



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

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Apparent molal volumes (ϕ_v) and apparent molal adiabatic compressibilities (ϕ_K) have been calculated from the measured densities for the binary liquid mixtures of cellosolves namely 2-methoxy ethanol (2ME), 2-ethoxy ethanol (2EE) and 2-butoxy ethanol (2BE) with water at 303.15, 308.15, 313.15, 318.15 and 323.15 K. The apparent molal volumes data has been analyzed using Mason's equation and calculated the apparent molal volumes at infinite dilution (ϕ_v^∞), the slope values (S_v) and the apparent molal expansibilities ($\phi_E^\infty = \partial\phi_v^\infty/\partial T$). From the measurements of ultrasonic velocity (u) and density (ρ) the apparent molal adiabatic compressibilities at infinite dilution (ϕ_K^∞) 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 2ME < 2EE < 2BE.

Key Words: Apparent molal volumes, Apparent molal adiabatic compressibilities.

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). 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 cellosolves are chosen as non electrolytes in view of their special industrial importance. The water is considered as highly polar liquid with high dielectric constant where as alkoxy ethanols are moderately polar, associating and amphiprotic solvents with low dielectric constants. Therefore, these are hardly dissociating liquids¹. Thus the aqueous liquid mixtures of cellosolves 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 (SD Fine Chemicals, Bombay) samples of the cellosolves, namely 2-methoxy ethanol, 2-ethoxy ethanol and 2-butoxy ethanol were further purified by standard methods²

and dried over 4 Å molecular sieves and fractionally distilled. The cellosolves GC analysis indicated a mole percentage 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 described³. 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 °C.

RESULTS AND DISCUSSION

The apparent molal volumes (ϕ_v) of 2-methoxy ethanol, 2-ethoxy ethanol and 2-butoxy ethanol in water at different concentrations and temperatures 30, 35, 40, 45 and 50 °C are evaluated from the density measurements using the relation⁶

$$\phi_v = \frac{M}{d_0} - \frac{100(d - d_0)}{d_0 C}$$

where d_0 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.

m (mol kg^{-1})	ϕ_v (mL mol^{-1})				
	30 °C	35 °C	40 °C	45 °C	50 °C
2-Methoxy ethanol + water					
0.0315	75.47	75.90	76.05	76.20	76.70
0.0634	75.49	75.76	76.05	76.37	76.53
0.1170	75.48	75.68	76.00	76.32	76.58
0.1701	75.43	75.71	76.03	76.31	76.59
0.2290	75.40	75.70	75.97	76.26	76.57
0.2790	75.39	75.68	75.95	76.26	76.57
0.3178	75.36	75.64	75.94	76.26	76.56
0.3816	75.34	75.67	75.93	76.22	76.55
0.4271	75.33	75.65	75.91	76.21	76.55
2-Ethoxy ethanol + water					
0.0497	91.56	91.92	92.29	92.69	92.90
0.0757	91.62	91.90	92.21	92.67	93.01
0.1161	91.51	91.84	92.27	92.64	92.94
0.1584	91.45	91.86	92.22	92.54	92.95
0.2255	91.41	91.79	92.14	92.52	92.91
0.2559	91.39	91.74	92.12	92.51	92.88
0.3011	91.34	91.73	92.10	92.48	92.88
0.3560	91.28	91.66	92.06	92.45	92.85
0.4106	91.23	91.61	92.01	92.44	92.82
2-Butoxy ethanol + water					
0.0125	123.55	123.76	124.80	125.09	126.18
0.0356	123.53	124.03	124.84	125.39	125.97
0.0780	123.40	124.00	124.63	125.32	125.84
0.0989	123.45	124.07	124.62	125.30	125.90
0.1325	123.34	124.01	124.64	125.22	125.82
0.1629	123.31	123.96	124.58	125.22	125.83
0.2630	123.17	123.86	124.53	125.17	125.85
0.3398	123.09	123.76	124.46	125.11	125.84
0.4216	122.97	123.69	124.40	125.09	125.85

The ϕ_v is varying linearly with molality in the concentration range studied. The limiting partial molal volume, ϕ_v° (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 (as used by Millero *et al.*⁷).

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

using the method of least squares also. As both the values agree well, the least square fit values alone are presented in Table-2.

It is observed that the ϕ_v values decrease with concentration and increase with temperature. It is suggested from Table-1 that the ϕ_v° value increases with the successive addition of CH_2 group and also with increase of temperature. From this it can be presumed that hydrophobic hydration is enhanced around CH_2 group as has been generally accepted by Neal and Goring studies⁸.

From the ϕ_v° values, quantitative evaluation of the solvation and interaction parameters of the cellosolves in water is possible. This can be understood with the increment of ϕ_v° value by the addition of CH_2 group in the cellosolves as can be seen from the Table-2. At each temperature studied, the ϕ_v°

Solution	T (°C)	ϕ_v° (mL mol^{-1})	S_v (mL kg mol^{-2})
2-Methoxy ethanol + water	30	75.51	-0.43
	35	75.81	-0.42
	40	76.06	-0.37
	45	76.31	-0.20
	50	76.62	-0.18
2-Ethoxy ethanol + water	30	91.64	-1.00
	35	91.96	-0.84
	40	92.32	-0.73
	45	92.71	-0.72
	50	92.99	-0.37
2-Butoxy ethanol + water	30	123.55	-1.40
	35	124.01	-0.64
	40	124.77	-0.95
	45	125.29	-0.46
	50	125.98	-0.45

value increases as the cellosolves chain length increases. This indicates that the solute-solvent interactions are increased. This may be attributed to the accumulation of more number of water molecules surrounding the CH_2 group, as the CH_2 group increases in the cellosolves. Table-2 indicates that the magnitude of ϕ_v° at all the temperatures studied, is in the order of 2-methoxy ethanol < 2-ethoxy ethanol < 2-butoxy ethanol. This further indicates the order of solute-solvent interactions in the solutions of cellosolves in water.

From Table-2 it can be seen that S_v is negative and becomes more negative with increase in CH_2 group of cellosolves and becomes less negative with increase in temperature. As the adjacent hydrophilic groups *i.e.*, OH groups and ethereal oxygen atom present in cellosolves, a compact structure with water molecules is expected. This may be attributed to the decrease in volume with increase of concentration of cellosolves in water.

It can be seen from the Table-3 that the ϕ_v° of cellosolves in water are smaller than the molar volumes of the pure cellosolves. These results indicate that solute-solvent interactions between cellosolves and water are very large. This is in accordance with the observations made by Millero *et al.*⁹.

Solute	t (°C)	ϕ_v°	Molar volume of pure liquid
2-Methoxy ethanol	30	75.51	79.61
	35	75.81	79.98
	40	76.06	80.35
	45	76.31	80.72
	50	76.62	81.10
2-Ethoxy ethanol	30	91.64	98.01
	35	91.96	98.56
	40	92.32	99.12
	45	92.71	99.68
	50	92.99	100.25
2-Butoxy ethanol	30	123.55	132.48
	35	124.01	133.12
	40	124.77	133.76
	45	125.29	134.42
	50	125.98	135.08

TABLE-4
APPARENT MOLAL EXPANSIBILITIES OF CELLOSOLVES IN WATER

Solute	ϕ_v° (mL mol ⁻¹)			$\partial\phi_v^\circ/\partial t \times 10^2$ (mL mol ⁻¹ deg ⁻¹)		$\partial^2\phi_v^\circ/\partial t^2 \times 10^3$ (mL mol ⁻¹ deg ⁻²)
	30 °C	40 °C	50 °C	35 °C	45 °C	40 °C
2-Methoxy ethanol	75.51	76.06	76.62	5.5	5.6	0.1
2-Ethoxy ethanol	91.66	92.32	93.00	6.6	6.8	0.2
2-Butoxy ethanol	123.55	124.70	126.02	12.2	12.5	0.3

According to Hepler¹⁰ and Neal and Goring⁸ a good correlation exists between the sign of $\partial^2\phi_v^\circ/\partial T^2$ value of the solute and its structure making/breaking property. Accordingly, $\partial^2\phi_v^\circ/\partial T^2$ will be positive for structure makers and negative for structure breakers. It is evident from Table-4 that the apparent molal expansibilities ($\partial\phi_v^\circ/\partial T$) of these three cellosolves in water increase with temperature. This behaviour of these non electrolytes can be interpreted as an evidence for the structure making ability in water⁸.

The ability of solute to perturb the structure of water may be regarded as a sum of group effects. In order to understand the group effects of the cellosolves their chemical structure is considered. All these solutes have a common ethylene glycol group and the hydrogen atom of the hydroxyl group in ethylene glycol is replaced by methyl, ethyl and butyl groups, respectively. Two types of group effects are observed in the present study. One is the structure breaking effect of ethylene glycol group and the other is structure making effect of hydrocarbon group. The net effect of the solute can be considered as due to the resultant effect of these two functional groups. The structure making ability of the solutes is in the order, 2-methoxy ethanol < 2-ethoxy ethanol < 2-butoxy ethanol. This trend clearly indicates that the structure making ability of these solutes increased gradually as the hydrogen of the hydroxyl group of ethylene glycol is replaced by methyl, ethyl and butyl groups.

This can be attributed to the fact that the methyl, ethyl and butyl groups are supposed to have a hydrophobic character (structure making) and their hydrophobicity increases with increase in chain length, from methyl to butyl as has been reported from maximum density^{10,11} and minimum adiabatic compressibility and maximum sound velocity studies^{12,13}. The absorption studies carried out by Nishikawa *et al.*¹⁴ also confirm that the hydrophobicity of these solutes is in the order propyl cellosolve < isobutyl cellosolve < butyl cellosolve.

Apparent molal adiabatic compressibility studies: The adiabatic compressibilities (β_s) of these liquid mixtures are calculated from the measured density and ultrasonic velocity data which are further used in the evaluation⁷ of apparent molal adiabatic compressibilities using the equation

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

where d_o is the density of water, m is the molality, M is the molecular weight of the solute and β_s° is the adiabatic compressibility for water.

Apparent molal adiabatic compressibility studies of cellosolves namely, 2-methoxy ethanol, 2-ethoxy ethanol and 2-butoxy ethanol in water at different concentrations and temperatures are studied in order to understand the solute-water interactions. The apparent molal adiabatic compressibilities

(ϕ_k) of 2-methoxy ethanol, 2-ethoxy ethanol and 2-butoxy ethanol in water at different concentrations and at temperatures 30, 35, 40, 45 and 50 °C are evaluated from the density and ultrasonic velocity measurements (Table-5).

TABLE-5
MOLAL CONCENTRATION (M) AND APPARENT MOLAL ADIABATIC COMPRESSIBILITIES (ϕ_k) OF CELLOSOLVES AT DIFFERENT TEMPERATURES

m (mol/kg)	$\phi_k \times 10^3$ (mL mol ⁻¹ bar ⁻¹)				
	@ 30 °C	@ 35 °C	@ 40 °C	@ 45 °C	@ 50 °C
2 ME + water					
0.0315	8.40	10.79	13.03	15.19	16.89
0.0634	8.51	10.84	13.17	15.42	17.00
0.1170	8.70	11.03	13.38	15.66	17.30
0.1701	8.86	11.25	13.63	15.91	17.59
0.2290	9.06	11.48	13.86	16.17	17.89
0.2790	9.23	11.66	14.06	16.41	18.16
0.3178	9.35	11.80	14.23	16.60	18.36
0.3816	9.56	12.05	14.50	16.89	18.68
0.4271	9.72	12.23	14.69	17.10	18.92
2EE + water					
0.0497	6.77	10.01	13.31	16.52	19.15
0.0757	6.87	10.08	13.34	16.57	19.25
0.1161	6.95	10.16	13.47	16.65	19.30
0.1584	7.05	10.29	13.55	16.71	19.39
0.2255	7.24	10.45	13.69	16.85	19.51
0.2559	7.32	10.51	13.75	16.91	19.56
0.3011	7.43	10.63	13.86	17.00	19.65
0.3560	7.58	10.75	13.99	17.11	19.74
0.4106	7.72	10.88	14.10	17.22	19.84
2BE + water					
0.0125	4.86	9.89	15.20	20.27	24.70
0.0356	5.16	10.32	15.51	20.71	24.91
0.0780	5.65	10.87	15.98	21.23	25.42
0.0989	5.95	11.17	16.25	21.51	25.72
0.1325	6.34	11.59	16.70	21.92	26.13
0.1629	6.73	11.97	17.07	22.32	26.54
0.2630	7.98	13.24	18.37	23.63	27.87
0.3398	8.95	14.21	19.35	24.61	28.88
0.4216	9.98	15.26	20.39	25.68	29.97

The ϕ_k (m) is varying linearly relative to molality 'm' in the concentration range studied. The limiting partial molal adiabatic compressibility, ϕ_k° (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 (as used by Millero *et al.*⁷).

$$\phi_v = \phi_v^\circ + S_k m$$

using the method of least squares. As both the values agree well, the least square fit values alone are presented in Table-6. It can be seen from the Table-6 that the ϕ_k° values of each cellosolve increase with increase in temperature. It is also

TABLE-6
PARTIAL MOLAL ADIABATIC COMPRESSIBILITIES AND
EXPERIMENTAL SLOPES OF CELLOSOLVES 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)
2-Methoxy ethanol	30	8.30	3.3
	35	10.62	3.7
	40	12.90	4.2
	45	15.09	4.7
	50	16.70	5.2
2-Ethoxy ethanol	30	6.65	2.6
	35	9.89	2.4
	40	13.19	2.2
	45	16.42	1.9
	50	19.10	1.8
2-Butoxy ethanol	30	4.70	12.5
	35	9.85	12.9
	40	15.02	12.7
	45	20.19	13.0
	50	24.40	13.0

observed from the table, that the ϕ_k^o values decrease at lower temperatures from methoxy ethanol to butoxy ethanol in water. However the reverse trend is observed at higher temperatures (beyond 40 °C). From the above results it may infer that cellosolves (*n*-alkoxy ethanols) are structure making at low temperatures but exhibit structure breaking effect at higher temperatures.

Although some of the studies at 25 °C reveal a slightly hydrophobic nature for *N*-alkoxy ethanols, since the structural interactions are sensitive to temperature it is quite possible that the trend may change at higher temperatures, as was revealed in the temperature effect on adiabatic compressibility minimum (TACM) studies^{13,14}.

The structure breaking nature at higher temperatures reflected in temperature effect on adiabatic compressibility minimum studies was attributed to a reduction of the structure making ability of the alkyl group or to an increase in the structure breaking ability of the ethylene glycol group with increase in temperature. It is interesting to note that when the hydrogen attached to a carbon atom of ethylene glycol is replaced by a methyl group, as in the case of 1,2-propane diol, the solute behaves as structure maker, as reflected in density maximum studies¹⁵. This indicates that when the hydrogen of the hydrocarbon group (or that of the hydroxyl group of ethylene glycol) is replaced by an alkyl group, the resultant

trend is to shift the structural propensity of the substituted glycol towards structure promotion.

It can be observed that the slope (S_k) increases with increase in temperature for 2-ethoxy ethanol and 2-butoxy ethanol while it decreases with increases in temperature for 2-methoxy ethanol (data not shown). The slopes are also found to decrease with functional groups from 2-methoxy ethanol to 2-ethoxy ethanol and increase from 2-ethoxy ethanol to 2-butoxy ethanol.

Table-7 gives the $\partial\phi_k^o/\partial T$ values of all the three cellosolves under study which are in the order of 2-methoxy ethanol < 2-ethoxy ethanol < 2-butoxy ethanol 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 above.

TABLE-7
 $\partial\phi_k^o/\partial T$ VALUES OF CELLOSOLVES

Solute	$\partial\phi_k^o/\partial T \times 10^3$ (mL mol ⁻¹ deg ⁻²)				
	30 °C	40 °C	50 °C	35 °C	45 °C
2-Methoxy ethanol	8.3	12.9	16.7	4.6	3.8
2-Ethoxy ethanol	6.7	13.2	19.1	6.5	5.9
2-Butoxy ethanol	4.7	15.0	24.4	10.3	9.4

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