INTERFACIAL TENSION ON MOLECULAR INTERACTION IN N-ETHYL-2-PYRROLIDONE WITH ETHANOLAMINE/ DIETHANOLAMINE AND TRIETHANOLAMINE SYSTEMS

Abstract

Author

The surface tension of binary mixtures of n-ethyl-2-pyrrolidone with ethanolamine, diethanolamine, and triethanolamine was calculated using theoretical models including the Sudgen method, Hildebrand-Scott theories for ideal solutions (HSIS), extensions of Guggenheim's equation (HSEG), Volume Fraction Statistics, Auerbach relation, and Sanchez method at temperatures ranging from 293.15 K to 313.15 K. An equation based on the Redlich-Kister polynomial was used to correlate the excess surface tension using theoretical models. In addition, surface tension measurements were used to determine surface entropy, surface enthalpy, and lyophobicity factor.

Keywords: Surface tension; n-ethyl-2 pyrrolidone; alkanolamines; models; lyophobicity.

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I. INTRODUCTION

Interfaces play an apparent role in every aspect of our lives. The development in the surface chemistry domain has produced innumerable possibilities across a wide range of fields, such as pharmaceuticals, biotechnology, and biomedical science, where interfaces play a critical role. Understanding surface tension is crucial for overcoming obstacles and creating intriguing, better-performing goods. In a specific dimension, surface characteristics and their adaptation are crucial because surface science addresses chemical reactions at an interface between two phases. This paper discusses how surface tension is used to investigate intermolecular interactions existing between solute-solute, solute-solvent and solvent-solvent molecules in binary mixtures of n-ethyl-2-pyrrolidone with ethanolamine/ diethanolamine and triethanolamine.

There is typically a significant distinction in compositions across the liquid's bulk region and the surface region owing to an enrichment of molecules with lower surface tension in the surface region. Surface enrichment is exposed to the relationship between the geometry, dimension, orientation, and length of the chain of the molecule [1-3]. For the absorption of carbon dioxide during the gas purification process, N-ethyl-2-pyrrolidone is an appropriate solvent. The use of tertiary amines, such as ethanolamine, diethanolamine, and triethanolamine, to remove carbon dioxide and acid gases is made possible by their high absorption capacity and little power regeneration costs [4, 5].

As a follow-up of our prior studies [6–15], this paper states the surface tension values of binary blends of n-ethyl-2-pyrrolidone with ethanolamine, diethanolamine, and triethanolamine using a variety of theoretical models, including the Sudgen method [16], Hildebrand-Scott theories for ideal solutions (HSIS), and Hildebrand-Scott theories extensions of Guggenheim's equation (HSEG) [17], as well as the Volume Fraction Surface tension experimental data were collected from the literature [21]. Using theoretical models, excess surface tension E was calculated and fitted to the Redlich-Kister polynomial equation [22]. Additionally, the extended Langmuir model was used to determine surface entropy S^S , enthalpy H^S per unit surface area and lyophobicity β for the systems under study.

II. THEORY

Using six distinct theoretical models at various concentrations and temperatures, the present work estimates the surface tension of binary mixtures of n-ethyl-2-pyrrolidone with ethanolamine, diethanolamine, and triethanolamine.

1. Surface Tension Models

- Sudgen [16] revised the MacLeod's equation [23] using parachor P, a temperature independent parameter [24, 25] to obtain the surface tension of liquid mixtures.
- Hildebrand and Scott proposed the HSIS model [17].

- The HSEG model was proposed [17] using Guggenheim's ideal solution equation and taking into account the molecules' various sizes. It is believed that the HSIS and HSEG models fit quasi-spherical molecules effectively.
- Volume Fraction statistics was projected by Goldsach and Sarvas [18] to attain the values of surface tension.
- Auerbach relation gives the simplest expression for calculating surface tension as [19]:

$$
\sigma = 6.3 \times 10^{-4} \, u^{3/2} \, \rho \tag{1}
$$

Sanchez method uses the values of isothermal compressibility β_T and density ρ of the liquid to deduce surface tension as [20]:

$$
\sigma = \frac{\left(A_0^{1/2}\right)}{\left(\beta_{T,m}/\rho\right)^{1/2}}\tag{2}
$$

where,

$$
\beta_{T,m} = \sum_{i=1}^{2} \varphi_i \cdot \beta_{T,i} \tag{3}
$$

$$
A_0 = \sum_{i=1}^3 x_i A_i^{1/2} \tag{4}
$$

$$
A_i = \sigma_i^2 \left(\beta_{T,i} / \rho_i \right) \tag{5}
$$

The excess values of surface tension σ^E using the six different methods were calculated and fitted to the Redlich-Kister polynomial equation as [22]:

$$
\sigma^E = x_1 x_2 \sum_{k=0}^n B_k (2x_1 - 1)^k
$$
\n(6)

where,

 B_k represent Redlich-Kister coefficients and SD refers to the standard deviation.

• **Interfacial thermodynamics:** According to the thermodynamic equation given by Clapeyron to determine the surface enthalpy per unit surface area and surface entropy per unit surface area HS for liquid mixes as a result of interface creation is as follows [26–29]:

$$
SS = -(\partial \sigma / \partial T)P
$$

\n
$$
HS = \sigma - T(\partial \sigma / \partial T)P
$$
\n(3)

Surface tension of binary liquid mixtures is revealed by the extended Langmuir model [30] which depends on the bulk composition. According to this paradigm, the surface is a thin membrane with a definite thickness. At a state of equilibrium, the relationship between the volume fraction of the solute in this layer and its bulk volume fraction and lyophobicity is as follows:

$$
\varphi_2^S = \frac{\beta \varphi_2}{1 + (\beta - 1)\varphi_2} \tag{9}
$$

Where, is a measure of lyophobicity of the component 2 (ethanolamine) diethanolamine/ triethanolamine) with respect to the component 1 (n-ethyl-2 pyrrolidone), φ_1 is bulk volume fraction of the component 1. The slope of $\left(\frac{\sigma - \sigma_1}{\sigma_2 - \sigma}\right)$ versus $\left(\frac{\varphi_2}{\varphi_1}\right)$ gives the value of lyophobicity β [30].

III. RESULTS AND DISCUSSION

The surface tension of binary mixtures of EP with MEA/ DEA and TEA were estimated using theoretical models viz., Sudgen method, HSIS model, HSEG model, Volume Fraction Statistics, Auerbach relation and Sanchez method at temperatures 293.15 K to 313.15 K over the whole composition range and listed in Tables 1-3, respectively. The values of surface tension using all the six models are found to decrease linearly with composition as well as temperature. The excess surface tension using the theoretical models were fitted to Redlich-Kister polynomial equation and shown as Figs. 1-7, for all the binary systems. The Redlich-Kister coefficients B_k and standard deviation SD are listed in Table 4. The average percentage deviations APDs from the six theoretical models are also listed in Table 5. The values of surface entropy S^S and surface enthalpy H^S per unit surface area are plotted as a function of concentration of EP (Fig. 8). The values of lyophobicity factor β at 293.15 to 313.15 K for the three binaries are recorded in Table 6.

Figures 1-7 display the variation of excess surface tension with increasing concentrations of EP at varying temperatures and atmospheric pressure for the three binary systems. The values of σ^E are found to be non-linear and negative over the entire composition range for EP with MEA/ DEA mixtures using all the methods except Auerbach relation which shows an S-shaped trend. For EP + TEA system, σ^E shows a negative and nonlinear trend using Sudgen, Auerbach an and Sanchez method while an S-shaped profile is observed using HSEG and HSIS models while positive σ^E variations are observed using volume fraction statistics at all temperatures. In the mixture EP + MEA/ DEA/ TEA, σ^E becomes less negative as the chain length of the aminoalcohols increase.

The excess surface tension primarily rests on the two key features i.e., the surface region and the bulk region. The close proximity of surface and bulk behaviour affects the surface tension of liquid mixtures which consequently can be examined in terms of the intermolecular interaction and structural effects occurring during mixing. The physical effects and dipolar–dipolar interaction suggest a negative contribution to the excess surface tension values, but some stronger interactions like chemical associations may affect the surface thermodynamics such as structural changes of the component species, attraction or repulsion between the unlike molecules, credited to stronger interactions lead to a positive contribution [31, 32]. Such interactions can cause the more surface-active component to remain in the bulk phase leading to positive excess surface tension values [33].

It has been experimentally observed that the magnitude of the interaction of EP with TEA is stronger than the interaction of EP with DEA and MEA. On the basis of available data, it is suggested that the magnitude of hydrogen bonding between EP and TEA having three hydroxyl (-OH) functions makes the developed system more stable. Thus, three molecules of EP are involved per molecule of TEA in the formation of the developed structures. An alternative possibility is the formation of hydrogen bonds between HO- and - OH groups. Since, EP possesses an α-hydrogen atom in its molecular architecture, the generated enol will be more reactive. Since, enols are more reactive than -C=O, this possibility seems more likely. Extent of bonding with DEA involves only two molecules and for MEA only one and therefore gives comparatively weaker interactions. It appears that the basicity of the amino alcohols contributes negligibly in deciding the magnitude of interactions.

The average percentage deviation APDs obtained for all the binary systems (Table 5) show the applicability of Sudgen, HSEG, HSIS, volume fraction statistics, Auerbach and Sanchez method being in good agreement with the experimental findings.

Surface entropy S^S measures the discrepancy in entropy or disorder per unit surface area due to the formation of an interface and is equal to the negative temperature coefficient of surface tension. Figure 8 reveals that the surface entropy S^S increases linearly with increasing concentration of EP for EP + DEA and EP + TEA systems but decreases almost steadily with composition for $EP + MEA$ system. Surface enthalpy H^S is the total surface free energy needed to spread the surface and the latent heat required to sustain isothermal state. If the plot of surface enthalpy against composition is a protruding curve, then physical effects are prevalent in the binary system. However, if surface enthalpy versus composition is a concave curve, a chemical hetero-association is ubiquitous in the binary system. The surface enthalpy H^S is almost linearly decreasing with the composition of EP for EP + MEA system (Fig. 8). H^S shows a concave curve for EP + DEA and EP + TEA systems which is indicative of the formation of EP -DEA/ TEA aggregates at surface formation [31]. The tendency of S^S or H^S for the EP + MEA system is almost linear, which suggests there is no aggregate complex formation rather weak interactions dominate [34].

The lyophobicity factor β affects the nature of surface tension. Examining the behaviour of surface phase in the binary liquid mixtures require a possible complex formation between the EP and MEA/ DEA/ TEA molecules in the liquid phase. Subsequently, the molecules with lower surface tension move towards the free surface of the liquid. The lyophobicity of the surfactant molecules MEA/ DEA/ TEA with respect to EP molecule exposes it to be adsorbed by the surface (Table 6). Generally, values of $\beta \approx 1$ exemplify the equal affinity of the surfactant molecules for both the bulk phase region and the surface, though $\beta > 1$ confides to the greater affinity of the surfactant molecules for the surface. Table 6 shows $\beta > 1$ confirming the greater affinity of MEA/ DEA/ TEA for the surface. The value of β is highest for MEA followed by DEA and TEA. The probable reason for this may be due to the increased hydrocarbon chain in aminoalcohol molecules [35]. In addition, the self-association of monomers decrease with the increase in the hydrocarbon chain [31, 35].

IV. CONCLUSIONS

Using six theoretical models, the excess surface tension for combinations of n-ethyl-2-pyrrolidone and ethanolamine, diethanolamine, and triethanolamine was calculated in the temperature range from 293.15 to 313.15 K. The downward, nonlinear pattern of σ^E supports the existence of particular intermolecular interactions between the constituents of the binary liquid combination. Additionally, the surface enthalpies and entropies per unit surface area were calculated. Using the extended Langmuir model, the lyophobicity of the surfactants MEA, DEA, and TEA was calculated, demonstrating their higher surface affinities.

V. CONFLICT OF INTEREST

The author declares no potential conflict of interest.

VI.FUNDING

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VII. AUTHOR CONTRIBUTION

Conceptualization; Data curation; Formal analysis; Investigation; Software; Validation; Visualization; Writing – original draft; Writing – review & editing.

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Table 1: Values of Surface tension for EP (1) + MEA (2) system.

0.7002	39.3	38.5	39.1	39.2	38.0	39.4
0.7999	38.3	37.8	38.1	38.2	37.6	38.4
0.8997	37.3	37.1	37.2	37.3	37.2	37.4
1.0000	36.5	36.5	36.5	36.5	36.5	36.5
303.15 K						
0.0000	47.8	47.8	47.8	47.8	47.8	47.8
0.1000	46.5	45.2	46.2	45.9	42.9	45.7
0.2002	44.9	43.2	44.6	44.2	41.1	44.0
0.2999	43.9	41.5	43.0	42.7	39.8	42.5
0.4002	41.9	40.1	41.6	41.3	38.7	41.2
0.4999	40.3	39.0	40.2	40.0	37.8	40.0
0.5996	38.9	38.0	38.9	38.9	36.9	38.9
0.7002	37.8	37.2	37.8	37.8	36.3	37.9
0.7999	36.9	36.4	36.8	36.9	35.9	37.0
0.8997	36.0	35.8	35.9	36.0	35.5	36.1
1.0000	35.2	35.2	35.2	35.2	35.2	35.2
313.15 K						
0.0000	47.1	47.1	47.1	47.1	47.1	47.1
0.1000	45.7	44.5	45.4	45.2	41.3	44.9
0.2002	44.1	42.4	43.8	43.4	39.5	43.1
0.2999	42.5	40.7	42.2	41.9	38.2	41.6
0.4002	41.0	39.3	40.7	40.5	37.2	40.3
0.4999	39.4	38.1	39.3	39.2	36.2	39.1
0.5996	38.0	37.1	38.0	38.0	35.2	38.0
0.7002	36.9	36.2	36.9	36.9	34.7	36.9
0.7999	35.9	35.5	35.8	35.9	34.3	36.0
0.8997	35.0	34.8	34.9	35.0	33.9	35.1
1.0000	34.2	34.2	34.2	34.2	34.2	34.2

Table 2: Values of Surface tension for EP (1) + DEA (2) system.

0.8995	37.2	37.1	37.2	37.4	37.7	37.2
1.0000	36.5	36.5	36.5	36.5	36.5	36.5
303.15						
$\mathbf K$						
0.0000	46.6	46.6	46.6	46.6	46.6	46.6
0.1000	45.0	44.8	45.0	45.2	46.4	44.9
0.2005	43.5	43.2	43.6	43.8	44.5	43.4
0.3001	42.2	41.8	42.2	42.5	42.8	42.0
0.4002	40.9	40.5	40.9	41.3	41.3	40.8
0.4999	39.7	39.4	39.7	40.2	40.0	39.6
0.6000	38.6	38.3	38.6	39.1	38.8	38.6
0.7001	37.6	37.4	37.6	38.0	37.8	37.7
0.8001	36.7	36.6	36.7	37.0	36.9	36.8
0.8995	35.9	35.9	35.9	36.1	36.0	36.0
1.0000	35.2	35.2	35.2	35.2	35.2	35.2
313.15						
$\mathbf K$						
0.0000	46.0	46.0	46.0	46.0	46.0	46.0
0.1000	44.3	44.2	44.4	44.5	45.0	44.2
0.2005	42.8	42.5	42.9	43.1	43.1	42.6
0.3001	41.4	41.0	41.4	41.7	41.4	41.2
0.4002	40.1	39.7	40.1	40.5	39.9	39.9
0.4999	38.8	38.5	38.8	39.3	38.5	38.7
0.6000	37.7	37.4	37.7	38.2	37.3	37.7
0.7001	36.7	36.5	36.7	37.1	36.2	36.7
0.8001	35.8	35.6	35.7	36.1	35.4	35.8
0.8995	34.9	34.9	34.9	35.1	34.4	35.0
1.0000	34.2	34.2	34.2	34.2	34.2	34.2

Table3: Values of Surface tension for EP (1) + TEA (2) system.

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Table 4: Coefficients (Bi) and standard deviations (SD) for σ E using Redlich-Kister Equation

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Table 5: Average Percentage Deviations (APD) between experimental surface tension and theoretical models

Table 6: Lyophobicity factor (β) for the binary systems

Figure 1: Variation of excess surface tension, σ^E against mole fraction, x_1 of EP for (**a**) EP + MEA (**b**) EP + DEA and (**c**) EP + TEA at T= 293.15 K (\circ), 303.15 K (\bullet), 313.15 K (\blacktriangle) and 323.15 K (**×**). The solid lines represent values calculated from Redlich-Kister equation.

Figure 2: Variation of excess surface tension, σ^E (Sudgen method) against mole fraction, x_1 of EP for (**a**) $EP + MEA$ (**b**) $EP + DEA$ and (**c**) $EP + TEA$ at $T = 293.15$ K (\circ), 303.15 K (\bullet), 313.15 K (▲) and 323.15 K (**×**). The solid lines represent values calculated from Redlich-Kister equation.

Figure 3: Variation of excess surface tension, σ^E (HSEG method) against mole fraction, x_1 of EP for (**a**) EP + MEA (**b**) EP + DEA and (**c**) EP + TEA at T= 293.15 K (○), 303.15 K (), 313.15 K (▲) and 323.15 K (**×**). The solid lines represent values calculated from Redlich-Kister equation.

Figure 4: Variation of excess surface tension, σ^E (HSIS method) against mole fraction, x_1 of EP for (**a**) EP + MEA (**b**) EP + DEA and (**c**) EP + TEA at T= 293.15 K (\circ), 303.15 K (\bullet), 313.15 K (▲) and 323.15 K (**×**). The solid lines represent values calculated from Redlich-Kister equation.

Figure 5: Variation of excess surface tension, σ^E (Volume fraction) against mole fraction, x_1 of EP for (**a**) EP + MEA (**b**) EP + DEA and (**c**) EP + TEA at T= 293.15 K (○), 303.15 K (), 313.15 K (▲) and 323.15 K (**×**). The solid lines represent values calculated from Redlich-Kister equation.

Figure 6: Variation of excess surface tension, σ^E (Auerbach) against mole fraction, x_1 of EP for (**a**) EP + MEA (**b**) EP + DEA and (**c**) EP + TEA at T= 293.15 K (\circ), 303.15 K (\bullet), 313.15 K (▲) and 323.15 K (**×**). The solid lines represent values calculated from Redlich-Kister equation.

Figure 7: Variation of excess surface tension, σ^E (Sanchez) against mole fraction, x_1 of EP for (**a**) EP + MEA (**b**) EP + DEA and (**c**) EP + TEA at T= 293.15 K (\circ), 303.15 K (\bullet), 313.15 K (▲) and 323.15 K (**×**). The solid lines represent values calculated from Redlich-Kister equation.

Figure 8: Variation of Surface entropy, S^S and Surface enthalpy H^S against mole fraction, x_1 of EP for (**a**) $EP + MEA$ (\circ) (**b**) $EP + DEA$ (\bullet) and (**c**) $EP + TEA$ (Δ).