

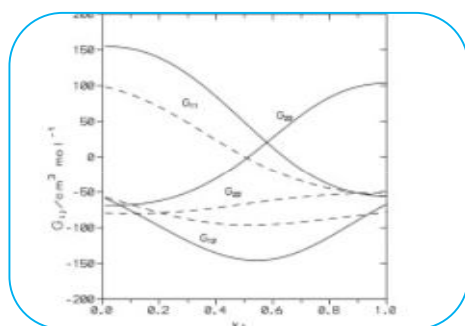


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## APPLICATIONS OF KIRKWOOD BUFF THEORY TO PEG

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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 Kirkwood–Buff. The application of these theories enabled us to obtain second virial coefficients of PEG's, the number of binding sites,  $\chi_{12}$  (Flory–Huggins interaction parameter), and the Kirkwood–Buff (KB)

integrals.

**KEYWORDS:** PEG, Osmotic Coefficients.

### 1. INTRODUCTION

We report in this communication, the osmotic coefficient data for aqueous PEG-400, PEG-1000, and PEG-4000 solutions in the concentration range of  $[(\sim 0.01 \text{ to } \sim 0.48) \text{ mol} \cdot \text{kg}^{-1}]$  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  $\text{g} \cdot \text{mol}^{-1}$  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  $[(\sim 0.04 \text{ to } \sim 0.47) \text{ mol} \cdot \text{kg}^{-1}]$ ,  $[(\sim 0.03 \text{ to } \sim 0.48) \text{ mol} \cdot \text{kg}^{-1}]$  and  $[(\sim 0.01 \text{ to } \sim 0.09) \text{ mol} \cdot \text{kg}^{-1}]$  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 activity coefficient of solute ( $\gamma_2$ ) thus obtained is converted to mole-fraction scale activity coefficient ( $f_2$ ). The data of activity coefficient of water ( $\gamma_1$ ) and activity coefficient of solute ( $f_2$ ) on mole-fraction scale are collected. 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 ( $\Delta G^M$ ) and excess free energy change ( $\Delta G^E$ ) in solution.

The data of activity coefficient along with partial molar volumes of PEG's in aqueous solutions have been used to evaluate the KB integrals by means of the following equations

$$G_{AB}(A \neq B) = G_{BA} = RTK_T - V_1 V_2 / DV$$

### 3. RESULT:

The trends of KB integral parameter with concentration indicate that for small molecular weight compound PEG-400, both hydrophobic hydration and interaction contribute to the thermodynamic properties while for higher molecular weight PEGs, hydrophobic interactions persist upto the lowest concentration studied and of which strength increases with increase in concentration. The magnitudes of second virial coefficients are positive which increase with molecular weight of PEGs. The attractive contributions to the virial coefficient are negative for higher PEGs, while the same is similar for solute-solvent interaction as that of partial molar volumes of PEGs. The studies of concentration fluctuation parameter and non-ideality show presence of micro-heterogeneity, the extent depends upon the chain length of PEG molecules in solution phase.

Limiting values of Kirkwood-Buff integrals and values of second virial coefficients for aqueous PEG's at 298.15 K.

	$10^3 G_{AB}^0$ /mm <sup>3</sup> ·mol <sup>-1</sup>	$10^3 G_{AA}^0$ /mm <sup>3</sup> ·mol <sup>-1</sup>	$10^3 G_{BB}^0$ /mm <sup>3</sup> ·mol <sup>-1</sup>	$10^3 NB_2$ * /mm <sup>3</sup> ·mol <sup>-1</sup>
PEG-400	-346	16.94	-810	405
PEG-1000	-865	-16.94	-10,777	5389
PEG-4000	-3329	-16.	92 -63,633	31,817

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