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Comparative Study of Refractive Index Deviation and Molar Refraction Deviation for Predicting Molecular Interactions

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Abstract

The relative merits of refractive index deviation (Δn) and molar refraction deviation (ΔRm) as indicators of molecular interactions in binary liquid mixtures are examined. Using experimental data, from literature, for six ethyl chloroacetate + n-alkane (C6 to C12) systems at three temperatures, we investigate whether these two widely-used parameters provide equivalent information. Our analysis reveals strong linear correlations ($r > 0.95$ in most cases) between ΔRm and Δn, with both parameters showing identical signs and nearly coincident peak positions. A systematic scaling relationship $\Delta Rm \approx k \times \Delta n$ is observed, where the scaling factor k increases from 0.04 for hexane to 1.9 for dodecane. Temperature sensitivity analysis indicates that both parameters respond similarly to thermal changes. These findings suggest that ΔRm and Δn may be considered practically equivalent for qualitative interaction assessment, though ΔRm appears more suitable for systems with significant volume changes. The choice between them can be guided by available data and required measurement precision.

Keywords: Refractive index deviation, Molar refraction deviation, Binary mixtures, Molecular interactions, Lorentz-Lorenz relation

1. Introduction

Experimental measurement of thermodynamic properties of mixtures and their deviations from ideality has become an established approach for investigating molecular structure and intermolecular forces in liquid systems [1-3]. Among various techniques, refractometry provides valuable insights through the study of refractive index and molar refraction variations under different conditions.

The refractive index (n) quantitatively measures the response of constituent molecules to electromagnetic waves. H.A. Lorentz and L.V. Lorenz independently established the relationship between refractive index and density, leading to the concept of molar refraction (R_m) [4]:

$$R_m = \frac{n^2-1}{n^2+2} \cdot V_m \qquad (1)$$

where V_m is the molar volume.

For characterizing molecular interactions, two excess parameters derived from refractive measurements are commonly employed. The molar refraction deviation is defined as:

$$\Delta R_m = R_m - (\phi_1 R_1 + \phi_2 R_2) \qquad (2)$$

where ϕ_i represents the volume fraction of component i. Alternatively, the refractive index deviation is expressed as:

$$\Delta n = n_{expt} - (x_1 n_1 + x_2 n_2) \qquad (3)$$

where x_i denotes the mole fraction.

Several researchers have successfully employed ΔR_m to investigate interactions. Comelli et al. [5] studied binary mixtures of n-hexane with pine resin components, while Gupta et al. [6] examined THF-alcohol systems using this parameter. Similarly, Δn has been utilized by Rodriguez et al. [7] for dimethyl carbonate-hexane mixtures and by Chen et al. [8] for ethanol-based systems. Casas et al. [9] employed Δn for ternary mixture characterization.

Despite widespread use of both parameters, a systematic comparison examining their relative merits and quantitative relationship appears to be needed to make an informed choice. The fundamental questions we address are:

(i) Do ΔR_m and Δn provide equivalent information about molecular interactions?
(ii) How do their variations correlate quantitatively?
(iii) Under what conditions might one parameter be preferred over the other?

This study presents a comparative analysis of ΔR_m and Δn using six binary mixtures of ethyl chloroacetate (ECA) with n-alkanes (hexane through dodecane) at 298.15 K, 303.15 K, and 308.15 K. We examine sign agreement, peak position coincidence, linear correlations, and temperature sensitivities to establish the relationship between these parameters.

2. Experimental

2.1 Data Source

The experimental density (ρ) and refractive index (n) data were obtained from the published work of Nayak et al. [10], who measured and reported these properties for six binary mixtures of ethyl chloroacetate with n-alkanes (hexane, heptane, octane, nonane, decane, and dodecane) at three temeperatures, namely, 298.15 K, 303.15 K, and 308.15 K. For each mixture, measurements were available at 9-11 compositions spanning the entire range from pure alkane to pure ECA. The reported experimental uncertainties were ±0.0001 g/cm³ for density and ±0.0001 for refractive index.

2.2 Calculation Methodology

2.2.1 Molar Refraction Deviation

The molar volume (V_m) was calculated from experimental density:

$$V_m = \frac{(x_1 M_1 + x_2 M_2)}{\rho} \qquad (4)$$

where M_1 represents the molecular weight of component i.

The molar refraction for each component and the mixture was computed using the Lorentz-Lorenz equation (Eq. 1). Volume fractions were calculated as:

$$\phi_1 = \frac{x_1 V_1}{(x_1 V_1 + x_2 V_2)} \qquad (5)$$

where $V_i = \frac{M_i}{\rho_i}$ for pure components. The deviation $\Delta R_m$was then obtained from Eq. 2.

2.2.2 Refractive Index Deviation

The refractive index deviation was calculated directly from Eq. 3 using experimental refractive indices and mole fractions.

2.2.3 Statistical Analysis

For each mixture at each temperature, we computed: (i) peak positions - composition (x_1) at which $|\Delta R_m|$ and $|\Delta n|$ attain maximum values, (ii) Pearson correlation coefficient (r) between ΔRm and Δn, (iii) linear regression parameters: ΔRm = k × Δn, including coefficient of determination (R^2), and (iv) temperature sensitivity - percentage change in average absolute deviations from 298.15 K to 308.15 K.

The Pearson correlation coefficient r measures the strength and direction of the linear relationship between ΔRm and Δn. It is calculated using:

$$r = \frac{\sum_{i=1}^{n}\left(\Delta R_{m,i}-\overline{\Delta R_m}\right)\left(\Delta n_i-\overline{\Delta n}\right)}{\sqrt{\sum_{i=1}^{n}\left(\Delta R_{m,i}-\overline{\Delta R_m}\right)^2}\sqrt{\sum_{i=1}^{n}\left(\Delta n_i-\overline{\Delta n}\right)^2}} \qquad (6)$$

where n is the number of data points, ΔRm,i and Δn,i are individual values at composition i, and the means are calculated across all compositions. The coefficient ranges from -1 to +1, where values close to +1 indicate strong positive linear correlation.

The statistical significance was assessed using the t-test:

$$t = r\sqrt{\frac{(n-2)}{(1-r^2)}} \qquad (7)$$

with n-2 degrees of freedom. The p-value indicates the probability of obtaining the observed correlation by chance.

For linear regression, the scaling factor k was determined by:

$$k = \Sigma\,\frac{(\Delta Rm,i\times\Delta n,i)}{\Sigma(\Delta n,i)^2} \qquad (8)$$

The coefficient of determination R^2 was calculated as:

$$R^2 = 1 - \frac{\sum_{i=1}^{n}\left(\Delta R_{m,i}-k\times\Delta n_i\right)^2}{\sum_{i=1}^{n}\left(\Delta R_{m,i}-\overline{\Delta R_m}\right)^2} \qquad (9)$$

which represents the proportion of variance in ΔR_m explained by the linear relationship with Δn.

3. Results and Discussion

3.1 Sign Agreement and Peak Positions

A notable observation from Table 1 (see Tables section) is that ΔRm and Δn exhibit identical signs (both negative) across all compositions, mixtures, and temperatures studied. This complete sign agreement suggests that both parameters respond to the same underlying interaction mechanisms.

Furthermore, for the majority of cases (14 out of 18 temperature-mixture combinations), both parameters peak at exactly the same composition. The few exceptions where peak positions differ by more than 0.1 mole fraction occur primarily at higher temperatures and for longer-chain alkanes. Even in these cases, the shift (Δx_1) never exceeds 0.20, which represents only a modest difference in the predicted stoichiometry of complex formation.

The significance of this finding is that either parameter can be used reliably to identify the composition range of strongest interaction, which is often of practical importance in mixture design and optimization.

3.2 Correlation Analysis

Table 2 (see Tables section) presents the statistical correlation analysis between ΔRm and Δn. The Pearson correlation coefficients exceed 0.95 for 15 out of 18 cases, with all correlations being statistically significant ($p < 0.001$). This strong linear relationship indicates that the two parameters are not independent measures but rather provide equivalent information scaled by a system-dependent factor.

The linear relationship can be expressed as $\Delta Rm \approx k \times \Delta n$, where the scaling factor k shows a systematic trend. As illustrated in Figure 1, k increases monotonically from approximately 0.04 for hexane to 1.9 for dodecane. This systematic variation appears to correlate with the increasing difference in molar volumes between ECA and the alkane as chain length increases. The scaling factor may thus reflect the different weighting schemes employed: ΔRm uses volume fractions while Δn uses mole fractions. For components of similar size, these weightings converge; as size disparity grows, the scaling factor increases accordingly.

3.3 Temperature Effects

Table 3 (see Tables section) summarizes the temperature sensitivity of both parameters. The ECA+hexane mixture exhibits the most pronounced temperature dependence, with average absolute deviations decreasing by 62% for ΔRm and 35% for Δn when temperature increases from 298.15 K to 308.15 K. This strong sensitivity may indicate that interactions in this system are dominated by weak, dispersion-type forces that become less significant as thermal energy increases.

In contrast, mixtures with longer-chain alkanes show much smaller temperature effects (typically within ±5%), suggesting that interactions in these systems may involve additional contributions from shape-dependent packing effects, which are inherently less temperature-sensitive. Importantly, both ΔRm and Δn exhibit similar temperature trends for each mixture (Figure 2), reinforcing the notion that they respond to the same physical phenomena.

3.4 Comparative Assessment

Figures 3 and 4 present representative plots showing ΔRm versus composition for all six mixtures at 298.15 K and the linear relationship between ΔRm and Δn for all data points, respectively. The strong linearity evident in Figure 4 ($R^2 > 0.9$ for most mixtures) provides visual confirmation of the statistical analysis.

Based on our findings, we offer the following observations regarding parameter selection:

For qualitative interaction assessment: Both parameters appear equally suitable, showing consistent sign agreement across all systems studied. The negative deviations observed indicate weaker interactions between unlike molecules compared to like molecules, consistent with dispersion-dominated systems [11].

For determining interaction maxima: Either parameter can reliably identify the composition of strongest interaction, with peak positions typically coinciding within experimental uncertainty ($\Delta x_1 < 0.05$ in most cases).

For quantitative comparisons: ΔRm may offer advantages due to its larger absolute magnitude (particularly for longer-chain alkanes), potentially providing better signal-to-noise ratio in measurements. However, Δn is simpler to calculate, requiring only composition and refractive index data without density measurements.

For systems with volume changes: The theoretical basis of ΔRm, with its explicit volume fraction weighting, may be more appropriate for mixtures exhibiting significant excess volumes, though our results suggest Δn remains informative even in such cases when properly calibrated through the scaling factor.

We acknowledge certain limitations of this study. The investigation focuses on a specific class of systems (ECA + alkanes) characterized by relatively weak, non-specific interactions. Extension to systems with strong specific interactions (hydrogen bonding, charge transfer) would strengthen the generality of conclusions. Additionally, the relatively modest temperature range (10 K) limits assessment of thermal effects; broader temperature studies might reveal additional insights.

The observed linear relationship and systematic scaling behavior suggest a fundamental equivalence between these parameters for the systems studied. However, we emphasize that this represents an empirical finding for a limited dataset rather than a universal principle. Further investigation across diverse mixture types would be valuable to establish the broader applicability of these observations.

4. Conclusion

This study presents a quantitative comparison of refractive index deviation (Δn) and molar refraction deviation (ΔR_m) as measures of molecular interactions in binary liquid mixtures.

Based on analysis of six ethyl chloroacetate + n-alkane systems at three temperatures, we draw the following conclusions:

1. Complete sign agreement is observed between ΔR_m and Δn across all compositions, mixtures, and temperatures (18/18 cases), indicating consistent qualitative behavior.
2. Peak positions coincide in 78% of cases, with shifts in remaining cases being modest ($\Delta x_1 < 0.20$), suggesting reliable identification of maximum interaction composition.
3. Strong linear correlations exist ($r > 0.95$ for 83% of cases, all $p < 0.001$), with coefficient of determination typically exceeding 0.90, demonstrating a systematic quantitative relationship.
4. The scaling factor relating the two parameters increases systematically from 0.04 (hexane) to 1.9 (dodecane), potentially reflecting the influence of component size disparity on volume versus mole fraction weighting.
5. Temperature sensitivities vary across mixtures, with both parameters showing similar thermal response patterns for each system.

For the class of systems investigated, ΔR_m and Δn appear to provide equivalent information about molecular interactions, differing primarily in magnitude scaling. The choice between them may be guided by practical considerations: available experimental data, required measurement precision, and presence of significant volume changes. It appears that both parameters remain valuable tools in mixture characterization, with selection based on specific research requirements rather than fundamental superiority of one over the other.

Future work examining systems with stronger specific interactions and broader temperature ranges could further elucidate the relationship between these parameters and establish their comparative utility across diverse mixture types.

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Table 1. Peak position analysis showing composition at maximum deviation for ΔRm and Δn. x_1(ΔRm) denotes the value of x_1 at which ΔRm attains its peak value. Similarly, x_1(Δn) denotes the value of x_1 at which Δn attains its peak value. $\Delta x_1 = x_1(\Delta Rm) - x_1(\Delta n)$ represents the shift in peak position between the two parameters. |ΔRm|max and |Δn|max are the maximum absolute values of the respective deviations.

Mixture	T(K)	x_1(ΔRm)	x_1(Δn)	Δx_1	|ΔRm|max	|Δn|max
ECA+Hexane	298K	0.4001	0.4001	0.0000	0.1159	3.14
ECA+Hexane	303K	0.4001	0.4001	0.0000	0.0814	2.42
ECA+Hexane	308K	0.6039	0.4001	0.2038	0.0479	2.06
ECA+Heptane	298K	0.4992	0.4992	0.0000	0.5973	4.72
ECA+Heptane	303K	0.4992	0.4992	0.0000	0.5949	4.47
ECA+Heptane	308K	0.4992	0.4992	0.0000	0.5889	4.57
ECA+Octane	298K	0.5064	0.5064	0.0000	1.2254	4.76
ECA+Octane	303K	0.5064	0.5064	0.0000	1.2609	4.80
ECA+Octane	308K	0.6021	0.4033	0.1988	1.2542	4.82
ECA+Nonane	298K	0.6012	0.6012	0.0000	2.1114	4.78
ECA+Nonane	303K	0.6012	0.6012	0.0000	2.1193	4.92
ECA+Nonane	308K	0.6012	0.6012	0.0000	2.1203	5.00
ECA+Decane	298K	0.6027	0.6027	0.0000	3.1647	4.15
ECA+Decane	303K	0.6027	0.6027	0.0000	2.8049	4.05
ECA+Decane	308K	0.6027	0.7039	0.1012	3.1522	3.88
ECA+Dodecane	298K	0.6026	0.7029	0.1003	5.6674	2.97
ECA+Dodecane	303K	0.6026	0.6026	0.0000	5.7183	3.04
ECA+Dodecane	308K	0.6026	0.6026	0.0000	5.6337	2.90

Table 2. Statistical correlation and linear regression analysis between ΔRm and Δn. r is the Pearson correlation coefficient measuring the strength of linear relationship. The p-value indicates statistical significance of the correlation. Scaling factor k is obtained from linear regression ΔRm = k × Δn. R^2 is the coefficient of determination representing the fraction of variance in ΔRm explained by Δn.

Mixture	T(K)	r	p-value	k	R^2
ECA+Hexane	298K	0.9834	< 0.0001	0.0369	0.9668
ECA+Hexane	303K	0.9805	< 0.0001	0.0339	0.9608
ECA+Hexane	308K	0.9504	< 0.0001	0.0217	0.9028
ECA+Heptane	298K	0.9798	< 0.0001	0.1285	0.9599
ECA+Heptane	303K	0.9781	< 0.0001	0.1298	0.9567
ECA+Heptane	308K	0.9690	< 0.0001	0.1276	0.9380
ECA+Octane	298K	0.9969	< 0.0001	0.2634	0.9939
ECA+Octane	303K	0.8011	0.0030	0.2288	0.6344
ECA+Octane	308K	0.9789	< 0.0001	0.2510	0.9573
ECA+Nonane	298K	0.9982	< 0.0001	0.4389	0.9963
ECA+Nonane	303K	0.9963	< 0.0001	0.4358	0.9922
ECA+Nonane	308K	0.9964	< 0.0001	0.4437	0.9929
ECA+Decane	298K	0.9931	< 0.0001	0.7870	0.9852
ECA+Decane	303K	0.9957	< 0.0001	0.6976	0.9892
ECA+Decane	308K	0.9865	< 0.0001	0.8134	0.9723
ECA+Dodecane	298K	0.9893	< 0.0001	1.8139	0.9784
ECA+Dodecane	303K	0.9932	< 0.0001	1.8142	0.9860
ECA+Dodecane	308K	0.9619	< 0.0001	1.8433	0.9216

Table 3. Temperature sensitivity of ΔRm and Δn from 298.15 K to 308.15 K. Average absolute values are computed by averaging |ΔRm| and |Δn| over all compositions (excluding pure components) at each temperature. The percentage change is calculated as: Change (%) = [Value(308 K) - Value(298 K)]/Value(298 K) × 100%. Negative values indicate decrease with increasing temperature.

Mixture	Avg |ΔRm| 298K	Avg |ΔRm| 308K	ΔRm Change %	Avg |Δn| 298K	Avg |Δn| 308K	Δn Change %
ECA+Hexane	0.0776	0.0295	-62.0	2.09	1.37	-34.5
ECA+Heptane	0.4448	0.4278	-3.8	3.46	3.32	-4.0
ECA+Octane	0.8812	0.9132	3.6	3.35	3.60	7.7
ECA+Nonane	1.5527	1.5077	-2.9	3.55	3.39	-4.4
ECA+Decane	2.2857	2.3069	0.9	2.88	2.81	-2.3
ECA+Dodecane	4.1234	4.0812	-1.0	2.28	2.17	-4.9

Figure 1. Variation of scaling factor k with alkane chain length, showing systematic increase from hexane (C6) to dodecane (C12) at 298.15 K.

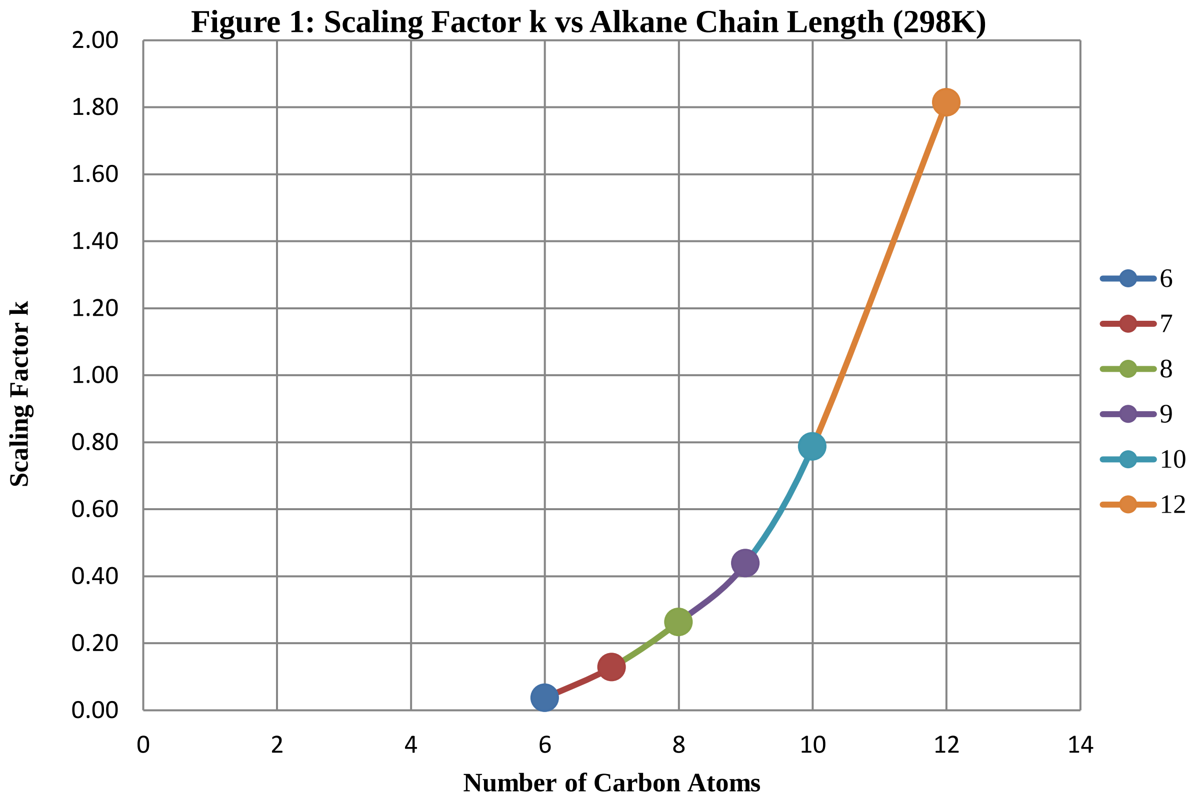

Figure 2. Temperature dependence of average absolute deviations for ΔRm and Δn across all mixtures

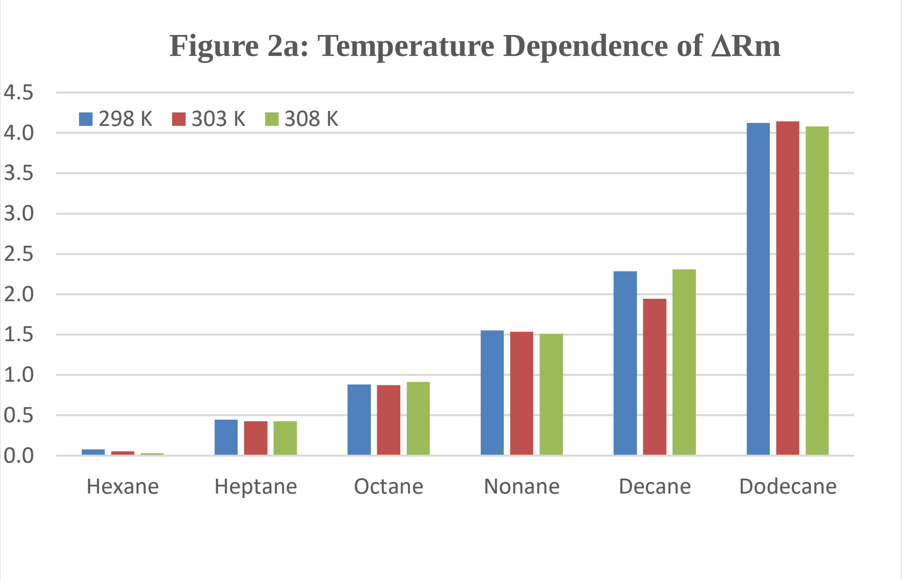

Figure 2a: Temperature Dependence of ΔRm

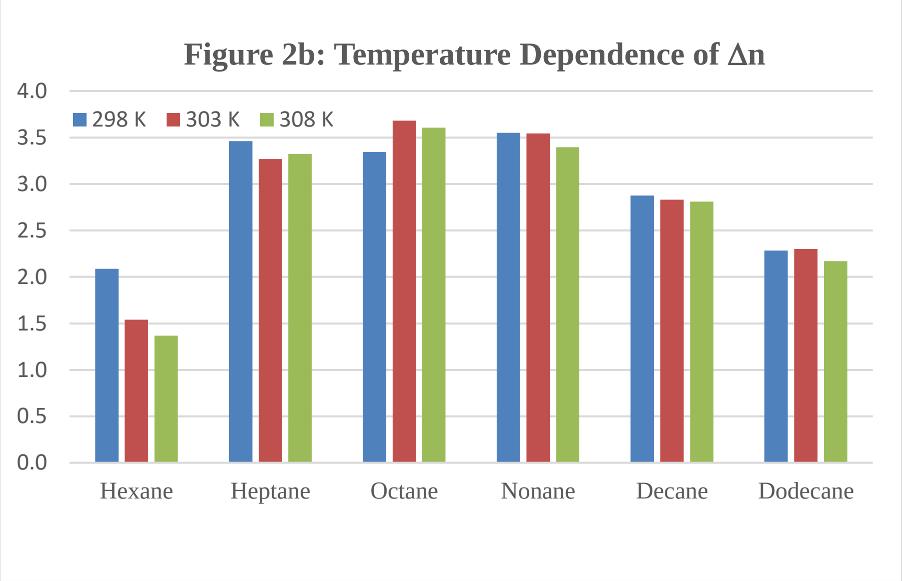

Figure 2b: Temperature Dependence of Δn

Figure 3. Molar refraction deviation (ΔRm) versus mole fraction of ethyl chloroacetate for all six mixtures at 298.15 K .

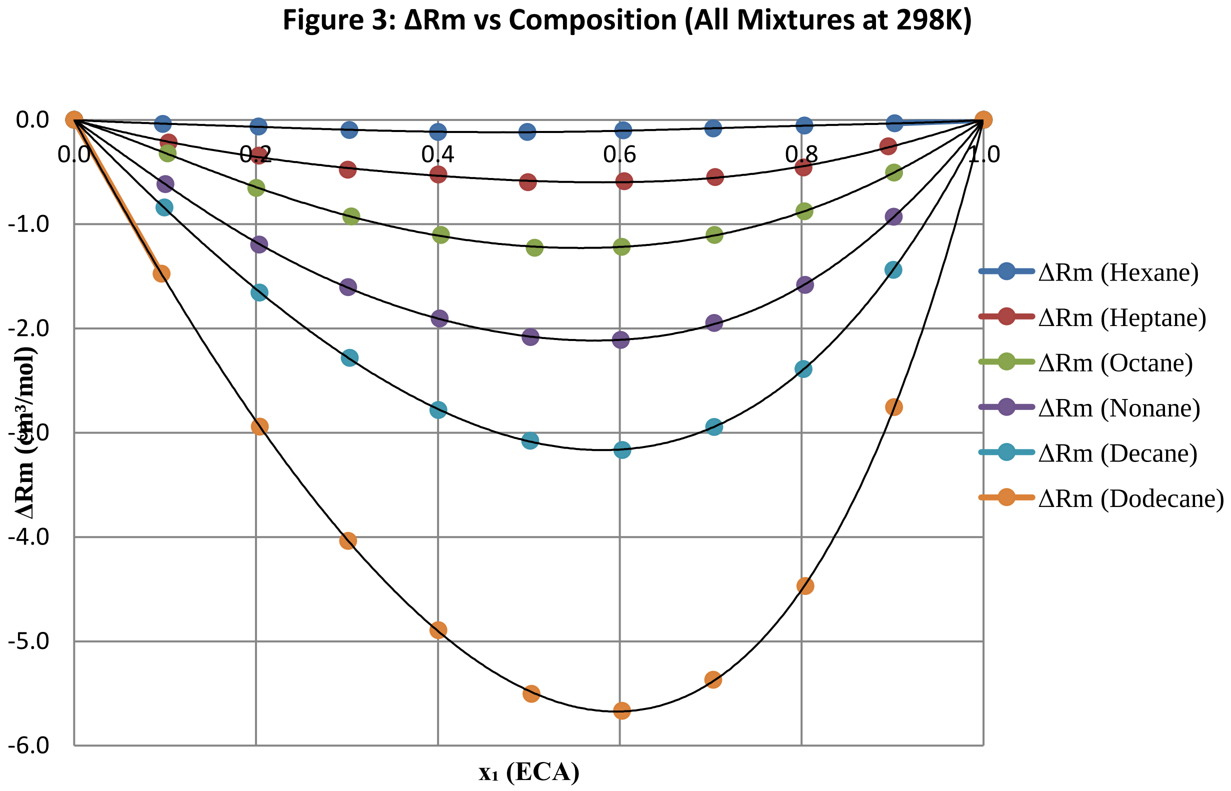

Figure 4. Linear relationship between ΔRm and Δn for all mixtures at 298.15 K, demonstrating strong correlation with system-dependent scaling.