Volumetric and Viscosity Studies of Aqueous Solutions of the Potassium Salt of Penicillin-G at Different Temperatures and at Ambient Pressure

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Density and viscosity measurements are reported for aqueous solutions of the potassium salt of penicillin-G at different temperatures (293.15 K to 308.15 K) and at ambient pressure. The density data are used to obtain apparent molar volumes of the potassium salt of penicillin-G (PGK). Also, the coefficient of thermal expansion and apparent molar expansivity data has been obtained using the density data at different temperatures. The relative viscosities (η_r) and the viscosity *A*, *B*, and *D* coefficients in the Jones−Dole equation $\eta_r = 1 + Ac^{1/2} + Bc + Dc^2$, with c = concentration of the potassium salt of penicillin-G in aqueous solutions (0.005 mol·dm^{-3} to 0.12 mol·dm^{-3}), have been determined. The values of the *B* and *D* coefficients were found to be high compared to simple 1:1 electrolytes. The values of the *A* coefficient do not show any trend as a function of temperature; however, the *B* coefficient decreases with an increase in temperature. The results are explained in terms of hydrophobic hydration of the anion and hydrophobic interactions between penicillin-G molecules in the premicellar region.

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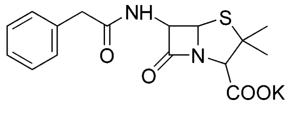
1. Introduction

At present, a large collection of data on an ionic viscosity *B* coefficient of the Jones−Dole[1] empirical equation are available for electrolytes in both aqueous and nonaqueous solvents at ambient and other temperatures.[2−7] Similarly, the data for such a coefficient for neutral solutes like alcohols, ethers, urea, carbohydrates, amines, and amides in aqueous solutions are available.[8−11] The said parameter is used to derive information about structure making/breaking properties of the solutes, shape effect, calculation of radii, hydration number, etc., in aqueous solutions, whereas the constancy of the Walden product is being tested in aqueous/nonaqueous solutions with a combination of conductivity data.[12] Such investigations are also made in mixed aqueous solvent systems. However, we noted that information about large anions in aqueous solutions is very much limited.

Many microorganisms produce chemical substances internally which interfere with the growth or metabolism of other microorganisms. Such compounds are known as antibiotics. They are chemotherapeutic agents. Penicillin is one of the most familiar antibiotics. Penicillin G (a molecule of the 20th century) is a natural penicillin, is obtained from cultures of *Penicillium chrysogenum*, and is available in several different salt forms. Penicillin G potassium (also known as benzylpenicillin potassium, aqueous or crystalline penicillin) occurs as colorless or white crystals or as white crystalline powder. The general structure of penicillin-G potassium is



Penicillin is a unique molecule containing an unstable highly strained and reactive β-lactam ring. The degradation of penicillin takes place in various conditions, viz., alkaline or acidic, in the presence of the enzyme β-lactamase or on treatment with weak nucleophiles like water and metal ions. Penicillin-G is a fairly strong monobasic acid (pK_a = 2.5) with an optical rotation $[\alpha]_D$ = +280. It is soluble in common fat solvents and in water. The sodium and potassium salts of penicillin are most stable in solutions of pH 6.0 to 6.8. In solution outside this pH range, activity is soon lost.[13−16]

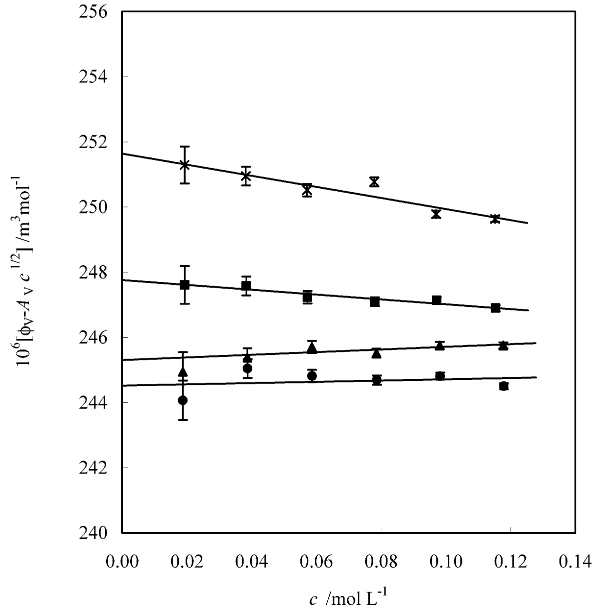


Figure 1. Apparent molar volume of potassium salt of penicillin-G in aqueous solutions at different temperatures: ●, 293.15 K; ▲, 298.15 K; ■, 303.15 K; and *, 308.15 K.

In this study, we report the volumetric and viscosity properties of aqueous solutions of the potassium salt of penicillin-G in the concentration range of (0.005 to 0.12) mol·kg^{-1} (i.e., in the premicellar region) at different temperatures (293.15 K to 308.15 K with 5 K intervals). Penicillin-G forms micelles in aqueous solutions having a cmc value of 0.22 mol·dm^{-3} at 298.15 K.[17]

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Table 1. Density and Volume Data for Potassium Salt of Penicillin-G in Aqueous Solutions at Different Temperatures

m / $\mathrm{mol \cdot kg^{-1}}$	d / $\mathrm{kg \cdot m^{-3}}$	$10^6 \cdot \phi_V$ / $\mathrm{m^3 \cdot mol^{-1}}$	$10^6 \cdot \phi_E^0$ / $\mathrm{m^3 \cdot mol^{-1} \cdot K^{-1}}$	m / $\mathrm{mol \cdot kg^{-1}}$	d / $\mathrm{kg \cdot m^{-3}}$	$10^6 \cdot \phi_V$ / $\mathrm{m^3 \cdot mol^{-1}}$	$10^6 \cdot \phi_E^0$ / $\mathrm{m^3 \cdot mol^{-1} \cdot K^{-1}}$
	T/K = 293.15				T/K = 298.15		
0.00000	998.206	244.5[a]		0.00000	997.047	245.3*	0.09[a]
0.01891	1000.623	244.3		0.01891	999.450	245.2	
0.03922	1003.152	245.4		0.03922	1001.984	245.7	
0.05967	1005.702	245.3		0.05967	1004.498	246.2	
0.08039	1008.259	245.2		0.08039	1007.044	246.0	
0.10085	1010.738	245.4		0.10085	1009.497	246.3	
0.12167	1013.281	245.1		0.12167	1011.986	246.4	
	T/K = 303.15				T/K = 308.15		
0.00000	995.650	247.8[a]	0.71[a]	0.00000	994.035	251.6[a]	
0.01952	998.081	247.9		0.01952	996.399	251.6	
0.03888	1000.467	248.0		0.03888	998.730	251.4	
0.05831	1002.854	247.7		0.05831	1001.061	251.0	
0.07995	1005.481	247.6		0.07995	1003.592	251.4	
0.10000	1007.876	247.8		0.10000	1006.020	250.4	
0.11934	1010.194	247.6		0.11934	1008.281	250.3	

[a] Extrapolated values to infinite dilution.

2. Experimental Section

Penicillin-G potassium salt (> 98 % pure) procured from MERCK Schurchardt was used without further purification. All the solutions were prepared in fresh doubly quartz distilled water on a molality basis and converted to the molarity scale when required using density data at different temperatures. A Mettler Toledo AB204-S balance, having a readability of 0.1 mg, was used to determine weight. The uncertainty in composition of solutions is negligibly small and is of the order of $\pm\ 5 \cdot 10^{-5}$ $\mathrm{mol \cdot kg^{-1}}$.

The density measurements of these solutions were made using an Anton Paar digital densiometer (model DMA 60/602) at different temperatures (293.15 K to 308.15 K). The temperature constancy of the vibrating tube is better than ± 0.02 K, as is maintained constant by circulating water through a Julabo Cryostat (± 0.01 K). After applying humidity and laboratory pressure corrections, the reproducibility in the density values is found to be of the order of $\pm\ 5 \cdot 10^{-3}$ $\mathrm{kg \cdot m^{-3}}$.

Viscosity measurements were made using a Ubbelohde viscometer suspended in the thermostatic bath having 60 L capacity and temperature fluctuations less than ± 0.005 K. The details were reported previously. The flow time of water for the Ubbelohde viscometers is (1093.1 ± 0.1) s at 298.15 K, the time being monitored using a stopwatch with least count of 0.1 s. All the flow time measurements reported in this work are averaged over three separate measurements of the same solutions. The calibration of the Ubbelohde viscometer has been described previously.[10] The uncertainty in viscosity measurements with reference to water is estimated using the guide to the expression of uncertainty in measurements (International Organization for Standardization, Geneva) to be of the order of ± 0.00015 mPa·s.

3. Results

The apparent molal volume (ϕ_V) of the potassium salt of penicillin-G (PGK) in aqueous solutions was calculated using eq 1

$$\phi_V = \frac{1000(d_0 - d)}{mdd_0} + \frac{M_2}{d} \qquad (1)$$

where m is the molality of PGK in aqueous solution; d and d_0 are the densities of solution and water, respectively; and M_2 is the molar mass of PGK. It is assumed that in the studied concentration range hydrolysis if any is negligible.

Errors in ϕ_V were considered on the basis of the equation given by Redlich and Bigeleisen[18]

$$\delta\phi_V = -\frac{1000\delta d}{d_0 c} + \frac{1000(d - d_0)}{c}\,\delta c \qquad (2)$$

where $\delta\phi_V$, δd, and δc are the uncertainties in volume, density, and concentration, respectively. The estimated uncertainty in ϕ_V at the concentration of 0.02m is about $\pm\ 0.5 \cdot 10^{-6}$ $\mathrm{m^3 \cdot mol^{-1}}$, and it is about $\pm\ 0.2 \cdot 10^{-6}$ $\mathrm{m^3 \cdot mol^{-1}}$ for 0.04m (where m is molality). The data of density and ϕ_V for aqueous solutions of PGK at different temperatures are collected in Table 1. The limiting values of the apparent molar volume (ϕ_V^0) were obtained by smooth extrapolation of ϕ_V data to infinite dilution (zero concentration) of PGK using the Debye−Hückel limiting law correction at different temperatures.[19] The data of ϕ_V and ϕ_V^0 are collected in Table 1, and the concentration variation of the parameter ($\phi_V - A_V\sqrt{c}$) is shown in Figure 1; here A_V is the Debye−Hückel limiting slope. The apparent molar expansivities (ϕ_E) at 298.15 K and 303.15 K have been calculated from densities and their temperature coefficients using eq 3

$$\phi_E = \frac{1000}{mdd_0}(d_0\alpha - d\alpha_0) + \frac{M_2}{d}\alpha \qquad (3)$$

where α, $[\alpha = -(1/d)(\partial d/\partial T)]$, is the coefficient of the thermal expansion of solution. The accuracy in the α data is of the order of $\pm\ 5 \cdot 10^{-6}$ $\mathrm{K^{-1}}$. Using the method of propagation of errors, the uncertainty in the derived apparent molar expansivity (ϕ_E) was estimated and found to be $\pm\ 0.067 \cdot 10^{-6}$ $\mathrm{m^3 \cdot mol^{-1} \cdot K^{-1}}$ at the lowest concentration studied for aqueous solutions. The details about error analysis are given elsewhere.[20] The limiting apparent molar expansivity (ϕ_E^0) values were obtained by writing $\phi_E = \phi_E^0 + S_E\sqrt{c}$ where S_E is the limiting slope, and plotting them against the square root of concentration, the intercept yields the value of ϕ_E^0. The ϕ_E^0 values are also collected in Table 1.

The relative viscosities (η_r) of aqueous solutions of PGK were evaluated using an expression[2]

$$\eta_r = \frac{\eta}{\eta_0} = \frac{td}{t_0 d_0}K \qquad (4)$$

Table 2. Viscosity Data for Potassium Salt of Penicillin-G in Aqueous Solutions at Different Temperatures

T / K	c / $\text{mol}\cdot\text{dm}^{-3}$	d / $\text{kg}\cdot\text{m}^{-3}$	η_r	A / $(\text{dm}^3\cdot\text{mol}^{-1})^{1/2}$	B / $\text{dm}^3\cdot\text{mol}^{-1}$	D / $(\text{dm}^3\cdot\text{mol}^{-1})^2$	h
293.15	0.00000	998.206	1.0000	0.0055	1.0678	0.5547	11.2
	0.00507	998.859	1.0064				
	0.00992	999.481	1.0099				
	0.02049	1000.835	1.0234				
	0.03938	1003.245	1.0433				
	0.05948	1005.801	1.0685				
	0.07975	1008.381	1.0899				
	0.09729	1010.623	1.1101				
	0.12274	1013.905	1.1416				
298.15	0.00000	997.047	1.0000	0.0075	1.0408	0.4308	11.0
	0.00507	997.697	1.0064				
	0.00991	998.316	1.0107				
	0.02047	999.664	1.0224				
	0.03934	1002.064	1.0418				
	0.05941	1004.606	1.0673				
	0.07966	1007.164	1.0866				
	0.09717	1009.378	1.1082				
	0.12258	1012.596	1.1363				
303.15	0.00000	995.650	1.0000	0.0003	0.9883	0.7918	7.9
	0.00506	996.285	1.0049				
	0.00989	996.892	1.0097				
	0.02044	998.217	1.0209				
	0.03928	1000.587	1.0395				
	0.05932	1003.112	1.0621				
	0.07954	1005.661	1.0842				
	0.09703	1007.868	1.1028				
	0.12239	1011.070	1.1330				
308.15	0.00000	994.035	1.0000	0.0060	0.9281	0.8850	7.7
	0.00505	994.653	1.0049				
	0.00988	995.244	1.0096				
	0.02040	996.533	1.0202				
	0.03921	998.841	1.0388				
	0.05922	1001.305	1.0601				
	0.07939	1003.804	1.0816				
	0.09685	1005.980	1.0987				
	0.12216	1009.166	1.1291				

where η, t, and d are viscosity, time of flow, and density, respectively, of solution and η_0, t_0, and d_0 are, respectively, viscosity, time of flow, and density of the solvent. The kinetic energy correction was found to be negligible, and the correction factor (K) is taken to be unity. The relative viscosity of the solutions can be expressed as a sum of terms in different powers of concentration (c) as given by

$$\eta_r = 1 + Ac^{1/2} + Bc + Dc^2 \tag{5}$$

The B coefficient is a measure of hydrodynamic or size and shape effects, solvation effects, and structural effects, and the D coefficient includes the contribution due to the higher terms of the hydrodynamic effects and interactions arising from changes in solute−solute interactions with concentration.

The effective volume of the flowing unit (V_e) is calculated using the Breslau−Miller equation[21] (derived from the Thomas equation[22] [$\eta_r = 1 \pm 2.5V_ec + 10.05\ V_e^2c^2$]), which is applicable for solutes with nonspherical shapes as well

$$V_e = \frac{\{-2.5c + [(2.5c)^2 - 4(10.05c^2)(1-\eta_r)]^{1/2}\}}{2(10.05c^2)} \tag{6}$$

The hydration numbers (h), i.e., the number of water molecules associated with one PGK molecule, have been estimated using eq 7 and are reported in Table 2

$$h = \frac{V_e{}^0 - \phi_V^0}{V_{H_2O}} \tag{7}$$

where V_{H_2O} is the molar volume of water. The $V_e{}^0$ is the limiting value of the effective volume of the flowing unit (PGK + nH$_2$O) obtained by smooth extrapolation of V_e values to zero concentration of PGK.

4. Discussion

It is observed from Figure 1 that if we write the expression $\phi_V = \phi_V^0 + A_V\sqrt{c} + B_Vc$ the deviation parameter B_V varies in a peculiar fashion; i.e., at low temperatures (293.15 K and 298.15 K), it is small and positive, whereas it is negative at higher temperatures. In general, negative B_V is observed for large structure making cations[23,24] such as Bu_4N^+, BPh_4^-, or higher n-alkylamine hydrobromides[25] and is interpreted as being due to a solvent-induced cosphere overlap effect due to solute−solute hydrophobic interactions. Our results in Figure 1 suggest that at higher temperatures these effects predominate in agreement with the concept of hydrophobic interaction and water−structure making effects.[26] Similar effects are also observed for large tetralkylammonium salts and $NaBPh_4$ where ($\partial B_V/\partial T$) is positive and have been attributed to similar types of ion−ion interactions.[24] It appears that anion−anion interactions give rise to a peculiar type of variation of B_V (positive at lower temperature and negative at higher temperature). The role of the water structure around such anions is not clear, but H-bonding is postulated for anion−water interactions. Such interactions might show typical temperature dependence in tune with the concept of hydrophobic interactions in this case due to anions. There is also a possibility of some sort of packing effect, but whether the packing is caused by mutual penetration of the hydrocarbon portion of these ions or the filling of the void space between large ions is not known with certainty. These

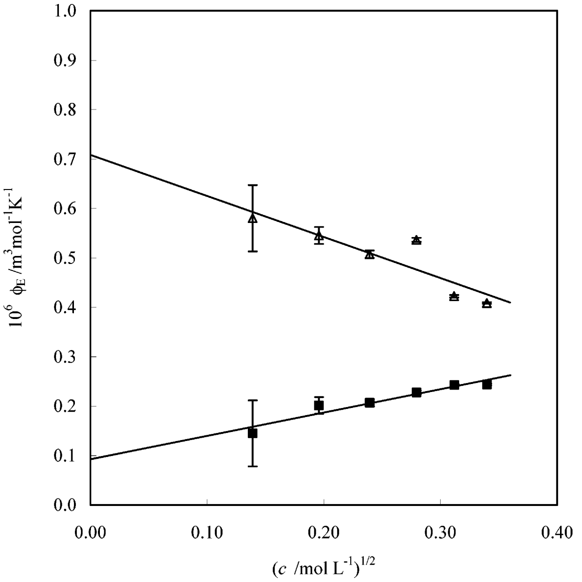

Figure 2. Apparent molar expansivity of potassium salt of penicillin-G in aqueous solutions at different temperatures: ■, 298.15 K; Δ, 303.15.

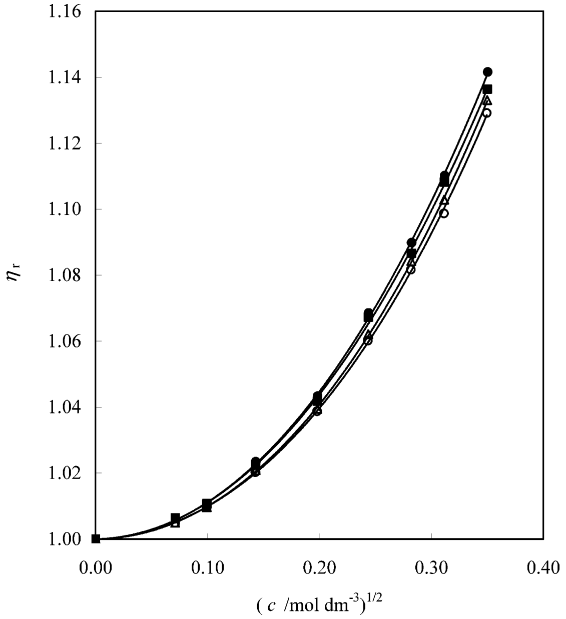

Figure 3. Relative viscosity of potassium salt of penicillin-G in aqueous solutions at different temperatures: ●, 293.15 K; ■, 298.15 K; Δ, 303.15 K; and ○, 308.15 K.

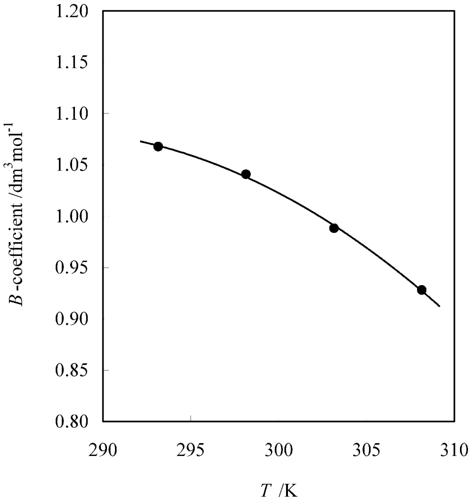

Figure 4. Variation viscosity *B* coefficient as a function of temperature for potassium salt of penicillin-G in aqueous solutions.

arguments also get supported by the variation of the ϕ_E parameter as a function of the square root of concentration as shown in Figure 2. The ϕ_E values are positive and increase with an increase in concentration at 298.15 K, whereas they decrease as a function of concentration at 303.15 K. Thus, the positive values of ϕ_E indicate that more energy is required to melt the structured region (H-bonded) around the solute molecule. For normal uni-univalent electrolytes, very small +ve ϕ_E values are being observed.[27]

The limiting values of these apparent properties, i.e., ϕ_V^0 and ϕ_E^0, signify the effect due to solute−solvent interactions. We do not decompose the parameters in individual ionic components as it requires nonthermodynamic assumptions. The ϕ_V^0 and ϕ_E^0 increase with an increase in temperature and in tune with accepted concepts. It is noted, however, that the temperature variation of ϕ_V^0 is not linear but is small at lower temperature and comparatively large at higher temperatures. This must be associated with the structural interactions of PGK with the solvent which are affected by thermal effects.

The relative viscosity for solutions of PGK in water at all studied temperatures increases with an increase in concentration as shown in Figure 3. The viscosity *A*, *B*, and *D* coefficients are determined using eq 5 with a least-squares fitting procedure. The values are collected in Table 2 along with density and relative viscosity data. The viscosity *A* coefficients for PGK are small and quite temperature insensitive. It describes the effect exerted by Coulombic interactions between the ions, and also, its magnitude can be calculated using conductance data and the Falkenhegen equation.[3] We did not do this as precise data of conductance are not available for this electrolyte and the experimental values of *A* coefficients obtained closely match those of usual 1:1 electrolytes.

The important observation from this work is about the magnitude and temperature variation of the viscosity *B* coefficient of PGK as shown in Figure 4. We observe a high-viscosity *B* coefficient for the salt that decreases as the temperature is increased. Such a behavior is generally observed for neutral nonelectrolytes like 18-crown-6[10] and amines,[11] for salts having large water structure making abilities such as Bu_4N^+ cations,[5−7] and for salts of long chain fatty acids.[28,29] It is known that the K^+ ion is a structure breaking ion having an ionic *B* coefficient value of −0.007 $dm^3{\cdot}mol^{-1}$ at 298.15 K.[3] Seen in this light, we attribute that the high *B* coefficient values obtained for PGK are due to the structure making PG anion. We found that the value of the hydration number (*h*), calculated using eq 7, varies from 11 at 293.15 K to 7.7 at 308.15 K, meaning that the extent of cosphere water around the ions decreases if the temperature is increased. The hydration number for the K^+ ion is about 2 to 4,[30] meaning that the PG anion gets hydrated to a large extent.

It is known from the literature that the viscosity *D* coefficient represents solute−solute structural interactions and depends mainly on higher terms of hydrodynamic effects, structural interactions, and to some extent higher terms of Coulombic forces.[7] With large ions, the hydrodynamic effect is the most important, whereas with small ions, Coulombic forces and solute−solute structural interactions predominate. From Table 2, we note that the *D* coefficient values are positive and go through a minimum at 298.15 K. In the absence of similar studies for salts consisting of large anions, it is difficult to account for these observations. We may suggest that the large values of the *D* coefficient probably indicate the existence of solute−solute interactions along with solute−solvent interactions. Further, the increase of the *D* coefficient at higher temperature may suggest that the contribution to solute−solute interactions predominates at higher temperatures. Thus, in the temperature range of 293 K to 303 K, there may be some structural transitions for the solute molecule or its hydration sheath resulting in such a behavior for the *D* coefficient.

5. Conclusions

Density and relative viscosity data have been obtained for aqueous solutions of the potassium salt of penicillin-G at different temperatures. It is observed that the PGK molecule dissolves in water with a water structure making effect based on the results of the studies of apparent molar volume and the viscosity *B* coefficient. The high positive *B* coefficients and hydration number calculated signify that the anion of PGK is a structure making ion of which structural interactions decrease with an increase in temperature. The results of volume and expansivity also show a structure making effect and the presence of hydrophobic interactions in the premicellar concentration region for aqueous PGK solutions.

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