



SUPPLEMENTARY MATERIAL TO
Thermophysical investigation of glycol ethers in mannitol solutions at various temperatures

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Partial molar volume of transfer

To determine the Transfer of partial molar volume of glycol ethers from water to aqueous solutions of mannitol at infinite dilution, the formula used is

$$\Delta V_{\phi}^0 = V_{\phi}^0(\text{in aqueous d-Mannitol}) - V_{\phi}^0(\text{water}) \quad (\text{SEq1})$$

The partial molar volume of transfer allows for qualitative and quantitative studies of solvent and solute interactions within the mixture, excluding interactions resulting from solute-solute molecules. The results of this parameter are presented in **Table S-I**, revealing that all ΔV_{ϕ}^0 values are positive. This indicates the presence of strong ion-ion interactions between mannitol and glycol ethers, both of which contain polar groups. According to the co-spheres overlap theory, the solute's ability to form structures is enhanced through their interactions in the solution, resulting in a positive value that is attributed to the structural interactions between the two co-spheres.¹⁻² The ΔV_{ϕ}^0 values reflect the different types of interactions in the solution, such as ion-hydrophilic interactions, ion-hydrophobic interactions, hydrophilic-hydrophilic interactions, and hydrophobic-hydrophobic interactions. These values primarily control the solute-solute interactions, which are almost nonexistent in this case. The positive ΔV_{ϕ}^0 values suggest the presence of ion-hydrophilic and hydrophilic-hydrophilic contacts, as indicated by the co-spheres overlap model. On the other hand, ion-hydrophobic and hydrophobic-hydrophobic interactions would have a negative impact on the partial molar volume of transfer. Based on the current investigation of the mannitol-water-glycol ethers system, the findings support the existence of ion-hydrophilic and hydrophilic-hydrophilic interactions.

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Consequently, the results are interpreted as the following interactions-

- i. (hydrophobic-hydrophobic) interactions:
Between the alkyl groups of mannitol and glycol ethers
- ii. (hydrophilic- hydrophobic) interactions:
Between -OH group of mannitol and alkyl group of glycol ethers.
- iii. (hydrophilic-hydrophilic) interactions:
Between -OH group of mannitol and hydrophilic group of glycol ethers
- iv. (ion-hydrophobic) interactions:
Between alkyl groups of mannitol and zwitterions of glycol ethers
- v. (ion- hydrophilic) interactions:
Between -OH group of mannitol and zwitterions of glycol ethers.

It can be seen that the ΔV_{ϕ}^0 values of the solutions are increasing along the concentrations of mannitol at specific temperature. The dominance of (ion-hydrophilic) interactions in the system is established and is increasing with the molar mass of the glycol ethers i.e., from BE to PE as $\Delta V_{\phi}^0(\text{BE}) < \Delta V_{\phi}^0(\text{PE})$.³⁻¹²

Partial molar isentropic compression of transfer

The transfer of partial molar isentropic compression is determined using the undermentioned formula at infinite dilution

$$\Delta K_{\phi,s}^0 = K_{\phi,s}^0(\text{in aqueous d- Mannitol}) - K_{\phi,s}^0(\text{in water}) \quad (\text{SEq 2})$$

The results presented in **Table S-I** reveal that all ($\Delta K_{\phi,s}^0$) values are positive and exhibit an increasing trend with increasing mannitol concentration. However, these values do not follow a consistent pattern with temperature. These findings suggest that the interaction between the zwitterionic center of glycol ethers and mannitol contributes to a structure-making tendency in the ions. This tendency becomes more pronounced as the mannitol concentration increases and the electrostriction decreases. The compressibility of bulk water experiences a significant decrease as the mannitol concentration increases, resulting in positive ($\Delta K_{\phi,s}^0$) values. In contrast, for (BE/PE) at different concentrations of mannitol, the $K_{\phi,s}^0$ values are negative. The cause of this behavior is due to incorporation of more solute water molecules with solvent molecules, leading to increased interactions within the ions. At lower mannitol concentrations and temperatures, the water molecules are more likely to interact with each other, contributing to the negative $K_{\phi,s}^0$ values for (BE/PE).¹³⁻¹⁵

Table S-I. Values of Partial molar volumes of transfer (ΔV_{ϕ}^0), and partial molar isentropic compression transfer, ΔK_{ϕ}^0 of (BE/PE) in aqueous solution of d-Mannitol at different temperatures.

mb/ (mol·kg ⁻¹)	$\Delta V_{\phi}^0 * 106 / (\text{m}^3 \cdot \text{mol}^{-1})$				$\Delta K_{\phi}^0 * 106 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{GPa}^{-1})$			
	288.15 K	293.15 K	298.15 K	303.15 K	288.15 K	293.15 K	298.15 K	303.15 K
	BE							
0.02	0.0844	0.0979	0.0921	0.1046	0.1836	0.1474	0.1824	0.1503
0.06	0.1934	0.1803	0.1713	0.1906	0.4224	0.4000	0.4138	0.4073
0.10	0.2843	0.2864	0.2655	0.2812	0.6328	0.6109	0.6695	0.6671
	PE							
0.02	0.1348	0.1362	0.1262	0.1107	0.1523	0.1165	0.1520	0.1202
0.06	0.2237	0.2174	0.1990	0.1800	0.3909	0.3691	0.3833	0.3771
0.10	0.3339	0.3244	0.2920	0.3097	0.5974	0.5761	0.6350	0.6331

m_b is the concentration of d-mannitol

Temperature dependent partial molar volume

The given equation describes the change in the apparent molar volume at finite dilution corresponding the temperature

$$V_{\phi}^0 = a + b(T - T_{ref}) + c(T - T_{ref})^2 \quad (\text{SEq 3})$$

The constants a , b , and c represent empirical values, and the values of these constants for three types of glycol ethers, where T is the experimental temperature and T_{ref} is the reference temperature, i.e., 298.15 K.

Utilizing these empirical parameters to derive deviations known as ARDs (σ), estimated and experimental values of V_{ϕ}^0 are used to obtain the deviations. These deviations (ARD) are obtained by applying the following relation.

$$\sigma = (1/n) \sum [\text{abs}((Y_{\text{Exptl.}} - Y_{\text{Calc.}})/Y_{\text{Exptl.}})] \quad (\text{SEq 4})$$

Here, $Y = V_{\phi}^0$

After this above-mentioned substitution, equation (9) becomes-

$$\sigma = (1/n) \sum [\text{abs}((V_{\phi, \text{Exptl.}}^0 - V_{\phi, \text{Calc.}}^0)/V_{\phi, \text{Exptl.}}^0)] \quad (\text{SEq 5})$$

To calculate the deviations, we employed equation (10). The present investigation's R^2 results demonstrate that the polynomial equation is fully appropriate, and the deviation values are considerably lower.¹⁶ **Table S-II** displays the values of the empirical parameters (a , b , and c), ARDs (σ), and R^2 . The theoretical values of V_{ϕ}^0 are evaluated using these empirical constants, and they are then compared with the outcomes of the experiments.¹² With regard to temperature, the values of partial molar expansibility E_{ϕ}^0 is obtained by differentiating equation (8) which becomes equation (11), mentioned as below:

$$E_{\phi}^0 = (\partial E_{\phi}^0 / \partial T)_n = b + 2c(T - T_{ref}) \quad (\text{SEq 6})$$

These values are used to determine the partial molar expansibilities at infinite dilution, which is considered to be a significant property for characterizing the interactions between solute and solvent that take place in solution.¹⁴⁻¹⁷ The values of E_{ϕ}^0 are not showing any discrete trend but are all positive, as shown in **Table S-III**, indicating that the volume is decreased following the between the glycol ethers and aqueous mannitol solution.

In order to determine whether solute molecules tend to support or intervene with the structure of the solvent molecules, Hepler proposed a mathematical relationship that is assessed by the following equation.¹⁷

$$\left(\frac{\partial E_{\phi}^0}{\partial T}\right)_{\infty} = \left(\frac{\partial^2 V_{\phi}}{\partial T^2}\right)_{\infty} = 2c \quad (\text{Seq 7})$$

according to Hepler's constant $\left(\frac{\partial^2 V_{\phi}}{\partial T^2}\right)_{\infty}$, even a solute in a solution can operate as a structural forming or deforming agent. Values with positive $\left(\frac{\partial^2 V_{\phi}}{\partial T^2}\right)_{\infty}$ values revealed the structure making property in the solutions. **Table S-III** summarizes the computed $\left(\frac{\partial^2 V_{\phi}}{\partial T^2}\right)_{\infty}$ data for all mixes under investigation. The results showed that $\left(\frac{\partial^2 V_{\phi}}{\partial T^2}\right)_{\infty}$ values for aqueous mannitol solutions containing glycol ethers are positive, demonstrating the solute's ability to promote structure. This is shown by the fact that water molecules develop weak intermolecular contacts with single charged ions with low charge densities, and that these interactions have only a minimal impact on H-bonding. These ions are classified as "structure deformer" or chaotropic ions. On the other hand, stronger interactions with water molecules are produced by charged ions with higher charge densities and can strengthen the H bonding in water structure. These ions are referred to as kosmotropes or "structure-former" ions.¹⁸⁻²¹ Positive or small negative values of $\left(\frac{\partial E_{\phi}^0}{\partial T}\right)_{\infty}$ implies the structure making capability solute, while negative values imply a structure breaker. In summary, the thermodynamic equation provides a measure of the solute's ability to influence the structure of the solution, and the sign of the partial molar expansibility derivative determines whether the solute breaks or builds structures. In Table 8 values of $\left(\frac{\partial E_{\phi}^0}{\partial T}\right)_{\infty}$ are found to be positive which implies the structure making property of glycol ethers in aqueous mannitol solutions.¹⁶⁻²⁵

Table S-II. Values of Empirical parameters (a, b, c) of (BE/PE) in aqueous solution of d-Mannitol.

$^a m_B / (\text{mol} \cdot \text{kg}^{-1})$	$a \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$	$b \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	$c \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$	R ²	ARD
BE					
0.00	116.18813	0.01343	-0.00007	0.9999	0.00043
0.02	116.28039	0.01400	-0.00007	0.9999	0.00044
0.06	116.36480	0.01244	0.00002	0.9999	0.00041
0.10	116.46561	0.01279	-0.00003	0.9999	0.00055
PE					
0.00	133.48155	0.00937	0.00004	0.9999	0.00027
0.02	133.61688	0.00897	-0.00001	0.9999	0.00025
0.06	133.69722	0.00819	0.00000	0.9999	0.00023
0.10	133.79504	0.00764	0.00010	0.9999	0.00029

m_b is the concentration of d-mannitol

Table S-III. Values of Partial molar expansibilities, (E_ϕ^0), and its first derivatives ($(\partial E_\phi^0 / \partial T)_p$) for (BE/PE) in aqueous solution of d-Mannitol at different temperatures.

$^a m_B / (\text{mol} \cdot \text{kg}^{-1})$	$E_\phi^0 \cdot 10^6 / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$				$(\partial E_\phi^0 / \partial T)_p / (\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$
	288.15 K	293.15 K	T298.15 K	303.15 K	
BE					
0.00	0.01474	0.01408	0.01343	0.01277	-0.00013
0.02	0.01537	0.01469	0.01400	0.01332	-0.00014
0.06	0.01214	0.01229	0.01244	0.01259	0.00003
0.10	0.01343	0.01311	0.01279	0.01247	-0.00006
PE					
0.00	0.00864	0.00900	0.00937	0.00973	0.00007
0.02	0.00909	0.00903	0.00897	0.00891	-0.00001
0.06	0.01474	0.01474	0.01474	0.01474	-0.00013
0.10	0.00555	0.00659	0.00764	0.00868	0.00021

m_b is the concentration of d-mannitol

Pair and triplet coefficients

The partial molar volume of transfer (ΔV_ϕ^0) and partial molar isentropic compression of transfer (ΔK_ϕ^0) can be calculated using the given equation, where *A* represents glycol ethers, *B* represents d-mannitol, and m_B is the molality of the aqueous d-mannitol solution. The interaction between the glycol ethers and d-mannitol is characterized by pair and triplet interaction coefficients, denoted by V_{AB} , V_{ABB} , K_{AB} , and K_{ABB} , which are listed in **Table S-IV** and calculated by the undermentioned formula-

$$\Delta V_\phi^0(\text{water to aqueous d- Mannitol solution}) = 2V_{AB}m_B + 3V_{ABB}m_B^2 \quad (\text{Seq 8})$$

$$\Delta K_\phi^0(\text{water to aqueous d- Mannitol solution}) = 2K_{AB}m_B + 3K_{ABB}m_B^2 \quad (\text{Seq 9})$$

The separation of effects in liquid mixtures is examined using the McMillan and Mayer hypothesis, which has been later studied by Krishnan-Friedman, and Franks.²³⁻²⁵ At all temperatures for all glycol ethers, the triplet interaction

coefficient V_{ABB} is negative and the pair interaction coefficient V_{AB} is positive. For, the pair interaction coefficient K_{AB} is positive; however, K_{ABB} it is negative for both glycol ethers, except at 303.15 K for PE. According to this hypothesis of co-sphere, the water is released and enters the bulk, changing the volume.⁴⁻⁵ Given that the water molecules are grouped in distinct structures, the change is positive when the bulk is more structured than the co-sphere and it is negative when the reverse is true. Additionally, because the interaction that took place was a non-bonding one, the water molecules from the hydration co-spheres are released into the bulk. The dominance of pair-wise interactions in the current investigation is established by the higher positive values of the pair interaction coefficients in the mixture of (mannitol + water + PE/ BE) compared to the triplet interaction coefficients.^{26, 27}

Table S-IV. Pair (V_{AB} , K_{AB}) and triplet (V_{ABB} , K_{ABB}) of (BE/PE) in aqueous solutions of d-Mannitol at different temperatures

T/K	$V_{AB} * 10^6$ ($m^3 \cdot mol^{-2} \cdot kg$)	$V_{ABB} * 10^6$ ($m^3 \cdot mol^{-3} \cdot kg^2$)	$K_{AB} * 10^6$ ($m^3 \cdot mol^{-2} \cdot kg \cdot GPa^{-1}$)	$K_{ABB} * 10^6$ ($m^3 \cdot mol^{-3} \cdot kg^2 \cdot GPa^{-1}$)
BE				
288.15	2.02	-4.08	4.35	-8.04
293.15	1.97	-3.75	3.78	-4.86
298.15	1.90	-3.95	4.02	-4.66
303.15	2.21	-5.53	3.61	-1.87
PE				
288.15	2.70	-7.10	3.78	-5.33
293.15	2.68	-7.29	3.22	-2.21
298.15	2.49	-7.12	3.47	-2.04
303.15	1.97	-3.06	3.06	0.71

T/K is the temperature

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