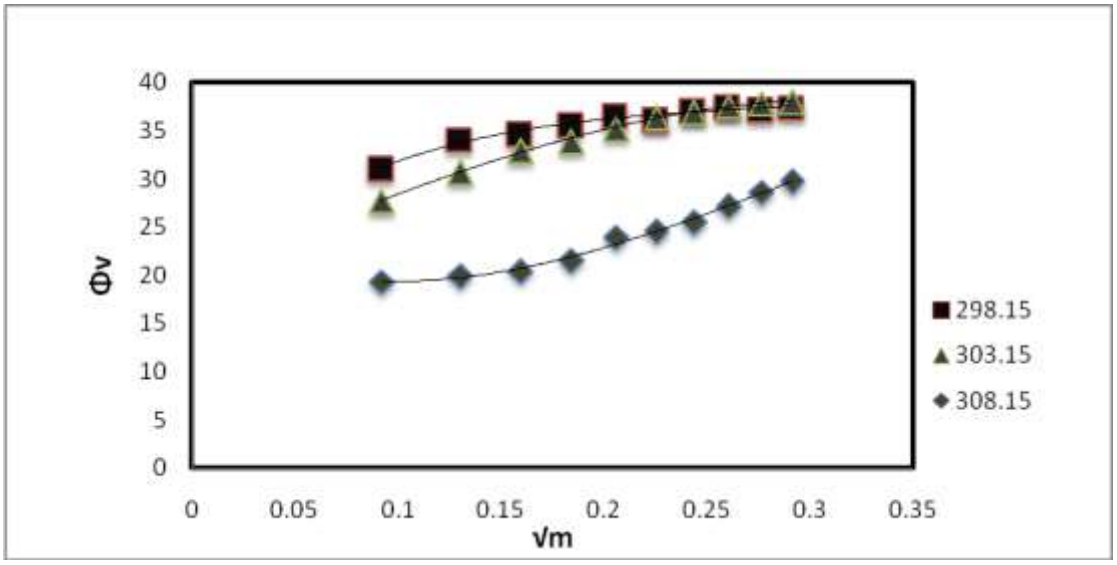


Figure (2) plots of apparent molar volume ($Ø_v$) versus √ m of Urea in Ammonium phosphate solution at 298.15, 303.15 and 308.15K.

To describe the variety of interactions among different species in the solution according to equation (6) we give the following explanation:

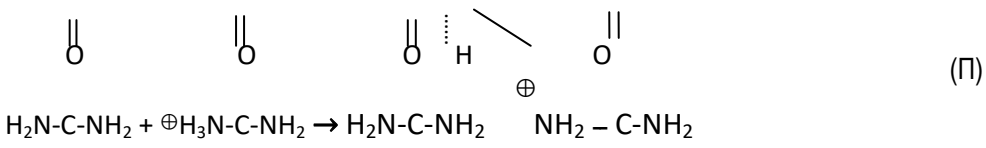
(a) Parameter is analogous to (Φ_v^0) in equation (5) describe the interactions between solute and solvent qualitatively not quantitatively because the deviations that take place as a result of ionization at low concentrations will get a large deviation in (Φ_v^0) value, for this reason the values of (Φ_v^0) obtained from equation (5) are considered more realist than that obtained from eq. (6) especially they much close to the theoretical molecular volume of urea molecule.

(b), (c) and (d) values are analogous to (S_v) they describe the interactions among solute species as follows:

(b) Define the interaction between ions mainly between unions and cations in the solution.

(c) Define none ionic binary interactions between molecules.

(d) Define the interactions among ions and neutral molecules of solute such as:



(П)

From table (2) we observed the decreasing of (Φ_v^v) value with increase temperature and they were largely positive suggesting strong solute- solvent interaction and this interaction decreased by increasing temperature , (S_v) values are found to be positive indicate strong solute – solute interaction , by increasing temperature (S_v) increases which show that the interactions become more strong.

Solute – solute interactions can be represented more clearly by considering the coefficients of equation (6) that shown in table (2) the ionic type solute – solute interaction which be predicted from coefficient (b) weakened by increasing temperature this may be due to decrease in ionization of urea by increasing temperature. eq (I)

None – ionic interaction type between urea molecules which represented by (c) coefficient is negative indicate weak interaction, this interaction become stronger with increasing temperature. eq (Π)

Remaining (d) coefficient that give indication to ionic – nonionic solute – solute interactions also begin with large positive value meaning strong solute – solute interaction and this interaction become weak with increasing temperature as shown from (d) values this result may be explained as the explanation of ionic solute – solute interaction [coefficient (b) because the decrease of ionization of urea in water with increasing temperature.

The temperature dependence of (Φ_v^0) follows the equation (7):

$$\Phi_v^0 = \alpha + \beta T + \gamma T^2 \qquad (7)$$

Values of coefficients (α), (β) and (γ) have been calculated and are listed with first and second derivatives in table (3), first derivative called partial molar expansibility [18] 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 [19] 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:

$$\left(\frac{\partial C_P^0}{\partial P}\right)_T = -T\left(\frac{\partial^2 \Phi_v^0}{\partial T^2}\right)_P \qquad (8)$$

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 $[\frac{\partial^2 \Phi_v^0}{\partial T^2}]_P$ on the other hand , positive values of $[\frac{\partial^2 \Phi_v^0}{\partial T^2}]_P$ should be associated with structure – making solutes.

In the present study the values of second derivative have been obtained from equation (7) and are listed in table (3) shows that the values are negative thus urea behave as structure - breaking in the liquid ammonium phosphate solution and these results are in agreement with the results that obtained from partial molar expansibility .

Table (3) Limiting partial molar volume with its derivatives

T	Φ_v^0	$\partial\Phi_v^0$v/∂T	$\partial^2\Phi_v^0/\partial T^2$
K	cm^3mol^{-1}	$Cm^3\ mol^{-1}\ k^{-1}$	$Cm^3\ mol^{-1}\ k^{-2}$
298.15	32.54	0.217	-0.312
303.15	28.87	-1.343	-0.312
308.15	17.38	-2.903	-0.312

The viscosity data were analyzed by using the Jones- Dole equation

$$\frac{\eta_r - 1}{\sqrt{m}} = A + B\sqrt{m} \quad (9)$$

Where η_r is the relative viscosity of the solution which obtained from dividing the viscosity of the solutions that contain urea on the viscosity of the solution that contains ammonium phosphate which is treated as solvent, A and B are Jones- Dole constants where A accounts for The solute- solute interactions and B is a measure of structural modifications induced by the solute- solvent interactions, the values of A and B are included in table (4) , this table show the increase of A value with increasing temperature at the time that decrease B coefficient with increasing temperature this mean the solute- solute interactions become stronger by increasing temperature while the solute solvent become weak this support our earlier conclusion drawn from apparent molal results.

The temperature derivatives of B coefficient ($\partial B/\partial T$) have also been calculated it's sign provide important information regarding the structure- making structure- breaking ability of the solute in solvent media in general it's value is negative which means urea act as structure-breaker in aqueous ammonium phosphate solvent.

Table (4) Jones-Dole constants with B derivative

T K	A $Dm^{3/2}\ mol^{-1/2}$	B $dm^3\ mol^{-1}$	$\frac{\partial B}{\partial T}$ $dm^3\ mol^{-1}\ k^{-1}$
298.15	0.004	0.234	-0.001222
303.15	0.008	0.225	-0.000622
308.15	0.15	0.219	-2.2E-05

The activation free energy of viscose flow has been calculated by using the Eyring relation [20, 21]

$$\Delta G^* = RT \ln \frac{\eta \bar{V}_{1,2}}{hN_A} \quad (10)$$

Where (ΔG^*) is the activation energy (R) gas constant (T) absolute temperature (η) viscosity of solution ($\bar{V}_{1,2}$) is the molar volume of solution (h) Planck constant (N_A) Avogadro number , furthermore the entropies (ΔS^*) and enthalpies (ΔH^*) of activation of viscous flow have been calculated from the free energy of activation by using the relations:

$$\Delta S^* = -d(\Delta G^*)/dT \quad (11)$$

$$\Delta H^* = \Delta G^* + T\Delta S^* \quad (12)$$

Equations (11) and (12) applied at constant pressure, the values of (ΔG^*), (ΔH^*) and ΔS^* are listed in table (5).

Table (5) thermodynamic functions for viscous flow ΔG^* and ΔH^* in J/mol, ΔS^* in J/mol.K the ΔG^* that shown for three temperatures while ΔH^* for 298.15 K and ΔS^* is constant with temperature molar concentration is used here because it is constant with temperature.

C	ΔG*	ΔG*	ΔG*	ΔS*	ΔH*
mol. L	298/J. mol^{-1}	303/J. mol^{-1}	308/J. mol^{-1}	J/mol. K	298/J. mol^{-1}
0	20627.28	20369.51	20129.7	49.75742	3545.99
0.008333	20633.71	20376.79	20137.8	49.59125	35411.91
0.016667	20639.09	20381.66	20144.1	49.49938	35389.91
0.025	20644.36	20387.56	20149.64	49.49938	35395.45
0.033333	20650.45	20393.59	20155.46	49.49835	35400.95
0.041667	20656.15	20398.97	20160.79	49.53613	35417.92
0.05	20661.08	20404.57	20166.13	49.49492	35410.57
0.058333	20666.7	20409.59	20171.06	49.56378	35436.7
0.066667	20672.7	20415.68	20176.67	49.60205	35454.1
0.075	20678.09	20421.08	20186.11	49.19803	35339.1
0.083333	20683.68	20427.32	20187.68	49.59946	35464.32

In general $\Delta G^{*(14)}$ values are positive increasing with increasing concentration and decreasing with increasing temperature these results can be explained by the increase of activation energy that needed for viscous flow with by the raising the concentration of urea due to the increase f hydrogen bonding among the urea molecules and formation of long range aggregations among them but with increasing temperature these aggregations are destroyed so the activation energy will be smaller, ΔS^* positive values indicate that viscous flow is take place through deferent types of conformations that consume an appreciable amount of energy to stabilize (positive ΔH^*value).

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