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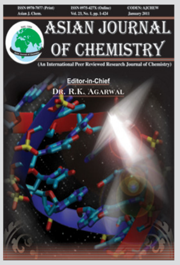

Apparent Molal Volumes and Apparent Molal Adiabatic Compressibilities of Digols in Water at Different Temperatures

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Apparent molal volumes (ϕ_V) and apparent molal adiabiatic compressibilities (ϕ_K) have been calculated from the measured densities for the binary liquid mixtures of digols namely diethylene glycol monomethyl ether (methyl digol-MD), diethylene glycol dimethyl ether (dimethyl digol-DD) and diethylene glycol monobutyl ether (butyl digol-BG) with water at 303.15, 308.15, 313.15, 318.15 and 323.15 K. The apparent molal volume data has been analyzed using Mason's equation and calculated the apparent molal volumes at infinite dilution (ϕ_V^o), the slope values (S_V) and the apparent molal expansibilities ($\phi_E^o = \partial\phi_V^o/\partial T$). From the measurements of ultrasonic velocity (u) and density (ρ) the apparent molal adiabatic compressibilities at infinite dilution (ϕ_k^o) and the experimental slopes (S_k) are computed. The analysis of the results indicates the presence of solute solvent interactions in these liquid mixtures and the solutes are found to be the structure makers in water and their structure making ability is in the order of methyl digol < dimethyl digol < butyl digol.

Key Words: Apparent molal volume, Apparent molal adiabatic, Compressibilities, Digols.

INTRODUCTION

Water is a polar solvent and is associated with intermolecular hydrogen bonding leading to polymeric nature. It is expected that the addition of other liquids to water may cause rupture of the association of like molecules (water-water) and promote the association of unlike molecules if possible (solute-water)[1]. With the addition of non electrolytes to water, the studies throw light on the structure making or breaking ability of the solutes. In the present study digols are chosen as they form a group of compounds of interesting properties. They are water soluble ethers, which can dissolve some halogenic salts. They form a series of solvents in which one can study reactions with water sensitive materials. Thus the aqueous liquid mixtures of digols are taken up to understand their behaviour through the apparent molal volume and apparent molal adiabatic compressibility studies, which will be interesting binary solvent systems for the study of inter molecular interactions.

EXPERIMENTAL

AR grade (S.D. Fine Chemicals, Bombay) samples of the digols namely diethylene glycol monomethyl ether (methyl digol-MD), diethylene glycol dimethyl ether (dimethyl digol-DD) and diethylene glycol monobutyl ether (butyl digol-BG) were further purified by standard methods[2] and dried over 4 Å molecular sieves and fractionally distilled. The cellosolves GC analasis indicated a mole % purity of 99.6 %. Triple distilled water (specific conductance 2.8 × 10^{-6} mhos/cm) was used as a standard liquid for preparing the solutions.

Mixtures were prepared by weighing an appropriate value of each liquid component and were kept in special air tight bottles. All solutions were prepared in dry box. Densities were measured by a bicapillary pycnometer as described in earlier paper[3]. Purity of all the samples were checked by measuring densities and found to be in good agreement with the available literature data[4,5]. The precision in the density measurements was with in ± 2 parts in 10^4. The ultrasonic velocity measurements were made by a single frequency (2 MHz) variable path interferometer with an accuracy of ± 0.03 %. The temperature water bath used had an accuracy of ± 0.05 ºC.

RESULTS AND DISCUSSION

The apparent molal volume studies of digols namely, diethylene glycol monomethyl ether (methyl digol), diethylene glycol dimethyl ether (dimethyl digol), diethylene glycol monobutyl ether (butyl digol) in water at different concentrations and temperatures. Based on their chemical structure methyl digol, dimethyl digol and butyl digol can also be regarded as diethylene glycol monomethyl ether, diethylene glycol dimethyl ether and diethylene glycol monobutyl ether, respectively. From their chemical structure one can understand that all these solutes have a common diethylene glycol group and the variation is with respect to the substituted methyl, dimethyl and monobutyl groups in the place of terminal hydroxyl hydrogen atoms of the diethylene glycol group.

Adiabatic compressibility minimum and density maximum studies carried out in the case of aqueous ethylene glycol, diethylene glycol, triethylene glycol and polyethylene glycols[1-4] indicate that all these solutes behave as structure breakers. Structure breaking ability of these solutes increases with increase in chain length. As such there is unquestionable evidence that diethylene glycol acts as water structure breaker at different concentrations and different temperatures in the studies carried out so far.

The fact that diethylene glycol dimethyl ether is a maker at lower temperature as indicated by density maximum studies[4] can be attributed due to the either increasing structure making ability of the alkyl groups or the decrease in structure breaking ability of the diethylene glycol at lower temperatures. In the case of diethylene glycol, it is found that its structure breaking ability decreases with decrease of temperature as observed from the sound velocity maximum, adiabatic compressibility minimum and acoustic impedance maximum studies[3] and as such the behaviour of diethylene glycol dimethyl ether is a structure maker at lower temperatures.

The apparent molal volumes (ϕ_v) of diethylene glycol monomethyl ether, diethylene glycol dimethyl ether, diethylene glycol monobutyl ether in water at different temperatures 30, 35, 40, 45 and 50 °C are evaluated from the density measurements of the present study using the relation[5]:

$$\phi_v = \frac{M}{d_o} - \frac{1000(d-d_o)}{d_o C}$$

where d_o and d are the densities of the water and of the solution, respectively, M is the molecular weight of the solute and C is the molar concentration ('m' in the case of molal concentration, molality). The results are presented in Table-1.

It can be seen that the ϕ_v is varying linearly relative to molality in the concentration range studied. The limiting partial molal volume, ϕ_v^o (the apparent molal volume at infinite dilution) and S_v (experimental slope) are obtained graphically from ϕ_v *versus* molality plots as well as by fitting the experimental data into the following equation[2]:

$$\phi_v = \phi_v^o + S_v m$$

using the method of least squares. As both the values agree well, the least square fit values alone are presented in Table-2. The data indicates that the magnitude of ϕ_v^o at all the temperatures studied is in the order of methyl digol < dimethyl digol < butyl digol, which also indicates the order of solute-solvent interactions in the solutions of digols in water. At each temperature studied, as the chain length of digols increases ϕ_v^o value also increases, indicating that solute-solvent interactions are predominant.

It can be seen from the Table-3 that the ϕ_v^o of digols in water are smaller than the molar volumes of the pure digols. These results indicate that solute-solvent interactions in digols and water are very large. This is in accordance with the observations made by Millero *et al.*[6] .

TABLE-1
MOLAL CONCENTRATION (m) AND APPARENT MOLAL VOLUME (ϕ_V) AT DIFFERENT TEMPERATURES

m (mol kg^{-1})	ϕ_V (mL mol^{-1})				
	30 °C	35 °C	40 °C	45 °C	50 °C
Methyl digol + Water					
0.0355	97.86	100.27	103.86	106.05	107.41
0.0581	97.63	100.20	103.86	105.97	107.59
0.0767	97.62	100.13	103.74	105.92	107.47
0.0885	97.68	100.11	103.72	105.87	107.47
0.1357	97.55	100.01	103.71	105.79	107.44
0.1965	97.45	99.92	103.64	105.76	107.40
0.3497	97.17	99.70	103.43	105.59	107.30
0.3912	97.10	99.62	103.38	105.54	107.26
0.4498	97.02	99.53	103.33	105.48	107.22
Dimethyl digol + Water					
0.0318	133.17	133.71	134.27	134.86	135.48
0.0520	133.20	133.81	134.25	134.91	135.41
0.0687	133.14	133.80	134.34	134.91	135.50
0.0793	133.10	133.70	134.33	134.86	135.41
0.1215	133.08	133.63	134.21	134.82	135.46
0.1759	133.01	133.57	134.17	134.79	135.39
0.3131	132.75	133.40	134.02	134.66	135.29
0.3503	132.69	133.35	133.99	134.62	135.28
0.4028	132.60	133.27	133.93	134.57	135.24
Butyl digol + Water					
0.0263	144.94	149.78	156.23	161.99	165.86
0.0430	144.86	149.80	155.99	162.02	165.97
0.0568	144.78	149.83	156.03	161.94	165.93
0.0655	144.85	149.89	156.08	161.89	165.88
0.1005	144.71	149.81	156.01	161.87	165.95
0.1454	144.62	149.72	155.89	161.78	165.88
0.2588	144.36	149.46	155.73	161.68	165.74
0.2896	144.28	149.42	155.65	161.61	165.74
0.3329	144.18	149.33	155.58	161.61	165.69

TABLE-2
LIMITING PARTIAL MOLAL VOLUMES (ϕ_V^o) AND EXPERIMENTAL SLOPES (S_V) OF DIGOLS IN WATER AT DIFFERENT TEMPERATURES

Solution	T (°C)	ϕ_V^o (mL mol^{-1})	S_V (mL kg mol^{-2})
Methyl digol + Water	30	97.81	-1.81
	35	100.28	-1.68
	40	103.88	-1.26
	45	106.02	-1.24
	50	107.53	-0.67
Dimethyl digol + Water	30	133.25	-1.60
	35	133.83	-1.37
	40	134.38	-1.04
	45	134.94	-0.89
	50	135.49	-0.62
Butyl digol + Water	30	144.97	-2.37
	35	149.92	-1.71
	40	156.16	-1.69
	45	162.02	-1.42
	50	165.96	-0.78

It is evident from Table-4 (ϕ_E values) that the apparent molal expansibilities ($\phi_E = \phi_v^o/T$) of methyl digol and butyl digol in water decrease with temperature and that of dimethyl digol in water increase with temperature. This behaviour of these non-electrolytes can be interpreted as evidence for the breaking of structure in the water[1] in case of methyl digol and butyl digol and making of structure in water by dimethyl digol[7].

TABLE-3
COMPARISON BETWEEN ϕ_v^o AND MOLAR VOLUMES OF PURE DIGOLS AT DIFFERENT TEMPERATURES

Solution	T (ºC)	ϕ_V^o	Molar volume of pure liquid
Methyl digol	30	97.81	118.87
	35	100.28	119.37
	40	103.88	119.88
	45	106.02	120.39
	50	107.53	120.92
Dimethyl digol	30	133.25	143.63
	35	133.83	144.33
	40	134.38	145.06
	45	134.94	145.80
	50	135.49	146.55
Butyl digol	30	144.97	171.81
	35	149.92	172.59
	40	156.16	173.37
	45	162.02	174.14
	50	165.96	174.91

TABLE-5
MOLAL CONCENTRATION (m) AND APPARENT MOLAL ADIABATIC COMPRESSIBILITIES (ϕ_K) AT DIFFERENT TEMPERATURES

m (mol kg^{-1})	$\phi_K \times 10^4$ (mL mol^{-1})				
	30 ºC	35 ºC	40 ºC	45 ºC	50 ºC
Methyl digol + Water					
0.0355	8.23	12.91	16.49	19.92	22.81
0.0581	8.19	12.94	16.54	19.94	22.94
0.0767	8.24	12.95	16.53	19.96	22.92
0.0885	8.30	12.97	16.56	19.96	22.95
0.1357	8.37	13.05	16.67	20.03	23.04
0.1965	8.49	13.17	16.68	20.16	23.15
0.3497	8.80	13.49	17.06	20.43	23.48
0.3912	8.88	13.56	17.14	20.51	23.50
0.4498	9.00	13.67	17.26	20.61	23.61
Dimethyl digol + Water					
0.0318	11.30	16.08	20.71	25.77	30.19
0.0520	11.40	16.20	21.04	25.86	30.22
0.0687	11.45	16.27	21.14	25.92	30.31
0.0793	11.48	16.27	21.17	25.93	30.31
0.1215	11.66	16.41	21.28	26.06	30.46
0.1759	11.88	16.61	21.47	26.23	31.59
0.3131	12.39	17.10	21.93	26.64	31.98
0.3503	12.52	17.23	22.06	26.75	31.09
0.4028	12.73	17.41	22.23	26.91	31.23
Buty digol + Water					
0.0263	5.02	12.12	15.42	23.41	25.02
0.0430	5.21	12.33	15.50	23.57	25.18
0.0568	5.35	12.50	15.66	23.65	25.26
0.0655	5.50	12.63	15.77	23.70	25.29
0.1005	5.90	13.01	16.11	23.99	25.56
0.1454	6.45	13.51	16.54	24.32	25.84
0.2588	7.83	14.74	17.67	25.23	26.55
0.2896	8.20	15.09	17.97	25.46	26.76
0.3329	8.73	15.57	18.40	25.79	27.03

These results are in conformity with the sound velocity maximum, adiabatic compressibility minimum and specific acoustic impedance maximum studies[2,3,8,9].

Apparent molal adiabatic compressibilities: The apparent molal adiabatic compressibility studies of digols namely, methyl digol (diethylene glycol monomethyl ether), dimethyl digol (diethylene glycol dimethyl ether) and butyl digol (diethylene glycol monobutyl ether) in water at different concentrations and temperatures. Similar to apparent molal volumes, the apparent molal adiabatic compressibilities were calculated[6] from the density, d and adiabatic compressibility, β_s of the solution using the equation:

$$\phi_{k(s)} = \frac{1000(\beta_s d_o - \beta_s^o d)}{m d d_o} + \frac{\beta_s M}{d}$$

where d_o is the density of water, m is the molality, M is the molecular weight of the solute and β_s^o is the adiabatic compressibility for water. The adiabatic compressibilities (β_s) of the aqueous solutions at different temperatures were determined from the density and the velocity of sound values.

The apparent molal adiabatic compressibilities (ϕ_K) of the above solutions at different concentrations and at temperatures 30, 35, 40, 45 and 50 °C are evaluated from the density and ultrasonic velocity measurements and the results are presented in Table-5.

The ϕ_k (m) is varying linearly relative to molality 'm' in the concentration range studied. The limiting partial molal adiabatic compressibility, ϕ_k^o (the apparent molal adiabatic compressibility at infinite dilution) and S_k (experimental slope) are obtained graphically from ϕ_k *versus* molality plots as well as by fitting the experimental data into the following equation[6]:

$$\phi_K = \phi_K^o + S_k m$$

using the method of least squares. As both the values agree well, the least square fit values alone are presented in Table-6.

From the partial molal adiabatic compressibilities of aqueous non-electrolytes, Millero *et al.*[6] concluded that lower ϕ_K^o values indicate higher hydration nature and higher ϕ_K^o values indicate the lower hydration nature of molecules. Similarly in the present study, the relatively smaller values of methyl digol and butyl digol at lower temperature indicate higher hydration nature of these molecules in water, as against dimethyl digol which has relatively higher ϕ_K^o. The ϕ_K^o value increases with increase in temperature for all the three digols in water. This may be interpreted in terms of the release of structural water molecules from around the digols with increase in temperature and may be attributed to the hydration nature of these molecules. The experimental slopes on the other hand decrease

TABLE-4
APPARENT MOLAL EXPANSIBILITIES OF DIGOLS

Solute	ϕ_v^o (mL mol^{-1})			$\partial\phi_v^o/\partial t \times 10^2$ (mL mol^{-1} deg^{-1})		$\partial^2\phi_v^o/\partial t^2 \times 10^3$ (mL mol^{-1} deg^{-2})
	30 ºC	40 ºC	50 ºC	35 ºC	45 ºC	40 ºC
Methyl digol	97.81	103.88	107.53	60.7	36.5	-24.2
Dimethyl digol	133.25	134.38	135.49	11.0	11.4	0.4
Butyl digol	144.97	156.16	165.90	111.9	97.4	-14.5

TABLE-6
PARTIAL MOLAL ADIABATIC COMPRESSIBILITIES AND EXPERIMENTAL SLOPES OF DIGOLS IN WATER AT DIFFERENT TEMPERATURES

Solution	T (°C)	$\phi_K^o \times 10^4$ (mL mol^{-1} bar^{-1})	$S_K \times 10^4$ (mL kg mol^{-2} bar^{-1})
Methyl digol + Water	30	8.11	2.0
	35	12.81	1.9
	40	16.41	1.8
	45	19.83	1.7
	50	23.54	1.7
Dimethyl digol + Water	30	11.19	3.8
	35	16.00	3.5
	40	20.88	3.3
	45	25.69	3.0
	50	30.10	2.8
Butyl digol + Water	30	4.69	12.2
	35	11.87	11.1
	40	15.12	9.8
	45	23.21	7.7
	50	24.90	6.4

with increase in temperature and increase with the increase in functional groups.

Table-7 gives the compressibility behaviour ($\partial\phi_K^o/T$ values) of all the three digols under study which are in the order of methyl digol < dimethyl digol < butyl digol and may be considered as the order of the solute solvent interactions. This also confirms the order as revealed from the apparent molal volume studies discussed before.

TABLE-7
$\partial\phi_K^o/\partial T$ VALUES OF THE DIGOLS

Solute	$\phi_K^o \times 10^4$ (mL mol^{-1} bar^{-1})			$\partial\phi_K^o/\partial T \times 10^5$ (mL mol^{-1} bar^{-1} deg^{-1})	
	30 °C	40 °C	50 °C	35 °C	45 °C
Methyl digol	8.11	16.4	23.5	8.3	7.1
Dimethyl digol	11.2	20.9	30.1	9.7	9.2
Butyl digol	4.7	15.1	24.9	10.4	9.8

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