

Different Volumes of Ceftazidime Antibiotic in Mixed Solvents (Density Measurements)

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D ensities and apparent molar volumes for mixed (MeOH+H₂O) and (DMSO+H₂O) solutions of Ceftazidime antibiotic at 298.15K were reported. It was observed that, all the volumes of CFZ in mixed (MeOH+H₂O) increase by increasing concentration due to more solvation whereas; they decrease in case of mixed (DMSO+H₂O). All the partial molar volume (V_{Φ}^{0}) values are negative showing high solvation effect of solvent on CFZ and indicate that the solvent effect is higher in MeOH than the other solvent does.

Introduction

The solubility of any electrolyte in solvents depends on the properties for both solute and solvent. Debye-Hückel recognizes solvents by their bulk properties, namely relative permittivity, viscosity and density of pure solvent. Also the bulk properties of the solvents decrease as the electrolyte concentration increase. On the molecular scale solvents may be classified according to hard and soft donor and acceptor properties of both solvent and solute [1]. Interactions of solvent and solute depend on the electron distribution between donor and acceptor atoms in these substances.

The solubility of solutes in mixed solvents is of great practical importance since many industrial process as well as laboratory procedures call for the use of solvent mixtures [2]. The solubility of solutes in mixed solvents depends primarily on the solvation of solutes or their constituent ions by the components of solvent mixtures.

Intermolecular forces are those which can occur between closed-shell molecules. These are also called van der Waals forces, since Van der Waals recognized them as the reason for the non-ideal behavior of real gases. Intermolecular forces are usually classified into two distinct categories. The first category comprises the so-called directional, induction, and dispersion forces, which are non-specific and cannot be completely saturated (just as Coulomb forces between ions cannot). The second group consists of hydrogen-bonding forces, and charge-transfer or electron-pair donor–acceptor forces. The latter group is specific, directional forces, which can be saturated and lead to stoichiometric molecular compounds. For the sake of completeness, in the following the Coulomb forces between ions and electrically neutral molecules (with permanent dipole moments) will be considered first, even though they do not belong to the intermolecular forces in the narrower sense.

Ceftazidime is a third-generation cephalosporin antibiotic. Like other third-generation cephalosporin's, it has broad spectrum activity against Gram-positive and Gram-negative bacteria. Ceftazidime pentahydrate is slightly soluble in water and in methanol, practically insoluble in acetone and in ethanol (96 per cent). It dissolves in acid and alkali solutions.

Experimental

Chemicals and Reagents

Ceftazidime Antibiotic (CFZ)



Solvents

Systematic name	Methanol (MeOH)	Dimethylsulfoxide (DMSO)
Molecular formula	H H—C—OH H CH₄O	$H_3C^{S}CH_3$ C_2H_6OS
Molar mass	32.04 g/mol	78.13 g/mol
Liquid density	0.7918 g/cm ³	1.1004 g/cm ³
Melting point	-97.6°C	19°C
Boiling point	64.7°C	189°C
Dipole moment	1.69 D	3.96 D

All solvents were provided from El Nasr Pharmaceutical Chemicals Co and used directly without purification.

Experimental Method

Density measurements

A very precise method by pycknometer is used for density determination which is a glass flask with a close-fitting ground glass stopper with a capillary hole through it. This fine hole releases a spare liquid after closing a top-filled pycknometer and allows for obtaining a given volume of measured and/or working liquid with a high accuracy.

Weighting bottle (1ml of pycknometeric type) was used for measuring the density of mixed (MeOH+H₂O) and (DMSO+H₂O) at 298.15K, weighing using four digital weighing balance of the type Mettler AE 240. Also, the density of the solution of CFZ in mixed (MeOH+H₂O) and (DMSO+H₂O) were measured at 298.15K by the same method. Weighing the solvents and mixed solvents firstly alone and then measuring the used antibiotic in the same vessel, subtracting both weights gave the density on the using the pycknometer. The experiment was repeated at least three times and then the mean absolute density was taken. The maximal error was to be ± 0.001 gm.

Results and Discussion

Different volumes of Ceftazidime antibiotic (CFZ) in mixed (MeOH+ H_2O) and (DMSO+ H_2O) at 298.15K (Density measurements).

The densities of different concentrations of CFZ ranging from 0.0001 to 0.0006 M were measured in different mixed solvents at 298.15K, Tables (1, 2). The mixed solvents used are (MeOH+H₂O) and (DMSO+H₂O).

The molar volume (V_m) of CFZ in different mixed solvents at 298.15K was obtained by dividing the molar mass of the solute by the experimental densities.

$$V_{\rm m} = M/d \tag{1}$$

where, (M) is the molecular weight of CFZ and (d) is the density of the used solutions.

The packing density (P) as reported by Kim and Gomaa [3-13], i.e. the relation between Van der Waals volume (V_w) and the molar volume (V_m) of relatively large molecules (M. W. > 35) was found to be a constant value equals 0.661.

$$P = \frac{V_{w}}{V_{m}} = 0.661$$
 (2)

The electrostriction volume (V_e) [14-19] is the volume of solute which impressed by the solvent was calculated by using equation (23) after Kim [20] and King [21-60].

$$V_e = V_w - V_m \tag{3}$$

The apparent molar volume V_{Φ} [22, 23] was calculated by using equation (4):

$$V_{\rm F} = -[(\frac{M}{d_{\rm o}}) * \frac{d - d_{\rm o}}{dd_{\rm o}}] \frac{1000}{C_{\rm m}}$$
(4)

where, (M) is the molar mass of CFZ and the molar concentration is (C_m) , (d) and (d_o) are the densities of CFZ and the solvent used, respectively.

The values of the V_m , V_w , V_e and V_{Φ} for CFZ in mixed (MeOH+H₂O) and (DMSO+H₂O) are presented in Table 3 (a, b, c, d, e), Table 4 (a, b, c, d, e), respectively.

The partial dilution (V_{Φ}^{0}) was obtained by linear extrapolation of (V_{Φ}) against C_{m} to zero concentration, Fig. 1. The intercept of Masson relation [24], equation (5) gives (V_{Φ}^{0}) , Table 5.

$$\mathbf{V}_{\Phi} = \mathbf{V}_{\Phi}^{0} + \mathbf{S}_{v} \cdot \mathbf{C}_{m} \tag{5}$$

where; (V_{Φ}^{0}) is the limiting value of the apparent molar volume which equals to the partial molar volumes.

The proportionality constant S_v (the slopes of V_{Φ}^{0} vs. C_m relations), obtained from equation (5) are given in Table 6. S_v values obtained in the used mixtures are negative values indicating association behavior in solvents.



Fig. 1. Variation of apparent molar volume (V_{ϕ}) with C_m of CFZ in mixed (a) (MeOH+H₂O) and (b) (DMSO+H₂O) at 298.15K.

Table 1. The densities of CFZ in mixed ($MeOH+H_2O$) at 298.15K.

Concentration	Density (d _{solution})					
(C _m)	20% MeOH	40% MeOH	60% MeOH	80% MeOH	100% MeOH	
1.00 x 10 ⁻⁴	9.139	8.86	8.676	8.203	7.336	
2.00 x 10 ⁻⁴	10.28	9.923	9.728	9.092	8.211	
3.00 x 10 ⁻⁴	11.372	11.088	10.867	10.037	9.046	
4.00 x 10 ⁻⁴	12.472	12.308	12.048	10.958	9.912	
5.00 x 10 ⁻⁴	-	13.448	13.093	12.119	10.778	
6.00 x 10 ⁻⁴	-	14.579	14.151	13.145	11.63	

Table 2. The densities of CFZ in mixed (DMSO+ H_2O) at 298.15K.

$Concentration (C_{i})$	Density (d _{solution})				
Concentration (Cm)	20% DMSO	40% DMSO	60% DMSO	80% DMSO	100% DMSO
1.00 x 10 ⁻⁴	9.664	10.054	9.635	10.201	10.34
2.00 x 10 ⁻⁴	10.835	11.261	10.915	11.428	11.522
3.00 x 10 ⁻⁴	11.996	12.487	12.168	12.68	12.674
4.00 x 10 ⁻⁴	13.221	13.607	13.411	14.052	13.927
5.00 x 10 ⁻⁴	14.386	14.853	14.694	15.38	15.165
6.00 x 10 ⁻⁴	15.606	16.082	15.949	16.597	16.331

Table 3(a). The molar volume (V_m) , solvated Van der Waals (V_w) , electrostatriction volumes (V_e) and apparent molar volume (V_{Φ}) of CFZ in mixed (20% MeOH+ 80% H₂O) at 298.15K in cm³/mole.

Concentration (C _m)	V _m	V _w	Ve	$V_{\Phi} \times 10^{6}$
1.00 x 10 ⁻⁴	69.662	46.047	-23.615	-5.8
2.00 x 10 ⁻⁴	61.93	40.936	-20.994	-2.96
3.00 x 10 ⁻⁴	55.984	37.005	-18.978	-2.01
4.00 x 10 ⁻⁴	51.046	33.741	-17.304	-1.52

Table 3(b). The molar volume (V_m) , solvated Van der Waals (V_w) , electrostatriction volumes (V_e) and apparent molar volume (V_{Φ}) of CFZ in mixed (40% MeOH+ 60% H₂O) at 298.15K in cm³/mole.

Concentration (C _m)	V _m	V _w	Ve	$V_{\Phi} \times 10^{6}$
1.00 x 10 ⁻⁴	71.856	47.497	-24.359	-6.8
2.00 x 10 ⁻⁴	64.159	42.409	-21.749	-3.46
3.00 x 10 ⁻⁴	57.417	37.953	-19.464	-2.34
4.00 x 10 ⁻⁴	51.726	34.191	-17.535	-1.78
5.00 x 10 ⁻⁴	47.341	31.292	-16.048	-1.44
6.00 x 10 ⁻⁴	43.668	28.865	-14.803	-1.21

Table 3(c). The molar volume (V_m) , solvated Van der Waals (V_w) , electrostatriction volumes (V_e) and apparent molar volume (V_{Φ}) of CFZ in mixed (60% MeOH+ 40% H₂O) at 298.15K in cm³/mole.

Concentration (C _m)	V _m	V _w	Ve	$V_{\Phi} \times 10^{6}$
1.00 x 10 ⁻⁴	73.3805	48.504	-24.876	-8.39
2.00 x 10 ⁻⁴	65.4451	43.259	-22.185	-4.26
3.00 x 10 ⁻⁴	58.585	38.725	-19.86	-2.87
4.00 x 10 ⁻⁴	52.842	34.929	-17.913	-2.18
5.00 x 10 ⁻⁴	48.625	32.141	-16.483	-1.76
6.00 x 10 ⁻⁴	44.989	29.738	-15.251	-1.47

Table 3(d). The molar volume (V_m) , solvated Van der Waals (V_w) , electrostatriction volumes (V_e) and apparent molar volume (V_{Φ}) of CFZ in mixed (80% MeOH+ 20% H₂O) at 298.15K in cm³/mole.

Concentration (C _m)	V _m	V _w	Ve	$V_{\Phi} \times 10^{6}$
1.00 x 10 ⁻⁴	77.611	51.301	-26.31	-9.5
2.00 x 10 ⁻⁴	70.023	46.285	-23.737	-4.81
3.00 x 10 ⁻⁴	63.43	41.927	-21.502	-3.24
4.00 x 10 ⁻⁴	58.099	38.403	-19.695	-2.45
5.00 x 10 ⁻⁴	52.533	34.724	-17.808	-1.98
6.00 x 10 ⁻⁴	48.432	32.014	-16.418	-1.66

Concentration (C _m)	V _m	V _w	Ve	$V_{\Phi} \times 10^{6}$	
1.00 x 10 ⁻⁴	86.784	57.364	-29.419	-10.6	
2.00 x 10 ⁻⁴	77.536	51.251	-26.284	-5.36	
3.00 x 10 ⁻⁴	70.3791	46.52	-23.858	-3.61	
4.00 x 10 ⁻⁴	64.23	42.456	-21.774	-2.73	
5.00 x 10 ⁻⁴	59.069	39.044	-20.024	-2.2	
6.00 x 10 ⁻⁴	54.742	36.184	-18.557	-1.84	

Table 3(e). The molar volume (V_m) , solvated Van der Waals (V_w) , electrostatriction volumes (V_e) and apparent molar volume (V_{Φ}) of CFZ in 100% MeOH at 298.15K in cm³/mole.

Table 4(a). The molar volume (V_m) , solvated Van der Waals (V_w) , electrostatriction volumes (V_e) and apparent molar volume (V_{Φ}) of CFZ in mixed (20% DMSO+ 80% H₂O) at 298.15K in cm³/mole.

Concentration (C _m)	V _m	$\mathbf{V}_{\mathbf{w}}$	Ve	$V_{\Phi} \times 10^{6}$
1.00 x 10 ⁻⁴	65.878	43.545	-22.332	-5.65
2.00 x 10 ⁻⁴	58.758	38.839	-19.919	-2.88
3.00 x 10 ⁻⁴	53.071	35.08	-17.991	-1.95
4.00 x 10 ⁻⁴	48.154	31.83	-16.324	-1.48
5.00 x 10 ⁻⁴	44.254	29.252	-15.002	-1.2
6.00 x 10 ⁻⁴	40.795	26.965	-13.829	-1.01

Table 4(b). The molar volume (V_m) , solvated Van der Waals (V_w) , electrostatriction volumes (V_e) and apparent molar volume (V_{Φ}) of CFZ in mixed (40% DMSO+ 60% H₂O) at 298.15K in cm³/mole.

Concentration (C _m)	V _m	$\mathbf{V}_{\mathbf{w}}$	Ve	$V_{\Phi} \times 10^{6}$
1.00 x 10 ⁻⁴	63.323	41.856	-21.466	-6.16
2.00 x 10 ⁻⁴	56.535	37.37	-19.165	-3.13
3.00 x 10 ⁻⁴	50.985	33.701	-17.283	-2.12
4.00 x 10 ⁻⁴	46.788	30.927	-15.861	-1.61
5.00 x 10 ⁻⁴	42.863	28.332	-14.53	-1.3
6.00 x 10 ⁻⁴	39.587	26.167	-13.42	-1.09

Table 4(c). The molar volume (V_m) , solvated Van der Waals (V_w) , electrostatriction volumes (V_e) and apparent molar volume (V_{Φ}) of CFZ in mixed (60% DMSO+ 40% H₂O) at 298.15K in cm³/mole.

Concentration (C _m)	V _m	V _w	Ve	$V_{\Phi} \times 10^{6}$
1.00 x 10 ⁻⁴	66.076	43.676	-22.4	-6.77
2.00 x 10 ⁻⁴	58.327	38.554	-19.773	-3.45
3.00 x 10 ⁻⁴	52.321	34.584	-17.737	-2.33
4.00 x 10 ⁻⁴	47.472	31.379	-16.093	-1.77
5.00 x 10 ⁻⁴	43.327	28.639	-14.687	-1.43
6.00 x 10 ⁻⁴	39.917	26.385	-13.532	-1.2

Table 4(d). The molar volume (V_m) , solvated Van der Waals (V_w) , electrostatriction volumes (V_e) and apparent molar volume (V_{Φ}) of CFZ in mixed (80% DMSO+ 20% H₂O) at 298.15K in cm³/mole.

Concentration (C _m)	Vm	$\mathbf{V}_{\mathbf{w}}$	Ve	$V_{\Phi} \times 10^{6}$	
1.00 x 10 ⁻⁴	62.41	41.253	-21.157	-7.42	
2.00 x 10 ⁻⁴	55.709	36.824	-18.885	-3.76	
3.00 x 10 ⁻⁴	50.208	33.188	-17.02	-2.54	
4.00 x 10 ⁻⁴	45.306	29.947	-15.359	-1.92	
5.00 x 10 ⁻⁴	41.394	27.361	-14.032	-1.55	
6.00 x 10 ⁻⁴	38.359	25.355	-13.003	-1.3	

Table 4(e). The molar volume (V_m) , solvated Van der Waals (V_w) , electrostatriction volumes (V_e) and apparent molar volume (V_{Φ}) of CFZ in 100% DMSO at 298.15K in cm³/mole.

Concentration (C _m)	V _m	V_w	V _e	$V_{\Phi} \times 10^{6}$
1.00 x 10 ⁻⁴	61.571	40.698	-20.872	-8.17
2.00 x 10 ⁻⁴	55.255	36.523	-18.731	-4.14
3.00 x 10 ⁻⁴	50.232	33.203	-17.028	-2.78
4.00 x 10 ⁻⁴	45.713	30.216	-15.496	-2.11
5.00 x 10 ⁻⁴	41.981	27.749	-14.231	-1.7
6.00 x 10 ⁻⁴	38.984	25.768	-13.215	-1.42

9/ Salvant	$V_{\Phi}^{0} \times (10^{6})$	
76 Solvent	МеОН	DMSO
20%	-3.921	-3.506
40%	-4.21	-3.814
60%	-5.182	-4.914
80%	-5.852	-4.577
100%	-6.521	-5.035

Table 5. The intercept of Masson relation (V_{Φ}^{0}) , partial molar volumes in cm³/mole.

Table 6. S_V factor (the slopes of V_{ϕ}^0 vs. C_m relations).

9/ Solvent	$S_V \times (10^9)$		
% Solvent	MeOH	DMSO	
20%	5.191	4.503	
40%	5.413	4.914	
60%	6.687	5.405	
80%	7.561	5.91	
100%	8.432	6.518	

Conclusion

It was observed that, all the volumes of CFZ in different MeOH mixtures with water increase by increasing concentration due to more solvation whereas; they decrease in case of DMSO mixtures with water. All the partial molar volume (V_{Φ}^{0}) values are negative showing high solvation effect of solvent on CFZ and indicate that the solvent effect is higher in MeOH than the other solvent does. All the evaluated S_V values for CFZ solutions are positive in their values indicating more association behavior in MeOH mixtures than do other solvent mixtures.



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