

Study on volumetric and acoustic properties of binary mixtures of p-Cymene with fluorobenzene, chlorobenzene and bromobenzene at various temperatures

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Volumetric and acoustic properties of p-cymene with fluorobenzene, chlorobenzene and bromobenzene have been investigated using density, (ρ), and speed of sound, (U) measurements over the entire composition range at T= (303.15, 308.15 and 313.15) K. From the experimentally measured density, (ρ); Excess molar volumes, (V_m^E), infinite dilution partial molar volume, ($\bar{V}_{m,i}^o$), excess partial molar volume, ($\bar{V}_{m,i}^{o,E}$), apparent molar volume, ($V_{m,\phi,i}$), infinite dilution apparent molar volume, ($V_{m,\phi,1}^o$), with empirical parameters, S_v , B_v and limiting apparent molar expansibility, (E_ϕ^o) have been calculated. Deviation in speed of sound, (ΔU), deviation in isentropic compressibility, ($\Delta\kappa_s$), deviation in acoustic impedance, (ΔZ), infinite dilution partial molar isentropic compressibility, ($\bar{K}_{s,m,i}^{o,E}$), excess partial molar isentropic compressibility, ($\bar{K}_{s,m,i}^{o,E}$), apparent molar isentropic compressibility, ($K_{s,m,\phi,i}$), infinite dilution apparent molar isentropic compressibility, ($K_{s,m,\phi,1}^o$) with empirical parameters S_k and B_k and intermolecular free length (L_f) have been calculated using experimentally measured speed of sound, (U). To derive fitting coefficients, (A_i) with standard deviation, (σ), excess properties were fitted to the Redlich-Kister type polynomial equation. Various theoretical speed of sound and average deviations have been calculated using well established equation like Nomoto, (U_{nmt}), Ideal Mixing Rule, (U_{imr}), Junji, (U_{junji}) and Jacobson's Free Length Theory, (U_{flt}). The variation of these properties with composition and temperature has been discussed in terms of molecular interaction on mixing and their interacting abilities have also been compared.

Keywords: Density, Speed of sound, Excess molar volume, Isentropic compressibility, Acoustic impedance

1 Introduction

A study on spectral, thermodynamic and transport properties such as FT-IR, density, viscosity, refractive index and speed of sound for binary and multicomponent liquid mixtures are reported by many research groups in recent years¹⁻⁷. Thermodynamic and transport properties are essential for a process design as well as understanding a structure orientation in liquid mixtures. The excess thermodynamic properties of binary liquid mixtures have been extremely helpful to get data on the intermolecular interactions and geometrical impacts in the frameworks^{8,9}.

The knowledge of physicochemical properties of binary liquid mixtures have significance importance in theoretical and applied areas of research, and such outcomes are frequently used in designing processes (flow, mass transfer or heat transfer calculations) in many chemical and industrial units. The excess property values obtained from these physical property

data reveal the physicochemical behaviour of the liquid mixtures regarding the arrangement of structure and intermolecular interactions between the component molecules in the mixture¹⁰. p-Cymene (1-methyl-4-(propan-2-yl) benzene) is a naturally obtained from oils of cypress and essential oils in various plant species. The study of volumetric and acoustic properties of p-cymene with organic solvents help us to understand the nature and behavior in binary mixture. The study of these parameters helps us in various separation techniques, mass transfer phenomena as well as in various analytical techniques^{11,12}.

In present study, the density, sound velocity and its related properties such as excess molar volumes and deviation in sound velocities were studied. Some theoretical sound velocities of binary mixture were calculated by using well known relations and were compared with experimental values. The results were interpreted in terms of intermolecular interaction between the components of binary mixture.

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2 Experimental

2.1 Chemicals

p-Cymene (with >95% purity, Tokyo chemical industry Co. Ltd., Tokyo, Japan), fluorobenzene (with 99% purity, S. D. Fine Chem. Ltd., India), chlorobenzene (with 99% purity, S. D. Fine Chem. Ltd., India), bromobenzene (with 99% purity, S. D. Fine Chem. Ltd., India) were used in this study as received. List of chemicals with details like CAS number, molar mass, chemical formula, supplier, purity and comparison of experimental values of densities (ρ) in g cm^{-3} and speed of sound (U) in m s^{-1} with literature values were reported in Table 1.

2.2 Apparatus and procedure

Binary mixtures were freshly prepared by gravimetrically with an electronic balance Reptech RA-2012 (supplied by Reptech India) with an accuracy of ± 0.0001 g. The uncertainty in the mole fraction of the mixtures was estimated to less than ± 0.0001 . Densities and sound velocity were measured by using automatic density and sound velocity meter (Anton Paar, DSA 5000 M, Anton Paar India Pvt. Ltd., Gurgaon, India). The instrument was calibrated by using highly pure deionized water provided by manufacturer. Temperature compensation in the instrument is achieved with inbuilt integrated Pt 1000 temperature sensor having measuring scale $0\text{ }^{\circ}\text{C}$ to $70\text{ }^{\circ}\text{C}$ ($32\text{ }^{\circ}\text{F}$ to $158\text{ }^{\circ}\text{F}$) with accuracy of $0.001\text{ }^{\circ}\text{C}$ ($0.002\text{ }^{\circ}\text{F}$) during the measurement

of density. The accuracy in densities and sound velocities were $\pm 0.000001\text{ g cm}^{-3}$ and $\pm 0.01\text{ ms}^{-1}$, respectively.

3 Calculations

3.1 Mathematical representation of excess or deviation functions

All the excess and deviation in properties have been fitting with the Redlich-Kister²¹ polynomial equation for representing excess or deviation functions for binary mixtures.

$$(Y)^E = x_1(1 - x_1) \sum_{i=1}^n A_i(2x_1 - 1)^i \quad \dots (1)$$

where, Y^E = excess/ deviation properties. x_i represents mole fraction of i^{th} component. A_i is fitting coefficient. The fourth-order form of equation of the Redlich-Kister equation gives the minimum standard deviation in Y^E . The standard deviation (σ) has been calculated using following relation.

$$\sigma(Y) = \left[\frac{\sum (Y_{exp}^E - Y_{cal}^E)^2}{N - P} \right]^{\frac{1}{2}} \quad \dots (2)$$

where, Y_{exp}^E , Y_{cal}^E represent experimental and calculated values of excess properties, respectively. N is the number of experimental points and P is the number of parameters of the Redlich-Kister equation. The values of Fitting coefficients (A_0, A_1, A_2, A_3, A_4) with standard deviation (σ) in least square representation of $V_m^E, \Delta U, \Delta \kappa_s, K_{s,m}^E, \Delta z$ for studied binary mixtures were reported in Table 2.

Table 1 — List of chemicals with details of CAS number, molar mass, chemical formula, supplier, purity and comparison of experimental values of Densities (ρ) in g cm^{-3} and Speed of sound (U) in m s^{-1} with literature values

Compound Name	CAS number	Molar mass g/mol	Chemical Formula	Supplier	Initial mass-fraction purity	Temp. in K	Densities (ρ) in g cm^{-3}		Speed of sound (U) in m s^{-1}	
							Exp.	Lit	Exp.	Lit
p-Cymene	99-87-6	134.21 g/mol	$\text{C}_{10}\text{H}_{14}$	TCI Co. Ltd. Tokyo, Japan	95%	303.15	0.847195	-----	1293.28	-----
						308.15	0.843178	-----	1273.89	-----
						313.15	0.839156	-----	1254.90	-----
Fluorobenzene	462-06-6	96.103 g/mol	$\text{C}_6\text{H}_5\text{F}$	S.D. Fine Chemicals Ltd. India	99%	303.15	1.013097	1.01316[34]	1145.29	1171[34]
						308.15	1.007057	-----	1125.26	-----
						313.15	1.000977	-----	1105.04	-----
Chlorobenzene	108-90-7	112.55 g/mol	$\text{C}_6\text{H}_5\text{Cl}$	S.D. Fine Chemicals Ltd. India	99.5%	303.15	1.095771	1.09547[35]	1249.33	1249[35]
						308.15	1.090368	1.09006[35]	1231.22	1235[35]
						313.15	1.084941	1.08366[36]	1212.98	1212.63 [38]
Bromobenzene	108-86-1	157.02 g/mol	$\text{C}_6\text{H}_5\text{Br}$	S.D. Fine Chemicals Ltd. India	98%	303.15	1.481918	1.48148[35]	1138.27	1131[39]
						308.15	1.475155	1.47481[35]	1122.88	1122[40]
						313.15	1.468378	1.4670[37]	1107.62	1109[41]

Table 2 — Fitting coefficients (A_0, A_1, A_2, A_3, A_4) with Standard deviation (σ) for Least square representation of $V_m^E, \Delta U, \Delta \kappa_s, K_{s,m}^E, \Delta z$ of p-cymene (1) + fluoro-, chloro- and bromobenzene (2) binary mixtures

	T (K)	A_0	A_1	A_2	A_3	A_4	σ
p-Cymene (1) + Fluorobenzene (2)							
V_m^E	303.15	-0.699533	0.271621	0.513154	-0.183438	-0.395109	0.00097
	308.15	-0.703608	0.284997	0.525753	-0.210058	-0.432421	0.00097
	313.15	-0.709128	0.283548	0.533262	-0.202750	-0.444715	0.00113
ΔU	303.15	43.629	-6.419	-11.475	6.795	25.010	0.179
	308.15	42.765	-5.739	-7.753	4.872	19.361	0.258
	313.15	42.611	-4.027	-5.415	-1.740	10.351	0.186
$\Delta \kappa_s$	303.15	-13.90570	2.42337	18.43250	-9.41566	-32.86830	0.2193
	308.15	-15.46650	2.14497	14.27310	-7.54989	-27.01330	0.3276
	313.15	-18.36290	0.47332	11.94380	0.89897	-16.96790	0.2512
$K_{s,m}^E$	303.15	0.00072	0.00017	0.00254	-0.00146	-0.00424	0.000027
	308.15	0.00091	0.00011	0.00218	-0.00132	-0.00376	0.000038
	313.15	0.00102	-0.00021	0.00192	-0.00012	-0.00239	0.000030
Δz	303.15	-0.03106	0.00628	-0.01733	0.00860	0.02494	0.00017
	308.15	-0.02927	0.00630	-0.01454	0.00600	0.02140	0.00023
	313.15	-0.02694	0.00688	-0.01123	0.00160	0.01180	0.00017
p-Cymene (1) + Chlorobenzene (2)							
V_m^E	303.15	-0.577382	0.261057	0.554597	-0.294344	-0.455024	0.00160
	308.15	-0.569972	0.260869	0.581361	-0.304482	-0.496203	0.00191
	313.15	-0.564252	0.263156	0.582485	-0.305820	-0.496699	0.00204
ΔU	303.15	9.309	-0.852	1.089	1.137	-2.190	0.070
	308.15	8.653	-2.052	-0.357	3.173	0.299	0.077
	313.15	8.159	-0.568	-1.359	1.429	1.455	0.032
$\Delta \kappa_s$	303.15	25.76250	-1.95625	2.08067	-2.92608	-0.12849	0.0718
	308.15	27.15960	-0.71835	3.73242	-5.17225	-2.94719	0.0891
	313.15	28.50980	-2.42830	4.87536	-3.21915	-4.25777	0.0474
$K_{s,m}^E$	303.15	-0.00375	0.00060	0.00061	-0.00050	-0.00042	0.000008
	308.15	-0.00386	0.00080	0.00084	-0.00079	-0.00079	0.000012
	313.15	-0.00395	0.00064	0.00096	-0.00057	-0.00093	0.000007
Δz	303.15	-0.10982	0.02077	-0.00770	0.00561	0.00046	0.00008
	308.15	-0.10795	0.01906	-0.01248	0.00763	0.00815	0.00010
	313.15	-0.10621	0.02024	-0.01153	0.00517	0.00567	0.00005
p-Cymene (1) + Bromobenzene (2)							
V_m^E	303.15	-0.453247	0.176241	0.720204	-0.310766	-0.689489	0.00237
	308.15	-0.452467	0.175941	0.722299	-0.309228	-0.710914	0.00230
	313.15	-0.452334	0.180101	0.729574	-0.311519	-0.731033	0.00238
ΔU	303.15	-20.939	1.832	0.599	-0.336	3.105	0.030
	308.15	-21.116	1.019	4.349	-2.100	0.835	0.053
	313.15	-21.162	-0.495	-1.809	-1.483	7.095	0.056
$\Delta \kappa_s$	303.15	22.72340	-2.24533	2.42901	-1.42972	-6.34960	0.033
	308.15	23.70300	-1.37115	-1.37991	0.13539	-4.44265	0.052
	313.15	24.62380	0.37348	5.25418	-0.16174	-11.07170	0.071
$K_{s,m}^E$	303.15	-0.00697	0.00039	0.00064	-0.00041	-0.00118	0.000004
	308.15	-0.00733	0.00052	0.00018	-0.00026	-0.00091	0.000005
	313.15	-0.00769	0.00081	0.00107	-0.00026	-0.00174	0.000010
Δz	303.15	-0.22634	0.04637	-0.01721	0.00440	0.01236	0.00006
	308.15	-0.22384	0.04530	-0.01336	0.00162	0.01156	0.00008
	313.15	-0.22116	0.04290	-0.02044	0.00315	0.01989	0.00009

3.2 Molar volume (V_m)

Molar volumes have been calculated from experimental measured density data. The following equation has been used to determine molar volumes of for pure components and for mixtures, respectively:

$$V_i(\text{cm}^3 \cdot \text{mol}^{-1}) = M_i/\rho_i \quad \dots (3)$$

$$V_m(\text{cm}^3 \cdot \text{mol}^{-1}) = M_1x_1 + M_2x_2/\rho_m \quad \dots (4)$$

where, x_1 and x_2 , M_1 and M_2 and ρ_i and ρ_m are the mole fraction, molar mass and density of the components, respectively.

3.3 Excess molar volume (V_m^E)

Excess molar volume (V_m^E) has been calculated using following standard equation:

$$V_m^E(\text{cm}^3 \cdot \text{mol}^{-1}) = V_m - V_1x_1 - V_2x_2 \quad \dots (5)$$

$$V_m^E(\text{cm}^3 \cdot \text{mol}^{-1}) = \left(\frac{x_1M_1+x_2M_2}{\rho_m}\right) - \left(\frac{x_1M_1}{\rho_1}\right) - \left(\frac{x_2M_2}{\rho_2}\right) \quad \dots (6)$$

where, V_m , V_1 and V_2 , are the molar volumes of mixture and component 1 and 2, respectively. x_1 , x_2 & M_1 , M_2 represents the mole fraction and molar masses of component 1 and 2, respectively. ρ_m , ρ_1 and ρ_2 represents densities of a binary liquid mixture, component 1 and 2, respectively.

3.4 Partial molar volume ($\bar{V}_{m,i}^o$) and excess partial molar volume, ($\bar{V}_{m,i}^{o,E}$)

The partial molar volume ($\bar{V}_{m,i}^o$) and excess partial molar volume, ($\bar{V}_{m,i}^{o,E}$) of components in their binary mixtures have been calculated using following equations¹³:

$$\bar{V}_{m,1}^o = V_m^E + V_{m,1}^* + x_2 \left(\frac{\partial V_m^E}{\partial x_1}\right)_{T,P} \quad \dots (7)$$

$$\bar{V}_{m,2}^o = V_m^E + V_{m,2}^* - x_1 \left(\frac{\partial V_m^E}{\partial x_1}\right)_{T,P} \quad \dots (8)$$

where, $V_{m,1}^*$, $V_{m,2}^*$ and $\bar{V}_{m,1}^o$, $\bar{V}_{m,2}^o$ represent the molar volume and partial molar volume of component 1 and 2, respectively. Taking differentiation of $\left(\frac{\partial V_m^E}{\partial x_1}\right)_{T,P}$ derivative, the following relations were obtained.

$$\bar{V}_{m,1}^o = V_{m,1}^* + x_2^2 \sum_{i=0}^n A_i(1 - 2x_1)^i - 2x_1x_2^2 \sum_{i=1}^n A_i(1 - 2x_1)^{i-1} \quad \dots (9)$$

$$\bar{V}_{m,2}^o = V_{m,2}^* + x_1^2 \sum_{i=0}^n A_i(1 - 2x_1)^i + 2x_1^2x_2 \sum_{i=1}^n A_i(1 - 2x_1)^{i-1} \quad \dots (10)$$

The excess partial molar volume of binary mixtures has been calculated by following equations.

$$\bar{V}_{m,1}^{o,E}(\text{cm}^3 \cdot \text{mol}^{-1}) = \bar{V}_{m,1}^o - V_{m,1}^* \quad \dots (11)$$

$$\bar{V}_{m,2}^{o,E}(\text{cm}^3 \cdot \text{mol}^{-1}) = \bar{V}_{m,2}^o - V_{m,2}^* \quad \dots (12)$$

where, $\bar{V}_{m,1}^o$, $\bar{V}_{m,2}^o$ represent the partial molar volume of component 1 and 2, respectively.

3.5 Apparent molar volume ($V_{m,\phi,i}$)

Using two different relations, apparent molar volumes for all binary mixtures over the entire composition range have been calculated as under.

Relation 1¹⁴.

$$V_{m,\phi,i}(\text{cm}^3 \cdot \text{mol}^{-1}) = \frac{M}{\rho} - \frac{(\rho - \rho_o)}{m\rho\rho_o} \quad \dots (13)$$

where, M and m represents the molar mass and molality of solute molecules. ρ and ρ_o represents the density of solution and solute molecules, respectively.

Relation 2

$$V'_{m,\phi,1}(\text{cm}^3 \cdot \text{mol}^{-1}) = \left(\frac{V_m - (1-x_1)\bar{V}_{m,2}^o}{x_1}\right) \quad \dots (14)$$

$$V'_{m,\phi,2}(\text{cm}^3 \cdot \text{mol}^{-1}) = \left(\frac{V_m - x_1\bar{V}_{m,1}^o}{(1-x_1)}\right) \quad \dots (15)$$

Using the equation of V_m^E in above equations, we get:

$$V'_{m,\phi,1}(\text{cm}^3 \cdot \text{mol}^{-1}) = \bar{V}_{m,1}^o + \left(\frac{V_m^E}{x_1}\right) \quad \dots (16)$$

$$V'_{m,\phi,2}(\text{cm}^3 \cdot \text{mol}^{-1}) = \bar{V}_{m,2}^o + \left(\frac{V_m^E}{x_2}\right) \quad \dots (17)$$

where, $V'_{m,\phi,1}$, $V'_{m,\phi,2}$ represents the apparent molar volume of component 1 and 2, respectively.

3.6 Infinite dilution apparent molar volume ($V_{m,\phi,1}^o$) and empirical parameters S_v , B_v using the redlich-rosenberg-mayer equation

The infinite dilution apparent molar volume $V_{m,\phi,1}^o$ for all binary mixtures have been calculated using the Redlich-Rosenberg-Mayer relation¹⁴.

$$V_{m,\phi,1} = V_{m,\phi,1}^o + S_v m^{1/2} + B_v m \quad \dots (18)$$

where, S_v and B_v are empirical parameters.

3.7 Limiting apparent molar expansibility (E_{ϕ}^o)

The limiting apparent molar expansibility (E_{ϕ}^o) for all binary mixtures has been calculated using following relations¹⁴.

Temperature dependence for $V_{m,\phi,i}^o$ can be calculated using following relation.

$$V_{m,\phi,i}^o = A + BT + CT^2 \quad \dots (19)$$

The limiting apparent molar expansibility (E_{ϕ}^o) can be calculated by differentiation of the above equation with respect to temperature (T).

$$E_{\phi}^o = \left(\frac{\partial V_{\phi}^o}{\partial T}\right) = B + 2CT \quad \dots (20)$$

where, A , B and C are temperature dependence constants of $V_{m,\phi,i}^o$.

3.8 Deviation in speed of Sound (ΔU)

Deviation in the speed of sound (ΔU) has been calculated using the following relations.

$$\Delta U (m \cdot s^{-1}) = U_{exp} - (x_1 U_1 + x_2 U_2) \quad \dots (21)$$

$$\Delta U (m \cdot s^{-1}) = U_{exp} - (x_1 U_1 + x_2 U_2 + x_3 U_3) \quad \dots (22)$$

where, U_{exp} represents speed of sound of mixture. x_1, x_2 and U_1, U_2 represents mole fraction and speed of sound of pure component 1 and 2, respectively.

3.9 Isentropic compressibility (k_s), deviation in isentropic compressibility (Δk_s), acoustical impedance (Z), deviation in acoustical impedance (ΔZ) and intermolecular free length (L_f)

These properties have been calculated using following relations¹⁵.

$$k_s(T Pa^{-1}) = \frac{1}{U_i^2 \rho_i} \quad \dots (23)$$

$$Z (g \cdot m^{-2} \cdot s^{-1}) = U_i \rho_i \quad \dots (24)$$

$$L_f = K k_s^{1/2} \quad \dots (25)$$

$$\Delta k_s = k_{s_{exp}} - (x_1 k_{s_1} + x_2 k_{s_2}) \quad \dots (26)$$

$$\Delta Z = z_{exp} - (x_1 z_1 + x_2 z_2) \quad \dots (27)$$

where, $x_1, x_2, \phi_1, \phi_2, k_{s_1}, k_{s_2}$ and z_1, z_2 represent mole fraction, volume fraction, isentropic compressibility and acoustical impedance of component 1 and 2, respectively, $k_{s_{exp}}$ and z_{exp} represents isentropic compressibility and acoustical impedance of binary mixtures. U_i and ρ_i represent

speed of sound and density of i^{th} component respectively. K is the temperature dependent Jacobson constant.

3.10 Partial molar isentropic compressibility ($K_{s,m,\phi,i}$) and excess partial molar isentropic compressibility ($\bar{K}_{s,m,i}^{o,E}$)

These properties have been calculated using the following relations¹⁵.

$$\bar{K}_{s,m,1}^o = K_{s,m}^E + K_{s,m,1}^* + x_2 \left(\frac{\partial K_{s,m}^E}{\partial x_1}\right)_{T,P} \quad \dots (28)$$

$$\bar{K}_{s,m,2}^o = K_{s,m}^E + K_{s,m,2}^* - x_1 \left(\frac{\partial K_{s,m}^E}{\partial x_1}\right)_{T,P} \quad \dots (29)$$

Taking differentiation of $\left(\frac{\partial K_{s,m}^E}{\partial x_1}\right)_{T,P}$ derivative, we get following relations.

$$\bar{K}_{s,m,1}^o = K_{s,m,1}^* + x_2^2 \sum_{i=0}^n A_i (1 - 2x_1)^i - 2x_1 x_2^2 \sum_{i=1}^n A_i (1 - 2x_1)^{i-1} \quad \dots (30)$$

$$\bar{K}_{s,m,2}^o = K_{s,m,2}^* + x_1^2 \sum_{i=0}^n A_i (1 - 2x_1)^i + 2x_1^2 x_2 \sum_{i=1}^n A_i (1 - 2x_1)^{i-1} \quad \dots (31)$$

$$\bar{K}_{s,m,1}^{o,E} ((TPa)^{-1} \cdot m^3 \cdot mol^{-1}) = \bar{K}_{s,m,1}^o - K_{s,m,1}^* \quad \dots (32)$$

$$\bar{K}_{s,m,2}^{o,E} ((TPa)^{-1} \cdot m^3 \cdot mol^{-1}) = \bar{K}_{s,m,2}^o - K_{s,m,2}^* \quad \dots (33)$$

where, $K_{s,m}^E$ represents excess molar isentropic compressibility of mixture. $K_{s,m,1}^*, K_{s,m,2}^*$ and $\bar{K}_{s,m,1}^o, \bar{K}_{s,m,2}^o$ represents molar isentropic compressibility and partial molar isentropic compressibility of component 1 and 2, respectively.

3.11 Apparent molar isentropic compressibility ($K_{s,m,\phi,i}$) & redlich-rosenberg-mayer equation

Apparent molar isentropic compressibility ($K_{s,m,\phi,i}$) has been calculated using following two methods^{14,15}.

Relation 1

$$K_{s,m,\phi,i} = \frac{K_{sM}}{\rho} - \frac{1000(K_{s0}\rho - K_s\rho_0)}{m\rho\rho_0} \quad \dots (34)$$

Relation 2

$$K'_{s,m,\phi,1} = \bar{K}_{s,m,1}^o + \left(\frac{K_{s,m}^E}{x_1}\right) \quad \dots (35)$$

$$K'_{s,m,\phi,2} = \bar{K}_{s,m,2}^o + \left(\frac{K_{s,m}^E}{x_2}\right) \quad \dots (36)$$

where, $K'_{s,m,\phi,1}$ and $K'_{s,m,\phi,2}$ represents apparent molar isentropic compressibility of component 1 and

2, respectively. $K_s, K_{s_0}, \rho, \rho_0$ represents isentropic compressibility of mixture, isentropic compressibility of solvent, density of mixture and solvent, respectively.

3.12 Limiting apparent molar isentropic compressibility ($K_{s.m.\phi,i}^0$) and redlich-rosenberg-mayer equation

The limiting apparent molar isentropic compressibility ($K_{s.m.\phi,i}^0$) has been calculated using the following Redlich-Rosenberg-Mayer equation^{14,15}.

$$K_{s,m,\phi,i} ((TPa)^{-1} \cdot m^3 \cdot mol^{-1}) = K_{s.m,\phi,i}^0 + S_k m^{\frac{1}{2}} + B_k m \quad \dots (37)$$

where, $K_{s.m.\phi,i}^0$ represents limiting apparent molar isentropic compressibility of i^{th} component. S_k and B_k are the empirical parameters.

3.13 Theoretical models of speed of sound

Following models are used in the present study to calculate theoretical speed of sound.

(i) Junjie equation

Experimental values of speed of sound are generally compared with those obtained from the Junjie's equation¹⁶, which has the following form

$$U_{junji} = \left\{ \left(\frac{x_1 M_1}{\rho_1} \right) + \left(\frac{x_2 M_2}{\rho_2} \right) \right\} / \left\{ (x_1 M_1 + x_2 M_2)^{\frac{1}{2}} \left[\left(\frac{x_1 M_1}{\rho_1 U_1^2} \right) + \left(\frac{x_2 M_2}{\rho_2 U_2^2} \right)^{1/2} \right] \right\} \quad \dots (38)$$

where, x_i, M_i, ρ_i and U_i are the mole fraction, molecular weight, density and speed of sound for component 1 and component 2, respectively.

(ii) Nomoto equation

Theoretical values of speed of sound were also obtained using Nomoto equation¹⁷

$$U_{nom} = \left\{ \frac{x_1 R_1 + x_2 R_2}{x_1 V_1 + x_2 V_2} \right\} \quad \dots (39)$$

where, V_i is the molar volume of component 1 and component 2 and R_i is Wada's constant and is calculated as:

$$R_i = U_i^{1/3} V_i \quad \dots (40)$$

where, U_i is the speed of sound of i^{th} component.

(iii) Ideal mixture relation

Van deal and Van Geel¹⁸ proposed the following expression for the estimation of sound velocity u_{imr} in

an ideal mixture using sound velocities in the pure components:

$$U_{imr} = \left[\frac{1}{(x_1 M_1 + x_2 M_2)^{\frac{1}{2}}} \left\{ 1 / \left[\left(\frac{x_1}{M_1 U_1^2} \right) + \left(\frac{x_2}{M_2 U_2^2} \right) \right]^{1/2} \right\} \right] \quad \dots (41)$$

where M_1, M_2 and U_1, U_2 are the molar masses and sound velocities of first and second components, and U_{imr} is the ultrasonic velocity of ideal mixture.

(iv) Free length theory

According to Jacobson's theory [19] of free length, the ultrasonic velocity is given by:

$$U = K / (L_f \rho^{\frac{1}{2}}) = KY / (2V_a \rho^{\frac{1}{2}}) \quad \dots (42)$$

For the Binary liquid mixture Eq. 42 is

$$U = K(x_1 Y_1 + x_2 Y_2) / 2[V_M - (x_1 V_{0.1} + x_2 V_{0.2})] \rho^{1/2} \quad \dots (43)$$

Y is an adjustable parameter in the evaluation of velocity in liquid mixtures. Y can be obtained from velocity of pure liquids using equation 42

$$Y = 2V_a U \rho^{1/2} / K \quad \dots (44)$$

where K is the temperature dependent Jacobson's constant²⁰, V_a is the available molar volume, which is the difference between the molar volumes at $T(K)$ and $0(K)$, is a direct measure of the compactness and the strength of bonding between the molecules of a liquid in mixture. V_a is given by

$$V_a = V_M - V_0 \quad \dots (45)$$

when Y in equation 43 is replaced according to equation 44 and when the resulting expression is rearranged, we gets

$$U_{flt} = \left\{ [x_1 (V_{M1} - V_{0.1}) U_1 \rho_1^{1/2}] + [x_2 (V_{M2} - V_{0.2}) U_2 \rho_2^{1/2}] \right\} / [V_M - (x_1 V_{0.1} + x_2 V_{0.2})] \rho^{1/2} \quad \dots (46)$$

Equation 44 says that according to the free length theory the square root of the inverse of the adiabatic compressibility of liquid mixture ($U \rho^{1/2}$) is the sum of the available volume fraction average of the square root of the inverse of adiabatic compressibilities of the individual components.

4 Results and Discussion

4.1 Densities, (ρ) and excess molar volumes, (V_m^E)

The experimental values of densities, (ρ) and calculated excess molar volumes, (V_m^E) of p-cymene

+ fluoro-, chloro-, and bromobenzene binary mixtures with mole fraction, (x_1) of p-cymene at 303.15, 308.15 and 313.15 K are reported in Table 3. It can be seen from Fig. 1, the V_m^E values have negative deviation for all three binary mixtures over the whole composition range at all three temperatures. When mixtures changes from fluorobenzene to bromobenzene; the negative values of V_m^E become less

negative (i.e. increases). In general, the negative V_m^E values indicate for volume contraction on mixing and also means that the mixtures are more compressible than the corresponding ideal mixtures and it comes from specific intermolecular interactions²². These interactions may be due to charge transfer and the structural contributions due to geometrical fitting of one component into another due to differences in

Table 3 — Density (ρ) and Excess molar volume (V_m^E) of p-cymene (1) + fluoro-, chloro- and bromobenzene (2) binary mixtures

x_1	ρ (gm·cm ³)			V_m^E (cm ³ ·mol ⁻¹)		
	303.15 K	308.15 K	313.15 K	303.15 K	308.15 K	313.15 K
p-Cymene (1) + Fluorobenzene (2)						
0.0000	1.013097	1.007057	1.000977	0.0000	0.0000	0.0000
0.0624	0.996890	0.991074	0.985219	-0.0380	-0.0388	-0.0394
0.1302	0.980639	0.975029	0.969391	-0.0760	-0.0761	-0.0768
0.2042	0.964331	0.958933	0.953515	-0.1123	-0.1128	-0.1143
0.2853	0.947958	0.942796	0.937577	-0.1456	-0.1497	-0.1500
0.3745	0.931492	0.926502	0.921492	-0.1715	-0.1718	-0.1724
0.4732	0.914869	0.910079	0.905283	-0.1793	-0.1796	-0.1815
0.5828	0.898026	0.893438	0.888842	-0.1558	-0.1564	-0.1581
0.7055	0.881061	0.876666	0.872262	-0.1087	-0.1089	-0.1095
0.8435	0.864107	0.859907	0.855697	-0.0553	-0.0560	-0.0565
1.0000	0.847195	0.843178	0.839156	0.0000	0.0000	0.0000
p-Cymene (1) + Chlorobenzene (2)						
0.0000	1.095771	1.090368	1.084941	0.0000	0.0000	0.0000
0.0672	1.071199	1.065930	1.060642	-0.0284	-0.0278	-0.0274
0.1395	1.046614	1.041469	1.036324	-0.0589	-0.0567	-0.0565
0.2175	1.022012	1.017011	1.011998	-0.0914	-0.0897	-0.0885
0.3018	0.997369	0.992499	0.987625	-0.1233	-0.1205	-0.1191
0.3934	0.972627	0.967907	0.963177	-0.1466	-0.1452	-0.1443
0.4931	0.947684	0.943097	0.938506	-0.1454	-0.1431	-0.1418
0.6021	0.922567	0.918121	0.913670	-0.1180	-0.1157	-0.1141
0.7217	0.897420	0.893118	0.888810	-0.0812	-0.0795	-0.0781
0.8537	0.872293	0.868134	0.863969	-0.0414	-0.0405	-0.0396
1.0000	0.847195	0.843178	0.839156	0.0000	0.0000	0.0000
p-Cymene (1) + Bromobenzene (2)						
0.0000	1.481918	1.475155	1.468378	0.0000	0.0000	0.0000
0.0692	1.418655	1.412164	1.405657	-0.0162	-0.0169	-0.0174
0.1432	1.355386	1.349154	1.342911	-0.0345	-0.0348	-0.0352
0.2228	1.292143	1.286176	1.280199	-0.0584	-0.0586	-0.0589
0.3084	1.228901	1.223202	1.217494	-0.0867	-0.0868	-0.0869
0.4008	1.165595	1.160165	1.154729	-0.1131	-0.1129	-0.1130
0.5008	1.102034	1.096879	1.091720	-0.1140	-0.1135	-0.1136
0.6095	1.038271	1.033400	1.028518	-0.0876	-0.0875	-0.0870
0.7279	0.974533	0.969945	0.965348	-0.0582	-0.0582	-0.0578
0.8575	0.910852	0.906551	0.902241	-0.0306	-0.0310	-0.0309
1.0000	0.847195	0.843178	0.839156	0.0000	0.0000	0.0000

Standard uncertainties u , $u(T) = \pm 0.001$ K, $u(\rho) = \pm 0.000001$ g·cm⁻³, $u(x) = \pm 0.0001$. All physical quantities are measured at atmospheric pressure

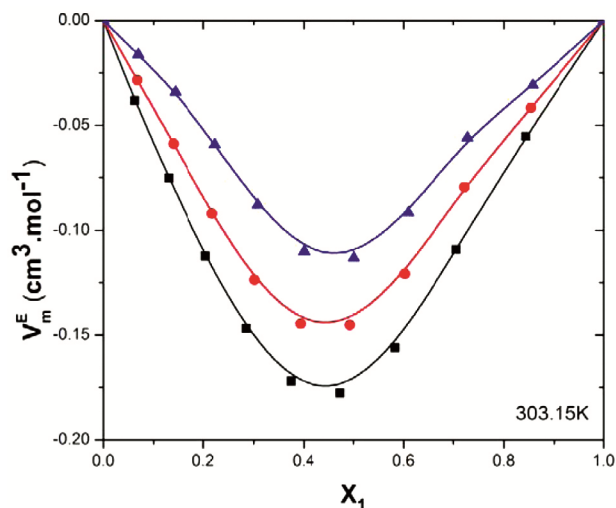


Fig. 1 — Excess molar volume (V_m^E) as a function of mole fraction (X_1) for p-Cymene (1) + Fluorobenzene (2) (■), p-Cymene (1) + Chlorobenzene (2) (●), p-Cymene (1) + Bromobenzene (2) (▲) at $T = 303.15\text{K}$.

molar volume of pure components²³. The negative contributions also come from changes of free volume in the real mixtures due to physical, chemical, and structural characteristics of liquids²⁴. In present case, negative V_m^E values indicate that there is a volume contraction on mixing which may result from physical and non-specific interactions between p-cymene and selected halo benzenes.

V_m^E values are negative and these values become less negative as the mixture changes from p-cymene + fluorobenzene to p-cymene + bromobenzene, suggesting that intermolecular interactions are strong in fluorobenzene binary mixture as compared to chloro- and bromobenzene binary mixtures. There are four possibilities for the interaction between these molecules; (i) due to high electronegativity of fluorine atom; fluorobenzene molecules are attracted by the hydrogen atom of p-cymene molecules which are hydrogen rich molecules, and bonding is possible between fluorine and hydrogen atom (ii) π - π interaction like benzene dimer and may be slipped parallel, T-shaped or sandwich between two molecules (iii) CH/ π interaction; the methyl group of p-Cymene is the potential electron donating group to the aromatic ring²⁵ causes the attraction between a C-H bond and π system of the aromatic ring of halo benzenes (iv) geometrical fitting of the halo benzene molecules in the void of the p-cymene molecules.

This may be due to fact that the size of the haloatom increases from fluorine to bromine atom and also electronegativity decreases. The H-bond

formation between the halo atom and hydrogen strongly depend on the electronegativity of the halo atoms. This interactions become weaker in chloro- and bromobenzene binary mixtures when compared to fluorobenzene binary mixtures. In case of π - π interactions and CH/ π interactions, size of the atom is more important; when moving from fluorine to bromine atom, the size of atom increases and results weakening in intermolecular attractions. The increment in size is also affect the geometrical fitting of one molecule into another. The order of interaction of p-cymene with halobenzenes is as under
fluorobenzene > chlorobenzene > bromobenzene

4.2 Infinite dilution partial molar volume, ($\bar{V}_{m,i}^o$), excess partial molar volume, ($\bar{V}_{m,i}^{o,E}$), apparent molar volume, ($V_{m,\phi,i}$),

Infinite dilution partial molar volume, ($\bar{V}_{m,i}^o$), excess partial molar volume, ($\bar{V}_{m,i}^{o,E}$) and apparent molar volume, ($V_{m,\phi,i}$) are calculated for both components present in the binary mixtures (e.g. for p-cymene and halo benzenes) and the values are presented in the Table 4. The graphical variation of these properties is also given in Figs 2 to 9. The values of excess partial molar volume, ($\bar{V}_{m,i}^{o,E}$) are negative for p-cymene for all fluoro-, chloro- and bromobenzene containing binary mixtures and positive for the halobenzenes. The negative values of excess partial molar volume, ($\bar{V}_{m,i}^{o,E}$) indicate that there is a strong interaction present between unlike molecules. When p-cymene is introduced into the halo benzene, the molar volume changes and the resultant excess partial molar volume, ($\bar{V}_{m,i}^{o,E}$) become negative. The negative values of $\bar{V}_{m,i}^{o,E}$ become less negative for p-Cymene with binary mixture changes from fluoro- to bromobenzene. It can be said that the interaction become weaker when binary mixture changes from fluoro- to bromobenzene.

Apparent molar volumes, ($V_{m,\phi,i}$) are calculated by two different methods and both results are shown in Table 5. Using Redlich-Rosenberg-Mayer equation, the infinite dilution apparent molar volume, ($V_{m,\phi,1}^o$) has been calculated and also the values of empirical parameters S_v , B_v and limiting apparent molar expansibility, (E_ϕ^o) are also calculated and the values are presented in Table 5.

Infinite dilution apparent molar volume, ($V_{m,\phi,1}^o$) are positive for all three binary mixtures and increase

Table 4 — Infinite dilution partial molar volume ($\bar{V}_{m,i}^o$), Excess partial molar volume ($\bar{V}_{m,i}^{o,E}$), Apparent molar volume ($V_{m,\phi,i}$) and Apparent molar volume ($V'_{m,\phi,i}$) of p-cymene (1) + fluoro-, chloro- and bromobenzene (2) binary mixtures

x_1	Molality m_1 (mol·Kg ⁻¹)	Molality m_2 (mol·Kg ⁻¹)	$\bar{V}_{m,1}^o$ (cm ³ ·mol ⁻¹)	$\bar{V}_{m,2}^o$ (cm ³ ·mol ⁻¹)	$\bar{V}_{m,1}^{o,E}$ (cm ³ ·mol ⁻¹)	$\bar{V}_{m,2}^{o,E}$ (cm ³ ·mol ⁻¹)	$V_{m,\phi,1}$ (cm ³ ·mol ⁻¹)	$V_{m,\phi,2}$ (cm ³ ·mol ⁻¹)	$V'_{m,\phi,1}$ (cm ³ ·mol ⁻¹)	$V'_{m,\phi,2}$ (cm ³ ·mol ⁻¹)
p-Cymene (1) + Fluorobenzene (2) at 303.15 K										
0.0000	-	-	157.747	94.861	-0.6697	0.0000	-	-	-	-
0.0624	0.6923	111.9884	157.849	94.863	-0.5683	0.0023	157.8079	94.8201	157.7727	94.8579
0.1302	1.5577	49.7726	157.924	94.871	-0.4926	0.0105	157.8334	94.7733	157.7630	94.8470
0.2042	2.6704	29.0340	157.983	94.889	-0.4339	0.0283	157.8668	94.7194	157.7563	94.8308
0.2853	4.1539	18.6647	158.035	94.922	-0.3822	0.0615	157.9064	94.6568	157.7524	94.8094
0.3745	6.2309	12.4432	158.089	94.976	-0.3275	0.1150	157.9591	94.5865	157.7670	94.7826
0.4732	9.3463	8.2954	158.155	95.049	-0.2618	0.1883	158.0379	94.5202	157.8283	94.7553
0.5828	14.5387	5.3328	158.234	95.128	-0.1826	0.2675	158.1497	94.4872	157.9582	94.7424
0.7055	24.9234	3.1108	158.319	95.184	-0.0975	0.3236	158.2628	94.4915	158.1277	94.7250
0.8435	56.0777	1.3826	158.390	95.204	-0.0272	0.3432	158.3513	94.5073	158.2877	94.6538
1.0000	-	-	158.417	95.354	0.0000	0.4933	-	-	-	-
p-Cymene (1) + Fluorobenzene (2) at 308.15 K										
0.0000	-	-	158.486	95.430	-0.6852	0.0000	-	-	-	-
0.0624	0.6932	111.8511	158.594	95.432	-0.5780	0.0024	158.5213	95.3862	158.5134	95.4266
0.1302	1.5596	49.7116	158.672	95.440	-0.4992	0.0107	158.5612	95.3381	158.5152	95.4167
0.2042	2.6736	28.9984	158.732	95.458	-0.4392	0.0288	158.5964	95.2817	158.5071	95.4005
0.2853	4.1590	18.6419	158.784	95.492	-0.3874	0.0624	158.6269	95.2118	158.4906	95.3747
0.3745	6.2385	12.4279	158.839	95.546	-0.3326	0.1167	158.6959	95.1443	158.5180	95.3541
0.4732	9.3578	8.2853	158.905	95.620	-0.2664	0.1908	158.7783	95.0758	158.5797	95.3280
0.5828	14.5565	5.3262	158.986	95.700	-0.1858	0.2702	158.8926	95.0392	158.7099	95.3143
0.7055	24.9540	3.1070	159.073	95.754	-0.0988	0.3249	159.0100	95.0419	158.8816	95.2965
0.8435	56.1465	1.3809	159.144	95.777	-0.0272	0.3470	159.1015	95.0510	159.0408	95.2181
1.0000	-	-	159.172	95.965	0.0000	0.5353	-	-	-	-
p-Cymene (1) + Fluorobenzene (2) at 313.15 K										
0.0000	-	-	159.233	96.009	-0.7014	0.0000	-	-	-	-
0.0624	0.6941	111.7087	159.347	96.012	-0.5880	0.0025	159.2460	95.9633	159.2665	96.0063
0.1302	1.5616	49.6483	159.430	96.020	-0.5048	0.0109	159.2926	95.9129	159.2721	95.9965
0.2042	2.6771	28.9615	159.492	96.038	-0.4422	0.0290	159.3283	95.8532	159.2620	95.9790
0.2853	4.1643	18.6181	159.546	96.072	-0.3890	0.0626	159.3680	95.7825	159.2518	95.9545
0.3745	6.2465	12.4121	159.601	96.126	-0.3337	0.1172	159.4397	95.7122	159.2786	95.9334
0.4732	9.3697	8.2747	159.667	96.201	-0.2674	0.1918	159.5227	95.6384	159.3373	95.9049
0.5828	14.5751	5.3195	159.748	96.281	-0.1868	0.2720	159.6415	95.5988	159.4685	95.8911
0.7055	24.9858	3.1030	159.835	96.337	-0.0995	0.3276	159.7645	95.6010	159.6425	95.8756
0.8435	56.2181	1.3791	159.907	96.359	-0.0274	0.3498	159.8600	95.6065	159.8026	95.7960
1.0000	-	-	159.935	96.549	0.0000	0.5398	-	-	-	-
p-Cymene (1) + Chlorobenzene (2) at 303.15 K										
0.0000	-	-	157.972	102.722	-0.4445	0.0000	-	-	-	-
0.0672	0.6401	103.4177	158.040	102.724	-0.3767	0.0014	157.9945	102.6918	157.9746	102.7189
0.1395	1.4402	45.9634	158.079	102.730	-0.3377	0.0075	157.9944	102.6537	157.9482	102.7085
0.2175	2.4689	26.8120	158.103	102.745	-0.3142	0.0232	157.9964	102.6053	157.9129	102.6927
0.3018	3.8405	17.2363	158.124	102.777	-0.2928	0.0549	158.0085	102.5457	157.8815	102.6722

(Contd.)

Table 4 — Infinite dilution partial molar volume ($\bar{V}_{m,i}^o$), Excess partial molar volume ($\bar{V}_{m,i}^{o,E}$), Apparent molar volume ($V_{m,\phi,i}$) and Apparent molar volume ($V'_{m,\phi,i}$) of p-cymene (1) + fluoro-, chloro- and bromobenzene (2) binary mixtures (*Contd.*)

x_1	Molality m_1 (mol·Kg ⁻¹)	Molality m_2 (mol·Kg ⁻¹)	$\bar{V}_{m,1}^o$ (cm ³ ·mol ⁻¹)	$\bar{V}_{m,2}^o$ (cm ³ ·mol ⁻¹)	$\bar{V}_{m,1}^{o,E}$ (cm ³ ·mol ⁻¹)	$\bar{V}_{m,2}^{o,E}$ (cm ³ ·mol ⁻¹)	$V_{m,\phi,1}$ (cm ³ ·mol ⁻¹)	$V_{m,\phi,2}$ (cm ³ ·mol ⁻¹)	$V'_{m,\phi,1}$ (cm ³ ·mol ⁻¹)	$V'_{m,\phi,2}$ (cm ³ ·mol ⁻¹)
p-Cymene (1) + Chlorobenzene (2) at 303.15 K										
0.3934	5.7607	11.4909	158.155	102.829	-0.2617	0.1063	158.0442	102.4805	157.8803	102.6503
0.4931	8.6411	7.6606	158.203	102.895	-0.2135	0.1724	158.1220	102.4353	157.9447	102.6430
0.6021	13.4417	4.9247	158.269	102.957	-0.1481	0.2345	158.2208	102.4256	158.0659	102.6497
0.7217	23.0430	2.8727	158.340	102.988	-0.0764	0.2655	158.3044	102.4304	158.2020	102.6286
0.8537	51.8467	1.2768	158.397	103.002	-0.0197	0.2797	158.3684	102.4391	158.3205	102.5543
1.0000	-	-	158.417	103.233	0.0000	0.5111	-	-	-	-
p-Cymene (1) + Chlorobenzene (2) at 308.15 K										
0.0000	-	-	158.730	103.231	-0.4412	0.0000	-	-	-	-
0.0672	0.6402	103.3980	158.805	103.233	-0.3666	0.0014	158.7520	103.2010	158.7393	103.2278
0.1395	1.4405	45.9547	158.846	103.238	-0.3253	0.0071	158.7597	103.1644	158.7218	103.2181
0.2175	2.4694	26.8069	158.869	103.253	-0.3029	0.0222	158.7543	103.1152	158.6796	103.2008
0.3018	3.8412	17.2330	158.887	103.284	-0.2844	0.0533	158.7679	103.0566	158.6491	103.1816
0.3934	5.7618	11.4887	158.915	103.336	-0.2568	0.1044	158.7986	102.9893	158.6414	103.1584
0.4931	8.6428	7.6591	158.960	103.402	-0.2114	0.1706	158.8782	102.9458	158.7060	103.1545
0.6021	13.4443	4.9237	159.024	103.463	-0.1477	0.2321	158.9769	102.9366	158.8260	103.1638
0.7217	23.0474	2.8722	159.095	103.492	-0.0763	0.2611	159.0598	102.9411	158.9608	103.1434
0.8537	51.8566	1.2765	159.152	103.506	-0.0196	0.2747	159.1233	102.9494	159.0771	103.0686
1.0000	-	-	159.172	103.760	0.0000	0.5284	-	-	-	-
p-Cymene (1) + Chlorobenzene (2) at 313.15 K										
0.0000	-	-	159.499	103.748	-0.4358	0.0000	-	-	-	-
0.0672	0.6403	103.3765	159.572	103.749	-0.3621	0.0013	159.5130	103.7172	159.5075	103.7443
0.1395	1.4408	45.9451	159.613	103.755	-0.3218	0.0070	159.5178	103.6800	159.4867	103.7341
0.2175	2.4699	26.8013	159.634	103.770	-0.3002	0.0220	159.5170	103.6315	159.4487	103.7180
0.3018	3.8420	17.2294	159.652	103.800	-0.2824	0.0529	159.5305	103.5728	159.4175	103.6991
0.3934	5.7630	11.4863	159.679	103.851	-0.2554	0.1038	159.5597	103.5045	159.4077	103.6754
0.4931	8.6446	7.6575	159.724	103.917	-0.2105	0.1695	159.6403	103.4613	159.4727	103.6726
0.6021	13.4471	4.9227	159.787	103.978	-0.1472	0.2302	159.7398	103.4529	159.5928	103.6834
0.7217	23.0522	2.8716	159.858	104.006	-0.0761	0.2579	159.8227	103.4575	159.7268	103.6640
0.8537	51.8674	1.2763	159.915	104.017	-0.0195	0.2696	159.8863	103.4660	159.8419	103.5904
1.0000	-	-	159.935	104.269	0.0000	0.5211	-	-	-	-
p-Cymene (1) + Bromobenzene (2) at 303.15 K										
0.0000	-	-	158.129	105.949	-0.2880	0.0000	-	-	-	-
0.0692	0.4733	100.2679	158.227	105.949	-0.1900	0.0002	158.1832	105.9317	158.1810	105.9459
0.1432	1.0649	44.5635	158.264	105.951	-0.1526	0.0014	158.1758	105.9088	158.1674	105.9343
0.2228	1.8256	25.9954	158.265	105.958	-0.1523	0.0092	158.1546	105.8739	158.1225	105.9176
0.3084	2.8398	16.7113	158.251	105.981	-0.1658	0.0322	158.1358	105.8238	158.0636	105.8977
0.4008	4.2597	11.1409	158.245	106.025	-0.1723	0.0762	158.1346	105.7603	158.0207	105.8755
0.5008	6.3895	7.4272	158.260	106.085	-0.1572	0.1358	158.1893	105.7208	158.0540	105.8785
0.6095	9.9392	4.7747	158.300	106.137	-0.1167	0.1882	158.2732	105.7249	158.1526	105.9070
0.7279	17.0386	2.7852	158.356	106.153	-0.0613	0.2037	158.3370	105.7353	158.2608	105.8992

(Contd.)

Table 4 — Infinite dilution partial molar volume ($\bar{V}_{m,i}^o$), Excess partial molar volume ($\bar{V}_{m,i}^{o,E}$), Apparent molar volume ($V_{m,\phi,i}$) and Apparent molar volume ($V'_{m,\phi,i}$) of p-cymene (1) + fluoro-, chloro- and bromobenzene (2) binary mixtures (*Contd.*)

x_1	Molality m_1 (mol·Kg ⁻¹)	Molality m_2 (mol·Kg ⁻¹)	$\bar{V}_{m,1}^o$ (cm ³ ·mol ⁻¹)	$\bar{V}_{m,2}^o$ (cm ³ ·mol ⁻¹)	$\bar{V}_{m,1}^{o,E}$ (cm ³ ·mol ⁻¹)	$\bar{V}_{m,2}^{o,E}$ (cm ³ ·mol ⁻¹)	$V_{m,\phi,1}$ (cm ³ ·mol ⁻¹)	$V_{m,\phi,2}$ (cm ³ ·mol ⁻¹)	$V'_{m,\phi,1}$ (cm ³ ·mol ⁻¹)	$V'_{m,\phi,2}$ (cm ³ ·mol ⁻¹)
p-Cymene (1) + Bromobenzene (2) at 303.15 K										
0.8575	38.3369	1.2379	158.402	106.164	-0.0149	0.2153	158.3812	105.7343	158.3454	105.8239
1.0000	-	-	158.417	106.506	0.0000	0.5571	-	-	-	-
p-Cymene (1) + Bromobenzene (2) at 308.15 K										
0.0000	-	-	158.864	106.435	-0.3078	0.0000	-	-	-	-
0.0692	0.4732	100.2858	158.971	106.435	-0.2004	0.0003	158.9386	106.4175	158.9236	106.4316
0.1432	1.0647	44.5715	159.015	106.436	-0.1570	0.0016	158.9390	106.3960	158.9188	106.4204
0.2228	1.8252	26.0000	159.018	106.444	-0.1535	0.0093	158.9183	106.3623	158.8759	106.4034
0.3084	2.8393	16.7143	159.006	106.467	-0.1656	0.0322	158.8991	106.3133	158.8181	106.3832
0.4008	4.2589	11.1429	159.000	106.511	-0.1718	0.0760	158.8976	106.2516	158.7763	106.3613
0.5008	6.3883	7.4286	159.015	106.570	-0.1569	0.1356	158.9515	106.2140	158.8098	106.3648
0.6095	9.9374	4.7755	159.055	106.623	-0.1166	0.1879	159.0332	106.2189	158.9076	106.3927
0.7279	17.0356	2.7857	159.110	106.638	-0.0612	0.2034	159.0954	106.2310	159.0157	106.3846
0.8575	38.3300	1.2381	159.157	106.652	-0.0148	0.2172	159.1374	106.2290	159.0993	106.3059
1.0000	-	-	159.172	107.009	0.0000	0.5744	-	-	-	-
p-Cymene (1) + Bromobenzene (2) at 313.15 K										
0.0000	-	-	159.612	106.926	-0.3224	0.0000	-	-	-	-
0.0692	0.4731	100.3035	159.726	106.926	-0.2081	0.0003	159.7056	106.9091	159.6781	106.9228
0.1432	1.0645	44.5793	159.774	106.928	-0.1606	0.0018	159.7098	106.8885	159.6780	106.9118
0.2228	1.8249	26.0046	159.779	106.936	-0.1551	0.0095	159.6898	106.8560	159.6371	106.8948
0.3084	2.8388	16.7173	159.768	106.958	-0.1666	0.0324	159.6702	106.8083	159.5800	106.8747
0.4008	4.2581	11.1448	159.762	107.002	-0.1727	0.0763	159.6680	106.7479	159.5384	106.8531
0.5008	6.3872	7.4299	159.777	107.062	-0.1579	0.1361	159.7208	106.7118	159.5721	106.8570
0.6095	9.9357	4.7764	159.817	107.114	-0.1174	0.1882	159.8022	106.7197	159.6712	106.8866
0.7279	17.0326	2.7862	159.873	107.129	-0.0615	0.2028	159.8625	106.7336	159.7793	106.8783
0.8575	38.3233	1.2383	159.920	107.143	-0.0148	0.2167	159.9024	106.7331	159.8625	106.7981
1.0000	-	-	159.935	107.511	0.0000	0.5852	-	-	-	-

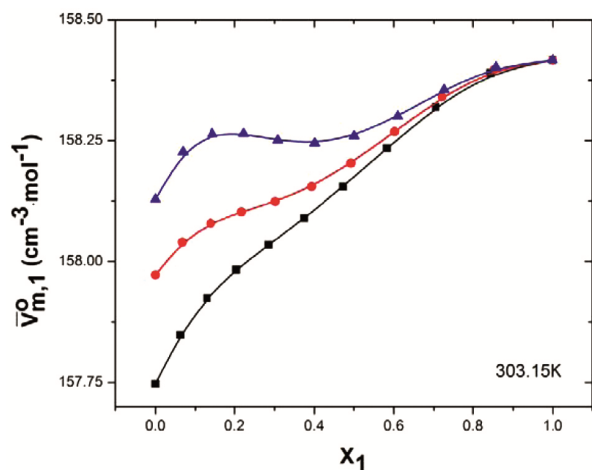


Fig. 2 — Infinite dilution partial molar volume ($\bar{V}_{m,1}^o$) as a function of mole fraction (X_1) for p-Cymene (1) + Fluorobenzene (2) (■), p-Cymene (1) + Chlorobenzene (2) (●), p-Cymene (1) + Bromobenzene (2) (▲) at T= 303.15K.

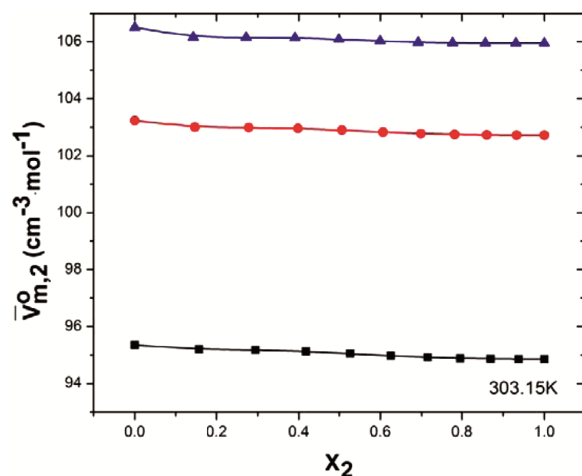


Fig. 3 — Infinite dilution partial molar volume ($\bar{V}_{m,2}^o$) as a function of mole fraction (X_2) for p-Cymene (1) + Fluorobenzene (2) (■), p-Cymene (1) + Chlorobenzene (2) (●), p-Cymene (1) + Bromobenzene (2) (▲) at T= 303.15K.

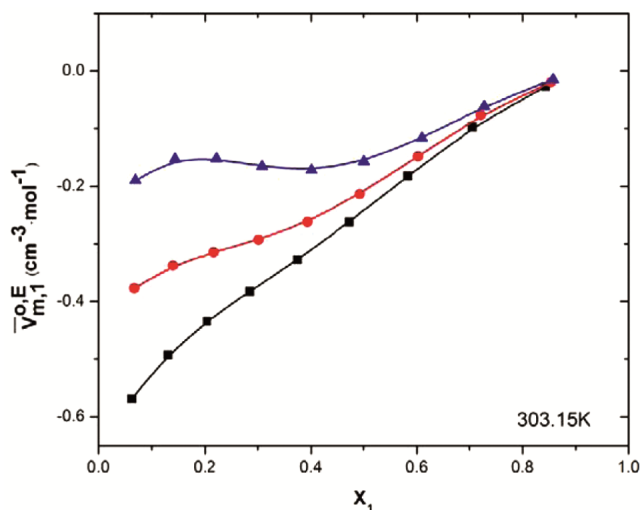


Fig. 4 — Infinite dilution excess partial molar volume ($\bar{V}_{m,1}^{o,E}$) as a function of mole fraction (X_1) for p-Cymene (1) + Fluorobenzene (2) (■), p-Cymene (1) + Chlorobenzene (2) (●), p-Cymene (1) + Bromobenzene (2) (▲) at T= 303.15K.

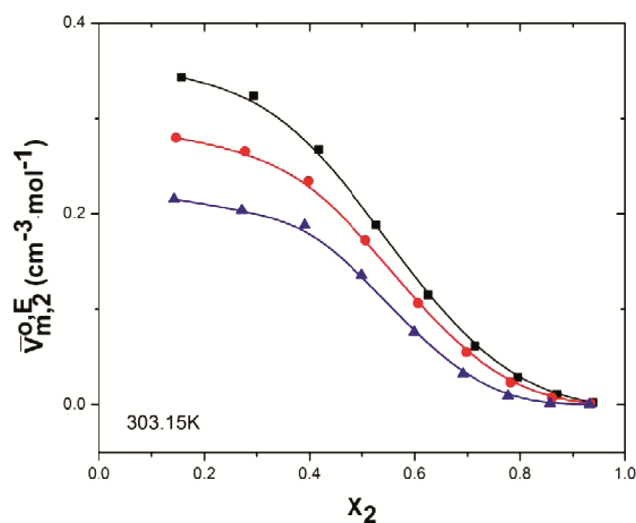


Fig. 5 — Infinite dilution excess partial molar volume ($\bar{V}_{m,2}^{o,E}$) as a function of mole fraction (X_2) for p-Cymene (1) + Fluorobenzene (2) (■), p-Cymene (1) + Chlorobenzene (2) (●), p-Cymene (1) + Bromobenzene (2) (▲) at T= 303.15K.

with rise in temperature. The increasing trend in $V_{m,\phi,1}^o$ suggest that attraction between the solvent and solute molecules become weaker at higher temperatures. The values of limiting apparent molar expansibility, (E_ϕ^o) also increases with temperature supports the view that at higher temperature solute molecules show expansion and the attraction towards the solvent molecules

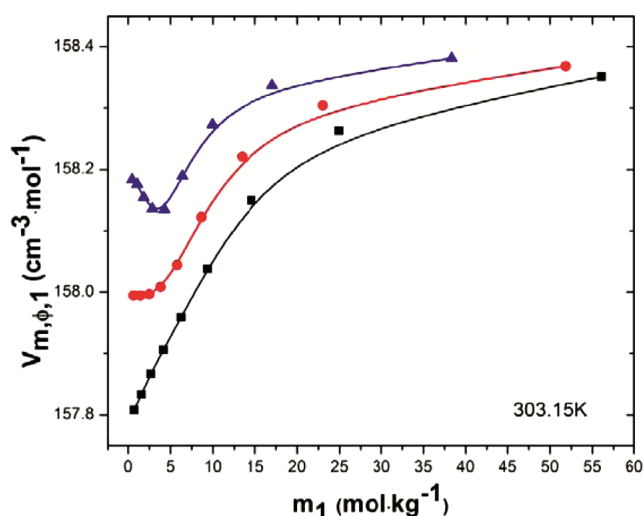


Fig. 6 — Apparent molar volume ($V_{m,\phi,1}$) as a function of molality, (m_1) for p-Cymene (1) + Fluorobenzene (2) (■), p-Cymene (1) + Chlorobenzene (2) (●), p-Cymene (1) + Bromobenzene (2) (▲) at T= 303.15K.

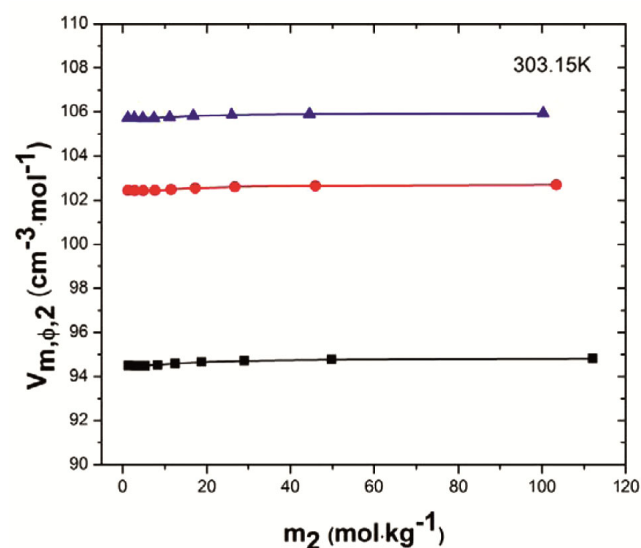


Fig. 7 — Apparent molar volume ($V_{m,\phi,2}$) as a function of molality (m_2) for p-Cymene (1) + Fluorobenzene (2) (■), p-Cymene (1) + Chlorobenzene (2) (●), p-Cymene (1) + Bromobenzene (2) (▲) at T= 303.15K.

become weaker. Empirical parameter S_v have negative and B_v have positive values for all binary mixtures. When there is a presence of strong electrostatic type interaction between the charged atoms, the empirical parameters S_v and B_v have large positive values²⁶.

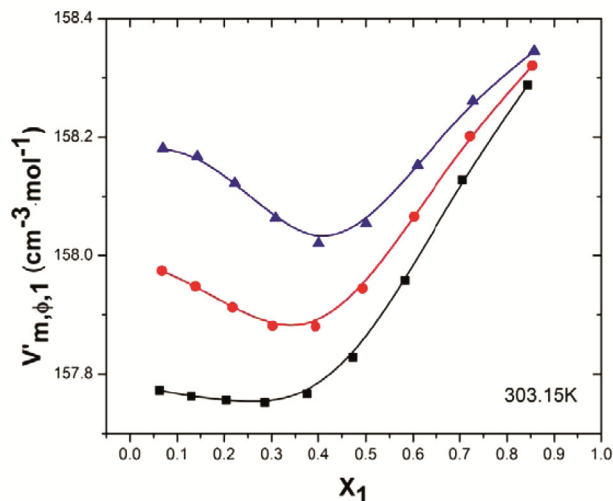


Fig. 8 — Apparent molar volume ($V'_{m,\phi,1}$) as a function of mole fraction (X_1) for p-Cymene (1) + Fluorobenzene (2) (■), p-Cymene (1) + Chlorobenzene (2) (●), p-Cymene (1) + Bromobenzene (2) (▲) at $T= 303.15\text{K}$.

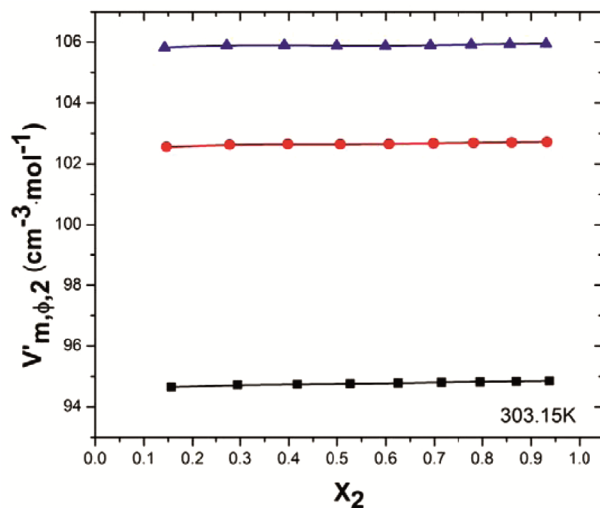


Fig. 9 — Apparent molar volume ($V'_{m,\phi,2}$) as a function of mole fraction (X_2) for p-Cymene (1) + Fluorobenzene (2) (■), p-Cymene (1) + Chlorobenzene (2) (●), p-Cymene (1) + Bromobenzene (2) (▲) at $T= 303.15\text{K}$.

Table 5 — Infinite dilution apparent molar volume ($V_{m,\phi,1}^o$), Empirical parameters S_v and B_v of Redlich-Rosenberg-Mayer equation with Standard deviation (σ) and The limiting apparent molar expansibility (E_ϕ^o) of p-cymene (1) + fluoro-, chloro- and bromobenzene (2) binary mixtures

T (K)	$V_{m,\phi,1}^o$ ($\text{cm}^3 \cdot \text{mol}^{-1}$)	S_v ($\text{cm}^3 \cdot \text{mol}^{(3/2)} \cdot \text{kg}^{(1/2)}$)	B_v ($\text{cm}^3 \cdot \text{mol}^{-2} \cdot \text{kg}$)	σ	E_ϕ^o ($\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
p-Cymene (1) + Fluorobenzene (2)					
303.15	157.887	-0.0400821	0.0299590	0.097732	0.1445
308.15	158.614	-0.0395755	0.0302123	0.105355	0.1463
313.15	159.350	-0.0390766	0.0304617	0.111912	0.1481
p-Cymene (1) + Chlorobenzene (2)					
303.15	158.018	-0.0419436	0.0290282	0.071438	0.1513
308.15	158.776	-0.0420395	0.0289803	0.070304	0.1519
313.15	159.537	-0.0419970	0.0290015	0.070842	0.1525
p-Cymene (1) + Bromobenzene (2)					
303.15	158.919	-0.0433418	0.0283291	0.933800	0.1512
308.15	158.919	-0.0434911	0.0282544	0.045245	0.1532
313.15	159.690	-0.0436318	0.0281841	0.044550	0.1552

4.3 Speed of sound, (U) and deviation in speed of sound, (ΔU)

Deviation in the speed of sound, (ΔU) are calculated from the experimentally measured speed of sound, (U) over the whole composition range and at all studied temperatures. The values of U and (ΔU) are given in Table 6. The graphical variation of ΔU values as function of mole fraction, (x_1) of p-cymene is shown in Fig. 10 at 303.15 K. ΔU values are positive for p-cymene + fluorobenzene and +

chlorobenzene binary mixtures and negative for p-cymene + bromobenzene binary mixtures. Highest ΔU values are obtained for p-cymene + fluorobenzene binary mixtures. With increase in temperature, ΔU values systematically decrease.

In general, positive deviation in Δu values indicate the presence of strong interaction and negative deviation in ΔU indicate the presence of weak interactions between the unlike molecules^{27,28}. The positive ΔU values support that there is a strong

Table 6 — Speed of sound (U) and Deviation in speed of sound (ΔU) of p-cymene (1) + fluoro-, chloro- and bromobenzene (2) binary mixtures

x_1	U ($\text{m}\cdot\text{s}^{-1}$)			ΔU ($\text{m}\cdot\text{s}^{-1}$)		
	303.15 K	308.15 K	313.15 K	303.15 K	308.15 K	313.15 K
p-Cymene (1) + Fluorobenzene (2)						
0.0000	1145.29	1125.26	1105.04	0.00	0.00	0.00
0.0624	1157.47	1137.43	1117.26	2.95	2.90	2.87
0.1302	1169.85	1149.91	1129.79	5.29	5.30	5.24
0.2042	1183.06	1163.18	1143.15	7.55	7.57	7.51
0.2853	1196.27	1176.18	1156.45	8.76	8.51	8.65
0.3745	1211.15	1191.14	1171.21	10.43	10.21	10.04
0.4732	1226.44	1206.61	1186.83	11.12	11.02	10.88
0.5828	1241.84	1222.03	1202.62	10.29	10.14	10.23
0.7055	1257.99	1238.31	1219.01	8.30	8.20	8.25
0.8435	1275.62	1256.07	1236.61	5.50	5.44	5.17
1.0000	1293.28	1273.89	1254.90	0.00	0.00	0.00
p-Cymene (1) + Chlorobenzene (2)						
0.0000	1249.33	1231.22	1212.98	0.00	0.00	0.00
0.0672	1252.82	1234.61	1216.27	0.54	0.52	0.47
0.1395	1256.70	1238.24	1219.77	1.24	1.07	0.94
0.2175	1260.41	1242.01	1223.43	1.52	1.51	1.33
0.3018	1264.64	1246.04	1227.32	2.05	1.94	1.69
0.3934	1268.93	1250.30	1231.49	2.31	2.30	2.02
0.4931	1273.35	1254.32	1235.67	2.35	2.06	2.02
0.6021	1277.98	1258.86	1240.11	2.19	1.95	1.89
0.7217	1282.88	1263.66	1244.83	1.83	1.64	1.59
0.8537	1287.99	1268.67	1249.76	1.14	1.02	0.99
1.0000	1293.28	1273.89	1254.90	0.00	0.00	0.00
p-Cymene (1) + Bromobenzene (2)						
0.0000	1138.27	1122.88	1107.62	0.00	0.00	0.00
0.0692	1147.70	1132.25	1116.71	-1.29	-1.08	-1.10
0.1432	1157.85	1142.16	1126.30	-2.62	-2.35	-2.42
0.2228	1169.14	1153.11	1136.92	-3.66	-3.41	-3.51
0.3084	1181.48	1165.11	1148.56	-4.59	-4.34	-4.48
0.4008	1195.30	1178.26	1161.57	-5.09	-5.14	-5.07
0.5008	1210.64	1193.21	1176.13	-5.26	-5.30	-5.25
0.6095	1227.85	1209.99	1192.20	-4.89	-4.92	-5.18
0.7279	1247.18	1228.87	1210.61	-3.92	-3.93	-4.22
0.8575	1268.92	1250.09	1231.33	-2.28	-2.29	-2.59
1.0000	1293.28	1273.89	1254.90	0.00	0.00	0.00

Standard uncertainties u , $u(T) = \pm 0.001$ K, $u(x) = \pm 0.0001$, $u(U) = \pm 0.1$ $\text{m}\cdot\text{s}^{-1}$. All physical quantities are measured at atmospheric pressure

interaction between p-cymene + fluorobenzene molecules. Due to close packing of molecules in the binary mixture, sound waves can easily pass through the molecules and deviation in speed of sound, (ΔU) values become positive.

4.4 Theoretical relations of speed of sound

Various theoretical speed of sound and average deviations were calculated using well established equation like Nomoto, (U_{nmt}), Ideal Mixing Rule,

(U_{imr}), Junji, (U_{junji}), and Jacobson's Free Length Theory, (U_{flt}) and their average deviation (σ) are listed in Table 7.

It can be observed from data that

- Ideal mixture relation (U_{imr}) have highest values for p-cymene + fluorobenzene and + chlorobenzene binary mixtures. For bromobenzene containing binary mixture, highest σ values are obtained for free length theory, (U_{flt}).

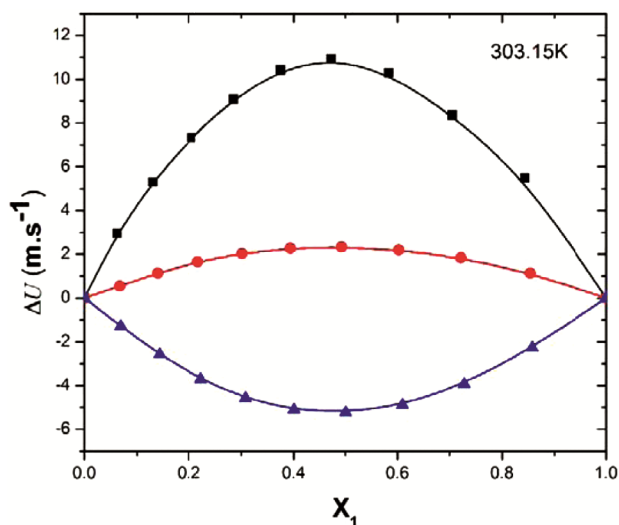


Fig. 10 — Deviation in speed of sound (ΔU) as a function of mole fraction (X_1) for p-Cymene (1) + Fluorobenzene (2) (■), p-Cymene (1) + Chlorobenzene (2) (●), p-Cymene (1) + Bromobenzene (2) (▲) at $T = 303.15\text{K}$.

(ii) Lowest σ values are obtained for U_{junji} , U_{nmt} and U_{imr} for p-cymene + fluorobenzene, + chlorobenzene and + bromobenzene binary mixtures respectively at all studied temperatures.

4.5 Isentropic compressibility, (κ_s), acoustical impedances, (Z) and intermolecular free length, (L_f)

From the experimentally measured speed of sound, (U); isentropic compressibility, (κ_s), acoustical impedances, (Z) and intermolecular free length, (L_f) are calculated and their values are listed in Table 8, 9 and 10 respectively.

Values of κ_s and L_f increase with increase in temperature for all three binary mixtures. The volume expansion of the mixture leads to increase in κ_s and L_f values with rise in temperature. The value of Z decrease with increase in temperature which results due to less close packing of molecules with increase in temperature²⁹.

4.6 Deviation in isentropic compressibility, ($\Delta\kappa_s$) and deviation in acoustical impedance, (ΔZ)

The calculated values of deviation in isentropic compressibility, ($\Delta\kappa_s$) and deviation in acoustical impedance, (ΔZ) for all binary mixtures over the whole composition range are reported in Tables 8 and 9, respectively. The graph of $\Delta\kappa_s$ and ΔZ vs x_1 of p-cymene are given in Figs 11 and 12

Table 7 — Average deviation (σ) in the Speed of sound from various theoretical relations of p-cymene (1) + fluoro-, chloro- and bromobenzene (2) binary mixtures

Parameters	T (K)		
	303.15	308.15	313.15
p-Cymene (1) + Fluorobenzene (2)			
U_{nmt}	0.403	0.419	0.432
U_{imr}	2.690	2.722	2.766
U_{junji}	0.193	0.205	0.213
U_{flt}	0.362	0.348	0.330
p-Cymene (1) + Chlorobenzene (2)			
U_{nmt}	0.132	0.136	0.143
U_{imr}	0.550	0.539	0.532
U_{junji}	0.333	0.330	0.323
U_{flt}	0.472	0.432	0.403
p-Cymene (1) + Bromobenzene (2)			
U_{nmt}	0.154	0.144	0.149
U_{imr}	0.019	0.020	0.033
U_{junji}	0.739	0.759	0.762
U_{flt}	1.224	1.140	1.078

nmt = Nomoto, imr = Ideal mixture relation, junji = Junji, flt = Free length Theory

respectively. $\Delta\kappa_s$ values are negative for p-cymene + fluorobenzene binary mixture and positive for p-cymene + chlorobenzene and + bromobenzene binary mixtures. The values of $\Delta\kappa_s$ change from negative to positive when binary mixture changes from fluorobenzene to bromobenzene. ΔZ values are negative for all binary mixture at all studied temperature. ΔZ values become negative to more negative when binary mixtures change from fluorobenzene to bromobenzene.

In general, negative $\Delta\kappa_s$ values indicate for strong interaction and positive $\Delta\kappa_s$ values indicate for weak interaction present between mixed components³⁰. Negative ΔZ values indicate for weak intermolecular interaction in binary mixture³¹. The trend and magnitude of $\Delta\kappa_s$ values show that there is strong interaction present between p-cymene + fluorobenzene binary mixture when compared to chlorobenzene and bromobenzene containing binary mixtures. When there is a strong interaction, the molecules in binary mixture are close to each other and resultant isentropic compressibility, (κ_s) are less than its pure value. ΔZ values also support the view that interaction become weaker when binary mixture changes from fluorobenzene to bromobenzene.

Table 8 — Isentropic compressibility (κ_s) and Deviation in isentropic compressibility ($\Delta\kappa_s$) of p-cymene (1) + fluoro-, chloro- and bromobenzene (2) binary mixtures

x_1	κ_s (TPa ⁻¹)			$\Delta\kappa_s$ (TPa ⁻¹)		
	303.15 K	308.15 K	313.15 K	303.15 K	308.15 K	313.15 K
p-Cymene (1) + Fluorobenzene (2)						
0.0000	752.52	784.22	818.13	0.00	0.00	0.00
0.0624	748.74	779.91	813.13	-0.86	-0.98	-1.17
0.1302	745.13	775.63	808.18	-1.30	-1.64	-1.96
0.2042	740.90	770.76	802.54	-2.06	-2.56	-3.05
0.2853	737.14	766.72	797.52	-2.02	-2.27	-3.09
0.3745	731.85	760.73	791.11	-3.14	-3.50	-4.02
0.4732	726.69	754.72	784.22	-3.69	-4.24	-4.85
0.5828	722.07	749.50	777.89	-3.17	-3.60	-4.45
0.7055	717.20	743.89	771.50	-2.30	-2.67	-3.31
0.8435	711.20	737.09	764.21	-1.85	-2.10	-2.12
1.0000	705.72	730.83	756.73	0.00	0.00	0.00
p-Cymene (1) + Chlorobenzene (2)						
0.0000	584.69	605.00	626.45	0.00	0.00	0.00
0.0672	594.77	615.48	637.34	1.95	2.02	2.13
0.1395	604.99	626.24	648.56	3.42	3.69	3.93
0.2175	615.91	637.42	660.18	4.90	5.05	5.40
0.3018	626.92	648.94	672.19	5.70	5.96	6.42
0.3934	638.53	660.90	684.59	6.23	6.41	6.90
0.4931	650.79	673.95	697.84	6.42	6.91	7.16
0.6021	663.67	687.30	711.69	6.12	6.54	6.80
0.7217	677.07	701.18	726.06	5.03	5.37	5.58
0.8537	691.06	715.68	741.05	3.04	3.25	3.38
1.0000	705.72	730.83	756.73	0.00	0.00	0.00
p-Cymene (1) + Bromobenzene (2)						
0.0000	520.82	537.65	555.11	0.00	0.00	0.00
0.0692	535.14	552.37	570.48	1.53	1.36	1.42
0.1432	550.34	568.18	587.01	3.04	2.86	3.02
0.2228	566.18	584.73	604.31	4.17	4.05	4.29
0.3084	582.95	602.24	622.62	5.11	5.02	5.34
0.4008	600.48	620.87	641.84	5.56	5.80	5.93
0.5008	619.12	640.34	662.18	5.70	5.94	6.10
0.6095	638.85	660.95	684.05	5.34	5.57	6.07
0.7279	659.70	682.72	706.82	4.29	4.45	4.95
0.8575	681.84	705.87	731.02	2.47	2.56	3.02
1.0000	705.72	730.83	756.73	0.00	0.00	0.00

4.7 Infinite dilution partial molar isentropic compressibility, $\bar{K}_{s,m,i}^o$, Excess partial molar isentropic compressibility, $\bar{K}_{s,m,i}^{o,E}$ and Apparent molar isentropic compressibility, $K_{s,m,\phi,i}$

$\bar{K}_{s,m,i}^o$, $\bar{K}_{s,m,i}^{o,E}$, and $K_{s,m,\phi,i}$ are calculated for both components of all binary mixtures and their value are presented in Table 11. The graphical

variation of $\bar{K}_{s,m,i}^{o,E}$ and $K_{s,m,\phi,i}$ is shown in Fig. 13 to 16. $\bar{K}_{s,m,1}^o$ and $\bar{K}_{s,m,2}^o$ values are positive for all binary mixtures at all studied temperatures. With increase in temperature, these values become more positive. When binary mixture changes from fluorobenzene to bromobenzene the value of $\bar{K}_{s,m,1}^o$ and $\bar{K}_{s,m,2}^o$ become less positive i.e. decreases. For

Table 9 — Acoustical impedance (z) and Deviation in acoustical impedance (Δz) of p-cymene (1) + fluoro-, chloro- and bromobenzene (2) binary mixtures

x_1	z ($\text{km}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) $\times 10^{-3}$			Δz ($\text{gm}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) $\times 10^{-3}$		
	303.15 K	308.15 K	313.15 K	303.15 K	308.15 K	313.15 K
p-Cymene (1) + Fluorobenzene (2)						
0.0000	1.1603	1.1332	1.1061	0.0000	0.0000	0.0000
0.0624	1.1539	1.1273	1.1007	-0.0024	-0.0022	-0.0021
0.1302	1.1472	1.1212	1.0952	-0.0047	-0.0043	-0.0040
0.2042	1.1409	1.1154	1.0900	-0.0062	-0.0057	-0.0053
0.2853	1.1340	1.1089	1.0843	-0.0078	-0.0074	-0.0067
0.3745	1.1282	1.1036	1.0793	-0.0079	-0.0075	-0.0070
0.4732	1.1220	1.0981	1.0744	-0.0077	-0.0071	-0.0066
0.5828	1.1152	1.0918	1.0689	-0.0074	-0.0070	-0.0063
0.7055	1.1084	1.0856	1.0633	-0.0063	-0.0059	-0.0054
0.8435	1.1023	1.0801	1.0582	-0.0035	-0.0033	-0.0032
1.0000	1.0957	1.0741	1.0531	0.0000	0.0000	0.0000
p-Cymene (1) + Chlorobenzene (2)						
0.0000	1.3690	1.3425	1.3160	0.0000	0.0000	0.0000
0.0672	1.3420	1.3160	1.2900	-0.0086	-0.0084	-0.0083
0.1395	1.3153	1.2896	1.2641	-0.0156	-0.0155	-0.0153
0.2175	1.2882	1.2631	1.2381	-0.0214	-0.0210	-0.0207
0.3018	1.2613	1.2367	1.2121	-0.0252	-0.0248	-0.0245
0.3934	1.2342	1.2102	1.1861	-0.0273	-0.0267	-0.0264
0.4931	1.2067	1.1829	1.1597	-0.0275	-0.0272	-0.0267
0.6021	1.1790	1.1558	1.1331	-0.0254	-0.0251	-0.0246
0.7217	1.1513	1.1286	1.1064	-0.0204	-0.0202	-0.0198
0.8537	1.1235	1.1014	1.0798	-0.0121	-0.0120	-0.0118
1.0000	1.0957	1.0741	1.0531	0.0000	0.0000	0.0000
p-Cymene (1) + Bromobenzene (2)						
0.0000	1.6868	1.6564	1.6264	0.0000	0.0000	0.0000
0.0692	1.6282	1.5989	1.5697	-0.0177	-0.0172	-0.0170
0.1432	1.5693	1.5409	1.5125	-0.0328	-0.0321	-0.0318
0.2228	1.5107	1.4831	1.4555	-0.0444	-0.0436	-0.0432
0.3084	1.4519	1.4252	1.3984	-0.0526	-0.0517	-0.0512
0.4008	1.3932	1.3670	1.3413	-0.0567	-0.0561	-0.0553
0.5008	1.3342	1.3088	1.2840	-0.0566	-0.0560	-0.0553
0.6095	1.2748	1.2504	1.2262	-0.0517	-0.0511	-0.0508
0.7279	1.2154	1.1919	1.1687	-0.0411	-0.0406	-0.0404
0.8575	1.1558	1.1333	1.1110	-0.0241	-0.0238	-0.0238
1.0000	1.0957	1.0741	1.0531	0.0000	0.0000	0.0000

p-cymene + fluorobenzene binary mixture $\bar{K}_{S,m,1}^o$ and $\bar{K}_{S,m,2}^o$ values are higher than chlorobenzene and bromobenzene binary mixture which suggest that p-cymene molecules are highly attracted by fluorobenzene molecules and resultant infinite dilution partial molar isentropic compressibility, ($\bar{K}_{S,m,i}^o$) are higher.

Apparent molar isentropic compressibility, $K_{S,m,\phi,i}$ are calculated by two different equations and calculated values are very close to each other. The values of infinite dilution apparent molar isentropic compressibility, $K_{S,m,\phi,1}^o$ with empirical parameters S_k and B_k of Redlich-Rosenberg-Mayer equation are given in Table 12 with standard deviation, (σ). The

Table 10 — Intermolecular free length (L_f) of p-cymene (1) + fluoro-, chloro- and bromobenzene (2) binary mixtures

x_1	L_f (\AA^0)		
	303.15 K	308.15 K	313.15 K
p-Cymene (1) + Fluorobenzene (2)			
0.0000	0.0000	0.0000	0.0000
0.0624	-0.0003	-0.0003	-0.0004
0.1302	-0.0005	-0.0006	-0.0007
0.2042	-0.0007	-0.0009	-0.0011
0.2853	-0.0007	-0.0008	-0.0011
0.3745	-0.0011	-0.0012	-0.0014
0.4732	-0.0013	-0.0015	-0.0017
0.5828	-0.0012	-0.0013	-0.0016
0.7055	-0.0008	-0.0009	-0.0012
0.8435	-0.0007	-0.0008	-0.0008
1.0000	0.0000	0.0000	0.0000
p-Cymene (1) + Chlorobenzene (2)			
0.0000	0.0000	0.0000	0.0000
0.0672	0.0010	0.0010	0.0011
0.1395	0.0017	0.0018	0.0019
0.2175	0.0025	0.0025	0.0027
0.3018	0.0029	0.0030	0.0032
0.3934	0.0031	0.0032	0.0034
0.4931	0.0032	0.0034	0.0035
0.6021	0.0030	0.0032	0.0033
0.7217	0.0025	0.0026	0.0027
0.8537	0.0015	0.0016	0.0016
1.0000	0.0000	0.0000	0.0000
p-Cymene (1) + Bromobenzene (2)			
0.0000	0.0000	0.0000	0.0000
0.0692	0.0011	0.0010	0.0011
0.1432	0.0021	0.0021	0.0022
0.2228	0.0029	0.0029	0.0030
0.3084	0.0035	0.0035	0.0037
0.4008	0.0038	0.0039	0.0040
0.5008	0.0039	0.0040	0.0041
0.6095	0.0036	0.0037	0.0040
0.7279	0.0029	0.0030	0.0032
0.8575	0.0017	0.0017	0.0019
1.0000	0.0000	0.0000	0.0000

value of $K_{s,m,\phi,1}^0$ are affected by two factors, such as (i) Presence of intermolecular free space gives more compressibility and gives positive effect due to solvent intrinsic compressibility of large sized organic

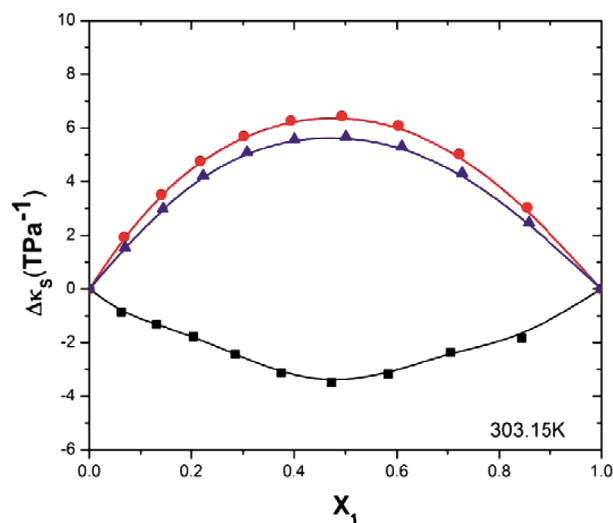


Fig. 11 — Deviation in isentropic compressibility ($\Delta\kappa_s$) as a function of mole fraction (X_1) for p-Cymene (1) + Fluorobenzene (2) (■), p-Cymene (1) + Chlorobenzene (2) (●), p-Cymene (1) + Bromobenzene (2) (▲) at $T=303.15\text{K}$.

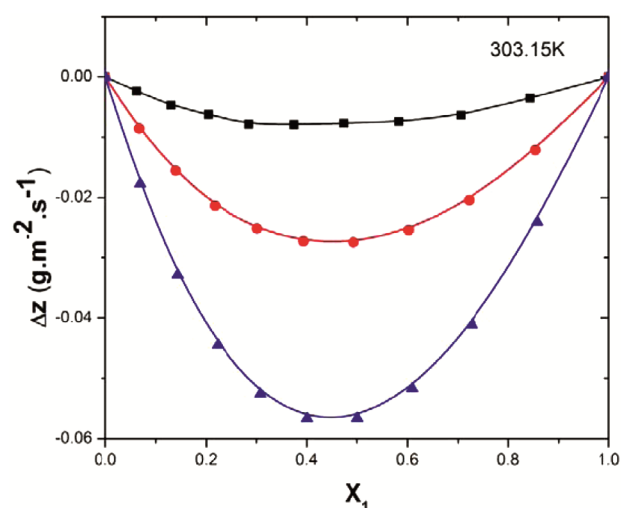


Fig. 12 — Deviation in acoustic impedance (Δz) as a function of mole fraction (X_1) for p-Cymene (1) + Fluorobenzene (2) (■), p-Cymene (1) + Chlorobenzene (2) (●), p-Cymene (1) + Bromobenzene (2) (▲) at $T=303.15\text{K}$.

group and (ii) Negative effect due to the more compressibility to the solution because of solvent molecules can penetrate into intra-group free space^{32,33}. Positive values of $K_{s,m,\phi,1}^0$ indicate that there is a higher solvent intrinsic compressibility than penetration effect in studied binary mixtures. From the above discussion the interaction trend of the mixtures is as under

Table 11 — Excess molar isentropic compressibility ($K_{s,m}^E$), Infinite dilution partial molar isentropic compressibility ($\bar{K}_{s,m,i}^o$), Excess partial molar isentropic compressibility ($\bar{K}_{s,m,i}^{o,E}$), Apparent molar isentropic compressibility ($K_{s,m,\phi,i}$) and Apparent molar isentropic compressibility ($K'_{s,m,\phi,i}$) of p-cymene (1) + fluoro-, chloro- and bromobenzene (2) binary mixtures

x_1	Molality m_1 (mol·Kg ⁻¹)	Molality m_2 (mol·Kg ⁻¹)	$K_{s,m}^E$ ((TPa) ⁻¹) ·m ³ ·mol ⁻¹	$\bar{K}_{s,m,1}^o$ ((TPa) ⁻¹) ·m ³ ·mol ⁻¹	$\bar{K}_{s,m,2}^o$ ((TPa) ⁻¹) ·m ³ ·mol ⁻¹	$\bar{K}_{s,m,1}^{o,E}$ ((TPa) ⁻¹) ·m ³ ·mol ⁻¹	$\bar{K}_{s,m,2}^{o,E}$ ((TPa) ⁻¹) ·m ³ ·mol ⁻¹	$K_{s,m,\phi,1}$ ((TPa) ⁻¹) ·m ³ ·mol ⁻¹	$K_{s,m,\phi,2}$ ((TPa) ⁻¹) ·m ³ ·mol ⁻¹	$K'_{s,m,\phi,1}$ ((TPa) ⁻¹) ·m ³ ·mol ⁻¹	$K'_{s,m,\phi,2}$ ((TPa) ⁻¹) ·m ³ ·mol ⁻¹
p-Cymene (1) + Fluorobenzene (2) at 303.15 K											
0.0000	-	-	0.000000	0.1095	0.0714	-	-	-	-	-	-
0.0624	0.6923	111.9884	0.000061	0.1114	0.0714	-0.00040	0.00000	0.112774	0.071449	0.112371	0.071446
0.1302	1.5577	49.7726	0.000146	0.1122	0.0714	0.00037	-0.00001	0.112921	0.071553	0.113296	0.071540
0.2042	2.6704	29.0340	0.000178	0.1123	0.0714	0.00049	-0.00003	0.112669	0.071608	0.113156	0.071581
0.2853	4.1539	18.6647	0.000271	0.1121	0.0713	0.00032	-0.00004	0.112746	0.071763	0.113065	0.071720
0.3745	6.2309	12.4432	0.000199	0.1120	0.0713	0.00015	-0.00007	0.112329	0.071703	0.112483	0.071636
0.4732	9.3463	8.2954	0.000151	0.1119	0.0713	0.00012	-0.00013	0.112116	0.071671	0.112240	0.071542
0.5828	14.5387	5.3328	0.000192	0.1120	0.0711	0.00019	-0.00030	0.112128	0.071846	0.112315	0.071549
0.7055	24.9234	3.1108	0.000218	0.1120	0.0707	0.00019	-0.00065	0.112107	0.072125	0.112300	0.071479
0.8435	56.0777	1.3826	0.000079	0.1119	0.0703	0.00007	-0.00104	0.111892	0.071890	0.111961	0.070847
1.0000	-	-	0.000000	0.1118	0.0711	-	-	-	-	-	-
p-Cymene (1) + Fluorobenzene (2) at 308.15 K											
0.0000	-	-	0.000000	0.1144	0.0748	-	-	-	-	-	-
0.0624	0.6932	111.8511	0.000071	0.1161	0.0748	-0.00020	0.00000	0.117452	0.074913	0.117265	0.074910
0.1302	1.5596	49.7116	0.000156	0.1168	0.0748	0.00050	-0.00002	0.117513	0.075016	0.118024	0.075001
0.2042	2.6736	28.9984	0.000188	0.1169	0.0748	0.00059	-0.00004	0.117238	0.075072	0.117842	0.075038
0.2853	4.1590	18.6419	0.000321	0.1168	0.0748	0.00043	-0.00006	0.117442	0.075283	0.117879	0.075225
0.3745	6.2385	12.4279	0.000249	0.1166	0.0747	0.00025	-0.00010	0.116984	0.075232	0.117246	0.075136
0.4732	9.3578	8.2853	0.000181	0.1165	0.0747	0.00020	-0.00018	0.116703	0.075176	0.116905	0.075002
0.5828	14.5565	5.3262	0.000232	0.1165	0.0745	0.00022	-0.00036	0.116721	0.075389	0.116946	0.075035
0.7055	24.9540	3.1070	0.000251	0.1165	0.0741	0.00020	-0.00071	0.116680	0.075684	0.116880	0.074979
0.8435	56.1465	1.3809	0.000095	0.1164	0.0737	0.00007	-0.00112	0.116439	0.075437	0.116508	0.074329
1.0000	-	-	0.000000	0.1163	0.0743	-	-	-	-	-	-
p-Cymene (1) + Fluorobenzene (2) at 313.15 K											
0.0000	-	-	0.000000	0.1212	0.0785	-	-	-	-	-	-
0.0624	0.6941	111.7087	0.000081	0.1218	0.0785	0.00075	0.00000	0.122293	0.078632	0.123070	0.078630
0.1302	1.5616	49.6483	0.000178	0.1219	0.0785	0.00084	-0.00002	0.122371	0.078749	0.123233	0.078736
0.2042	2.6771	28.9615	0.000214	0.1217	0.0785	0.00069	-0.00004	0.122050	0.078811	0.122765	0.078777
0.2853	4.1643	18.6181	0.000327	0.1215	0.0785	0.00049	-0.00007	0.122154	0.078999	0.122667	0.078932
0.3745	6.2465	12.4121	0.000301	0.1214	0.0784	0.00036	-0.00013	0.121815	0.079021	0.122187	0.078898
0.4732	9.3697	8.2747	0.000224	0.1213	0.0783	0.00031	-0.00024	0.121486	0.078961	0.121809	0.078732
0.5828	14.5751	5.3195	0.000238	0.1213	0.0781	0.00030	-0.00045	0.121426	0.079107	0.121734	0.078669
0.7055	24.9858	3.1030	0.000265	0.1212	0.0777	0.00022	-0.00081	0.121395	0.079432	0.121625	0.078639
0.8435	56.2181	1.3791	0.000157	0.1211	0.0773	0.00007	-0.00121	0.121209	0.079533	0.121284	0.078337
1.0000	-	-	0.000000	0.1210	0.0777	-	-	-	-	-	-
p-Cymene (1) + Chlorobenzene (2) at 303.15 K											
0.0000	-	-	0.000000	0.1083	0.0601	-	-	-	-	-	-
0.0672	0.6401	103.4177	-0.000232	0.1088	0.0601	-0.00296	0.00002	0.108349	0.059812	0.105385	0.059829
0.1395	1.4402	45.9634	-0.000467	0.1092	0.0601	-0.00258	0.00007	0.108451	0.059518	0.105873	0.059593
0.2175	2.4689	26.8120	-0.000640	0.1096	0.0602	-0.00224	0.00018	0.108854	0.059243	0.106611	0.059427
0.3018	3.8405	17.2363	-0.000816	0.1099	0.0604	-0.00190	0.00036	0.109093	0.058891	0.107188	0.059253
0.3934	5.7607	11.4909	-0.000926	0.1103	0.0607	-0.00153	0.00062	0.109444	0.058534	0.107914	0.059158

(Contd.)

Table 11 — Excess molar isentropic compressibility ($K_{s,m}^E$), Infinite dilution partial molar isentropic compressibility ($\bar{K}_{s,m,i}^o$), Excess partial molar isentropic compressibility ($\bar{K}_{s,m,i}^{o,E}$), Apparent molar isentropic compressibility ($K_{s,m,\phi,i}$) and Apparent molar isentropic compressibility ($K'_{s,m,\phi,i}$) of p-cymene (1) + fluoro-, chloro- and bromobenzene (2) binary mixtures (Contd.)

x_1	Molality m_1 (mol·Kg ⁻¹)	Molality m_2 (mol·Kg ⁻¹)	$K_{s,m}^E$ ((TPa) ⁻¹ ·m ³ ·mol ⁻¹)	$\bar{K}_{s,m,1}^o$ ((TPa) ⁻¹ ·m ³ ·mol ⁻¹)	$\bar{K}_{s,m,2}^o$ ((TPa) ⁻¹ ·m ³ ·mol ⁻¹)	$\bar{K}_{s,m,1}^{o,E}$ ((TPa) ⁻¹ ·m ³ ·mol ⁻¹)	$\bar{K}_{s,m,2}^{o,E}$ ((TPa) ⁻¹ ·m ³ ·mol ⁻¹)	$K_{s,m,\phi,1}$ ((TPa) ⁻¹ ·m ³ ·mol ⁻¹)	$K_{s,m,\phi,2}$ ((TPa) ⁻¹ ·m ³ ·mol ⁻¹)	$K'_{s,m,\phi,1}$ ((TPa) ⁻¹ ·m ³ ·mol ⁻¹)	$K'_{s,m,\phi,2}$ ((TPa) ⁻¹ ·m ³ ·mol ⁻¹)
p-Cymene (1) + Chlorobenzene (2) at 303.15 K											
0.4931	8.6411	7.6606	-0.000943	0.1107	0.0610	-0.00112	0.00099	0.109885	0.058200	0.108769	0.059186
0.6021	13.4417	4.9247	-0.000860	0.1111	0.0615	-0.00070	0.00146	0.110369	0.057899	0.109673	0.059360
0.7217	23.0430	2.8727	-0.000690	0.1115	0.0621	-0.00033	0.00206	0.110841	0.057580	0.110512	0.059636
0.8537	51.8467	1.2768	-0.000413	0.1117	0.0628	-0.00008	0.00278	0.111313	0.057235	0.111230	0.060012
1.0000	-	-	0.000000	0.1118	0.0637	-	-	-	-	-	-
p-Cymene (1) + Chlorobenzene (2) at 308.15 K											
0.0000	-	-	0.000000	0.1125	0.0625	-	-	-	-	-	-
0.0672	0.6402	103.3980	-0.000242	0.1132	0.0625	-0.00309	0.00002	0.112716	0.062195	0.109633	0.062213
0.1395	1.4405	45.9547	-0.000471	0.1137	0.0625	-0.00263	0.00008	0.112948	0.061907	0.110326	0.061985
0.2175	2.4694	26.8069	-0.000672	0.1140	0.0626	-0.00229	0.00019	0.113233	0.061595	0.110945	0.061788
0.3018	3.8412	17.2330	-0.000845	0.1143	0.0628	-0.00198	0.00038	0.113523	0.061242	0.111549	0.061622
0.3934	5.7618	11.4887	-0.000973	0.1147	0.0631	-0.00162	0.00065	0.113849	0.060847	0.112235	0.061505
0.4931	8.6428	7.6591	-0.000952	0.1151	0.0635	-0.00120	0.00104	0.114392	0.060572	0.113200	0.061612
0.6021	13.4443	4.9237	-0.000871	0.1156	0.0640	-0.00075	0.00153	0.114879	0.060262	0.114135	0.061798
0.7217	23.0474	2.8722	-0.000699	0.1160	0.0646	-0.00035	0.00214	0.115357	0.059938	0.115010	0.062083
0.8537	51.8566	1.2765	-0.000417	0.1162	0.0653	-0.00009	0.00287	0.115838	0.059597	0.115752	0.062474
1.0000	-	-	0.000000	0.1163	0.0663	-	-	-	-	-	-
p-Cymene (1) + Chlorobenzene (2) at 313.15 K											
0.0000	-	-	0.000000	0.1172	0.0650	-	-	-	-	-	-
0.0672	0.6403	103.3765	-0.000247	0.1179	0.0650	-0.00316	0.00002	0.117339	0.064727	0.114197	0.064746
0.1395	1.4408	45.9451	-0.000476	0.1183	0.0651	-0.00270	0.00008	0.117599	0.064437	0.114912	0.064518
0.2175	2.4699	26.8013	-0.000678	0.1187	0.0652	-0.00235	0.00020	0.117897	0.064123	0.115555	0.064322
0.3018	3.8420	17.2294	-0.000848	0.1190	0.0654	-0.00202	0.00038	0.118208	0.063774	0.116203	0.064163
0.3934	5.7630	11.4863	-0.000978	0.1194	0.0657	-0.00163	0.00066	0.118532	0.063375	0.116915	0.064043
0.4931	8.6446	7.6575	-0.000988	0.1198	0.0660	-0.00118	0.00104	0.119016	0.063036	0.117843	0.064084
0.6021	13.4471	4.9227	-0.000899	0.1203	0.0665	-0.00072	0.00153	0.119528	0.062724	0.118811	0.064261
0.7217	23.0522	2.8716	-0.000721	0.1207	0.0671	-0.00033	0.00213	0.120023	0.062389	0.119694	0.064529
0.8537	51.8674	1.2763	-0.000430	0.1209	0.0679	-0.00008	0.00288	0.120521	0.062038	0.120438	0.064936
1.0000	-	-	0.000000	0.1210	0.0690	-	-	-	-	-	-
p-Cymene (1) + Bromobenzene (2) at 303.15 K											
0.0000	-	-	0.000000	0.1043	0.0552	-	-	-	-	-	-
0.0692	0.4733	100.2679	-0.000465	0.1057	0.0552	-0.00612	0.00003	0.105069	0.054680	0.098950	0.054713
0.1432	1.0649	44.5635	-0.000865	0.1067	0.0553	-0.00505	0.00014	0.105759	0.054171	0.100705	0.054314
0.2228	1.8256	25.9954	-0.001222	0.1076	0.0555	-0.00418	0.00035	0.106313	0.053608	0.102129	0.053959
0.3084	2.8398	16.7113	-0.001495	0.1084	0.0559	-0.00339	0.00068	0.106949	0.053018	0.103558	0.053696
0.4008	4.2597	11.1409	-0.001692	0.1092	0.0563	-0.00261	0.00115	0.107577	0.052357	0.104968	0.053508
0.5008	6.3895	7.4272	-0.001742	0.1100	0.0570	-0.00183	0.00180	0.108320	0.051691	0.106487	0.053488
0.6095	9.9392	4.7747	-0.001628	0.1107	0.0578	-0.00112	0.00264	0.109126	0.051011	0.108011	0.053655
0.7279	17.0386	2.7852	-0.001341	0.1113	0.0589	-0.00053	0.00374	0.109955	0.050250	0.109421	0.053991
0.8575	38.3369	1.2379	-0.000834	0.1116	0.0604	-0.00015	0.00522	0.110825	0.049327	0.110676	0.054548
1.0000	-	-	0.000000	0.1118	0.0627	-	-	-	-	-	-

(Contd.)

Table 11 — Excess molar isentropic compressibility ($K_{s,m}^E$), Infinite dilution partial molar isentropic compressibility ($\bar{K}_{s,m,i}^o$), Excess partial molar isentropic compressibility ($\bar{K}_{s,m,i}^{o,E}$), Apparent molar isentropic compressibility ($K_{s,m,\phi,i}$) and Apparent molar isentropic compressibility ($K'_{s,m,\phi,i}$) of p-cymene (1) + fluoro-, chloro- and bromobenzene (2) binary mixtures (Contd.)

x_1	Molality m_1 (mol·kg ⁻¹)	Molality m_2 (mol·kg ⁻¹)	$K_{s,m}^E$ (TPa) ⁻¹ ·m ³ ·mol ⁻¹	$\bar{K}_{s,m,1}^o$ (TPa) ⁻¹ ·m ³ ·mol ⁻¹	$\bar{K}_{s,m,2}^o$ (TPa) ⁻¹ ·m ³ ·mol ⁻¹	$\bar{K}_{s,m,1}^{o,E}$ (TPa) ⁻¹ ·m ³ ·mol ⁻¹	$\bar{K}_{s,m,2}^{o,E}$ (TPa) ⁻¹ ·m ³ ·mol ⁻¹	$K_{s,m,\phi,1}$ (TPa) ⁻¹ ·m ³ ·mol ⁻¹	$K_{s,m,\phi,2}$ (TPa) ⁻¹ ·m ³ ·mol ⁻¹	$K'_{s,m,\phi,1}$ (TPa) ⁻¹ ·m ³ ·mol ⁻¹	$K'_{s,m,\phi,2}$ (TPa) ⁻¹ ·m ³ ·mol ⁻¹
p-Cymene (1) + Bromobenzene (2) at 308.15 K											
0.0000	-	-	0.000000	0.1085	0.0572	-	-	-	-	-	-
0.0692	0.4732	100.2858	-0.000515	0.1099	0.0573	-0.00641	0.00004	0.108887	0.056671	0.102472	0.056706
0.1432	1.0647	44.5715	-0.000944	0.1110	0.0574	-0.00532	0.00015	0.109746	0.056124	0.104419	0.056273
0.2228	1.8252	26.0000	-0.001319	0.1119	0.0576	-0.00440	0.00037	0.110414	0.055529	0.106005	0.055894
0.3084	2.8393	16.7143	-0.001609	0.1128	0.0579	-0.00356	0.00071	0.111117	0.054901	0.107549	0.055609
0.4008	4.2589	11.1429	-0.001777	0.1136	0.0584	-0.00275	0.00121	0.111901	0.054264	0.109146	0.055470
0.5008	6.3883	7.4286	-0.001830	0.1144	0.0591	-0.00196	0.00190	0.112679	0.053565	0.110717	0.055461
0.6095	9.9374	4.7755	-0.001712	0.1151	0.0601	-0.00122	0.00283	0.113524	0.052850	0.112297	0.055671
0.7279	17.0356	2.7857	-0.001413	0.1157	0.0613	-0.00061	0.00406	0.114390	0.052042	0.113777	0.056096
0.8575	38.3300	1.2381	-0.000878	0.1161	0.0630	-0.00018	0.00576	0.115306	0.051074	0.115126	0.056824
1.0000	-	-	0.000000	0.1163	0.0655	-	-	-	-	-	-
p-Cymene (1) + Bromobenzene (2) at 313.15 K											
0.0000	-	-	0.000000	0.1132	0.0594	-	-	-	-	-	-
0.0692	0.4731	100.3035	-0.000541	0.1146	0.0594	-0.00640	0.00004	0.113229	0.058777	0.106804	0.058812
0.1432	1.0645	44.5793	-0.000987	0.1156	0.0595	-0.00540	0.00016	0.114157	0.058208	0.108742	0.058364
0.2228	1.8249	26.0046	-0.001377	0.1164	0.0597	-0.00458	0.00039	0.114864	0.057590	0.110266	0.057977
0.3084	2.8388	16.7173	-0.001675	0.1172	0.0601	-0.00380	0.00076	0.115611	0.056942	0.111794	0.057697
0.4008	4.2581	11.1448	-0.001879	0.1180	0.0607	-0.00298	0.00130	0.116353	0.056231	0.113361	0.057520
0.5008	6.3872	7.4299	-0.001932	0.1189	0.0614	-0.00212	0.00203	0.117181	0.055499	0.115050	0.057515
0.6095	9.9357	4.7764	-0.001759	0.1197	0.0623	-0.00130	0.00299	0.118151	0.054870	0.116841	0.057841
0.7279	17.0326	2.7862	-0.001437	0.1204	0.0636	-0.00063	0.00424	0.119059	0.054095	0.118422	0.058314
0.8575	38.3233	1.2383	-0.000869	0.1208	0.0654	-0.00018	0.00600	0.120018	0.053284	0.119831	0.059256
1.0000	-	-	0.000000	0.1210	0.0683	-	-	-	-	-	-

Table 12 — Infinite dilution apparent molar isentropic compressibility ($K_{s,m,\phi,1}^o$), Empirical parameters S_k and B_k of Redlich-Rosenberg-Mayer equation with Standard deviation, (σ) of p-cymene (1) + fluoro-, chloro- and bromobenzene (2) binary mixtures

T (K)	$K_{s,m,\phi,1}^o$ (m ³ ·(TPa) ⁻¹ ·mol ⁻¹)	S_k (m ⁻³ ·(TPa) ⁻¹ ·mol ^{-(3/2)} ·kg ^(1/2))	B_k (m ⁻³ ·(TPa) ⁻¹ ·mol ⁻² ·kg)	σ
p-Cymene (1) + Fluorobenzene (2)				
303.15	0.112625	-0.05002	0.024992	0.00027
308.15	0.117258	-0.05002	0.024991	0.00028
313.15	0.122055	-0.05002	0.024991	0.00031
p-Cymene (1) + Chlorobenzene (2)				
303.15	0.108932	-0.04994	0.025028	0.00059
308.15	0.113362	-0.04994	0.025029	0.00062
313.15	0.118014	-0.04994	0.025029	0.00059
p-Cymene (1) + Bromobenzene (2)				
303.15	0.106510	-0.04986	0.025069	0.00115
308.15	0.110622	-0.04985	0.025075	0.00134
313.15	0.115060	-0.04984	0.025080	0.00140

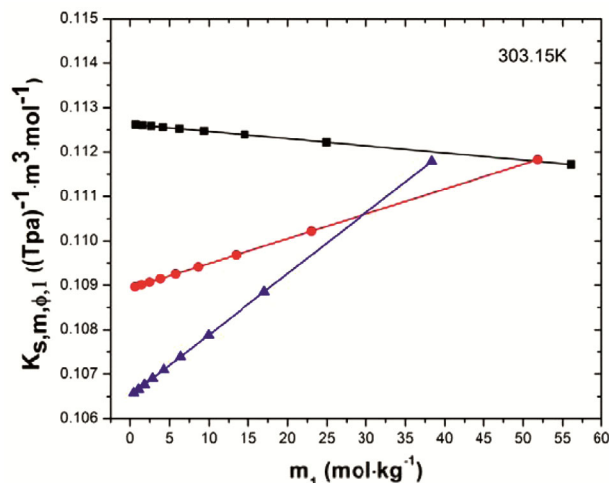


Fig. 13 — Apparent molar isentropic compressibility ($K_{s,m,\phi,1}$) as a function of molality (m_1) for p-Cymene (1) + Fluorobenzene (2) (■), p-Cymene (1) + Chlorobenzene (2) (●), p-Cymene (1) + Bromobenzene (2) (▲) at $T = 303.15$ K.

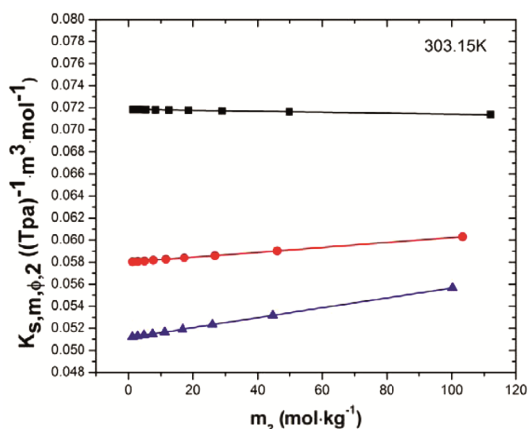


Fig. 14 — Apparent molar isentropic compressibility ($K_{s,m,\phi,2}$) as a function of molality (m_2) for p-Cymene (1) + Fluorobenzene (2) (■), p-Cymene (1) + Chlorobenzene (2) (●), p-Cymene (1) + Bromobenzene (2) (▲) at $T= 303.15\text{K}$.

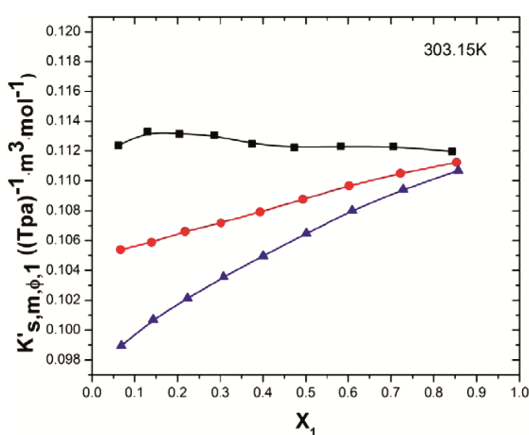


Fig. 15 — Apparent molar isentropic compressibility ($K'_{s,m,\phi,1}$) as a function of mole fraction (X_1) for p-Cymene (1) + Fluorobenzene (2) (■), p-Cymene (1) + Chlorobenzene (2) (●), p-Cymene (1) + Bromobenzene (2) (▲) at $T= 303.15\text{K}$.

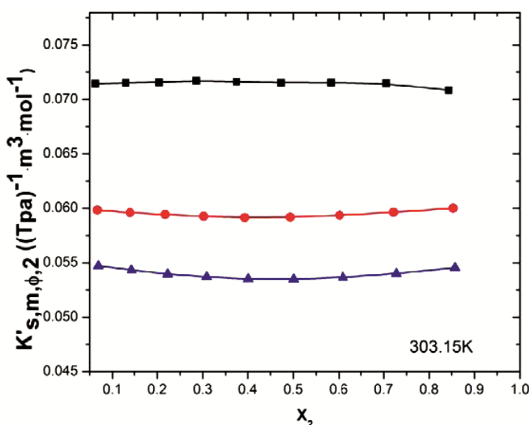


Fig. 16 — Apparent molar isentropic compressibility ($K'_{s,m,\phi,2}$) as a function of mole fraction (X_2) for p-Cymene (1) + Fluorobenzene (2) (■), p-Cymene (1) + Chlorobenzene (2) (●), p-Cymene (1) + Bromobenzene (2) (▲) at $T= 303.15\text{K}$.

fluorobenzene > chlorobenzene > bromobenzene

5 Conclusions

The density, (ρ), and excess molar volumes, (V_m^E), of *p*-cymene with halobenzenes (fluorobenzene, chlorobenzene and bromobenzene) are reported at temperatures 303.15, 308.15 K and 313.15 K. Negative deviations are observed in V_m^E values for all binary mixtures indicate for presence of strong interaction in binary mixtures. The negative values of excess partial molar volume, ($\bar{V}_{m,i}^{o,E}$) support the conclusion derived from excess molar volume. The positive values of ΔU , negative values of $\Delta\kappa_s$, and Δz suggest that there is a strong interaction between present between the molecules of binary mixtures. Interaction trend of the mixtures is fluorobenzene > chlorobenzene > bromobenzene. Theoretical relations of speed of sound were in good agreement with experimental values. From the result, it is anticipated that there is possibility of hydrogen bonding type of interaction between the *p*-cymene and halobenzene molecules. The interactions become weaker when binary mixture changes from fluorobenzene to bromobenzene and temperature changes from 303.15 to 313.15.

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