Thermodynamics of aqueous polyethylene-glycol (PEG) solutions at 298.15 K: Activity, activity coefficients and application of molecular theories

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ABSTRACT

Osmotic coefficients measured by vapor pressure osmometry are reported for aqueous polyethylene-glycol (PEG-400, PEG-1000, and PEG-4000) solutions. The derived properties such as activity and activity coefficients have been studied as a function of solute concentration. These data along with the partial molar volume data have been analyzed with the help of molecular theories such as Flory–Huggins, McMillan–Mayer, and Kirkwood–Buff. The application of these theories enabled us to obtain second virial coefficients of PEG's, the number of binding sites, χ_{12} (Flory–Huggins interaction parameter), and the Kirkwood–Buff (KB) integrals, defined by the equation: $Gij = \int_0^\infty (g_{ij} - 1)4\pi r^2 dr$. The highlight of the work is the observation that microheterogeneity in solution increases as the chain length of solute molecule increases [estimated through mean square concentration fluctuation $N\langle(\Delta x)^2\rangle$ and non-ideality (F) parameters], confirming the concept of solute association through hydrophobic interactions in aqueous solutions.

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1. Introduction

The peculiar thermodynamic properties of aqueous solutions of small molecules like rare gases, hydrocarbons, alcohols, amines, and diols can be measured to extreme dilutions and can be treated in a quantitative manner with the help of molecular theories like Kirkwood–Buff and McMillan–Mayer theories of solutions [1–9]. The concept of hydrophobic interaction introduced and developed by Kauzmann [10] and latter amplified by Ben-Naim [11] and others [12,13] has been found to be useful to understand aqueous solutions of supramolecules like crown-ethers, cyclodextrin and as well the solutions containing micellar equilibria [14–19]. In general water structural effects such as water structure making and breaking, hydrogen bonding between water and polar group of the solute, and hydrophobic interaction, that is, attraction between non-polar groups or moieties have been involved in affecting the excess free energy, enthalpy and partial molar entropy profiles as a function of concentration of solute in aqueous solutions. In dilute solutions of mono-functional solutes, hydrophobic hydration and followed by hydrophobic association (interaction) at higher concentration affect the properties showing maxima or minima as a function of solute concentration

[6,20]. Recently, Franks wrote in his book on water, that the competition between hydrophobic and direct hydration (hydrogen-bonding) effects plays a basic role in biology and many branches of technology [21]. Phase behavior, rheological properties of concentrated solutions and micellization, etc. all depend on this phenomenon which is peculiar to water as a solvent [22,23]. We thought to test such hypothesis; studies of aqueous solution of small oligomeric polymers of the type of polyethylene-glycols can be useful. As such the thermodynamic properties of water-soluble oligomers and polymers have been studied with special reference to application of Flory–Huggins lattice energy [24,25]. The interactions are accounted in terms of specific hydration model [26]. However at higher concentrations because of hydrophobic interactions many anomalies in the form of extrema occur for variety of properties and in extreme cases, phase separation or LCST, etc. occur [27,28].

In the last decade or so, we have developed the methodology of obtaining molecular weights, second virial coefficients, activity and activity coefficients of medium sized compounds like crown-ethers, cyclodextrins [15–19,29] in aqueous solutions by making measurements of osmotic coefficient and densities with the help of vapor pressure osmometer and digital densitometer. In this article, we describe the application of these techniques and measurements for the studies of the hydration of oligomers or polymers in aqueous solutions at 298.15 K. We have chosen the solutes: PEG-400, PEG-1000 and PEG-4000 for

our studies. These belong to a general class of polymers as polyethylene-glycols having structural units as: $-HO - CH_2 - [-CH_2 - O - CH_2-]_n - CH_2 - OH-$.

PEGs chosen are soluble in water and in case of PEG-4000, a solution upto 0.2 $mol \cdot kg^{-1}$ can be prepared at 298.15 K. The most wide-spread use of PEG aqueous solutions is in protein crystallization and cell fusion processes [30]. Also, investigation of local structure of water in aqueous polymeric solutions is of scientific relevance motivated by the interest in the role of H-bonding in the peculiar properties of water and its ability to interact with polymer chains giving rise to a large cluster formation or networking [31]. From this point of view, because of simple molecular structures PEGs represent an appropriate model system for the study of water structuring and other types of interaction in aqueous macromolecular solutions.

We report in this communication, the osmotic coefficient data for aqueous PEG-400, PEG-1000, and PEG-4000 solutions in the concentration range of [(~0.01 to ~0.48) $mol \cdot kg^{-1}$] at 298.15 K. The data are used to obtain the activity of solvent water and the activity coefficients of PEGs using appropriate methodology. The free energy changes due to mixing and excess free energy changes are calculated. The further analysis is made by applying three theories of solutions namely Flory–Huggins, McMillan–Mayer and Kirkwood–Buff to obtain second virial coefficients, number of binding sites, concentration variation of KB integrals and mean square concentration fluctuation $N\langle(\Delta x)^2\rangle$. The results are presented in the following pages and discussed in terms of solute–solvent and solute–solute (polymer–polymer) interactions.

2. Experimental

The chemicals polyethylene-glycol (PEG-400, PEG-1000 and PEG-4000), NaCl, and Sucrose were procured from Merck. The actual molecular weights estimated by using osmometry were found to be 405, 1022, and 4131 $g \cdot mol^{-1}$ for PEG-400, PEG-1000 and PEG-4000 respectively. These were used for calculations of concentrations in terms of molality or mole-fraction. The NaCl and Sucrose were dried in vacuum-oven for 10–12 h at 393 K before use. For preparation of solutions double quartz distilled water was used. All the weights were taken on the high precision analytical balance (Model: Mettler Toledo-AB204-S) having capacity to weigh minimum of 10 mg, maximum of 220 mg and with a readability of 0.1 mg. Solutions were made in a concentration range of [(~0.04 to ~0.47) $mol \cdot kg^{-1}$], [(~0.03 to ~0.48) $mol \cdot kg^{-1}$] and [(~0.01 to ~0.09) $mol \cdot kg^{-1}$] for PEG-400, PEG-1000, and PEG-4000 respectively. The molality concentrations were converted to other concentration scales such as molarity using density data.

The density measurements of aqueous solutions of PEG's were made using Anton Paar Digital Densitometer (Model: DMA 602) at 298.15 K. The osmotic coefficient (ϕ) of aqueous PEG's solutions were measured using a Knauer Vapor Pressure Osmometer (Model: K-7000) at 298.15 having temperature control of ± 0.001 K. The uncertainty in ϕ measurements was found to be better than $\pm 1 \cdot 10^{-3}$. The details about the density and osmotic coefficient measurements are given in our earlier publications [15,18,19,26].

3. Results and discussion

The data of osmotic coefficients (ϕ) in aqueous solutions for PEGs are represented by the following equations as:

$$\text{For PEG}-400: \quad \phi = 1 + 1.4341x_2 + 9815.3x_2^2 \tag{1}$$

$$\text{For PEG}-1000: \quad \phi = 1 + 264.23x_2 - 1735.8x_2^2 \tag{2}$$

$$\text{For PEG}-4000: \quad \phi = 1 + 1230.4x_2 + 3 \cdot 10^6 x_2^2 - 6 \cdot 10^8 x_2^3 \tag{3}$$

where x_2 is the mole-fraction of PEG.

It is observed that ϕ values are positive and high in magnitude for PEG-1000 and PEG-4000 respectively. One may ask the validity of osmometry technique to such a data based on colligative properties. However, we accept the experimental data and attribute the trend of increasing ϕ as a function of molality or mole-fraction to association of PEG-molecules.

The solvent activities (a_w) were calculated from the experimental osmotic coefficient data by making use of the following equation

$$\ln a_w = -\phi\left(\frac{x_2}{x_1}\right) \tag{4}$$

where x_1 is the mole-fraction of water.

The thermodynamic data of molality (m), solute mole-fraction (x_2), density (d), osmotic coefficient (ϕ), and water activity (a_w) are collected in Table 1. The variations of ϕ and a_w as a function of mole-fraction of solute for the three systems are shown in Figs. 1 and 2 respectively.

The density data have been used to compute apparent molar volumes (ϕ_V) of the PEGs. The data is in good agreement with the data previously reported [32]. The partial molar volume of PEGs ($\overline{V}_2$) is estimated using

$$\overline{V}_2 = \phi_V + m\frac{\delta\phi_V}{\delta m} \tag{5}$$

The partial molar volume of solvent ($\overline{V}_1$) is calculated using Gibb's–Duhem equation. The data of partial molar volumes ($\overline{V}_1 \text{ and } \overline{V}_2$) are collected in Table 1. The variation of $\overline{V}_2$ as a function of concentration (m) is shown for all the solutes in Fig. 3. The partial molar volumes of the solute ($\overline{V}_2$) if written as $\overline{V}_2 = \overline{V}_2^0 + B_V m$, show that B_V parameter is negative for all the solutes and $\overline{V}_2$ go through a minimum at 0.22, 0.20 and 0.07 $mol \cdot kg^{-1}$ for PEG-400, PEG-1000, and PEG-4000 respectively. The negative magnitude of Bv signifies the effects due to solvent induced solute–solute association and water structure making effect in solution phase. The $\overline{V}_2^0$ which depend upon solute–solvent interaction and were obtained by smooth extrapolation to infinite dilution of the solute molality.

The activity coefficients of PEG's (γ_2) were estimated using the osmotic coefficient data and Eq. (6).

$$\ln \gamma_2 = (\phi - 1) + \int_0^m (\phi - 1) d \ln m \tag{6}$$

The activity coefficient of solute (γ_2) thus obtained is converted to mole-fraction scale activity coefficient (f_2). The data of activity coefficient of water (γ_1) and activity coefficient of solute (f_2) on mole-fraction scale are collected in Table 1. We obtained high values of activity coefficients for the solutes at finite concentrations which are very unusual but probably signify the multiple solute association equilibria.

The activity coefficient data obtained for both the components have been used to obtain the free energy due to mixing (ΔG^M) and excess free energy change (ΔG^E) in solution by using the Eqs. (7) and (8) respectively.

$$\Delta G^M = RT \sum_{i=1}^{2} x_i \ln a_i \tag{7}$$

$$\Delta G^E = RT \sum_{i=1}^{2} x_i \ln \gamma_i \tag{8}$$

The data of ΔG^M and ΔG^E are incorporated in Table 1. These are also shown graphically in Figs. 4 and 5. It is observed that ΔG^M are negative in all the studied systems, but in PEG-4000, the values go