

Effect of the Temperature and Solvents on the Solvolysis of Barium Bromide in Aqueous-Organic Solutions: Volumetric and Viscometric Study

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Abstract: Volumetric and viscometric properties of solutions containing barium bromide in an aqueous solution of ethylene glycol and 1,4-dioxane have been discussed at different temperatures such as 298.15K, 303.15K, 308.15K, and 313.15K. The Masson's equation was used to determine the apparent molar volume, V_{ϕ} , standard partial molar volume, V_{ϕ}^0 , molar expansibilities, E_{ϕ}^0 by taking the density data. The values of viscosity and density were used in the Jones-Dole equation to find the viscosity B coefficients, which were used to estimate the ion-solvent interactions. The values of Hepler's constant $(\partial^2 V_{\phi}^0 / \partial T^2)_p$ and the viscosity B-coefficients have been used to deduce the solvent structure-promoting or structure breaking tendency of the salt in the studied mixtures. In the current study, the positive values of Hepler's constant and the negative values of dB/dT show that barium bromide in the considered solvents mainly behaves as a structure promoter.

Keywords: Apparent molar volume; Hepler's constant; barium bromide; Jones–Dole equation.

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1. Introduction

Partial molar volume and viscosity data provide valuable evidence about different types of forces of attractions present in the solutions [1-5]. The volumetric and viscometric studies of solutions help us illustrate solutes' organization and properties in mixed solvents [6-10]. Recently, many researchers have studied the solution properties of the different salts in mixed solutions [11-16]. Frank and Evan [17] have interpreted the thermodynamic properties of the aqueous-organic solutions in terms of water particles' organization about the non-polar solute. 1, 4-Dioxane is a heterocyclic colorless organic liquid having a faint sweet smell like to diether. It is used as a (i) versatile aprotic solvent for cellulose esters, inks, and adhesives, (ii) as a stabilizer for transporting chlorinated hydrocarbons in aluminum vessels. Due to its lower toxicity and higher boiling point, it substituted Tetrahydrofuran in some reactions and was used as an internal standard for NMR spectroscopy of deuterium oxide. It serves as a chelating diether ligand and can solvate many inorganic compounds due to the presence of two oxygen atoms in it. Similarly, ethylene glycol is used in many commercial and industrial applications, including antifreeze and coolant. The salt, barium bromide, BaBr₂ have many applications in



the field of chemical reactions. It is used as a precursor to chemicals used in photography and used to purify radium in the fractional crystallization process. This paper is dealt with the study of the ion-solvent, ion-ion, and solvent-solvent interactions of the barium bromide with the aqueous solutions of dioxane and ethylene glycol, as both the solute and the solvents are used for industrial processes. Therefore, the volumetric and viscometric properties of BaBr₂ in aqueous-organic solvents such as 1, 4-dioxane, and ethylene glycol, have been studied to evaluate the ion-solvent and ion-ion interactions existing among the solutes and solvents.

2. Materials and Methods

2.1. Chemicals.

Anhydrous barium bromide, ethylene glycol, and 1,4-dioxane used were taken from Sigma Aldrich, Germany, with more than 99% purity and then refined by standard methods [18]. The triply distilled water was used to prepare the solutions of 10, 20, and 30(v/v) % of each of ethylene glycol and dioxane solutions, which served as solvents. Barium bromide was further desiccated over anhydrous CaCl₂ before use [19]. The sample specification is given in Table 1.

Table 1. Specification of Chemicals.

Chemicals	Source	Mass fraction purity ^a	Purification method	CAS No	Mol.Mass/ g mol ⁻¹	Structure
Barium bromide	Sigma-Aldrich	0.99	Used as obtained	10553-31-8	297.14	BaBr ₂
Ethylene Glycol	Sigma-Aldrich	>0.998	By standard methods[18]	107-21-1	62.07	
1,4-Dioxane	Sigma-Aldrich	>0.99	By standard methods[18]	123-91-1	88.11	

^aAs declared by the supplier

2.2. Apparatus and procedure.

The masses of the solute and solvents were measured by electronic balance (KERN, model ABJ-220-4NM, made in Germany) with a precision of ± 0.01 mg. A double arm pycnometer was taken to determine the density (ρ) of the prepared solutions at $T=(298.15-313.15)$ K, which was calibrated with deionized triply distilled water with 997.017 kg/m³ as its density at temperature 298.15 K. The measurement of viscosity of the solutions was done with the help of Ostwald viscometer with appropriately long reflux period greater than 200 seconds to avoid the corrections in kinetic energy. The average of three readings from the Ostwald viscometer was taken into consideration. The density bottle and viscometer were calibrated [20-21] using distilled water. All the measurements are carried out by clamping pycnometer and viscometer in a water bath maintained at constant temperatures ± 0.01 K. The uncertainty in viscosity and density measurements were within ± 0.003 mPa and $\pm 1 \times 10^{-5}$ g cm⁻³ respectively. The water's viscosity was taken to be 0.7194×10^{-3} kg m⁻¹ s⁻¹ (at 303.15K) [22]. The molar concentrations of the solutions were converted to molality using the standard formula using the density values.

3. Results and Discussion

3.1. Viscometric study:

The properties of electrolytic solutions in aqueous media are highly particular to the individual ions of the respective electrolyte, so it is difficult to generalize these properties. Another parameter to find the ion solvent interactions is the determination of transport property in terms of viscosity. The formula: $\eta/\eta_0 = (t \times \rho) / (t_0 \times \rho_0)$ was used to calculate the relative viscosity of the solutions, where η is the absolute viscosity, t is the time of flow and ρ is the density of solution respectively, while η_0 , t_0 , and ρ_0 are the same measure for the solvent respectively. The densities of solutions are tabulated in Table 2.

The dependence of viscosities of BaBr₂ solutions in aqueous dioxane and ethylene glycol with the molality can be expressed by the Jones-Dole equation [23] as given below:

$$\eta_r = \eta / \eta_0 = 1 + A \sqrt{m_A} + B m_A \quad (1)$$

Where η_r is the relative viscosity of the studied solutions, η and η_0 are the viscosities of solutions and solvent, respectively. The constant A represents the interionic forces [24-25], and known as the Falkenhagen coefficient, the coefficient B is associated with the solute-solvent interactions and is understood as a degree of the structure-promoting or structure breaking nature of the ions in the said solutions [26]. The parameters A and B can be found by arranging equation 1 as follows:

$$(\eta/\eta_0 - 1) / \sqrt{m_A} = \eta_{sp}/\sqrt{m_A} = A + B \sqrt{m_A} \quad (2)$$

$(\eta/\eta_0 - 1)$ is known as specific viscosity and represented as η_{sp} . The values of $(\eta/\eta_0 - 1) / \sqrt{m_A}$ and the parameters A and B coefficients of the above equation are tabulated in Tables 3 and 4, respectively. The variation of $(\eta/\eta_0 - 1) / \sqrt{m_A}$ with molality ' $\sqrt{m_A}$ ' indicates the decrease of viscosity with the increase in temperature and viscosity increase with an increase of dioxane/ethylene glycol content in the solutions. The variation of viscosity with the molal concentration of solutions at 298.15 K is given in Figure 1.

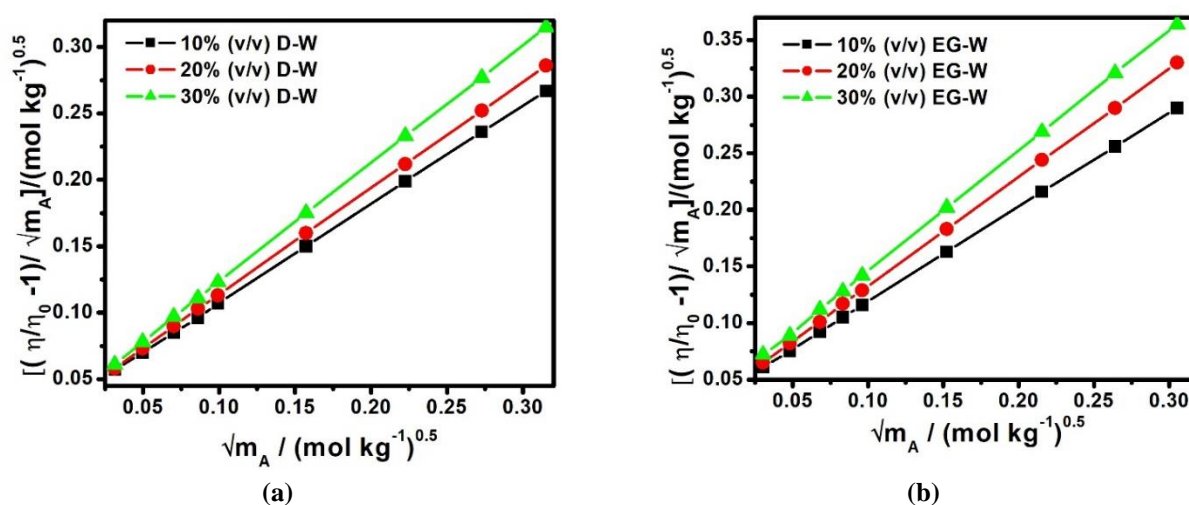


Figure 1. The plot $(\eta/\eta_0 - 1)/m_A^{1/2}$ vs. $m_A^{1/2}$ of BaBr₂ in (a) DO -Water and (b) EG -Water respectively at 298.15K.

The intermolecular force of attraction increases with an increase in the mass fraction of BaBr₂ in the solution; as a result, the viscosity of the solution increases. The positive values of

coefficient A at all temperatures for BaBr_2 prove the existence of substantial ion-ion interactions. The viscosity B coefficient of the Jones-Dole equation indicates the presence of ion-solvent interaction [22]. For all the solutions, the values of viscosity B coefficients may be positive or negative. If the solute attracts the water/solvent molecules, then its B coefficient value will be positive; otherwise, it will be negative. In the present study, the positive values of viscosity B coefficient for BaBr_2 in both dioxane-water and ethylene glycol-water media (Table 4) confirms the existence of ion-solvent interactions. The negative values of thermal coefficient (dB/dT) [25] indicate that there are strong ion-solvent interactions and the said solute is a structure promoter in the studied media. These data agree with the result obtained from the Hepler equation discussed in volumetric properties [27].

Table 2. Density, ρ , and apparent molar volume, V_ϕ of Barium bromide in ethylene glycol-water and 1,4-dioxane-water respectively at $T = (298.15 - 313.15)\text{K}$.

$m_A / \text{mol kg}^{-1}$	$\rho / \text{kg m}^{-3}$				$V_\phi \times 10^5 / \text{m}^3 \text{mol}^{-1}$			
	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
10:90 (v/v) 1,4-Dioxane-Water								
0.0000	1013.3	1010.0	1007.0	1003.9				
0.0010	1013.5	1010.2	1007.2	1004.1	5.1502	4.9399	4.5451	4.1607
0.0025	1013.9	1010.6	1007.6	1004.5	5.5678	5.3140	5.1351	4.8634
0.0049	1014.4	1011.2	1008.2	1005.1	6.1043	5.7958	5.5075	5.2943
0.0074	1015.0	1011.7	1008.7	1005.6	6.4401	6.2476	5.9790	5.6381
0.0099	1015.6	1012.3	1009.3	1006.2	6.6259	6.4674	6.2703	6.1036
0.0247	1019.0	1015.8	1012.8	1009.7	6.8233	6.6435	6.4444	6.2758
0.0495	1024.7	1021.5	1018.6	1015.5	6.8233	6.6298	6.4279	6.2793
0.0744	1030.4	1027.2	1024.4	1021.3	6.8233	6.6428	6.4505	6.2828
0.0994	1036.1	1033.0	1030.1	1027.0	6.8233	6.6503	6.4535	6.2868
20:80 (v/v) 1,4-Dioxane-Water								
0.000	1027.5	1024.2	1021.1	1018.2				
0.0010	1027.7	1024.4	1021.3	1018.4	5.0887	4.9308	4.8321	4.7113
0.0024	1028.1	1024.8	1021.7	1018.8	5.5433	5.3440	5.2375	5.0741
0.0049	1028.6	1025.3	1022.2	1019.3	6.0307	5.7412	5.5583	5.3740
0.0073	1029.2	1025.9	1022.8	1019.9	6.3362	6.1568	5.8777	5.7248
0.0097	1029.8	1026.5	1023.4	1020.5	6.5983	6.4128	6.2053	5.9554
0.0244	1033.1	1029.8	1026.8	1023.9	7.1183	6.9642	6.8318	6.6776
0.0488	1038.7	1035.5	1032.4	1029.5	7.1540	7.0025	6.8701	6.7172
0.0734	1044.3	1041.1	1038.1	1035.2	7.1717	7.0325	6.8960	6.7786
0.0980	1049.8	1046.6	1043.7	1040.8	7.2156	7.0743	6.9288	6.7949
30:70 (v/v) 1,4-Dioxane-Water								
0.0000	1040.6	1037.6	1034.5	1031.1				
0.0010	1040.8	1037.8	1034.7	1031.3	5.4409	5.1258	4.9442	4.7757
0.0024	1041.2	1038.2	1035.1	1031.7	5.9635	5.7599	5.5382	5.3099
0.0048	1041.7	1038.7	1035.7	1032.3	6.7727	6.5976	6.2695	6.0711
0.0072	1042.3	1039.3	1036.2	1032.8	7.1435	6.9335	6.7532	6.6015
0.0096	1042.8	1039.8	1036.7	1033.3	7.3617	7.2174	7.0618	6.8803
0.0241	1046.1	1043.1	1040.0	1036.6	7.5650	7.4405	7.3320	7.1682
0.0482	1051.5	1048.5	1045.5	1042.1	7.6052	7.4768	7.3510	7.2213
0.0725	1056.9	1054.0	1051.0	1047.6	7.6259	7.5030	7.3692	7.2395
0.0968	1062.4	1059.5	1056.5	1053.1	7.6052	7.4731	7.3718	7.2589
10:90 (v/v) Ethylene glycol-Water								
0.0000	1029.3	1026.1	1022.9	1020.1				
0.0010	1029.5	1026.3	1023.1	1020.4	4.7909	4.6093	4.4940	4.2312
0.0024	1029.9	1026.7	1023.5	1020.7	5.5514	5.3268	5.2447	5.1021
0.0049	1030.5	1027.3	1024.1	1021.3	5.9678	5.7101	5.5781	5.4309
0.0073	1031.0	1027.9	1024.7	1021.9	6.2968	6.0923	6.0090	5.9084
0.0097	1031.6	1028.4	1025.2	1022.4	6.5556	6.3522	6.2673	6.1455
0.0243	1035.0	1031.8	1028.7	1025.9	6.7251	6.5291	6.4054	6.2817
0.0487	1040.7	1037.5	1034.4	1031.6	6.7496	6.5736	6.4268	6.3243
0.0732	1046.4	1043.3	1040.2	1037.4	6.7578	6.5811	6.4219	6.3110
0.0978	1052.1	1049.0	1045.9	1043.2	6.7578	6.5946	6.4304	6.3118
20:80 (v/v) Ethylene glycol-Water								
0.0000	1047.9	1044.8	1041.5	1038.3				
0.0010	1048.1	1045.0	1041.7	1038.5	5.2452	4.7600	4.6564	4.4079

$m_A/$ $mol\ kg^{-1}$	$\rho / kg\ m^{-3}$				$V_\phi \times 10^5/ m^3\ mol^{-1}$			
	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
0.0024	1048.5	1045.4	1042.1	1038.9	5.7054	5.1947	5.3334	5.2514
0.0048	1049.1	1046.0	1042.7	1039.5	6.0659	5.9152	5.7675	5.5599
0.0072	1049.6	1046.5	1043.2	1040.0	6.4556	6.2779	6.1835	6.0356
0.0095	1050.2	1047.1	1043.8	1040.6	6.6821	6.5313	6.3868	6.2443
0.0239	1053.5	1050.5	1047.2	1044.0	6.8675	6.7016	6.5560	6.4257
0.0479	1059.1	1056.1	1052.8	1049.7	6.9143	6.7278	6.6085	6.4789
0.0720	1064.7	1061.8	1058.5	1055.4	6.9210	6.7453	6.6276	6.4892
0.0961	1070.3	1067.4	1064.2	1061.1	6.9363	6.7617	6.6295	6.4892
30:70 (v/v) Ethylene glycol-Water								
0.0000	1081.6	1064.0	1056.0	1047.9				
0.0009	1081.8	1064.2	1056.2	1048.1	5.3812	4.9981	4.8071	4.6325
0.0023	1082.2	1064.6	1056.6	1048.5	5.8372	5.5463	5.4131	5.4023
0.0046	1082.7	1065.1	1057.1	1049.0	6.2212	6.0071	5.9089	5.8170
0.0069	1083.3	1065.7	1057.7	1049.6	6.6128	6.3893	6.2976	6.1661
0.0093	1083.8	1066.2	1058.2	1050.1	6.8095	6.6536	6.6242	6.3898
0.0232	1087.1	1069.5	1061.5	1053.4	7.1047	6.8731	6.7934	6.5610
0.0464	1092.6	1075.0	1067.0	1058.9	7.1582	6.9222	6.8305	6.6052
0.0697	1098.1	1080.5	1072.5	1064.5	7.1716	6.9288	6.8644	6.6323
0.0932	1103.6	1086.0	1077.9	1070.0	7.1773	6.9353	6.8819	6.6478

Table 3. $(\eta/\eta_0-1)/m^{1/2}$ of BaBr₂ in 10-30 % (v/v) ethylene glycol-water and 1,4-dioxane-water respectively at T = (298.15-313.15) K and at atmospheric pressure.

$m_A/$ $mol\ kg^{-1}$	298.15K	303.15K	308.15K	313.15K	m_A $mol\ kg^{-1}$	298.15K	303.15K	308.15K	313.15K
	10:90 (v/v) 1,4-Dioxane-Water					10:90 (v/v) Ethylene glycol-Water			
0.0010	0.057	0.054	0.054	0.052	0.0010	0.061	0.059	0.055	0.052
0.0025	0.070	0.068	0.066	0.064	0.0024	0.075	0.072	0.067	0.063
0.0049	0.085	0.083	0.081	0.079	0.0049	0.092	0.088	0.082	0.077
0.0074	0.096	0.095	0.092	0.090	0.0073	0.105	0.101	0.093	0.087
0.0099	0.107	0.105	0.102	0.099	0.0097	0.116	0.111	0.102	0.097
0.0247	0.150	0.147	0.142	0.138	0.0243	0.163	0.156	0.143	0.134
0.0495	0.199	0.195	0.188	0.183	0.0487	0.216	0.206	0.189	0.177
0.0744	0.236	0.231	0.223	0.217	0.0732	0.256	0.246	0.225	0.211
0.0994	0.267	0.261	0.252	0.245	0.0978	0.290	0.278	0.254	0.238
20:80 (v/v) 1,4-Dioxane-Water					20:80 (v/v) Ethylene glycol-Water				
0.0010	0.058	0.058	0.058	0.058	0.0010	0.065	0.062	0.058	0.055
0.0024	0.073	0.071	0.071	0.070	0.0024	0.082	0.078	0.072	0.068
0.0049	0.090	0.087	0.086	0.084	0.0048	0.101	0.097	0.087	0.083
0.0073	0.103	0.099	0.097	0.094	0.0072	0.117	0.111	0.105	0.093
0.0097	0.113	0.110	0.107	0.104	0.0095	0.129	0.122	0.119	0.103
0.0244	0.160	0.155	0.151	0.146	0.0239	0.183	0.173	0.166	0.144
0.0488	0.212	0.205	0.200	0.194	0.0479	0.244	0.230	0.212	0.191
0.0734	0.252	0.244	0.238	0.230	0.0720	0.290	0.274	0.250	0.227
0.0980	0.286	0.277	0.270	0.261	0.0961	0.330	0.311	0.285	0.256
30:70 (v/v) 1,4-Dioxane-Water					30:70 (v/v) Ethylene glycol-Water				
0.0010	0.061	0.061	0.058	0.057	0.0009	0.072	0.069	0.066	0.062
0.0024	0.078	0.075	0.075	0.074	0.0023	0.089	0.085	0.083	0.079
0.0048	0.097	0.094	0.092	0.090	0.0046	0.112	0.106	0.103	0.099
0.0072	0.111	0.107	0.106	0.103	0.0069	0.128	0.121	0.119	0.113
0.0096	0.123	0.119	0.117	0.114	0.0093	0.142	0.135	0.131	0.124
0.0241	0.175	0.169	0.166	0.161	0.0232	0.202	0.191	0.186	0.175
0.0482	0.233	0.224	0.220	0.213	0.0464	0.269	0.254	0.248	0.234
0.0725	0.277	0.267	0.262	0.254	0.0697	0.321	0.303	0.295	0.278
0.0968	0.315	0.303	0.298	0.288	0.0932	0.364	0.344	0.328	0.315

Table 4. The values of A and viscosity B-coefficient of BaBr₂ in 10-30 % (v/v) ethylene glycol-water and 1,4-dioxane-water respectively at T = (298.15-313.15) K and at atmospheric pressure.

T/K	Parameters	10:90 DO-Water	20:80 DO-Water	30:70 DO-Water	10:90 EG-Water	20:80 EG-Water	30:70 EG-Water
298.15	A	0.033±0.000	0.033±0.000	0.034±0.000	0.036±0.0003	0.036±0.000	0.039±0.0004
	B	0.743±0.001	0.809±0.002	0.906±0.002	0.813±0.0017	0.949±0.002	1.066±0.0021
	σ	0.0004	0.0005	0.0006	0.0005	0.0005	0.0006
303.15	A	0.032±0.000	0.033±0.000	0.034±0.000	0.034±0.0002	0.035±0.000	0.038±0.0003
	B	0.730±0.002	0.778±0.001	0.867±0.002	0.778±0.0012	0.891±0.002	1.004±0.0020
	σ	0.0005	0.0004	0.0005	0.0004	0.0006	0.0006
308.15	A	0.032±0.000	0.033±0.000	0.033±0.000	0.032±0.0001	0.035±0.002	0.038±0.0014

T/K	Parameters	10:90 DO-Water	20:80 DO-Water	30:70 DO-Water	10:90 EG-Water	20:80 EG-Water	30:70 EG-Water
313.15	B	0.700±0.001	0.755±0.002	0.851±0.003	0.710±0.0006	0.811±0.012	0.964±0.0082
	σ	0.0002	0.0005	0.0007	0.0002	0.0035	0.0023
	A	0.031±0.000	0.033±0.001	0.033±0.000	0.031±0.0001	0.033±0.000	0.035±0.0004
	B	0.681±0.001	0.726±0.003	0.820±0.003	0.663±0.0008	0.723±0.001	0.919±0.0023
	σ	0.0004	0.0009	0.0007	0.0002	0.0002	0.0007

3.2. Volumetric study.

Apparent molar volume is the change in the volume of the solute molecules due to the interaction with the solvents in a solution. From the experimentally obtained density data, we can calculate the apparent molar volume, V_ϕ of the solute using the equation as follows [28]:

$$V_\phi = \frac{M_2}{\rho} + \frac{(\rho^0 - \rho)}{m_A \rho \rho^0} \quad (3)$$

Where $\rho_0 / \text{kg m}^{-3}$ is the density of the pure solvent, $\rho / \text{kg m}^{-3}$ is the solution's density, $m_A / \text{mol kg}^{-1}$ is the molality, and $M_2 / \text{kg mol}^{-1}$ is the molecular weight of solute. The V_ϕ values (Table 2) have been found to be positive and increase with an increase in solute concentration and decrease with rising in temperature. V_ϕ values of BaBr₂ in aqueous solvents increase in the following order: ethylene glycol-water < 1,4-dioxane-water. The Masson-type equation can be employed to calculate the partial molar volume, $V_\phi^0 / \text{m}^3 \text{mol}^{-1}$, [29] as given below:

$$V_\phi = V_\phi^0 + S_v^{ex} \sqrt{m_A} \quad (4)$$

The values of V_ϕ^0 and the coefficients S_v^{ex} of equation (4) are obtained by plotting the graph V_ϕ vs $\sqrt{m_A}$ at four different temperatures are given in Table 5. The plot of V_ϕ^0 vs. m_A are presented in Figure 2.

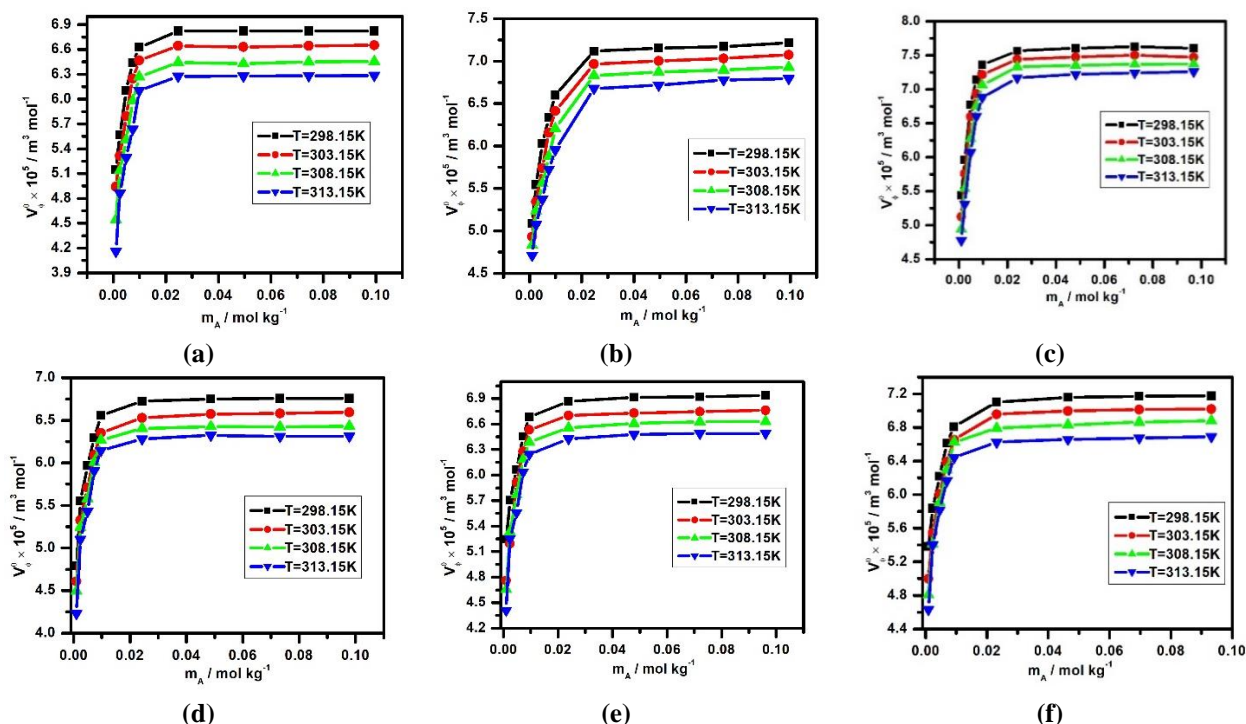


Figure 2. Plot of V_ϕ vs. m_A of BaBr₂ in (a) 10% (v/v) 1,4-dioxane –water, (b) 20% (v/v) 1,4-dioxane –water, (c) 30% (v/v) 1,4-dioxane –water, (d) 10% (v/v) ethylene glycol –water, (e) 20% (v/v) ethylene glycol –water, (f) 30% (v/v) ethylene glycol-water solutions at T=(298.15 – 313.15) K.

The standard deviation was calculated as per the formula, $\sigma = \sqrt{\left[\frac{(Y_{cal}-Y_{exp})^2}{f}\right]}$. It has been found that V_{ϕ}^0 for the investigated BaBr₂ solutions in the said solvents decrease with the concentration of dioxane and glycol. All the V_{ϕ}^0 values are found to be large and positive for all the solutions (Table 5). It is known the properties like density, viscosity, etc., are influenced by the presence of -OH group or oxygen atom in a molecule. The presence of such groups increases the hydrophilicity and electrostriction between water and solute particles. The decreasing trend of V_{ϕ}^0 values in dioxane-water and glycol-water indicate the ion-solvent interactions. In very dilute solutions, the ions are encircled by the solvent molecules so they are present far away from each other. So V_{ϕ}^0 is affected by ion-solvent interactions only. With an increase in temperature, some of the solvent molecules are freed from the loose solvation layers; as a result, the values of V_{ϕ}^0 decrease with an increase in temperature. With the addition of organic solvents, there will be the formation of strong solvation layers around the ions resulting increase in V_{ϕ}^0 values. In this case, the values of V_{ϕ}^0 of BaBr₂ in DO-water/EG-water is in the order:

In Water <10:90 DO-Water <20:80 DO-Water <30:70 DO-Water
 In Water <10:90 EG-Water <20:80EG-Water <30:70EG-Water

Table 5. Partial molar volume, V_{ϕ}^0 , experimental slope, S_v , and their standard deviations for BaBr₂ in pure water, 1,4-dioxane-water, and ethylene glycol-water at T=(298.15 – 313.15)K and at and 0.1 MPa Pressure.

Parameters	In Water	10:90 DO-Water	20:80 DO-Water	30:70 DO-Water	10:90 EG-Water	20:80 EG-Water	30:70 EG-Water
$V_{\phi}^0 \times 10^5 / m^3 mol^{-1}$	5.312 ± 0.16	5.67±0.25	5.818±0.25	6.145±0.33	5.498±0.28	5.720±0.23	5.838±0.24
$S_v \times 10^5 / m^{9/2} mol^{-3/2}$	3.651±0.78	4.667±1.45	6.637±1.47	6.044±1.93	5.154±1.64	4.924±1.36	5.492±1.40
$\sigma \times 10^5 / m^3 mol^{-1}$	0.301	0.422	0.423	0.553	0.474	0.390	0.394
$V_{\phi}^0 \times 10^5 / m^3 mol^{-1}$	5.221 ± 0.12	5.437±0.26	5.602±0.25	5.908±0.35	5.272±0.28	5.369±0.30	5.567±0.27
$S_v \times 10^5 / m^{9/2} mol^{-3/2}$	4.102 ±0.59	4.903±1.50	6.899±1.45	6.493±2.06	5.347±1.61	5.689±1.76	5.664±1.60
$\sigma \times 10^5 / m^3 mol^{-1}$	0.222	0.436	0.420	0.591	0.464	0.503	0.450
$V_{\phi}^0 \times 10^5 / m^3 mol^{-1}$	5.103 ± 0.12	5.147±0.28	5.133±0.24	5.671±0.36	5.188±0.29	5.318±0.28	5.435±0.29
$S_v \times 10^5 / m^{9/2} mol^{-3/2}$	4.230 ± 0.57	5.281±1.61	6.980±1.36	6.954±2.07	5.088±1.65	5.366±1.64	5.945±1.72
$\sigma \times 10^5 / m^3 mol^{-1}$	0.2	0.469	0.392	0.595	0.476	0.469	0.485
$V_{\phi}^0 \times 10^5 / m^3 mol^{-1}$	5.001 ± 0.12	4.837±0.31	4.954±0.22	5.465±0.36	5.013±0.31	5.143±0.30	5.336±0.28
$S_v \times 10^5 / m^{9/2} mol^{-3/2}$	5.32 ± 0.57	5.869±1.76	7.121±1.28	7.254±2.07	5.351±1.79	5.528±1.72	5.411±1.66
$\sigma \times 10^5 / m^3 mol^{-1}$	0.235	0.512	0.371	0.595	0.515	0.492	0.469

3.3. The temperature dependency of partial molar volume.

The temperature dependency of V_{ϕ}^0 values of BaBr₂ in aqueous solutions of dioxane and ethylene glycol can be evaluated from the following polynomial equation [30].

$$V_{\phi}^0 = a_0 + a_1T + a_2T^2 \tag{5}$$

The value of coefficient a_0 , a_1 , and a_2 in equation(5) has been evaluated from the least-squares fitting of the V_{ϕ}^0 values at T=(398.15-313.15)K and are presented in Table 6. The partial molar isobaric expansivity, E_{ϕ}^0 , is the factor that gives the change of partial molar volume with temperature can be found by different V_{ϕ}^0 concerning T at constant pressure is given below as:

$$E_{\phi}^0 = (\partial V_{\phi}^0 / \partial T)_p = a_1 + 2a_2T \tag{6}$$

The extent of solute-solvent interactions and solvation nature of the solute can be found from the values of E_{ϕ}^0 [31]. On the rising temperature, certain water molecules may be freed from the solvation sheet and hence increasing the volume of solution and E_{ϕ}^0 values become negative. It has been observed that the E_{ϕ}^0 values rise with rising temperatures that indicate the absence of caging effect.

Table 6. Values of various coefficients (Equation (5)), of BaBr₂ in 10-30 % (v/v) ethylene glycol-water and 1,4-dioxane-water respectively at T = (298.15-313.15) K and at 0.1 MPa pressure.

Solvents	$a_0 \times 10^5 / \text{m}^3 \text{mol}^{-1}$	$a_1 \times 10^5 / \text{m}^3 \text{mol}^{-1} \text{K}^{-1}$	$a_2 \times 10^9 / \text{m}^3 \text{mol}^{-1} \text{K}^{-2}$	$\sigma \times 10^5 / \text{m}^3 \text{mol}^{-1}$
10:90 DO-W	40.9±16.8	-0.20±0.11	2.764±1.80	0.009
20:80 DO-W	44.7±24.1	-0.22±0.16	3.100±2.58	0.013
30:70 DO-W	57.3±30.1	-0.30±0.20	4.361±3.23	0.016
10:90 EG-W	14.3±14.4	-0.03±0.09	-0.164±1.54	0.008
20:80 EG-W	50.3±23.1	-0.26±0.15	3.610±2.48	0.012
30:70 EG-W	49.1±12.8	-0.24±0.08	3.153±1.37	0.007

Hepler's equation[27] can be calculated by differentiating E_{ϕ}^0 w.r.t temperature T and given as follows:

$$(\partial E_{\phi}^0 / \partial T)_p = (\partial^2 V_{\phi}^0 / \partial T^2)_p = 2a_2 \quad (7)$$

For deciding whether the solute is a structure promoter or structure breaker, the sign of $(\partial^2 V_{\phi}^0 / \partial T^2)_p$ value is a better criterion [25]. The positive or small negative values of $(\partial^2 V_{\phi}^0 / \partial T^2)_p$ shows that the solute is a structure promoter, and the negative value indicates the reverse. In the present study, it has been found that the values of $(\partial^2 V_{\phi}^0 / \partial T^2)_p$ are all positive (Table 7), which indicates that BaBr₂ mostly acts as a structure promoter in the studied solutions over the entire ranges of temperature studied.

Table 7. Values of Limiting partial molar expansibilities (Equation 6)) and Hepler's constant (Equation (7)) of BaBr₂ in aqueous solutions of 1,4-dioxane(DO) and ethylene glycol (EG) at T=(298.15 to 313.15) K.

Solvents	$E_{\phi,v}^0 \times 10^7 / \text{m}^3 \text{mol}^{-1} \text{K}^{-1}$				$10^9 \left(\frac{dE_{\phi,v}^0}{dT} \right) / (\text{m}^3 \text{mol}^{-1})$
	298.15 K	303.15 K	308.15 K	313.15 K	
10:90 DO-W	-3.62	-3.34	-3.07	-2.79	5.528
20:80 DO-W	-3.84	-3.53	-3.22	-2.91	6.201
30:70 DO-W	-4.27	-3.83	-3.39	-2.96	8.722
10:90 EG-W	-3.54	-3.56	-3.58	-3.59	-0.328
20:80 EG-W	-4.26	-3.90	-3.54	-3.18	7.219
30:70 EG-W	-5.02	-4.71	-4.39	-4.08	6.305

The isobaric thermal expansion coefficient (α) can be calculated from equation 8 and presented in Table 8:

$$\alpha = (E_{\phi}^0 / V_{\phi}^0) \quad (8)$$

The structure-making or structure-breaking nature of a solute in an aqueous mixed solvent can best be understood by an equation given by L. G. Hepler[27].

$$(\partial C_p^0 / \partial P) = -T(\partial^2 V_{\phi}^0 / \partial T^2)_p \quad (9)$$

From this expression, it can be calculated that structure-making solutes have a negative value of $(\partial C_p^0 / \partial P)$, whereas the structure-breaking solutes have positive values. The values

of $(\partial C_p^0/\partial P)$ are found to be negative (Table 8) for both solvents. This indicates that BaBr₂ is a structure promoting solutes in the studied solutions.

3.4. Transport behavior.

The standard partial molar volumes of transfer, $\Delta_t V_\phi^0$ and B -coefficient of transfer $\Delta_t B$ of BaBr₂ from water to an aqueous solution of DO/EG were computed using the following equations:

$$\Delta_t V_\phi^0 = V_\phi^0(\text{BaBr}_2 \text{ in aqueous DO or EG}) - V_\phi^0(\text{in water}) \quad (10)$$

$$\Delta_t B = B(\text{BaBr}_2 \text{ in aqueous DO or EG}) - B(\text{in water}) \quad (11)$$

By definition, the values of $\Delta_t V_\phi^0$ deliver ideas about the ion-solvent interactions. The values of $\Delta_t V_\phi^0$ and $\Delta_t B$ obtained from equations (10 and 11) are listed in Table 9. The plot of $\Delta_t V_\phi^0$ and $\Delta_t B$ with percentage composition of DO and EG are given in Figure 3. The positive values of $\Delta_t V_\phi^0$ and $\Delta_t B$, can be interpreted by Krishnan and Friedman's cosphere overlap model [32]. The existence of ion-solvent interfaces is due to positive values of transfer volume. The increased value of $\Delta_t V_\phi^0$ and $\Delta_t B$ with an increase of the percentage of DO/EG in solution represents the presence of attraction of DO/EG with BaBr₂. The values of $\Delta_t V_\phi^0$ also, increases with the rise of temperatures are due to the lessening of electrostriction of BaBr₂ at higher values of temperature.

Table 8. The values of α and $(\partial C_p^0/\partial P)$ of BaBr₂ in ethylene glycol- -water and 1,4-dioxane- water at $T=(298.15- 313.15)$ K.

Solvents	$\alpha_1 \times 10^3 / \text{K}$				$(\partial C_p^0/\partial P) \times 10^9 / \text{m}^3 \text{mol}^{-1} \text{K}^{-1}$			
	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
10:90 DO-W	-6.91	-6.60	-6.29	-5.93	-0.165	-0.168	-0.170	-0.173
20:80 DO-W	-6.40	-6.07	-5.67	0.13	-0.185	-0.188	-0.191	-0.194
30:70 DO-W	-6.23	-5.75	-5.22	0.16	-0.260	-0.264	-0.269	-0.273
10:90 EG-W	-6.48	-6.73	-6.95	-0.01	0.010	0.010	0.010	0.010
20:80 EG-W	-6.90	-6.49	-5.99	0.14	-0.215	-0.219	-0.222	-0.226
30:70 EG-W	-8.06	-7.81	-7.46	0.12	-0.188	-0.191	-0.194	-0.197

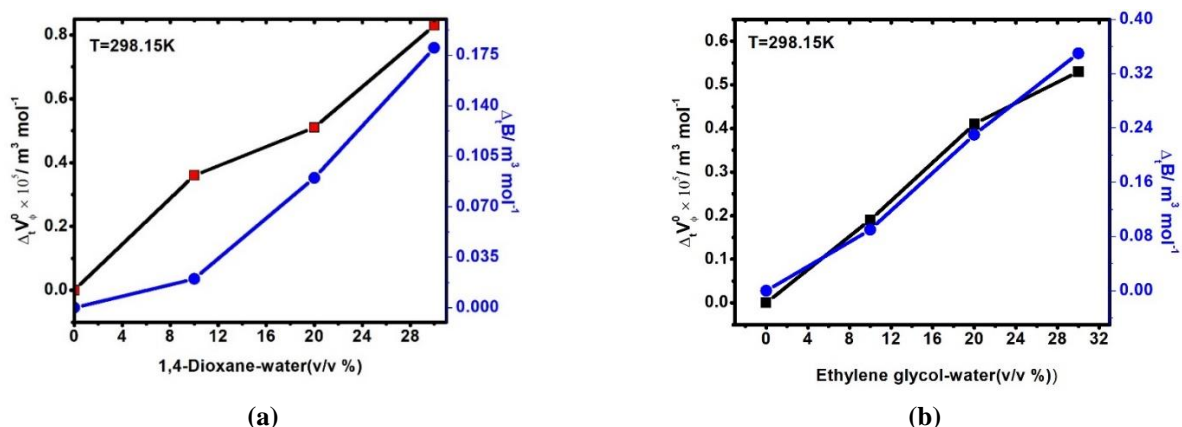


Figure 3. The Plot of $\Delta_t V_\phi^0$ and $\Delta_t B$ vs % (v/v) composition of (a) 1,4-dioxane –water and (b) ethylene glycol-water at $T=298.15\text{K}$ respectively.

Table 9. Values of $\Delta_t V_\phi^0$ and $\Delta_t B$ of BaBr₂ in ethylene glycol- water and 1,4-dioxane- water at $T=(298.15-313.15)$ K and 0.1 MPa Pressure.

% (v/v)	1,4-Dioxane-Water				Ethylene glycol -Water			
	$10^5 V_\phi^0/(\text{m}^3 \text{mol}^{-1})$	$10^5 \Delta_t V_\phi^0/(\text{m}^3 \text{mol}^{-1})$	B	$\Delta_t B$	$10^5 V_\phi^0/(\text{m}^3 \text{mol}^{-1})$	$10^5 \Delta_t V_\phi^0/(\text{m}^3 \text{mol}^{-1})$	B	$\Delta_t B$
T=298.15K								
0	5.312	0.00	0.721	0.00	5.312	0.00	0.721	0.00
10	5.677	0.36	0.743	0.02	5.498	0.19	0.813	0.09
20	5.818	0.51	0.809	0.09	5.720	0.41	0.949	0.23
30	6.145	0.83	0.906	0.18	5.838	0.53	1.066	0.35
T = 303.15K								
0	5.221	0.00	0.712	0.00	5.221	0.00	0.712	0.00
10	5.446	0.23	0.730	0.02	5.316	0.09	0.778	0.07
20	5.602	0.38	0.778	0.07	5.460	0.24	0.891	0.18
30	5.908	0.69	0.867	0.16	5.621	0.40	1.004	0.29
T = 308.15K								
0	5.103	0.00	0.692	0.00	5.103	0.00	0.692	0.00
10	4.876	-0.23	0.700	0.01	5.168	0.06	0.710	0.02
20	5.133	0.03	0.755	0.06	5.308	0.21	0.811	0.12
30	5.671	0.57	0.851	0.16	5.462	0.36	0.964	0.27
T=313.15K								
0	5.001	0.00	0.674	0.00	5.001	0.00	0.674	0.00
10	4.703	-0.30	0.681	0.01	5.013	0.01	0.663	-0.01
20	4.954	-0.05	0.726	0.05	5.143	0.14	0.723	0.05
30	5.465	0.46	0.820	0.15	5.288	0.29	0.919	0.25

4. Conclusions

The results obtained in the above discussions represent that the densities increase when the concentration of BaBr₂ and temperature increase. It has been observed that the density of the solutions increases with an increase in the mass fraction of DO and EG. The positive values of B coefficient at all temperatures represent the structure promoting the nature of the solute. The negative value of dB/dT may be attributed to the solid interactions between ions and solvents at the lower temperature. The positive values of V_ϕ^0 may be due to the existence of strong ion-solvent interactions. The negative values of E_ϕ^0 and the positive values of Hepler's constant say that the solute is a structure promoter. The negative values of isobaric thermal expansion, α_1 and the positive values of $(\partial C_p^0/\partial P)$ support the results obtained from the volumetric and viscometric studies.

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Conflicts of Interest

The authors declare no conflict of interest.

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