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Formulation and evaluation of a semi-empirical relation for estimating the thermal expansion coefficient of organic liquids

Bishan Datt Bhatt[1]

[1]bdbhatta@gmail.com, bishan.bhatt@trc.tu.edu.np

[1]https://orcid.org/0000-0002-3352-8173

[1]Department of Chemistry, Tri-Chandra Multiple Campus, Tribhuvan University, Nepal

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ABSTRACT

The thermal expansion coefficient (α), or thermal expansivity, is a fundamental thermophysical property that quantifies the volumetric response of a liquid to temperature variations. It plays a crucial role in a range of applications, including thermodynamic property estimation, chemical process design, and fluid system calibration. Moreover, it serves as a key parameter in the theoretical computation of various thermodynamic properties within the framework of statistical mechanical theories. Due to the challenges associated with its experimental determination and the demand for predictive approaches requiring minimal input data, a new semi-empirical relation has been developed for estimating the thermal expansion coefficient in pure organic liquids. The proposed relation was validated across a broad spectrum of polar and nonpolar organic liquids over a range of temperatures. Its performance was benchmarked against existing methods, with the results demonstrating strong agreement with experimental data. The analysis reveals that equations based on simplified hard-sphere models show significant deviations from experimental values, particularly at higher temperatures, due to their neglect of intermolecular forces and molecular complexity. The Stakhorsky relation provides better estimates but shows increased deviations as temperature rises. The newly proposed equation demonstrates low and consistent deviations across the studied temperature range. The accuracy, stability, and effectiveness of the model can be attributed to the inclusion of the molar volume term in the equation. This indicates the proposed relation's reliability and practical utility for estimating the thermal expansion coefficient using minimal input data, particularly in situations where experimental data are unavailable. Empirical and semi-empirical relations for estimating thermodynamic properties, such as the thermal expansion coefficient, using minimal input data are especially valuable when experimental data are limited. Additionally, developing simplified relations based on statistical theories offers the advantage of incorporating interaction parameters, which more accurately represent molecular behavior and thereby enhance the reliability of property predictions.

Keywords*:* Hard Sphere Model, Interaction Parameter, Molar Volume, Semi-Empirical Relation, Thermal Expansion Coefficient

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I. INTRODUCTION

Thermal expansion coefficient (thermal expansivity), α, is a fundamental thermodynamic property that quantifies the fractional change in volume of a substance with temperature at constant pressure. It plays a critical role in the calculation of thermodynamic functions, phase behavior analysis, and the development of equations of state, particularly for liquids and liquid mixtures.

A survey of the literature reveals that numerous researchers have utilized this parameter in various studies involving pure liquids and liquid mixtures. Sharma [1] employed the thermal expansion coefficient for the estimation of various nonlinear acoustic parameters in liquid systems. In a separate study, Sharma [2] used it in the evaluation of the Grüneisen parameter, and he also applied it in the estimation of multiple thermophysical properties, including the isochoric temperature coefficient of surface tension [3]. Pandey et al. [4] utilized the parameter α to estimate various thermodynamic properties of liquid argon and xenon. Pandey et al. [5] employed α to compute several thermoacoustical properties, including the available volume. The calculated values of available volume showed close agreement with experimental data, thereby validating the applicability of α in estimating this property in liquid systems. Reddy et al. [6] applied the parameter to explore correlations among the Moelwyn–Hughes parameter, available volume, and intermolecular free lengths in liquids. Pandey et al. [7] used α values of pure liquids to estimate the internal pressure of liquid mixtures. Similarly, Prabhune et al. [8] employed the parameter for the evaluation of various thermodynamic properties of liquid mixtures.

In industrial applications, liquid mixtures are more commonly used than pure liquids. But the experimental data for each composition of these mixtures are often unavailable. In applying statistical theories to estimate the thermodynamic properties of liquid mixtures, the thermal expansion coefficient of pure liquids serves as a critical input parameter. Notably, the experimental determination of the thermal expansion coefficient is both difficult and time-consuming. Consequently, various empirical and semi-empirical relations have been proposed to estimate this important property. However, a review of these relations reveals that many either fail to produce satisfactory results or exhibit significant temperature-dependent deviations.

In the present work, a new relation for the evaluation of the thermal expansion coefficient has been proposed. The relation is dimensionally correct and expected to provide satisfactory results. For the comparison purpose, some other relations are used for the estimation of the thermal expansion coefficient for a comparison purpose.

II. THEORETICAL FOUNDATION

The thermal expansion coefficient (α) quantifies the fractional change in volume of a substance per unit increase in temperature at constant pressure. In liquids, it reflects the degree of sensitivity of the liquid's volume to thermal energy. Thermodynamically, it is defined as

$$\alpha = \frac{1}{V}\left(\frac{dV}{dT}\right)_p$$

Where V is molar volume and T is absolute temperature.

Based on the studies conducted by several researchers [9–14], theoretical models have been proposed to estimate the thermal expansion coefficient using hard sphere approximations. Among these, two widely cited expressions are

Equation 1 (Scaled Particle Theory [12]) : $\alpha = \frac{1}{T}\frac{(1-y)}{(1+y)}$ … (1)

and

Equation 2 (Henderson model [14]) : $\alpha = \frac{1}{T}\frac{(8-y^2)(1-y)}{(8+8y+3y^2-y^3)}$ … (2)

In both expressions, y denotes the packing fraction, which is a measure of the volume occupied by molecules in a liquid. It can be computed from molecular parameters using the relation:

$$y = \frac{\pi\, d^3 N}{6V}$$

Where d is the molecular diameter, N is Avogadro's number, and V is the molar volume.

Additionally, Stakhorsky [15] proposed an empirical relation for evaluating the thermal expansion coefficient, given by

Equation 3 (Stakhorsky relation [15]): $\alpha = \frac{0.17\, T_c}{T(T_c - T)}$ … {3)

Where T_C is the critical temperature, a constant characteristic of a particular liquid.

The equation presented above is dimensionally correct; however, it does not explicitly incorporate the molar volume term. Nevertheless, molar volume is intrinsically linked to molecular packing, which plays a significant role in influencing the thermal expansion behavior of liquids. Along with temperature, molar volume critically affects the thermal expansion coefficient. For example, smaller molar volumes correspond to tighter molecular packing, which generally restricts the thermal expansion of a liquid. In contrast, larger molar volumes reflect looser molecular packing, thereby allowing greater expansion with temperature. This behavior is further supported by the presence of molar volume in the expression for packing fraction in hard-sphere models, underscoring its indirect yet crucial influence on the thermal expansion coefficient. Recognizing this interdependence, a new relation was developed to account for these effects. An empirical fitting parameter (0.1095) was obtained through analysis of a broad range of polar and nonpolar organic liquids at various temperatures. The dimensionless term $V_C/(V_C-V)$ was introduced to represent how closely the current molar volume V approaches the critical molar volume V_C, highlighting the divergence of thermodynamic properties such as compressibility and thermal expansion near the critical point. Based on these considerations, a new semi-empirical relation is proposed for estimating the thermal expansion coefficient in organic liquids, expressed as

Equation 4 (Newly Proposed Relation): $\boldsymbol{\alpha = 0.1095\, \frac{T_c}{T(T_c-T)}\frac{V_c}{(V_c-V)}}$ **… (4)**

Where, V_C and T_C represent the critical volume and critical temperature, respectively**,** both being constant for a given liquid**.**

III. RESULTS & DISCUSSION

The critical constants P_C, T_C, and V_C of pure liquids are readily available in standard physical data compilations. However, experimental data for the thermal expansion coefficient (α) and molar volume at specific temperatures are not consistently available from a single source. Therefore, in this study, the critical constants, molar volumes, and experimental values of α were collected from various literature sources [16–21]. Equations (1) to (4) were employed to compute the thermal expansion coefficients of several organic liquids at different temperatures. The results are presented in Table 1. Additionally, similar data for selected pure liquids at a single temperature are presented in Table 2. The column labeled "Eq. 4" shows the values obtained using the newly proposed relation. The last four columns in both tables display the percentage deviations of the calculated α values from experimental data, allowing comparison of the accuracy of each equation. The graphical representations showing the temperature dependence of the experimental and computed thermal expansion coefficient (α), using equations 3 and 4, for n-heptane and n-decane are presented in Figures 1 and 2, respectively.

Table 1

Thermal Expansion Coefficient (α) of Some Pure Liquids Obtained from Various Relations at Different Temperatures

(1-Scaled particle theory, 2-Henderson relation, 3-Stackhorshy relation, 4- Newly proposed relation)

Liquids	**T** K	**T_C** K	**V_C** (10^{-6} m^3mol^{-1})	**V** (10^{-6} m^3mol^{-1})	α_{expt} $10^{-3}K^{-1}$	α_{calc} **(10^{-3} K^{-1})**				**% Difference**			
						Eq (1)	Eq (2)	Eq (3)	**Eq (4)**	Eq (1)	Eq (2)	Eq (3)	Eq (4)
Cyclohexane	298.15	553.5	308	108.76	1.215	1.270	1.247	1.236	1.231	-4.56	-2.64	-1.72	-1.29
	313.15	553.5	308	110.80	1.265	1.248	1.226	1.250	1.258	1.31	3.08	1.17	0.58
	325.15	553.5	308	112.19	1.294	1.228	1.207	1.267	1.284	5.07	6.74	2.06	0.77
n-Pentane	283.15	469.7	311	113.46	1.517	1.439	1.414	1.512	1.533	5.09	6.73	0.32	-1.08
	288.15	469.7	311	114.31	1.548	1.430	1.405	1.526	1.555	7.66	9.25	1.43	-0.39
	293.15	469.7	311	115.22	1.579	1.421	1.397	1.543	1.579	10.01	11.54	2.30	0.03
	303.15	469.7	311	117.11	1.637	1.405	1.382	1.581	1.634	14.20	15.63	3.42	0.21
n-Hexane	293.15	507.6	368	130.39	1.374	1.354	1.330	1.373	1.369	1.39	3.14	0.07	0.32
	313.15	507.6	368	134.02	1.454	1.323	1.301	1.417	1.436	9.00	10.55	2.55	1.27
	333.15	507.6	368	137.56	1.526	1.299	1.278	1.485	1.527	14.89	16.28	2.73	-0.05
n-Heptane	293.15	540.2	432	146.66	1.250	1.302	1.278	1.268	1.237	-4.17	-2.26	-1.44	1.08
	313.15	540.2	432	150.39	1.309	1.269	1.246	1.292	1.276	3.04	4.76	1.31	2.48
	333.15	540.2	432	154.42	1.378	1.243	1.222	1.331	1.335	9.84	11.38	3.41	3.18
	353.15	540.2	432	158.78	1.462	1.223	1.203	1.390	1.416	16.37	17.74	4.92	3.17
n-Decane	293.15	617.7	624	194.99	1.036	1.194	1.171	1.104	1.034	-16.37	-14.12	-7.55	-0.76
	313.15	617.7	624	199.09	1.069	1.159	1.137	1.101	1.042	-8.47	-6.42	-3.03	2.54
	333.15	617.7	624	203.42	1.114	1.130	1.109	1.108	1.059	-1.46	0.42	0.58	4.98
	353.15	617.7	624	208.20	1.162	1.107	1.087	1.124	1.086	4.72	6.43	3.26	6.49
	363.15	617.7	624	210.61	1.187	1.097	1.078	1.136	1.104	7.54	9.18	4.26	6.92
Acetone	253.20	508.1	209	69.61	1.332	1.498	1.470	1.338	1.293	-12.46	-10.39	-0.48	2.96
	263.20	508.1	209	70.53	1.344	1.467	1.440	1.340	1.303	-9.16	-7.18	0.29	3.07
	273.20	508.1	209	71.48	1.361	1.440	1.414	1.346	1.318	-5.82	-3.93	1.10	3.19
	283.20	508.1	209	72.47	1.380	1.415	1.391	1.356	1.337	-2.57	-0.76	1.73	3.10
	293.20	508.1	209	73.48	1.398	1.393	1.369	1.371	1.362	0.35	2.08	1.94	2.59
	303.20	508.1	209	74.53	1.416	1.373	1.350	1.390	1.392	3.04	4.69	1.81	1.70
	308.20	508.1	209	75.07	1.435	1.364	1.341	1.402	1.409	4.95	6.56	2.30	1.79

Table 2
Thermal Expansion Coefficient (α) of Some Pure Liquids Obtained from Various Relations

(1-Scaled particle theory, 2-Henderson relation, 3-Stackhorshy relation, **4- Newly proposed relation**)

Liquids	**T**	**T$_C$**	**V$_C$** (10^{-6}	**V** (10^{-6}	α_{expt}	α_{calc} **(10^{-3} K^{-1})**				**% Difference**			
	K	K	m^{3}mol^{-1})	m^{3}mol^{-1})	10^{-3}K^{-1}	Eq (1)	Eq (2)	Eq (3)	**Eq (4)**	Eq (1)	Eq (2)	Eq (3)	**Eq (4)**
n-Hexane	298.15	507.6	368	131.56	1.381	1.339	1.316	1.382	1.385	3.02	4.73	-0.06	-0.31
n-Octane	298.15	568.7	492	163.53	1.160	1.245	1.222	1.199	1.156	-7.34	-5.33	-3.32	0.32
n-Decane	298.15	617.7	624	195.92	1.041	1.179	1.156	1.102	1.035	-13.26	-11.08	-5.88	0.59
n-Dodecane	298.15	658.0	754	228.58	0.978	1.128	1.106	1.043	0.964	-15.34	-13.06	-6.61	1.46
n-Tetradecane	298.15	693.0	894	261.34	0.931	1.084	1.062	1.001	0.911	-16.42	-14.09	-7.49	2.16
n-Hexadecane	298.15	723.0	1034	294.05	0.902	1.047	1.025	0.970	0.873	-16.04	-13.68	-7.57	3.17
Carbon tetrachl.	298.15	556.6	276	97.08	1.228	1.193	1.170	1.228	1.220	2.89	4.75	0.00	0.64
Benzene	298.15	562.2	259	89.41	1.218	1.255	1.232	1.214	1.194	-3.06	-1.14	0.33	1.95
p-xylene	298.15	616.2	379	123.92	1.019	1.182	1.159	1.105	1.057	-15.96	-13.72	-8.41	-3.75
Toluene	298.15	591.8	318	106.88	1.086	1.228	1.204	1.149	1.115	-13.03	-10.90	-5.82	-2.66
Ethyl Acetate	298.15	523.3	286	98.50	1.384	1.271	1.248	1.325	1.302	8.14	9.83	4.25	5.92
1,2-dichloroethane	303.15	566.0	225	79.92	1.162	1.185	1.162	1.208	1.206	-1.98	-0.04	-3.92	-3.81
Trichloroethene	303.15	572.0	256	90.52	1.139	1.180	1.158	1.193	1.189	-3.62	-1.64	-4.75	-4.38
Tetrachloroethene	303.15	620.2	290	103.62	1.025	1.128	1.106	1.097	1.100	-10.04	-7.89	-7.02	-7.34
Cyclohexane	303.15	553.5	308	109.41	1.233	1.260	1.237	1.240	1.239	-2.19	-0.32	-0.55	-0.45

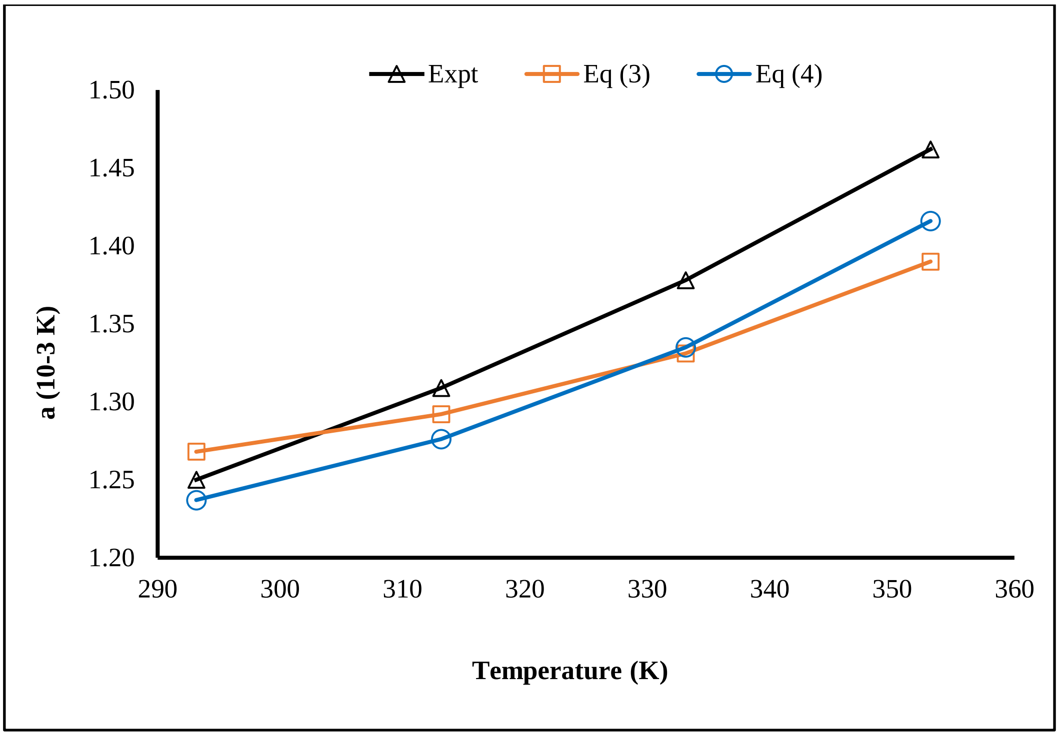

Figure 1
Temperature Dependence of Experimental and Computed α (Equations 3 and 4) for n-Heptane

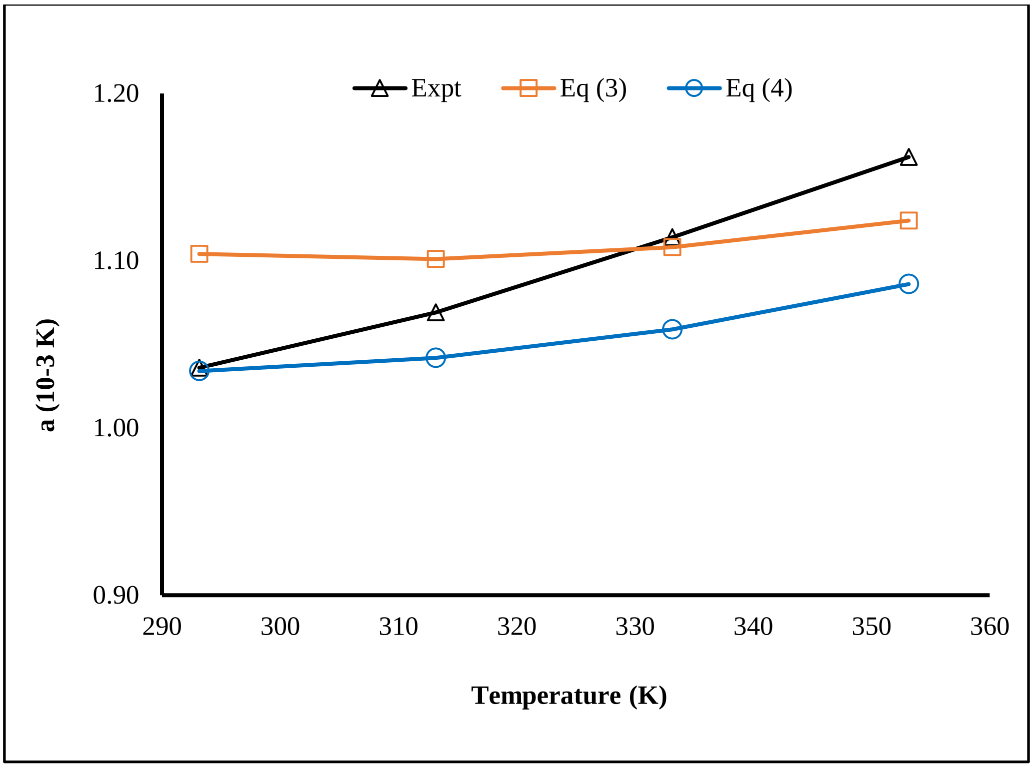

Figure 2
Temperature Dependence of Experimental and Computed α (Equations 3 and 4) for n-Decane

A closer examination of the results reveals that Equations (1) and (2) exhibit significant deviations from the experimental data. This behavior can be attributed to the fact that these equations are based on simplified hard-sphere approximations. The substantial deviations arise because the hard-sphere model neglects attractive intermolecular forces, molecular complexity, and the concept of free volume. These simplifications limit the model's ability to accurately predict thermodynamic properties, especially near phase transitions or in complex fluids. In contrast, Equation (3), the Stakhorsky relation, provides reasonably satisfactory results. However, a detailed review of Table 1 indicates that the deviations from experimental values increase noticeably with rising temperature. Figures 1 and 2 further show that the relation leads to unexpected deviations and an unusual trend in the variation of α between the computed and experimental values as the temperature increases. This increasing deviation can be attributed, in part, to the absence of an explicit molar volume term in the Stakhorsky relation, which limits its ability to capture the temperature-dependent expansion behavior of liquids. Despite these variations, Equation (3) remains a useful tool for estimating the thermal expansion coefficient of liquids, especially in situations where experimental data are scarce.

Tables 1 and 2 indicate that the newly proposed relation, Equation (4), exhibits relatively small deviations from the experimental values of the thermal expansion coefficient. This improved accuracy is primarily attributed to the incorporation of molar volume data, which is closely linked to thermal expansivity. A closer examination of Table 1 shows that the deviations from experimental values remain fairly consistent across the temperature range studied. Figures 1 and 2 show a regular increase in α with temperature, and this trend closely aligns with the experimental observations. Even over a broad temperature range (298.15 K to 363.15 K), the calculated values showed good agreement with experimental data. This demonstrates the applicability of the proposed relation under varying thermal conditions. Overall, the results validate its effectiveness in reliably estimating the thermal expansion coefficient of liquids across different temperatures using minimal input data. Notably, the equation requires only a few readily available parameters, viz., temperature, critical temperature, critical volume, and molar volume (or density). Moreover, the relation is dimensionally consistent and demonstrates close agreement with experimental data. All these results suggest that the newly proposed relation offers a promising approach for accurately computing the thermal expansion coefficient of polar and nonpolar organic liquids over a wide temperature range using minimal input data.

IV. CONCLUSIONS

This study evaluated some empirical and semi-empirical relations for estimating the thermal expansion coefficient of polar and nonpolar organic liquids across a broad temperature range. Relations based on hard-sphere models showed significant deviations due to their oversimplified assumptions, which fail to capture complex molecular interactions. The Stakhorsky relation provided reasonable estimates but demonstrated temperature-dependent variability. In contrast, the newly proposed relation consistently yielded low deviations and showed excellent agreement with experimental data under all tested conditions. Requiring only minimal and readily available input parameters, the proposed model offers a relatively accurate and highly practical approach for predicting the thermal expansion coefficients of a wide variety of organic liquids over a broad temperature range, especially useful when experimental data are limited or unavailable.

V. RECOMMENDATIONS

Although empirical and semi-empirical relations using minimal input data are strongly recommended, especially when experimental data are unavailable, the development of simplified relations grounded in statistical theories is highly advantageous. Such models incorporate molecular interaction parameters that more accurately represent real fluid behavior, which enhances the predictive reliability.

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