Computation of excess isentropic compressibility via Flory's statistical theory to investigate molecular interactions in n-alcohol–benzylamine mixtures

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ABSTRACT

Excess isentropic compressibility is a key thermodynamic property that offers valuable insight into molecular interactions within liquid mixtures. Understanding these interactions is crucial for characterizing solution structure, designing chemical processes, and developing predictive thermodynamic models. Statistical models play a vital role in interpreting thermodynamic behavior by connecting macroscopic properties with molecular-level interactions. They allow for the prediction and analysis of complex mixture behavior while minimizing the need for extensive experimental data. In this study, the excess isentropic compressibility of n-alcohol–benzylamine mixtures across various compositions was computed using the Flory statistical model. This model requires only minimal input data, specifically, the thermal expansion and isothermal compressibility of the pure components. The computed values were used to assess molecular interactions within the mixtures. A negative deviation in isentropic compressibility was observed, indicating stronger interactions between unlike molecules (i.e., α-alcohol and benzylamine) than between like molecules. The close agreement between experimental and calculated values confirms the effectiveness of this theoretical approach for analyzing molecular interactions. Overall, the method provides a reliable and efficient means to compute excess isentropic compressibility and investigate liquid mixture behavior.

Keywords: Isentropic compressibility, Thermal expansivity, Molecular interaction, Flory statistical theory, n-Alcohol-benzylamine mixture.

1. INTRODUCTION

Excess isentropic compressibility (β_S^E) is the difference between the isentropic compressibility of a mixture of a given composition and its ideal isentropic compressibility. The ideal isentropic compressibility (β_S^{id}) of a mixture is an average isentropic compressibility of its pure components, assuming no interaction between the molecules. The magnitude of β_S^E reflects deviations from ideal behavior due to molecular interactions like hydrogen bonding or dipole–dipole forces in mixtures. This property is significant for understanding the thermodynamic behavior and molecular interactions in a liquid mixture. Excess isentropic compressibility (β_S^E) has long been employed to investigate molecular interactions and the extent of complex formation in liquid mixtures. In addition to experimental determination, it can also be estimated theoretically using minimal input data. Common methods for determining β_S^E include density measurements using a densimeter or pycnometer, direct measurement of excess molar volume with a dilatometer, and theoretical calculations supported by ultrasonic velocity measurements obtained via an ultrasonic interferometer. A review of the literature reveals that a significant amount of work has been dedicated to measuring β_S^E and utilizing it to interpret molecular interactions in various liquid systems.

Blandamer and Waddington [1] analyzed sound velocity in terms of excess isentropic compressibility (β_S^E) in alcohol + water and alkyl cyanide + water systems. However, Bertrand and Smith [2] criticized the relation they used for the computation of β_S^E. Kiyohara et al. [3] investigated β_S^E and other thermodynamic properties in binary liquid mixtures containing carbon tetrachloride, cyclohexane, and benzene. Oswal [4] calculated β_S^E for various binary liquid mixtures with different combinations of alkanes, ethers, benzene, cyclohexane, ethyl acetate, and carbon tetrachloride by applying the Prigogine–Flory–Patterson theory along with the Lennard-Jones potential energy model to derive a relation for estimating b_S. Miyanaga et al. [5] measured densities using a densimeter and used the data to compute β_S^E for binary mixtures comprising benzene, N,N-dimethylformamide (DMF), and acetonitrile.

Reddy et al [7] determined the excess isentropic compressibility (β_S^E) of binary liquid mixtures comprising alcohols. Nath [8] utilized density measurements, obtained using a pycnometer, to calculate β_S^E for anisole + haloalkane mixtures, employing the volume fraction additivity relation for ideal isentropic compressibility (β_S^{id}). Rao et al. [8] reported β_S^E values for ethyl acetate + 2-alkoxyethanol mixtures and used them to study dipolar interactions and the self-

association behavior of the mixtures. Pal et al. [9] evaluated b_S^E for dipropylene glycol monopropyl ether mixtures with methanol, 1-propanol, 1-pentanol, and 1-heptanol. Zorębski and Deć [10] investigated β_S^E in binary mixtures of 1,2-ethanediol with various alcohols. Grozdanić et al. [11] examined β_S^E of binary mixtures consisting of isoamyl acetate and alcohols. Nakarov et al. [12] conducted volumetric studies on water–N-methylpyrrolidone mixtures.

The Flory statistical theory [13,14] has been successfully extended and applied in recent years to estimate various thermodynamic and transport properties. Flory statistical theory has been successfully utilized to evaluate the density of liquid mixtures [15], the internal pressure of liquid mixtures [16], and the thermodynamic behavior of liquid mixtures [17]. Awasthi et al [18] utilized the hard sphere model and Flory statistical theory to evaluate the expansion behavior of the ternary liquid mixtures. Reimann et al. [19] measured the excess molar volume (V^E) of alkanol + amine mixtures using a densitometer, and the data were employed to test theoretical models. These binary systems are particularly valuable for studying molecular interactions, as both alcohols and amines exhibit strong intermolecular interactions due to hydrogen bonding. Hevia et al. [20] measured the required data for n-alkanol + benzylamine mixtures and estimated their β_S^E, which was then used to analyze the nature of molecular interactions.

In the present work, the excess isentropic compressibility of n-alkanol + benzylamine mixtures at various compositions has been computed using Flory statistical theory. The rationale for using Flory's statistical theory lies in its capability to describe non-ideal mixing behavior in liquid mixtures. An additional advantage is the incorporation of the interaction parameter, which effectively accounts for intermolecular interactions. The computed results have been interpreted to understand the intermolecular interactions between the components. A key feature of this approach is its reliance on minimal input data, specifically the thermal expansivity and isothermal compressibility of the pure liquids, to compute the excess isentropic compressibility (β_S^E) for all compositions of the mixtures. The required parameters for the pure components, such as the thermal expansion coefficient and isothermal compressibility, have been sourced or calculated using literature data [20].

II. THEORETICAL FRAMEWORK

The excess isentropic compressibility (β_S^E) of the mixtures in various compositions were calculated using the relation

$$\beta_S^E = \beta_S - \beta_S^{id} \quad \ldots\ldots (1)$$

where β_S is the isentropic compressibility and β_S^{id} is the ideal isentropic compressibility of liquid mixtures.

The ideal isentropic compressibility (β_S^{id}) required in equation 1 was calculated using the relation

$$\beta_S^{id} = \beta_T^{id} - \frac{(\alpha^{id})^2 T V^{id}}{C_p^{id}} \quad \ldots\ldots (2)$$

Here β_T^{id}, a^{id}, V^{id}, and C_p^{id} are ideal values of isothermal compressibility, thermal expansivity, molar volume, and specific heat capacity at constant pressure, respectively and are given by the following relations:

$$\beta_T{}^{id} = \sum \varphi_i (\beta_T)_i \quad \ldots\ldots (3)$$

$$\alpha^{id} = \sum \varphi_i \alpha_i \quad \ldots\ldots (4)$$

$$V^{id} = \sum x_i V_i \quad \ldots\ldots (5)$$

$$C_P{}^{id} = \sum x_i (C_P)_i \quad \ldots\ldots (6)$$

Here, xi and φ_i represent the mole fractions and the volume fractions of i[th] components of the mixture. In these relations, $(\beta_T)_i$, a_i, V_i, and $(C_p)_i$ represent the isothermal compressibility, thermal expansivity, molar volume, and specific heat capacity at constant pressure of the i[th] component of the mixture.

The value of isentropic compressibility (β_S) required for equation (1) was computed using Flory statistical theory as

$$(\beta_S) = \frac{\alpha_{Flory} T \tilde{V}}{P*} \left(\tilde{V} - \frac{\tilde{\alpha}}{\tilde{C}_p} \right) \quad \ldots\ldots (7)$$

where α, T, $\tilde{V}$, P*, $\tilde{\alpha}$, and $\tilde{C}_p$ are thermal expansivity, temperature, reduced volume, characteristic pressure, reduced thermal expansivity, and reduced specific heat capacity at constant pressure, respectively.

In thermodynamics, characteristic properties refer to the intrinsic and substance-specific thermodynamic parameters, especially near critical or transition states. The reduced properties are dimensionless ratios that compare an actual thermodynamic state of a substance to its critical properties. In equation (7), α_{Flory} is the thermal expansivity of the liquid mixture computed using Flory statistical theory. The required parameters for equation (7) were computed using Flory theory and its extended forms with the help of the following relations.

Thermal expansivity $(\alpha_{Flory}) = \frac{3(\tilde{V}^{1/3} - 1)}{T(1 - 3(\tilde{V}^{1/3} - 1)}$ ……..(8)

Reduced volume of i^{th} component $(\tilde{V}_i) = \left[1 + \frac{\alpha_i T}{3(1 + \alpha_i T)}\right]^3$ ……..(9)

Characteristic pressure $(P^*) = \sum_i (\psi_i P_i^*) - \sum_{j \neq i} (\psi_i \theta_j x_{ij})$ …… (10)

Reduced thermal expansivity $(\tilde{\alpha}) = \alpha T^*$ …….. (11)

Reduced specific heat capacity at constant pressure

$(\tilde{C}_p) = \frac{C_P}{P^* V^* / T^*}$ ……. ... (12)

In the equations (8)-(12), ψ, θ, and χ_{ij} represent the segment fraction (refers to the fraction of the total number of segments in the system that belongs to a component), site fraction (refers to the fraction of total lattice sites occupied by component), and interaction parameter (refers to the parameter decided by the free energy of mixing) of the liquid mixture. The required parameters for equations (9)–(12) were computed using the expressions reported by the previous workers [15–18]. This computation requires minimal input data, primarily the thermal expansion coefficient and isothermal compressibility of the pure components.

III. RESULTS & DISCUSSION

The experimental values of density (ρ), sound velocity (u), thermal expansivity (α), isothermal compressibility (β_T), and heat capacity at constant pressure (C_p) for the pure liquids methanol, propan-1-ol, pentan-1-ol, and benzylamine were taken from the literature [20] and are presented in Table 1.

Table 1

Properties of pure liquids at 298.15 K and 0.1 MPa

Properties	Methanol	Propan-1-ol	Pentan-1-ol	Benzylamine
Molar mass (g mol^{-1})	32.04	60.10	88.15	107.15
Sound velocity, u (m s^{-1})	1102.3	1205.1	1275.3	1559.9
Density (kg m^{-3})	787.20	799.51	810.87	978.09
Thermal expansivity, a (10^{-3} K^{-1})	1.184	1.007	0.900	0.887
Isothermal compressibility, b_T (10^{-11} m^2 N^{-1})	125.32	101.60	88.49	54.45
Heat capacity, C_P (J mol^{-1} K^{-1})	81.92	146.88	207.45	206.74

Additionally, experimental values of density and sound velocity for the binary liquid mixtures methanol + benzylamine, propan-1-ol + benzylamine, and pentan-1-ol + benzylamine at various compositions were also sourced from the same reference. Unlike the aromatic amine (anilines), benzylamine is an aryl alkylamine and behaves more or less like an aliphatic amine. In computing the isentropic compressibility of these liquid mixtures at all compositions using Flory's statistical theory, the minimum required input data, thermal expansion coefficient and isothermal compressibility of the pure components, were utilized. Based on these inputs, the excess isothermal compressibility (β_S^E) of the mixtures was computed, and the results have been presented in Tables 2, 3, and 4.

Table 2.

Excess isentropic compressibility (β_S^E) of Methanol (1) + benzylamine (2) at 298.15 K and 0.1 MPa (Computed using Flory Statistical Theory)

x_1	$\tilde{V}$	$\tilde{T}$	β_S	β_S^{id}	β_S^E
			(10^{-11} m^2 N^{-1})	(10^{-11} m^2 N^{-1})	(10^{-11} m^2 N^{-1})
0.0521	1.2269	0.0537	42.55	42.92	-0.367
0.1123	1.2303	0.0543	43.18	44.01	-0.834
0.1523	1.2327	0.0547	43.62	44.79	-1.167
0.1970	1.2355	0.0552	44.13	45.69	-1.558
0.2527	1.2393	0.0559	44.82	46.88	-2.068
0.2970	1.2425	0.0564	45.41	47.89	-2.487
0.3542	1.2471	0.0572	46.24	49.28	-3.036
0.3994	1.2511	0.0579	46.98	50.44	-3.468

0.4505	1.2561	0.0587	47.90	51.85	-3.944
0.4999	1.2616	0.0596	48.91	53.29	-4.379
0.5514	1.2680	0.0605	50.12	54.91	-4.788
0.6029	1.2754	0.0616	51.51	56.64	-5.130
0.6503	1.2833	0.0627	52.99	58.35	-5.359
0.7004	1.2928	0.0640	54.80	60.28	-5.480
0.7489	1.3035	0.0653	56.86	62.30	-5.439
0.7998	1.3167	0.0669	59.39	64.56	-5.171
0.8506	1.3322	0.0687	62.40	67.00	-4.599
0.9003	1.3502	0.0707	65.90	69.55	-3.647
0.9501	1.3718	0.0729	70.10	72.28	-2.174

Table 3

Excess isentropic compressibility (β_S^E) of Propan-1-ol (1) + benzylamine (2) at 298.15 K and 0.1 MPa (Computed using Flory Statistical Theory)

x_1	$V^{\sim}$	$T^{\sim}$	β_S	β_S^{id}	β_S^E
			$(10^{-11}\ m^2\ N^{-1})$	$(10^{-11}\ m^2\ N^{-1})$	$(10^{-11}\ m^2\ N^{-1})$
0.0608	1.2257	0.0535	43.46	43.90	-0.445
0.1085	1.2270	0.0537	44.65	45.43	-0.775
0.1554	1.2283	0.0539	45.89	46.98	-1.082
0.2047	1.2297	0.0542	47.27	48.66	-1.381
0.2518	1.2310	0.0544	48.67	50.31	-1.642
0.3023	1.2325	0.0546	50.26	52.15	-1.892
0.3469	1.2338	0.0548	51.74	53.82	-2.085
0.3980	1.2353	0.0551	53.54	55.81	-2.268
0.4446	1.2366	0.0553	55.29	57.68	-2.397
0.4912	1.2380	0.0555	57.14	59.62	-2.486
0.5536	1.2398	0.0558	59.79	62.33	-2.535
0.5994	1.2411	0.0560	61.88	64.39	-2.516
0.6517	1.2426	0.0562	64.41	66.84	-2.431
0.7000	1.2438	0.0564	66.91	69.20	-2.289
0.7505	1.2451	0.0566	69.68	71.76	-2.073
0.7985	1.2462	0.0568	72.49	74.29	-1.800
0.8425	1.2471	0.0569	75.21	76.70	-1.492
0.8987	1.2481	0.0571	78.90	79.92	-1.023
0.9499	1.2488	0.0572	82.46	82.99	-0.529

Table 4

Excess isentropic compressibility (β_S^E) of Pentan-1-ol (1) + benzylamine (2) at 298.15 K and 0.1 MPa (Computed using Flory Statistical Theory)

x_1	V~	T~	β_S	β_S^{id}	β_S^E
			$(10^{-11}\ m^2\ N^{-1})$	$(10^{-11}\ m^2\ N^{-1})$	$(10^{-11}\ m^2\ N^{-1})$
0.0506	1.2248	0.0534	43.38	43.72	-0.342
0.1001	1.2256	0.0535	44.74	45.38	-0.638
0.1477	1.2262	0.0536	46.10	46.98	-0.886
0.1983	1.2269	0.0537	47.57	48.68	-1.111
0.2486	1.2275	0.0538	49.08	50.38	-1.294
0.2968	1.2280	0.0539	50.57	52.00	-1.431
0.3476	1.2285	0.0540	52.18	53.72	-1.536
0.3987	1.2289	0.0540	53.84	55.44	-1.601
0.4501	1.2293	0.0541	55.55	57.18	-1.626
0.4985	1.2296	0.0541	57.20	58.81	-1.613
0.5504	1.2298	0.0542	59.01	60.57	-1.562

0.6009	1.2299	0.0542	60.80	62.28	-1.477
0.6422	1.2299	0.0542	62.29	63.68	-1.384
0.6987	1.2298	0.0542	64.37	65.59	-1.224
0.7496	1.2297	0.0542	66.27	67.32	-1.052
0.8005	1.2294	0.0541	68.19	69.05	-0.858
0.8492	1.2290	0.0540	70.05	70.70	-0.657
0.9002	1.2284	0.0539	72.00	72.44	-0.435
0.9500	1.2277	0.0538	73.92	74.13	-0.216

The graphical representations of the excess isentropic compressibility (β_S^E) as a function of the mole fraction of n-alcohols for all the liquid mixtures are shown in Figures 1, 2, and 3.

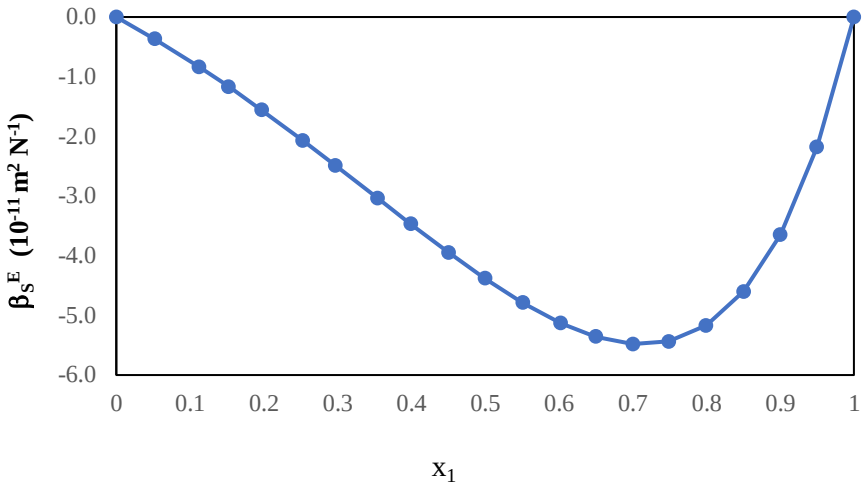

Figure 1
Excess isentropic compressibility (β_S^E) computed using Flory Statistical Theory for Methanol (1) + Benzylamine (2) at 298.15K

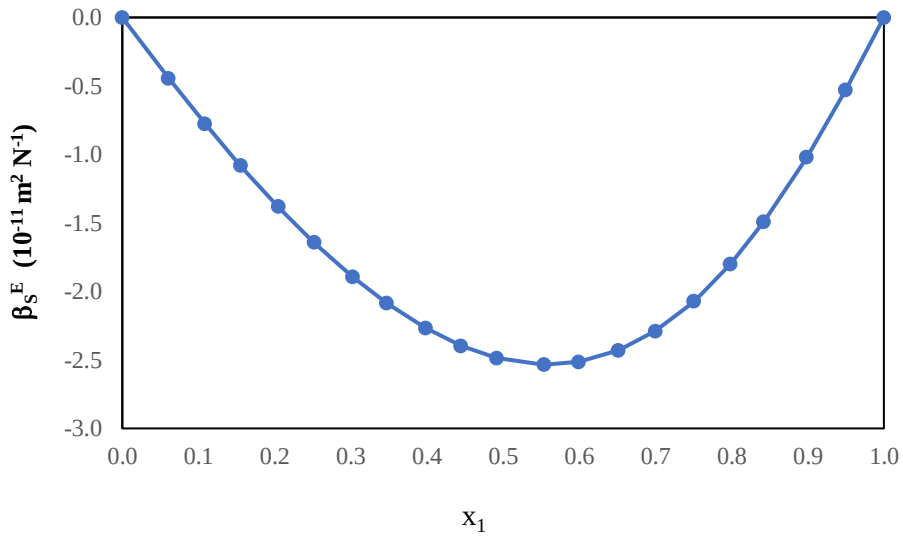

Figure 2
Excess isentropic compressibility (β_S^E) computed using Flory Statistical Theory for Propan-1-ol (1) + Benzylamine (2) at 298.15K

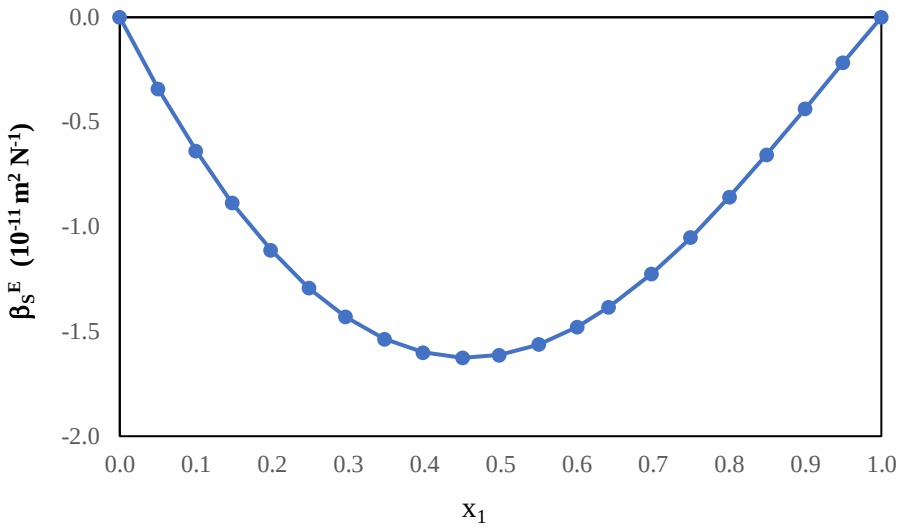

Figure 3

Excess isentropic compressibility (β_S^E) computed using Flory Statistical Theory for Pentan-1-ol (1) + Benzylamine (2) at 298.15K

The results show a negative deviation of excess isentropic compressibility (β_S^E) in all the mixtures and across all compositions under study. The large negative values of β_S^E observed in the benzylamine + n-alcohol mixtures indicate strong specific interactions between the unlike molecules, benzylamine and the alcohols. These interactions are primarily due to hydrogen bonding between the hydroxyl group of the alcohol and the amino group of benzylamine (O–H···N or N–H···O), leading to the formation of stable intermolecular complexes. As a result, the compressibility of the mixtures is reduced, signifying a negative deviation from ideal behaviour.

The observed decrease in the negative values of excess isentropic compressibility (β_S^E) from methanol to propan-1-ol to pentan-1-ol in their mixtures with benzylamine suggests a gradual weakening of specific interactions between the unlike molecules. This trend can be attributed to the increasing size and hydrophobic character of the alcohols, which introduce steric hindrance and reduce the effectiveness of hydrogen bonding with benzylamine. Additionally, the decreasing polarity of the alcohols with increasing chain length diminishes the strength of dipole–dipole interactions, leading to less efficient molecular association and a smaller negative deviation from ideal behaviour.

The values and trends of deviations in excess isentropic compressibility (β_S^E), as computed using the Flory statistical model in the present study, show close agreement with the values reported by Hevia et al. [20]. This consistency highlights the reliability and applicability of the Flory statistical theory in estimating the excess isentropic compressibility of liquid mixtures. Such estimations are crucial for understanding and quantifying the nature and strength of intermolecular interactions in liquid mixtures.

IV. CONCLUSION

The present study was focused on evaluating the excess isentropic compressibility (β_S^E) of *n*-alcohol + benzylamine mixtures using Flory statistical theory. The results revealed negative deviations in β_S^E across all mixtures, indicating strong specific interactions between the unlike molecules. These interactions, primarily hydrogen bonding between the hydroxyl group of the alcohol and the amino group of benzylamine, lead to the formation of stable intermolecular complexes. A decreasing trend in the magnitude of β_S^E from methanol to propan-1-ol to pentan-1-ol suggests a weakening of these interactions, attributed to increased steric hindrance and reduced polarity of the longer-chain alcohols. The values and trends obtained using Flory's statistical model closely matched the literature data [20], supporting the model's reliability in predicting excess compressibility and characterizing intermolecular interactions in binary liquid mixtures.

V. RECOMMENDATIONS

Although predictive methods based on statistical theories are highly valuable due to their reliance on minimal input data, there is a strong need to develop simpler and more efficient experimental techniques for determining key properties such as adiabatic and isothermal compressibility.

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