

MOLECULAR INTERACTION STUDIES IN MIXTURES OF METHYLCYCLOHEXANE WITH ALKANES: A THEORETICAL APPROACH

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ABSTRACT

Experimental values of density at (298.15, 303.15, and 308.15) K in the binary mixtures of methylcyclohexane with *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*-dodecane, and *iso*-octane are presented over the entire mole fraction range of the binary mixtures. Using these data, excess molar volume is calculated. The observed experimental V^E values are compared with Prigogine-Flory-Patterson (PFP) and Flory theories. Excess molar enthalpy and excess Gibbs free energy of mixing are calculated using PFP theory. All the computed quantities are fitted to Redlich and Kister equation to derive the coefficients and estimate the standard error values. Such a study on model calculations in addition to presentation of experimental data on binary mixtures are useful to understand the mixing behaviour of liquids in terms of molecular interactions and orientational order-disorder effects.

KEY WORDS

Methylcyclohexane, Aliphatic hydrocarbons, Excess molar volume, Isentropic compressibility, Molecular interaction

INTRODUCTION

Long-chain alkanes have been the subject of intense thermodynamic studies to understand the nature of molecular interactions when they are present with the other types of liquids. Aminabhavi and co-workers have studied molecular interactions and thermodynamic properties of several binary mixtures of bis (2-methoxyethyl) ether, cyclohexane, ethenylbenzene, bromoform, cyclohexanone, 2-ethoxyethanol, styrene, 1-chloronaphthalene and ethylchloroacetate as first components with *n*-alkanes as the second component¹⁻². Stella Dermini et al.³ measured excess volumes of cycloalkanes + *n*-alkanes. Tojo, J. et al.⁴ measured densities and excess properties of dimethyl carbonate with alkanes (C₆-C₉). Mixtures containing different alkanes with a variety of organic liquids, with respect to

different properties, have been extensively studied by different authors⁵⁻¹¹.

Juon B. Monton et al.¹² measured densities, refractive indices, and derived excess properties of toluene + *iso*-octane and methylcyclohexane + *iso*-octane binary mixtures only at 298.15 K. Excess volumes of methylcyclohexane with substituted benzenes were studied by D. Venkatesulu and co-workers¹³. M.C.S. Subha and S. Brahmajirao¹⁴ studied excess volumes and viscosities of propionic acid in methylcyclohexane. Only speed of sound and isentropic compressibility were studied for *n*-butanol + alkane mixtures by Nath and Jagan¹⁵. Flory and coworkers¹⁶⁻¹⁷ proposed theoretical relations to compute excess quantities of liquid mixtures. Aicart et al.¹⁸⁻²⁰ used Prigogine-Flory theory to correlate isothermal compressibility, k_T of the mixtures. Patterson and Delmas²¹

combined both the Prigogine²² and Flory⁷ theories to propose a more generalized equation, called Prigogine-Flory-Patterson (PFP) theory. From this theory, contributions from interactional, free volume and internal pressure towards excess quantities can be studied. PFP theory has been successfully used to obtain the theoretical estimates of excess thermodynamic functions of the non-electrolyte binary mixtures comprising *n*-alkanes.

Realizing the importance of the above mentioned theories, we have accumulated accurate data on density, ρ at 298.15 K, 303.15 K, and 308.15 K of methylcyclohexane with alkanes (*n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*-dodecane, and *iso*-octane). Using these data, excess molar volume, V^E are calculated²⁷. The experimental results are analysed by the Redlich and Kister polynomial equation to derive the binary coefficients and estimate the standard errors. Excess molar volumes are also calculated using Flory and PFP theories. The calculated results are discussed in terms of intermolecular interactions between methylcyclohexane and alkanes. Hence, an attempt is made here to investigate the detailed thermodynamic studies on these mixtures using the existing theories.

MATERIALS AND METHODS

Analytical reagent grade samples of methylcyclohexane, *n*-hexane, *n*-heptane, *n*-octane and *n*-decane were procured from s.d.fine-Chem. Pvt. Ltd., Mumbai, India. *N*-dodecane is an L.R.grade sample purchased from Spectrochem Pvt. Ltd., Mumbai, India. *Iso*-octane is also a L.R.grade sample procured from Qualigen Fine chemicals, Mumbai, India.

Excess molar volume, V^E at 298.15, 303.15 and 308.15K for the binary mixtures are calculated¹⁻² respectively, using the experimental values of ρ :

$$V^E = V_m - (V_1x_1 + V_2x_2) \quad (1)$$

Densities of pure components and their mixtures were determined at atmospheric pressure by using densitometer DMA 4500 (Anton Paar). The DMA 4500 is the oscillating U-tube density meter, which measures density with an uncertainty of $\pm 0.0001 \text{ g. cm}^{-3}$ in wide viscosity and temperature ranges. By measuring the damping of the U-tube's oscillation caused by the viscosity of the filled-in sample, the DMA 4500 automatically corrects viscosity related errors.

To perform the measurement, we select one out of a total of 10 individual measuring methods, and fill the sample into the measuring cell. An acoustic signal will inform us when the measurement is completed. The results are automatically converted (including temperature compensation wherever necessary) into concentration, specific gravity or other density-related units using the built-in conversion tables and functions. The density results, including sample number or name, shown on the programmable LC display, is transferred to the data memory. Temperature was controlled within an uncertainty of $\pm 0.01\text{K}$ using a constant temperature bath. A Julabo immersion cooler was used to cool water bath. This unit was installed at the intake of a heating circulating bath liquid. Immersion probe was connected to the instrument with a flexible and insulated tube which maintained the constant temperature of the bath.

Experimental data of density and refractive index at 298.15K temperature for pure liquids are compared with literature in **Table 1**. Average values of triplicate measurements of density at $T = (298.15, 303.15 \text{ and } 308.15) \text{ K}$ are given in **Table 2**.

Where, V_m is molar volume of the mixture, V_1 and V_2 are molar volumes of pure components; x_i , represents mole fraction of the i^{th} component of the mixture.

RESULTS

Excess molar volume data at 298.15 K are displayed in Graph 1. Points on the curves represent V^E values calculated from equation (1), while smooth curves are drawn from the best fitted values of V^E calculated from equation (2).

Effect of temperature on V^E has been studied for all the binary mixtures. A typical graph displaying the effect of temp on V^E vs x_1 for methylcyclohexane (1) + *n*-hexane (2) is shown in **Figure 2**.

The mixing quantities viz., V^E have been fitted to Redlich-Kister²⁵ equation by the method of least-squares using the Marquardt algorithm²⁶ to derive the binary coefficients, A_j and standard deviation, σ :

$$V^E(\Delta Y) = x_1 x_2 \sum_{i=k}^k A_j (x_2 - x_1)^{j-1} \quad (2)$$

In each case, the optimum number of coefficients, A_j was ascertained from an examination of the variation of the standard deviation, σ ,

$$\sigma = \left(\frac{\sum (Y_{\text{cal}}^E - Y_{\text{obs}}^E)^2}{(n - m)} \right)^{1/2} \quad (3)$$

Where n represents the number of measurements and m , the number of coefficients. The estimated values of A_j and σ for V^E are summarized in **Table 3**. In all the cases, the best fit was obtained by using only three fitting coefficients in all the cases.

In the above calculations, only the empirical equations have been used to compute excess functions. The nature or type of molecular- interactions have been studied based on these data. In an effort to quantify these data, it is essential to test them based on theories that are mentioned earlier. These will be discussed in the following sections.

Theoretical Calculations of Excess Molar Functions

(i) Flory Theory

By using Flory equation of state, excess molar volume (V^E) has been theoretically calculated^{16,17} which is given in the form.

$$V^E = \left(\sum_{i=1}^2 x_i V_i^* \right) \left(\tilde{V}^0 \right)^{7/3} \left[4/3 - (\tilde{V}^0)^{1/3} \right] (\tilde{T} - \tilde{T}^0) \quad (4)$$

$$\text{Where } \tilde{V}^0 \text{ is given by } \tilde{V}^0 = \Phi_1 \tilde{V}_1 + \Phi_2 \tilde{V}_2 \quad (5)$$

Here, $V_i^* = \frac{V_i}{\tilde{V}_i}$ is characteristic volume of the i -th component in the mixture. Reduced volume $\tilde{V}$ is calculated from thermal expansion coefficient, $\alpha \left[\equiv - (1/\rho) (\partial \rho / \partial T)_P \right]$ using the relation:

$$\tilde{V} = \left[\frac{1 + (4/3) \alpha T}{(1 + \alpha T)} \right]^3 \quad (6)$$

Reduced temperature, $\tilde{T}$ and ideal reduced temperature, $\tilde{T}^o$ in Eq. (4) are calculated as:

$$\tilde{T}^o = \frac{(\tilde{V}^o)^{1/3} - 1}{\tilde{V}^o^{4/3}} \quad (7)$$

The $\tilde{T}$ of the mixture is then calculated as:

$$\tilde{T} = \frac{(\Phi_1 P_1^* \tilde{T}_1 + \Phi_2 P_2^* \tilde{T}_2)}{(\Phi_1 P_1^* + \Phi_2 P_2^*)} \quad (8)$$

where the segment or hard-core volume fraction, Φ_i is calculated as:

$$\Phi_i = \frac{x_i V_i^*}{\sum_{i=1}^2 (x_i V_i^*)} \quad \text{And} \quad \Phi_1 = 1 - \Phi_2 \quad (9)$$

$$P^* = \frac{T \tilde{V}^2 \alpha}{k_T}$$

Characteristic pressure, P^* is calculated using:

(10)

Where k_T is computed from isentropic compressibility, k_S and heat capacity, C_p of liquids using:

$$k_T = k_S + T \alpha^2 V / C_p \quad (11)$$

From the experimental densities, the values of α have been calculated at different temperatures and are compared with literature values in **Table 4**. While calculating P^* from Eq. (10), we have used the C_p data of the mixtures as calculated from the additive relation. The parameters used in these calculations are presented in **Table 4**.

(ii) Prigogine-Flory-Patterson (PFP) Theory

V^E of the mixtures can be computed by using Prigogine-Flory-Patterson (PFP) Theory. The PFP theory for V^E given in the following form has been used to compute V^E of the mixtures:

$$\begin{aligned} \frac{V^E}{(x_1 V_1^* + x_2 V_2^*)} = & \frac{(\tilde{V}^{1/3} - 1) \tilde{V}^{2/3}}{[(4/3) \tilde{V}^{-1/3} - 1]} \psi_1 \theta_2 \left(\frac{X_{12}}{P_1^*} \right) \\ & - \frac{(\tilde{V}_1 - \tilde{V}_2)^2 [(14/9) \tilde{V}^{-1/3} - 1] \psi_1 \psi_2}{[(4/3) \tilde{V}^{-1/3} - 1] \tilde{V}} \\ & + \frac{(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)}{(P_1^* \psi_2 + P_2^* \psi_1)} \psi_1 \psi_2 \end{aligned} \quad (12)$$

The first term of Eq. (12) represents the interactional contribution (V_{int}^E) to V^E i.e., X_{12} parameter, often called contact interaction parameter; the second term is the difference in "free volume", V_{fv}^E , while the third term is the internal pressure contribution ($V_{p^*}^E$) i.e., p^* effect to V^E . In order to compute V^E from Eq. (12), the parameter values given in **Table 5** are used. To compute interactional contribution to V^E , one must evaluate contact interaction energy parameter, X_{12} . This can be calculated by employing the Marquardt algorithm in an optimization procedure using the experimental H^E data at 298.15 K from

Flory theory. The X_{12} values for each mixture at different compositions can be obtained so as to minimize $\sigma^2(X_{12})$ in the following equation:

$$\sigma_H^2(X_{12}) = \int_0^1 (H_{\text{exp}}^E - H_{\text{cal}}^E(X_{12}))^2 dx_1 \quad (13)$$

Where H_{exp}^E and $H_{\text{cal}}^E(X_{12})$ respectively, denote the experimental H^E data and those calculated from PFP theory. Because of the non-availability of experimental H^E data, X_{12} values are calculated using experimental V^E values at 298.15 K from Eq. (13a).

$$X_{12} = \frac{1}{(\Phi_1 \theta_2 \tilde{T}(X_{12}))} \left[\sum \Phi_i P_i^* (\tilde{T}(X_{12}) - \tilde{T}_i(X_{12})) \right] \quad (13a)$$

The results of X_{12} calculated in this way are presented in **Table 5** and do not show any systematic variation on the length of alkanes.

Reduced temperature of the mixture as a function of X_{12} was then calculated using:

$$\tilde{T}(X_{12}) = \frac{(\Phi_1 P_1^* \tilde{T}_1 + \Phi_2 P_2^* \tilde{T}_2)}{(\Phi_1 P_1^* + \Phi_2 P_2^* - \Phi_1 \theta_2 X_{12})} \quad (14)$$

Here, the surface site fraction θ_2 was calculated as:

$$\theta_2 = 1 - \theta_1 = \frac{\Phi_2}{\left[\Phi_2 + \Phi_1 \left(\frac{V_2^*}{V_1^*} \right)^{1/3} \right]} \quad (15)$$

The contact energy fraction ψ_i was calculated as:

$$\psi_1 = 1 - \psi_2 = \frac{x_1 P_1^* V_1^*}{\sum_{i=1}^2 (x_i P_i^* V_i^*)} \quad (16)$$

Next, by following Flory theory, excess enthalpy, H^E and excess free energy, G^E have been calculated using the following equations:

$$H^E = \sum_{i=1}^2 x_i P_i^* V_i^* \left(\frac{1}{\tilde{V}_i} - \frac{1}{\tilde{V}} \right) + \frac{x_1 \theta_2 V_1^* X_{12}}{\tilde{V}} \quad (17)$$

$$S^E = -3 \left[\frac{x_1 P_1^* V_1^*}{T_1^*} \ln \left(\frac{\tilde{V}_1^{1/3} - 1}{\tilde{V}^{1/3} - 1} \right) + \frac{x_2 P_2^* V_2^*}{T_2^*} \ln \left(\frac{\tilde{V}_2^{1/3} - 1}{\tilde{V}^{1/3} - 1} \right) \right] \quad (18)$$

$$G^E = \sum_{i=1}^2 x_i P_i^* V_i^* \left[\left(\frac{1}{\tilde{V}_i} - \frac{1}{\tilde{V}} \right) + 3 \tilde{T}_i \ln \left(\frac{\tilde{V}_i^{1/3} - 1}{\tilde{V}^{1/3} - 1} \right) \right] + \frac{x_1 \theta_2 V_1^* X_{12}}{\tilde{V}} \quad (19)$$

The computed values of θ_2 and X_{12} along with the comparison of experimental near equimolar V^E data with the literature and those of V^E results calculated from Flory and PFP theories are given in **Table 5**.

PFP contribution terms due to interactional, free volume and internal pressure are also included in Table 5.

Table 1: Comparison of Experimental Densities (ρ) and Refractive Indices (n_D) of Pure Liquids with Literature at 298.15 K

Liquids	(Mol% purity)	$\rho/(\text{kg.m}^{-3})$		n_D	
		Expt.	Lit.	Expt.	Lit.
Methylcyclohexane	(>99.0)	765.0	765.0 ²⁴	1.4217	1.4206 ²⁴
<i>n</i> -Hexane	(>99.0)	654.9	654.8 ²⁴	1.3736	1.3723 ²⁴
<i>n</i> -Heptane	(>99.5)	679.7	679.5 ²⁴	1.3860	1.3851 ²⁴
<i>n</i> -Octane	(>99.7)	698.6	698.6 ²⁴	1.3974	1.3951 ²⁴
<i>n</i> -Nonane	(>98.0)	714.8	714.8 ²⁴	1.4021	1.4031 ²⁴
<i>n</i> -Decane	(>99.0)	726.6	726.4 ²⁴	1.4108	1.4096 ²⁴
<i>n</i> -Dodecane	(>99.0)	746.2	746.0 ²⁴	1.4187	1.4192 ²⁴
<i>iso</i> -Octane	(>99.0)	687.8	687.8 ²⁴	1.3881	1.3889 ²⁴

Table2. Experimental Density (ρ) of Binary Mixtures at Different Temperatures

Methylcyclohexane (1) + <i>n</i> - Hexane (2)			
x_1	$\rho/(\text{kg. m}^{-3})$		
	298.15 K	303.15 K	308.15 K
0.0000	654.9	650.4	645.7
0.1042	666.5	662.0	657.4
0.2026	677.4	672.9	668.4
0.3010	688.4	683.9	679.4
0.4018	699.5	695.1	690.6
0.5026	710.7	706.3	701.8
0.6024	721.6	717.2	712.8
0.7021	732.5	728.1	723.7
0.8016	743.3	739.0	734.6
0.9011	754.1	749.8	745.4
1.0000	765.0	760.7	756.3

Methylcyclohexane (1) + <i>n</i> - Heptane (2)			
x_1	$\rho/(\text{kg. m}^{-3})$		
	298.15 K	303.15 K	308.15 K
0.0000	679.7	675.4	671.1
0.1021	683.4	683.2	678.9
0.2033	695.2	691.1	686.7
0.3044	703.3	699.0	694.7
0.4036	713.4	707.1	702.8
0.5029	719.7	715.4	711.1
0.6033	728.3	724.1	719.8
0.7038	737.2	732.9	728.6
0.8022	746.2	741.9	737.6
0.9006	755.4	751.1	746.7
1.0000	765.0	760.7	756.3

Methylcyclohexane (1) + <i>n</i> - Octane (2)			
x_1	$\rho/(\text{kg. m}^{-3})$		
	298.15 K	303.15 K	308.15 K
0.0000	698.6	694.6	690.5
0.1044	704.1	700.0	696.0
0.2066	709.7	705.6	701.5
0.3045	715.3	711.2	707.1
0.4068	721.5	717.4	713.3
0.5043	727.7	723.6	719.4
0.6015	734.3	730.0	725.9
0.7015	741.3	737.1	732.9
0.8023	748.8	744.6	740.3
0.8984	756.4	752.1	747.8
1.0000	765.0	760.7	756.3

Methylcyclohexane (1) + <i>n</i> - Nonane (2)			
x_1	$\rho/(\text{kg. m}^{-3})$		
	298.15 K	303.15 K	308.15 K
0.0000	714.8	710.9	707.0
0.1052	718.6	714.7	710.7
0.1980	722.1	718.1	714.2
0.2990	726.2	722.2	718.2
0.4018	730.7	726.7	722.6
0.4978	735.2	731.0	727.1
0.5982	740.2	736.1	732.0
0.6991	745.7	741.6	737.4
0.7995	751.6	747.4	743.2
0.9012	758.1	753.9	749.6
1.0000	765.0	760.7	756.3

Methylcyclohexane (1) + <i>n</i> - Decane (2)			
x_1	$\rho/(\text{kg. m}^{-3})$		
	298.15 K	303.15 K	308.15 K
0.0000	726.6	722.9	719.1
0.1014	729.1	725.3	721.5
0.2034	731.8	728.0	724.2
0.3035	734.7	730.9	727.0
0.4055	738.0	734.1	730.2
0.5004	741.3	737.3	733.4
0.5998	745.1	741.1	737.0
0.7041	749.4	745.4	741.3
0.8039	754.1	749.9	745.8
0.8993	759.1	754.8	750.6
1.0000	765.0	760.7	756.3

Methylcyclohexane (1) + <i>n</i> - Dodecane (2)			
x_1	$\rho/(\text{kg. m}^{-3})$		
	298.15 K	303.15 K	308.15 K
0.0000	746.3	742.7	739.0
0.1004	747.2	743.6	739.9
0.2017	748.3	744.6	740.9
0.2968	749.5	745.7	742.0
0.4060	750.9	747.2	743.4
0.5059	752.5	748.7	744.8
0.6011	754.2	750.3	746.4
0.6993	756.2	752.3	748.3
0.7989	758.7	754.6	750.5
0.8980	761.5	757.3	753.1
1.0000	765.0	760.7	756.3

Methylcyclohexane (1) + <i>iso</i> - Octane (2)			
x_1	$\rho/(\text{kg. m}^{-3})$		
	298.15 K	303.15 K	308.15 K
0.0000	687.8	683.7	679.5
0.1050	694.4	690.3	686.1
0.2010	700.7	696.6	692.4
0.3024	707.7	703.5	699.3
0.4039	715.0	710.8	706.5
0.4998	722.1	717.9	713.7
0.6064	730.4	726.2	721.9
0.6991	738.0	733.7	729.5
0.8004	746.6	742.4	738.1
0.9007	755.6	751.3	747.0
1.0000	765.0	760.7	756.3

Table 3: Estimated Parameters of Eq. (2) and Standard Errors, σ from Eq. (3) for Various Functions of the Binary Mixtures at Different Temperatures.

Function	Temp/K	A_1	A_2	A_3	σ
Methylcyclohexane (1) + <i>n</i>- Hexane (2)					
$V^E/10^{-6}(\text{m}^3.\text{mol}^{-1})$	298.15	-0.821	-0.101	0.259	0.003
	303.15	-0.876	-0.080	0.280	0.003
	308.15	-0.951	-0.094	0.261	0.004
Methylcyclohexane (1) + <i>n</i>- Heptane (2)					
$V^E/10^{-6}(\text{m}^3.\text{mol}^{-1})$	298.15	-0.052	-0.028	0.019	0.001
	303.15	-0.094	-0.122	-0.118	0.012
	308.15	-0.133	-0.056	-0.009	0.003
Methylcyclohexane (1) + <i>n</i>- Octane (2)					
$V^E/10^{-6}(\text{m}^3.\text{mol}^{-1})$	298.15	0.266	-0.098	0.101	0.004
	303.15	0.253	-0.125	0.089	0.005
	308.15	0.230	-0.099	0.045	0.002
Methylcyclohexane (1) + <i>n</i>- Nonane (2)					
$V^E/10^{-6}(\text{m}^3.\text{mol}^{-1})$	298.15	0.376	-0.075	-0.046	0.002
	303.15	0.366	-0.064	-0.119	0.006
	308.15	0.320	-0.036	-0.085	0.003
Methylcyclohexane (1) + <i>n</i>- Decane (2)					
$V^E/10^{-6}(\text{m}^3.\text{mol}^{-1})$	298.15	0.481	-0.116	0.130	0.004
	303.15	0.445	-0.122	0.085	0.004
	308.15	0.416	-0.121	0.040	0.003
Methylcyclohexane (1) + <i>n</i>- Dodecane (2)					
$V^E/10^{-6}(\text{m}^3.\text{mol}^{-1})$	298.15	0.592	-0.149	-0.070	0.002
	303.15	0.538	-0.125	-0.074	0.002
	308.15	0.478	-0.098	-0.077	0.003
Methylcyclohexane (1) + <i>iso</i>-Octane (2)					
$V^E/10^{-6}(\text{m}^3.\text{mol}^{-1})$	298.15	-0.525	0.030	0.064	0.003
	303.15	-0.553	0.014	0.040	0.002
	308.15	-0.577	0.013	0.012	0.001

Table 4: Molar volume (V), Critical Temperature (T_c), Heat capacity (C_p), Thermal Expansion Coefficient (α), Characteristic Pressure (P^*), and Isothermal Compressibility (k_T) for Methylcyclohexane and Pure Alkanes

Liquid	V ($\text{cm}^3 \cdot \text{mol}^{-1}$)	T_c	$C_p^{[65]}$ ($\text{J} \cdot \text{K} \cdot \text{mol}^{-1}$)	$\alpha \cdot 10^3$ (K^{-1}) (lit)	$\alpha \cdot 10^3$ (K^{-1}) (expt)	$P^* \cdot 10^6$ ($\text{J} \cdot \text{cm}^{-3}$)	k_T (TPa^{-1})
Methylcyclohexane	128.3	572.1	185.3	1.136	1.135	479	1148
<i>n</i> - Hexane	131.6	507.7	195.4	1.391	1.397	427	1697
<i>n</i> - Heptane	147.4	540.7	224.9	1.235	1.258	431	1430
<i>n</i> - Octane	163.5	568.8	254.1	1.164	1.159	437	1302
<i>n</i> - Nonane	179.4	594.6	284.5	1.077	1.092	436	1175
<i>n</i> - Decane	195.8	617.6	314.5	1.050	1.044	466	1064
<i>n</i> - Dodecane	228.3	658.3	375.9	0.970	0.971	455	984
<i>iso</i> -Octane	166.0	543.9	238.5	1.207	1.209	383	1560

Table 5: Comparison of excess molar volume data with theoretical calculations at 298.15K for Methylcyclohexane (MeC) + Alkanes mixtures near equimolar compositions

MeC with alkanes	θ_2	$X_{12}/(\text{J} \cdot \text{mol}^{-1})$		$V^E/10^{-6}(\text{m}^3 \cdot \text{mol}^{-1})$			PFP Contributions $V^E/10^{-6}$ ($\text{m}^3 \cdot \text{mol}^{-1}$)			G^E Jmol^{-1}
		H^E	V^E	Expt	Flory	PFP	$V^E(\text{int})$	$V^E(\text{fv})$	$V^E(\text{ip})$	
C ₆	0.4954	-2.44	0.465	-0.208	-0.285	-0.042	-0.065	0.084	-0.137	-31.4
C ₇	0.5177	1.960	2.130	-0.013	-1.700	-0.018	0.051	0.014	-0.054	42.94
C ₈	0.5353	6.296	3.200	0.067	0.149	0.016	0.165	0.001	-0.014	134.1
C ₉	0.5593	3.742	2.560	0.093	0.123	0.023	0.096	0.006	0.033	84.05
C ₁₀	0.5717	6.237	4.700	0.119	0.158	0.030	0.156	0.013	0.014	145.1
C ₁₂	0.5932	-13.8	5.779	0.149	-0.345	0.041	-0.348	0.052	0.055	-318
C _{8 (iso)}	0.5412	-2.33	-1.24	-0.13	-0.162	-0.030	-0.066	0.008	-0.087	-47.9

int- interactional contribution ;

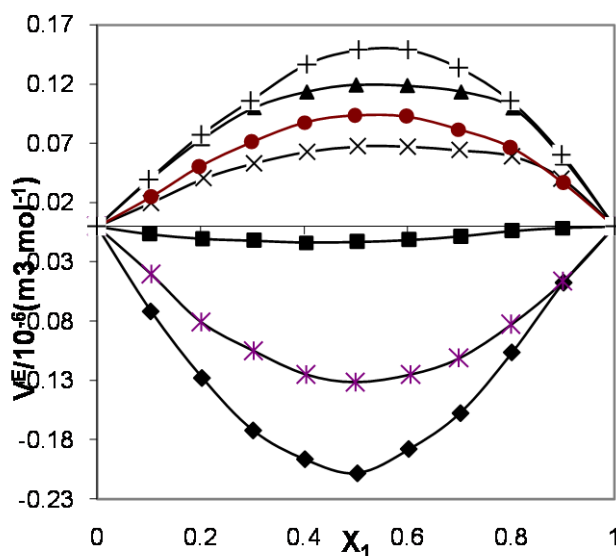
fv-free volume contribution

ip- internal pressure contribution ;

C₆- C₁₂ are the chain carbon atoms of alkanes

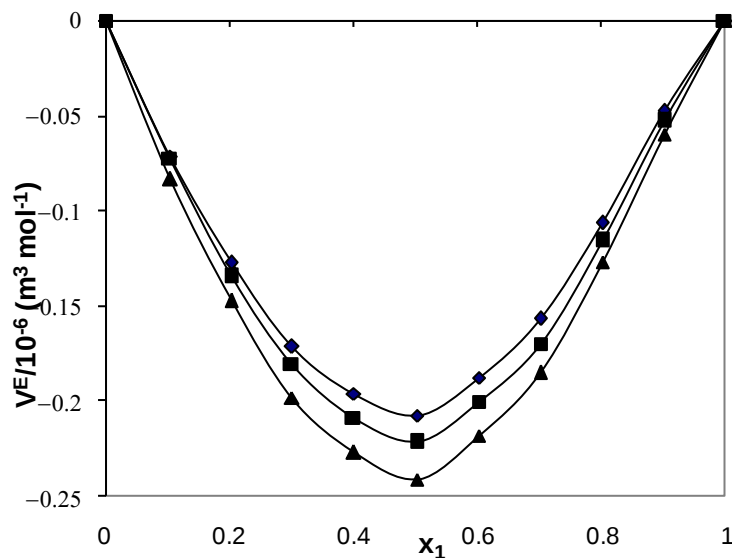
C_{8 (iso)}- *iso*-Octane

Graph 1



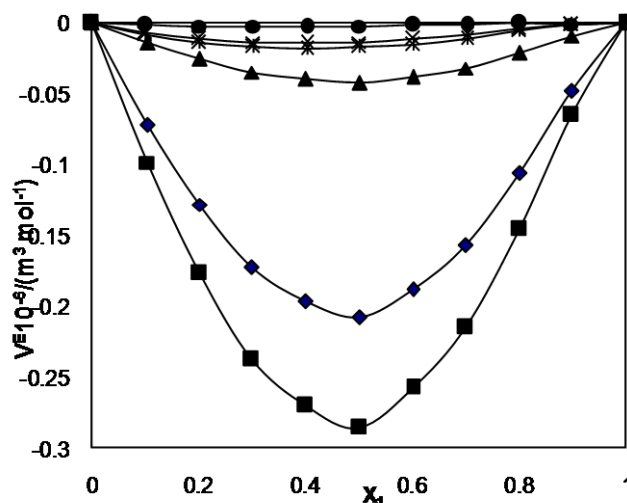
Excess molar volume (V^E) versus mole fraction of methylcyclohexane with ($\diamond$) *n*-hexane, ($\blacksquare$) *n*-heptane, ($\times$) *n*-octane, ($\bullet$) *n*-nonane, ($\blacktriangle$) *n*-decane ($+$) *n*-dodecane and ($*$) *iso*-octane at 298.15 K.

Graph 2



Effect of temperature on V^E versus mole fraction for methylcyclohexane (1) + *n*-hexane (2) at 298.15 K ($\diamond$), 303.15 K ($\blacksquare$) and 308.15 K ($\blacktriangle$).

Graph 3



Comparison of V^E vs x_1 for mixtures of methyl cyclohexane with n -hexane : (◆) Expt., (■) Flory theory (▲) PFP theory and for mixtures of methylcyclohexane with n -heptane : (x) Expt., (*) Flory theory and (●) PFP theory at 298.15

DISCUSSION

Excess molar volume data at 298.15 K are displayed in Graph 1. Large negative deviation of V^E observed for methylcyclohexane + n -hexane ($-0.21 \times 10^{-6} \text{ m}^3/\text{mol}$ at $x_1=0.5$) mixtures may be due to interstitial accommodation of hexane molecules in the voids created by methylcyclohexane molecules.

For methylcyclohexane + n -heptane mixtures V^E values are slightly negative ($-0.013 \times 10^{-6} \text{ m}^3/\text{mol}$ at $x_1=0.5$), while in case of n -octane, n -nonane, n -decane and n -dodecane V^E values increase systematically [(0.067, 0.09, 0.12 and 0.15) $\times 10^{-6} \text{ m}^3/\text{mol}$ at near $x_1=0.5$] as chain length increases indicating volume expansion upon mixing of alkanes with methylcyclohexane. This signifies that with increasing size of alkanes, volume expansion will be larger, indicating dispersion type of interactions between the component liquids. V^E values for methylcyclohexane + iso -octane ($-0.13 \times 10^{-6} \text{ m}^3/\text{mol}$ at $x_1=0.5$) are negative which may be due to compactness of iso -octane molecules and their interstitial accommodation

in the voids created by the methylcyclohexane molecules. Similar increasing trend in V^E values is commonly observed for mixtures from hexane to n -dodecane except iso -octane in literature. Effect of temperature on V^E has been studied for all the binary mixtures. With increase of temperature, V^E values decrease for all the mixtures in the mole fraction range. A typical graph displaying the effect of temp on V^E vs x_1 for methylcyclohexane (1) + n -hexane (2) is shown in Graph 2. As temperature increases the more negative values of V^E are observed.

Theoretical Calculations of Excess Molar Functions

(i) Flory Theory

By using Flory equation of state, excess molar volume (V^E) has been theoretically calculated. From the experimental densities, the values of α have been calculated at different temperatures and are compared with literature values in Table 4. While calculating P^* from Eq. (10), we have used the C_p data of the mixtures as calculated

from the additive relation. The parameters used in these calculations are presented in **Table 4**.

(ii) Prigogine-Flory-Patterson (PFP) Theory V^E of the mixtures can be computed by using Prigogine-Flory-Patterson (PFP) Theory. PFP contribution terms due to interactional, free volume and internal pressure are also included in **Table 5**. It may be noted that the PFP contributions from free volume and internal pressure are very small by both the calculations of X_{12} i.e., using enthalpy and excess volume data. In the original PFP theory, interactional term is generally positive in the absence of H-bond and other specific interactions. This is indeed the case for lower alkanes except hexane and dodecane. However, internal pressure contribution terms from PFP theory are negative for mixtures with hexane, heptane, octane and iso-octane, whereas for other mixtures the values are positive. The interactional term is usually dominant in H^E whereas, internal pressure contribution can be positive or negative depending upon the sign of $(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)$ term.

The P^* contribution from PFP theory depends either on the difference of thermal expansion coefficient or internal pressure of liquids. The P^* term often dominates V^E particularly, if one of the components has a higher P^* value and lower $\tilde{V}$ than the other. The P^* contribution to V^E is positive for all the mixtures and ultimately, this term dominates and decides the sign of V^E . A comparison of V^E typically for mixtures of methylcyclohexane with hexane and with heptane, with the values calculated from Flory and PFP theories is made in **Graph 3**. In both the cases, the V^E curves calculated from Flory and experimental data are lower than those calculated from PFP theory. The higher values of V^E from PFP theories is probably due to the contribution of the interactional term. This is true in all the cases. However, the magnitude of

V^E data of all the alkane containing mixtures vary depending upon the length of the chain of alkane molecule rather than their other physical properties.

CONCLUSION

The present chapter is a continuing effort towards the understanding of the mixing behavior of binary liquid mixtures comprising of methylcyclohexane and alkanes (C_6 - C_{12}). The measured physico-chemical properties of these mixtures have been used to predict the excess functions. These data when compared with the computed values using the available theoretical models agreed within the limits of experimental error.

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