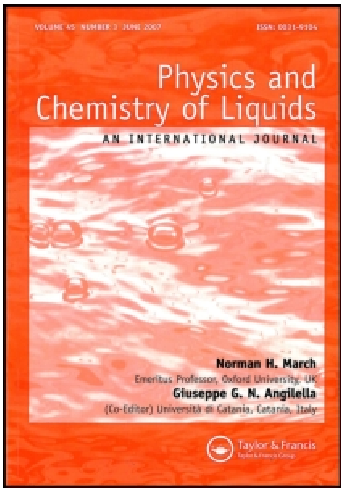

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Theoretical estimations of thermodynamic properties of liquid mixtures by Flory's statistical theory

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Flory's statistical theory has been employed for the computation of ultrasonic velocity (u), density (ρ), internal pressure (P_i), thermal expansion coefficient (α), isothermal compressibility (β_T), adiabatic compressibility (β_S), heat capacity at constant pressure (C_P), heat capacity at constant volume (C_V), heat capacities ratio (γ), pseudo-Gruneisen parameter (Γ), excess volume (V^E) and excess heat capacity at constant pressure (C_P^E) at varying temperatures for 10 binary and 5 ternary systems. The binary systems under investigation are: acetonitrile + benzene, benzene + DMF, acetonitrile + DMF, cyclohexanol + cyclohexane, piperidine + tetrahydropyran, piperidine + cyclohexane, tetrahydropyran + cyclohexane, benzene + *p*-xylene, benzene + *p*-dioxan, acetone + methyliodide, and the ternary systems are: benzene + chloroform + cyclohexane, toluene + chloroform + cyclohexane, chlorobenzene + chloroform + cyclohexane, dioxane + chloroform + cyclohexane and chlorobenzene + cyclohexane + *n*-heptane. The results of calculations show that for all the systems under consideration, the calculated values of various thermodynamic parameters show the same trend as observed experimentally. Fairly good agreement is found between theoretical and experimental values. The ultrasonic velocity of liquid mixtures is obtained using the most popular Flory theory without the help of any empirical relation.

Keywords: Flory's statistical theory; Ultrasonic velocity; Thermal expansivity; Isothermal compressibility

1. Introduction

For liquid mixtures, the most widely accepted Flory's statistical theory [1–5] has been successfully employed to evaluate theoretically, the ultrasonic velocity [6–11], isentropic compressibility [12–14], excess volume [11,15–21], isothermal compressibility [22], viscosity and other properties e.g., excess enthalpy, excess Gibbs free energy and activity coefficient. In the case of binary liquid mixture, excess volume and excess enthalpy were interpreted in the light of Prigogine–Flory–Patterson theory. Starting with the Flory equation of state, the excess volumes of binary, ternary and quaternary

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liquid mixtures have been theoretically evaluated [15–17]. This theory has also been extended to multicomponent liquid systems for computing thermodynamic [23–30] and transport [31–33] properties. Flory theory has also been utilised to evaluate ultrasonic velocity in liquid mixtures. The traditional approach, employed by most of the workers, is to use Auerback [34] and Altenberg [35] empirical equations between ultrasonic velocity, density and surface tension. Surface tension is first deduced from Flory theory using Patterson–Rastogi method [36], then it is transformed to ultrasonic velocity via the aforesaid empirical relations. In this approach, the values of experimental density of mixture are desired for obtaining ultrasonic velocity. In another advance approach, developed during recent year [12], the experimental density, heat of mixing and excess heat capacity data of mixture is required.

In the present work, we are presenting an entirely different formalism for computing ultrasonic velocity (u), density (ρ), internal pressure (P_i), thermal expansion coefficient (α), isothermal compressibility (β_T), isentropic compressibility (β_S), heat capacity at constant pressure (C_P), heat capacity at constant volume (C_V), heat capacities ratio (γ), pseudo-Gruneisen parameter [37] (Γ), excess volume (V^E) and excess heat capacity at constant pressure [13] (C_P^E) of binary and ternary liquid mixtures using Flory's statistical theory. The present approach has the following merits:

(i) No empirical relation is used.
(ii) We do not need experimental values of any property of mixture before hand.
(iii) The method does not involve any approximation.
(iv) Only experimental values of thermal expansivity, isothermal compressibility, heat capacity at constant pressure and density of pure components are desired for computing all the thermodynamic properties of binary and multicomponent mixtures.

In the present work, we are applying Flory's theory for estimating the values of various aforesaid thermodynamic properties of 10 binary and 5 ternary liquid mixtures. In earlier approaches, ultrasonic velocity of liquid mixture has been calculated on the basis of Flory–Patterson theory in conjunction with Auerbach and Altenberg empirical relations. But the present approach is purely theoretical and no empirical relation is used. Except mole fraction, no other property of liquid mixture is desired. The present approach is entirely new, as far as our knowledge is concerned, and nobody has, so far, succeeded in estimating the ultrasonic velocity of liquid mixtures using the most popular Flory theory without the help of any empirical relation, which is very novel approach. The sound velocity of any type of liquid mixture can be predicted simply from the knowledge of α, β_T, C_P and V of pure components. The density of any type of liquid mixture can be predicted simply from the knowledge of α, β_T and V of pure components. The computed values obtained by Flory theory are compared with the experimental findings [16,38–44].

2. Theoretical

From the knowledge of α, β_T and V of pure components, the values of $\tilde{V}$, V^*, P^*, $\tilde{T}$ and T^* for pure components can be obtained. Segment fraction (ψ) and site fraction (θ) of liquid mixtures have been computed by the method suggested earlier [23]. With the help of segment and site fraction reduced volume, $\tilde{V}$, of the mixture is calculated by the method given by earlier workers [1–4,23,25,28,29].

The molar volume (V) of the mixture is related with the characteristic volume (V^*) and reduced volume ($\tilde{V}$) of the mixture as,

$$V = V^* \tilde{V} \tag{1}$$

$$\text{where} \quad V^* = \Sigma x_{\mathrm{i}} V_{\mathrm{i}}^* \tag{2}$$

Density of the mixture is given by

$$\rho_{\mathrm{m}} = \frac{M_{\mathrm{m}}}{V} \tag{3}$$

where M_{m} is the molar mass of the mixture expressed as

$$M_{\mathrm{m}} = \Sigma x_{\mathrm{i}} M_{\mathrm{i}} \tag{4}$$

where x_{i} is the mole fraction and M_{i} is the molar mass of the i-th pure component. Equation (3) in conjunction with equation (1) can be used to compute ρ_{m} of the liquid mixture.

Isothermal compressibility of the liquid mixture can be calculated by the following expression:

$$\beta_{\mathrm{T}} = \frac{\alpha T \tilde{V}^2}{P^*} \tag{5}$$

Thermal expansion coefficient of the mixture is obtained by the equation

$$\alpha = \frac{\left(\tilde{V}^{1/3} - 1\right)}{T\left(1 - 3(\tilde{V}^{1/3} - 1)\right)} \tag{6}$$

Internal pressure (P_{i}) is related with the thermal expansion coefficient and isothermal compressibility through the relation,

$$P_{\mathrm{i}} = \frac{\alpha T}{\beta_{\mathrm{T}}} \tag{7}$$

Heat capacity at constant pressure of the mixture is defined as,

$$C_{\mathrm{P}} = C_{\mathrm{P}}^{\mathrm{E}} + C_{\mathrm{P(idl)}} \tag{8}$$

where $C_{\mathrm{P(idl)}}$ is ideal heat capacity of the mixture and defined as,

$$C_{\mathrm{P(idl)}} = \Sigma x_{\mathrm{i}} C_{\mathrm{P,i}} \tag{9}$$

where $C_{\mathrm{P,i}}$ = heat capacity of i-th pure component. $C_{\mathrm{P}}^{\mathrm{E}}$ is defined by Khanwalkar *et al.* [13] according to Flory theory, as

$$C_{\mathrm{P}}^{\mathrm{E}} = \frac{P^* V^*}{T^*}\left[\frac{1}{\left((4/3)\tilde{V}^{-1/3} - 1\right)} - \Sigma\left\{\frac{x_i}{(4/3)\tilde{V}_i^{-1/3} - 1}\right\}\right] \tag{10}$$

β_s is calculated with the help of well-known thermodynamic relation,

$$\beta_S = \beta_T - \frac{\alpha^2 TV}{C_P} \tag{11}$$

Ultrasonic velocity (u) of the mixture is obtained with the help of the following relation:

$$u = \left(\frac{1}{\beta_S \rho}\right)^{1/2} \tag{12}$$

The excess volume of the mixture is calculated with the help of Equation (18) of [25].

$$V^E = (\Sigma x_i V_i^*)\tilde{V}^E \tag{13}$$

Heat capacities ratio, γ, for the mixture can be calculated by the well-known relation,

$$\gamma = \frac{\beta_T}{\beta_S} \tag{14}$$

The heat capacity of mixture at constant volume (C_V) is computed by the following relation:

$$C_V = \frac{C_P}{\gamma} \tag{15}$$

Pseudo-Gruneisen parameter (Γ) of the mixture can be calculated using the following relation:

$$\Gamma = \frac{\gamma - 1}{\alpha T} \tag{16}$$

3. Results and discussion

The values of ultrasonic velocity, density, internal pressure, thermal expansion coefficient, isothermal compressibility, adiabatic compressibility, heat capacity at constant pressure, heat capacity at constant volume, specific heat ratio, pseudo-Gruneisen parameter, excess volume and excess heat capacity at constant pressure for the 10 binary and 5 ternary liquid mixtures have been evaluated with the help of Flory's statistical theory at different temperatures. Following liquid systems are studied in the present work.

3.1. *Binary liquid mixtures*

Acetonitrile + benzene, benzene + DMF, acetonitrile + DMF, cyclohexanol + cyclohexane, piperidine + tetrahydropyran, piperidine + cyclohexane, tetrahydropyran + cyclohexane, benzene + *p*-xylene, benzene + *p*-dioxan, acetone + methyliodide.

3.2. *Ternary liquid mixtures*

Benzene + chloroform + cyclohexane, toluene + chloroform + cyclohexane, chlorobenzene + chloroform + cyclohexane, dioxane + chloroform + cyclohexane and chlorobenzene + cyclohexane + *n*-heptane.

All the parameters of pure components are listed in table 1. The necessary data needed, for the calculation, have been taken from different sources [16,38–44]. Tables 2 and 3 enlist the computed values of all aforementioned properties of only 4 binary and 5 ternary liquid mixtures, respectively. In table 4, average percentage deviations (APD) of all the 10 binary and 5 ternary liquid mixtures have been presented. The computed values of the desired thermodynamic properties of rest of binary liquid mixtures can be obtained from the authors on request.

For the comparison of theoretically computed values with the observed values under consideration, the experimental values of liquid mixtures were taken from different sources [16,38–44]. Those systems for which experimental values of α and β_T are not known, we have used the following empirical equations [45]:

$$\alpha_{\exp} = \frac{75.6 \times 10^{-3}}{T^{1/9} u^{1/2} \rho^{1/3}} \, \mathrm{K}^{-1} \tag{17}$$

$$\beta_{\mathrm{T(exp)}} = \frac{1.71 \times 10^{-3}}{T^{4/9} \rho^{4/3} u^2} \, \mathrm{cm}^2 \, \mathrm{dyne}^{-1} \tag{18}$$

where u is in $\mathrm{m\,sec}^{-1}$ and ρ in $\mathrm{g\,cm}^{-3}$.

The experimental values of β_S, C_P, γ, C_V, Γ and P_i of liquid mixtures were obtained by the following equations:

$$\beta_{\mathrm{S(exp)}} = \frac{1}{u^2_{(\exp)} \rho_{(\exp)}} \tag{19}$$

$$C_{\mathrm{P(exp)}} = \frac{\alpha^2_{(\exp)} T V_{(\exp)}}{\beta_{T(\exp)} - \beta_{S(\exp)}} \tag{20}$$

$$\gamma_{\exp} = \left(\frac{\beta_{T(\exp)}}{\beta_{S(\exp)}} \right) \tag{21}$$

$$C_{V(\exp)} = \frac{C_{P(\exp)}}{\gamma_{(\exp)}} \tag{22}$$

$$\Gamma_{(\exp)} = \frac{\gamma_{(\exp)} - 1}{\alpha_{(\exp)} T} \tag{23}$$

$$\text{and} \quad P_{\mathrm{i(exp)}} = \frac{\alpha_{(\exp)} T}{\beta_{T(\exp)}} \tag{24}$$

Table 1. Parameters of pure components at different temperatures.

Components	T (K)	V ($\mathrm{cm^3\,mol^{-1}}$)	ρ ($\mathrm{g\,cm^{-3}}$)	$\alpha \times 10^3$ ($\mathrm{K^{-1}}$)	$\beta_T \times 10^{12}$ ($\mathrm{cm^2\,dyne^{-1}}$)	$\tilde{V}$	P^* ($\mathrm{J\,cm^{-3}}$)	T^* (K)	C_P ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
Benzene	298.15	89.42	0.87363	1.229	97.41	1.2928	628.75	4697.7	135.90
	303.15	90.03	0.86770	1.320	102.70	1.3138	672.17	4578.6	147.81
	313.15	91.08	0.85775	1.256	109.53	1.3097	616.03	4769.0	138.90
p-Xylene	298.15	123.94	0.85662	1.013	88.91	1.2504	531.60	5193.8	181.70
	313.15	125.86	0.84358	1.038	98.88	1.2659	526.77	5244.9	186.20
p-Dioxan	298.15	85.71	1.02792	1.132	75.79	1.2742	721.41	4896.7	147.90
	303.15	86.51	1.01850	1.115	78.71	1.2744	697.09	4973.9	143.25
	313.15	87.20	1.01037	1.164	84.49	1.2916	719.86	4947.1	153.70
Toluene	303.15	107.92	0.85390	1.065	96.00	1.2643	537.34	5094.4	147.77
n-Heptane	298.15	147.47	0.67951	1.258	142.40	1.2985	444.42	4642.9	224.68
Acetone	253.2	69.61	0.83436	1.332	91.60	1.2740	597.60	4159.7	120.33
	263.2	70.53	0.82348	1.344	98.40	1.2847	593.35	4220.3	121.08
	273.2	71.48	0.81253	1.361	106.90	1.2963	584.46	4273.9	122.05
	283.2	72.47	0.80144	1.380	115.80	2.3081	577.53	4325.6	123.22
	293.2	73.48	0.79042	1.398	125.50	1.3198	568.92	4380.1	124.73
	303.2	74.53	0.77928	1.416	136.30	1.3315	558.40	4435.7	126.44
	308.2	75.07	0.77368	1.435	143.00	1.3391	554.56	4450.2	127.28
Methyl iodide	253.2	59.50	2.38956	1.167	91.60	1.2459	628.28	4464.6	81.59
	263.2	60.10	2.36173	1.184	98.40	1.2569	626.35	4508.0	81.25
	273.2	60.82	2.33377	1.200	106.90	1.2678	623.58	4554.9	80.96
	283.2	61.56	2.30572	1.214	115.80	1.2783	619.38	4606.9	81.17
	293.2	62.32	2.27760	1.229	125.50	1.2890	616.57	4658.1	82.05
	303.2	63.10	2.24945	1.242	136.30	1.2993	612.42	4714.1	83.47
	308.2	63.49	2.23563	1.254	143.00	1.3055	612.13	4732.5	84.22
Cyclohexane	293.15	108.08	0.77868	1.224	111.60	1.2880	533.37	4667.1	153.34
	298.15	108.76	0.77380	1.215	112.77	1.2902	534.72	4724.3	156.84
	303.15	109.84	0.76620	1.239	119.90	1.2985	527.96	4718.8	151.80
	313.15	110.80	0.75959	1.265	128.97	1.3114	528.25	4752.8	163.60
	323.15	112.19	0.75019	1.294	141.11	1.3248	520.08	4783.8	166.00
Cyclohexanol	298.15	105.98	0.94510	0.804	59.07	1.2061	590.32	5938.7	208.30
	313.15	107.28	0.93368	0.823	64.55	1.2192	593.51	5971.5	211.90
	323.15	108.16	0.92600	0.836	68.61	1.2281	593.90	5994.6	213.80
Piperidine	293.15	98.86	0.86132	1.055	79.80	1.2553	610.71	5041.6	181.88
	313.15	100.98	0.84324	1.077	91.80	1.2740	596.30	5144.6	185.64
Tetrahydropyran	293.15	97.44	0.88403	1.129	93.40	1.2698	571.40	4863.3	149.62
	313.15	99.69	0.86408	1.155	108.10	1.2898	556.64	4965.8	156.61
Acetonitrile	298.15	52.85	0.77674	1.372	111.67	1.3193	637.59	4458.2	90.03
DMF	298.15	77.43	0.94392	0.559	54.78	1.1498	402.20	7541.7	147.22
Chlorobenzene	298.15	102.24	1.10092	0.982	75.50	1.2440	600.13	5284.0	150.78
	303.15	102.73	1.09570	0.990	78.90	1.2490	593.05	5299.0	148.96
Chloroform	303.15	81.40	1.46650	1.300	108.60	1.3100	622.48	4611.4	117.10

In all the cases, the calculated values of all the properties of binary and ternary liquid mixtures by Flory's statistical theory show the same trend as observed experimentally.

A careful study of table 4 demonstrates that the APD values of density in all the cases are below 1%, which is in excellent agreement. The APD values of ultrasonic velocity is

Table 2. Computed values of thermodynamic properties of binary liquid mixtures by Flory theory.

x_1	V^E	$\alpha \times 10^3$ (K^{-1})	$\beta_T \times 10^{12}$ ($cm^2\,dyne^{-1}$)	$\beta_S \times 10^{12}$ ($cm^2\,dyne^{-1}$)	C_p ($J\,K^{-1}\,mol^{-1}$)	$P_i \times 10^{-7}$ ($dyne\,cm^{-2}$)	C_P^E	ρ ($g\,cm^{-3}$)	γ	u ($m\,sec^{-1}$)	Γ	C_v ($J\,K^{-1}\,mol^{-1}$)
Benzene(x_1) + *p*-xylene(x_2)												
At 298.15 K												
0.7501	0.0666	1.158	95.29	68.64	147.21	362.34	−0.1403	0.8676	1.388	1295.85	1.125	106.04
0.5015	0.0836	1.103	92.99	68.58	158.55	353.63	−0.1776	0.8631	1.356	1299.81	1.082	116.93
0.2617	0.0606	1.057	90.93	68.35	169.58	346.57	−0.1315	0.8596	1.330	1304.61	1.048	127.47
At 313.15 K												
0.7501	0.0660	1.188	106.50	77.19	150.57	349.37	−0.1551	0.8527	1.380	1232.61	1.021	109.12
0.5015	0.0834	1.131	103.75	76.98	162.28	341.33	−0.1955	0.8489	1.348	1237.05	0.982	120.40
0.2617	0.0604	1.083	101.31	76.60	173.68	334.79	−0.1447	0.8461	1.323	1242.17	0.951	131.32
Benzene(x_1) + *p*-dioxan(x_2)												
At 298.15 K												
0.7503	−0.0135	1.199	91.74	64.41	138.89	389.82	−0.0089	0.9110	1.424	1305.41	1.186	97.51
0.5005	−0.0184	1.177	86.12	60.65	141.88	407.32	−0.0125	0.9492	1.420	1317.91	1.197	99.92
0.2497	−0.0156	1.154	80.85	57.11	144.89	425.55	−0.0111	0.9883	1.416	1331.03	1.208	102.36
At 313.15 K												
0.7503	−0.0107	1.232	102.60	72.55	142.59	376.16	−0.0065	0.8948	1.414	1241.19	1.073	100.82
0.5005	−0.0131	1.209	96.15	68.25	146.28	393.86	−0.0078	0.9325	1.409	1253.51	1.080	103.83
0.2497	−0.0096	1.186	90.10	64.19	150.00	412.35	−0.0058	0.9712	1.404	1266.52	1.086	106.87
Acetone(x_1) + methyl iodide(x_2)												
At 253.2 K												
0.8000	−0.0213	1.300	87.80	62.14	112.59	374.76	0.0036	1.1081	1.413	1205.03	1.255	79.69
0.6000	−0.0323	1.267	84.04	58.65	104.84	381.68	0.0052	1.3990	1.433	1103.96	1.349	73.17
0.4000	−0.0329	1.234	80.31	55.13	97.09	388.96	0.0049	1.7083	1.457	1030.48	1.463	66.64
0.2000	−0.0227	1.201	76.63	51.55	89.34	396.65	0.0026	2.0379	1.487	975.68	1.601	60.09
At 263.2 K												
0.8000	−0.0205	1.312	94.35	66.93	113.12	366.13	0.0045	1.0940	1.410	1168.69	1.186	80.24
0.6000	−0.0317	1.281	90.34	63.11	105.15	373.11	0.0061	1.3814	1.431	1070.96	1.280	73.46
0.4000	−0.0322	1.249	86.38	59.25	97.19	380.47	0.0057	1.6874	1.458	1000.07	1.393	66.67
0.2000	−0.0217	1.216	82.47	55.33	89.22	388.25	0.0037	2.0135	1.490	947.43	1.532	59.86

(*Continued*)

Table 2. Continued.

x_1	V^E	$\alpha \times 10^3$ (K^{-1})	$\beta_T \times 10^{12}$ ($cm^2\,dyne^{-1}$)	$\beta_S \times 10^{12}$ ($cm^2\,dyne^{-1}$)	C_P ($J\,K^{-1}\,mol^{-1}$)	$P_i \times 10^{-7}$ ($dyne\,cm^{-2}$)	C_P^E	ρ ($g\,cm^{-3}$)	γ	u ($m\,sec^{-1}$)	Γ	C_v ($J\,K^{-1}\,mol^{-1}$)
At 273.2 K												
0.8000	−0.0263	1.329	102.27	72.89	113.83	355.02	0.0002	1.0798	1.403	1127.24	1.110	81.12
0.6000	−0.0388	1.297	97.72	68.49	105.62	362.59	0.0011	1.3639	1.427	1034.67	1.204	74.02
0.4000	−0.0389	1.265	93.24	64.05	97.40	370.58	0.0011	1.6664	1.456	967.92	1.319	66.91
0.2000	−0.0265	1.232	88.83	59.55	89.18	379.03	0.0004	1.9891	1.492	918.82	1.460	59.78
At 283.2 K												
0.8000	−0.0257	1.347	110.58	79.15	114.81	344.92	0.0018	1.0653	1.397	1089.04	1.041	82.17
0.6000	−0.0403	1.314	105.46	74.20	106.40	352.76	0.0013	1.3461	1.421	1000.59	1.133	74.86
0.4000	−0.0411	1.280	100.44	69.22	97.99	361.03	0.0008	1.6453	1.451	937.03	1.244	67.53
0.2000	−0.0280	1.247	95.52	64.19	89.58	369.78	0.0001	1.9645	1.488	890.54	1.382	60.19
At 293.2 K												
0.8000	−0.0309	1.364	119.54	86.11	116.19	334.55	−0.0018	1.0510	1.388	1051.17	0.971	83.70
0.6000	−0.0470	1.330	113.72	80.49	107.65	342.92	−0.0031	1.3285	1.413	967.06	1.059	76.20
0.4000	−0.0475	1.296	108.04	74.87	99.12	351.78	−0.0033	1.6242	1.443	906.83	1.166	68.69
0.2000	−0.0324	1.263	102.50	69.21	90.58	361.16	−0.0027	1.9400	1.481	863.02	1.299	61.16
At 303.2 K												
0.8000	−0.0382	1.381	129.40	93.99	117.84	323.49	−0.0069	1.0366	1.377	1013.11	0.900	85.59
0.6000	−0.0557	1.346	122.71	87.58	109.24	332.48	−0.0088	1.3107	1.401	933.36	0.983	77.97
0.4000	−0.0556	1.311	116.21	81.21	100.65	341.99	−0.0084	1.6030	1.431	876.43	1.084	70.34
0.2000	−0.0377	1.276	109.91	74.85	92.06	352.08	−0.0060	1.9153	1.468	835.18	1.210	62.69
At 308.2 K												
0.8000	−0.0409	1.398	135.43	98.52	118.66	318.14	−0.0084	1.0294	1.375	993.00	0.870	86.32
0.6000	−0.0603	1.361	128.11	91.58	110.04	327.52	−0.0115	1.3018	1.399	915.85	0.951	78.66

0.4000	−0.0604	1.325	121.04	84.72	101.43	337.45	−0.0113	1.5926	1.429	860.93	1.050	70.99
0.2000	−0.0411	1.289	114.20	77.89	92.82	347.99	−0.0080	1.9032	1.466	821.31	1.173	63.31
Cyclohexanol(x_1) + cyclohexane(x_2)												
At 298.15 K												
0.1977	−0.2628	1.110	97.83	74.03	166.75	338.43	−0.2613	0.8089	1.322	1292.27	0.971	126.18
0.3178	−0.3476	1.054	90.09	69.49	172.86	348.76	−0.3387	0.8299	1.296	1316.75	0.943	133.33
0.4185	−0.3797	1.010	84.26	65.94	178.01	357.35	−0.3641	0.8474	1.278	1337.74	0.922	139.32
0.5050	−0.3812	0.974	79.66	63.07	182.47	364.68	−0.3605	0.8623	1.263	1356.06	0.906	144.45
0.6828	−0.3154	0.907	71.26	57.62	191.69	379.60	−0.2903	0.8924	1.237	1394.51	0.875	154.99
0.7871	−0.2377	0.871	66.90	54.69	197.13	388.28	−0.2155	0.9099	1.223	1417.53	0.859	161.16
0.9001	−0.1242	0.835	62.58	51.73	203.05	397.61	−0.1107	0.9287	1.210	1442.83	0.843	167.83
At 313.15 K												
0.1977	−0.3223	1.150	110.51	84.21	172.83	325.83	−0.3216	0.7955	1.312	1221.82	0.867	131.70
0.3178	−0.4254	1.088	101.11	78.41	178.53	337.05	−0.4162	0.8169	1.289	1249.46	0.849	138.46
0.4185	−0.4637	1.041	94.09	73.95	183.37	346.39	−0.4467	0.8346	1.272	1272.83	0.836	144.12
0.5050	−0.4644	1.003	88.61	70.39	187.55	354.37	−0.4417	0.8497	1.259	1293.03	0.825	148.98
0.6828	−0.3819	0.931	78.70	63.75	196.22	370.63	−0.3545	0.8804	1.235	1334.90	0.804	158.94
0.7871	−0.2863	0.893	73.61	60.23	201.35	380.10	−0.2623	0.8981	1.222	1359.67	0.794	164.77
0.9001	−0.1476	0.855	68.59	56.71	206.94	390.29	−0.1338	0.9170	1.210	1386.71	0.783	171.08
At 323.15 K												
0.1977	−0.3673	1.173	119.93	91.75	175.09	315.99	−0.3617	0.7865	1.307	1177.17	0.811	133.94
0.3178	−0.4831	1.109	109.27	85.01	180.72	327.83	−0.4672	0.8082	1.285	1206.47	0.797	140.59
0.4185	−0.5253	1.059	101.36	79.87	185.50	337.70	−0.5009	0.8261	1.269	1231.09	0.786	146.16
0.5050	−0.5251	1.020	95.22	75.79	189.64	346.13	−0.4950	0.8414	1.256	1252.27	0.778	150.94
0.6828	−0.4304	0.947	84.19	68.27	198.24	363.35	−0.3970	0.8723	1.233	1295.90	0.762	160.75
0.7871	−0.3220	0.908	78.56	64.32	203.33	373.39	−0.2937	0.8901	1.221	1321.57	0.754	166.49
0.9001	−0.1658	0.868	73.04	60.39	208.88	384.22	−0.1498	0.9093	1.209	1349.46	0.746	172.71

Table 3. Computed values of thermodynamic properties of tarnery liquid mixtures by Flory theory.

x_1	x_2	V^E	$\alpha \times 10^3$ (K^{-1})	$\beta_T \times 10^{12}$ ($cm^2\,dyne^{-1}$)	$\beta_S \times 10^{12}$ ($cm^2\,dyne^{-1}$)	C_P ($J\,K^{-1}\,mol^{-1}$)	$P_i \times 10^{-7}$ ($dyne\,cm^{-2}$)	C_P^E	ρ ($g\,cm^{-3}$)	γ	u ($m\,sec^{-1}$)	Γ	C_v ($J\,K^{-1}\,mol^{-1}$)
Benzene(x_1) + chloroform(x_2) + cyclohexane(x_3)													
At 303.15 K													
0.1015	0.3019	0.0827	1.266	115.69	81.44	140.93	331.78	0.0151	0.9482	1.421	1137.96	1.096	99.21
0.2019	0.2990	0.1031	1.276	114.12	79.95	140.65	338.86	0.0306	0.9593	1.427	1141.90	1.105	98.53
0.2998	0.2993	0.1120	1.285	112.45	78.39	140.26	346.30	0.0417	0.9727	1.434	1145.19	1.116	97.78
0.4001	0.3002	0.1098	1.293	110.63	76.73	139.84	354.39	0.0487	0.9875	1.442	1148.77	1.127	96.99
0.5045	0.2983	0.0962	1.302	108.67	74.99	139.49	363.16	0.0510	1.0018	1.449	1153.75	1.138	96.25
0.6031	0.2976	0.0721	1.310	106.72	73.27	139.11	372.00	0.0479	1.0168	1.456	1158.54	1.150	95.52
Toluene(x_1) + chloroform(x_2) + cyclohexane(x_3)													
At 303.15 K													
0.0911	0.3685	0.0473	1.241	113.98	80.54	138.61	330.13	−0.0386	0.9862	1.415	1122.00	1.103	97.94
0.2198	0.2939	0.0348	1.212	111.29	79.29	140.65	330.08	−0.0676	0.9523	1.403	1150.80	1.098	100.22
0.3004	0.3036	0.0359	1.197	109.08	77.86	139.97	332.55	−0.0860	0.9661	1.401	1152.95	1.105	99.91
0.4013	0.3026	0.0393	1.177	106.53	76.27	139.58	335.04	−0.1027	0.9754	1.397	1159.38	1.111	99.94
0.5016	0.2999	0.0463	1.159	104.10	74.76	139.26	337.43	−0.1141	0.9835	1.392	1166.26	1.117	100.01
0.5976	0.3035	0.0581	1.141	101.77	73.27	138.74	340.00	−0.1222	0.9951	1.389	1171.13	1.124	99.89
Chlorobenzene(x_1) + chloroform(x_2) + cyclohexane(x_3)													
At 303.15 K													
0.1001	0.3034	−0.0063	1.225	111.84	79.40	140.91	332.03	−0.0763	0.9721	1.409	1138.25	1.100	100.04
0.1988	0.3034	−0.0462	1.195	106.85	76.12	140.57	339.10	−0.1331	1.0074	1.404	1141.95	1.114	100.15
0.3150	0.2875	−0.0759	1.161	101.53	72.68	140.75	346.71	−0.1794	1.0391	1.397	1150.75	1.128	100.75
0.4005	0.2994	−0.0805	1.138	97.57	69.99	140.07	353.55	−0.2082	1.0781	1.394	1151.20	1.142	100.48
0.5023	0.2982	−0.0749	1.111	93.28	67.14	139.80	360.99	−0.2275	1.1148	1.389	1155.94	1.156	100.62
0.5997	0.3007	−0.0549	1.086	89.35	64.50	139.43	368.38	−0.2366	1.1527	1.385	1159.77	1.171	100.64

Dioxan(x_1) + chloroform(x_2) + cyclohexane(x_3)													
At 303.15 K													
0.1023	0.2998	0.0249	1.243	112.44	79.45	140.51	335.17	−0.0074	0.9613	1.415	1144.27	1.102	99.29
0.2024	0.3000	0.0038	1.230	107.81	76.07	139.65	345.94	−0.0131	0.9890	1.417	1152.89	1.119	98.54
0.2981	0.3011	−0.0125	1.218	103.45	72.90	138.78	356.86	−0.0212	1.0173	1.419	1161.23	1.135	97.80
0.3991	0.2912	−0.0252	1.204	99.07	69.76	138.25	368.39	−0.0300	1.0409	1.420	1173.53	1.151	97.35
0.5001	0.3007	−0.0334	1.191	94.52	66.43	137.04	381.86	−0.0457	1.0797	1.423	1180.81	1.172	96.32
0.6046	0.2966	−0.0363	1.176	90.09	63.25	136.28	395.71	−0.0612	1.1115	1.424	1192.70	1.191	95.67
Chlorobenzene(x_1) + cyclohexane(x_2) + n-heptane(x_3)													
At 298.15 K													
X_2(cyclohexane) = 0.1883													
0.0773	0.1737	−0.1148	1.230	131.59	101.74	207.18	278.65	−0.0012	0.7173	1.293	1170.54	0.800	160.19
0.1375	0.1624	−0.1829	1.213	127.29	98.24	203.49	284.08	−0.0120	0.7367	1.296	1175.45	0.818	157.05
0.1954	0.1515	−0.2385	1.197	123.24	94.94	199.94	289.48	−0.0208	0.7560	1.298	1180.37	0.835	154.04
0.2975	0.1323	−0.3125	1.168	116.31	89.30	193.69	299.44	−0.0325	0.7914	1.302	1189.54	0.868	148.71
0.4062	0.1118	−0.3577	1.138	109.22	83.53	187.04	310.71	−0.0399	0.8313	1.308	1200.04	0.906	143.04
0.5038	0.0934	−0.3688	1.112	103.11	78.55	181.07	321.47	−0.0422	0.8694	1.313	1210.15	0.944	137.93
0.5918	0.0769	−0.3549	1.088	97.80	74.21	175.69	331.74	−0.0410	0.9055	1.318	1219.87	0.980	133.32
0.6974	0.0570	−0.3086	1.060	91.67	69.21	169.24	344.83	−0.0357	0.9515	1.325	1232.32	1.027	127.78
0.7969	0.0382	−0.2357	1.034	86.13	64.69	163.17	358.00	−0.0269	0.9975	1.331	1244.90	1.075	122.55
0.8660	0.0252	−0.1684	1.016	82.41	61.65	158.95	367.68	−0.0190	1.0312	1.337	1254.18	1.111	118.91
0.9380	0.0117	−0.0840	0.998	78.65	58.58	154.56	378.26	−0.0093	1.0679	1.343	1264.35	1.152	115.11
X_2(cyclohexane) = 0.3138													
0.0766	0.2898	−0.1097	1.225	128.37	98.59	199.36	284.54	0.0013	0.7273	1.302	1180.91	0.827	153.11
0.1233	0.2751	−0.1588	1.212	125.19	96.03	196.90	288.64	−0.0095	0.7424	1.304	1184.35	0.840	151.04
0.2040	0.2498	−0.2296	1.189	119.82	91.72	192.63	295.96	−0.0252	0.7692	1.306	1190.58	0.864	147.45
0.3078	0.2172	−0.2947	1.161	113.18	86.38	187.16	305.81	−0.0398	0.8052	1.310	1199.11	0.897	142.84
0.4009	0.1880	−0.3283	1.136	107.45	81.77	182.25	315.11	−0.0478	0.8391	1.314	1207.29	0.928	138.69
0.5028	0.1560	−0.3385	1.109	101.43	76.92	176.89	325.83	−0.0513	0.8780	1.319	1216.82	0.964	134.14
0.5868	0.1297	−0.3262	1.086	96.66	73.07	172.47	335.12	−0.0502	0.9117	1.323	1225.18	0.996	130.38
0.6983	0.0947	−0.2812	1.058	90.58	68.17	166.61	348.12	−0.0436	0.9587	1.329	1236.98	1.042	125.39
0.7952	0.0643	−0.2159	1.033	85.52	64.09	161.52	360.11	−0.0334	1.0018	1.334	1247.95	1.086	121.05
0.8683	0.0413	−0.1508	1.015	81.85	61.13	157.69	369.60	−0.0232	1.0359	1.339	1256.69	1.121	117.77
0.9379	0.0195	−0.0763	0.997	78.45	58.38	154.03	379.04	−0.0116	1.0697	1.344	1265.41	1.156	114.64

Table 4. Average percentage deviation of different thermodynamic properties.

Systems	T (K)	APD									
		ρ	u	α	β_T	β_S	P_i	γ	C_P	C_V	Γ
Acetonitrile + benzene	298.15	0.09	0.38	0.17	0.71	0.84	0.61	0.17	0.28	0.30	0.61
Benzene + DMF	298.15	0.83	4.73	1.34	9.79	11.37	7.50	1.37	0.26	1.52	8.10
Acetonitrile + DMF	298.15	0.61	3.05	0.53	5.79	7.15	5.87	1.24	0.11	1.16	6.36
Cyclohexanol + cyclohexane	298.15	0.51	1.90	3.59	3.58	4.01	1.60	1.37	2.96	3.40	6.72
	313.15	0.32	1.95	2.38	3.57	4.07	1.88	0.86	2.33	2.84	4.73
	323.15	0.36	2.18	2.14	4.07	4.54	2.52	0.94	2.12	2.61	4.39
Piperidine + tetrahydropyran	293.15	0.18	0.78	5.49	1.13	1.40	4.40	2.49	2.66	1.87	4.39
	313.15	0.18	0.70	6.65	0.98	1.23	5.72	2.19	5.68	3.57	2.39
Piperidine + cyclohexane	293.15	0.26	0.30	4.37	2.22	0.34	2.19	2.55	2.72	4.14	5.43
	313.15	0.30	0.24	5.70	2.34	0.29	3.43	2.52	2.64	2.97	4.50
Tetrahydropyran + cyclohexane	293.15	0.18	0.25	2.01	2.29	0.33	0.58	2.61	5.06	7.87	7.19
	313.15	0.21	0.11	3.56	2.63	0.25	0.96	2.61	2.74	5.50	6.31
Benzene + *p*-xylene	298.15	0.10	0.10	0.12	0.21	0.23	0.33	0.05	0.35	0.37	0.25
	313.15	0.09	0.21	0.09	0.44	0.51	0.54	0.07	0.31	0.25	0.16
Benzene + *p*-dioxan	298.15	0.05	0.23	0.08	0.89	0.51	0.83	0.38	1.60	1.97	1.23
	313.15	0.07	0.06	0.09	0.34	0.18	0.25	0.16	0.44	0.59	0.45
Acetone + methyl iodide	253.20	0.70	0.27	3.95	3.78	0.64	0.62	3.42	1.94	0.32	6.49
	263.20	0.72	0.32	3.63	3.82	0.97	0.69	3.08	1.89	0.30	5.81
	273.20	0.76	0.31	2.95	3.27	0.85	0.60	2.61	1.77	0.53	5.12
	283.20	0.77	0.31	2.46	3.09	0.92	0.98	2.29	2.22	1.35	4.73
	293.20	0.79	0.38	2.09	3.21	1.29	1.27	1.94	1.85	1.27	4.11
	303.20	0.80	0.52	1.60	3.33	1.71	1.79	1.65	1.32	0.96	3.78
	308.20	0.81	0.49	1.04	2.66	1.68	1.67	1.00	1.13	1.49	2.29
Benzene + chloroform + cyclohexane	303.15	0.49	1.53	7.71	3.80	3.33	3.94	5.77	3.35	8.57	13.12
Toluene + chloroform + cyclohexane	303.15	0.37	1.23	1.67	0.67	2.77	1.74	2.79	8.84	11.32	11.51
Chlorobenzene + chloroform + cyclohexane	303.15	0.46	0.73	1.75	3.36	1.89	4.63	5.34	18.37	22.83	23.83
Dioxan + chloroform + cyclohexane	303.15	0.39	1.99	3.13	1.90	4.22	2.08	6.24	11.25	16.33	21.41
Chlorobenzene + cyclohexane + *n*-heptane	298.15	0.10	0.23	8.10	8.12	0.56	6.05	7.71	25.30	36.13	21.19

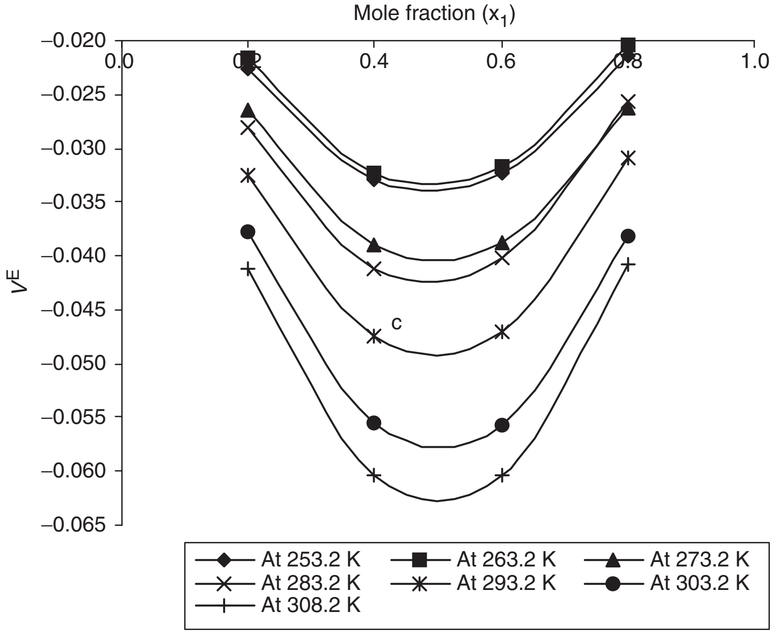

Figure 1. A graph between excess volume *vs*. mole fraction (x_1) of acetone(x_1) + methyl iodide(x_2) system at different temperatures.

below 2% for all the systems except benzene + DMF and acetonitrile + DMF for which APDs are 4.73 and 3.05%, respectively. It is due to the special nature of DMF. It is clear from table 4 that for the liquid systems cyclohexanol + cyclohexane, benzene + *p*-xylene, benzene + *p*-dioxan and acetone + methyl iodide, the agreement between computed values and experimental values for all the properties are quite good. For these systems, all experimental values are known [39–41]. For other systems, the APD values are slightly higher because the experimental values of α and β_T were obtained with the help of empirical equations (17) and (18).

The V^E and C_P^E for binary system acetone + methyl iodide at different temperatures are presented graphically in figures 1 and 2, respectively. From figure 1 it is clear that as temperature increases, the dip of the curves increase, indicating that the interaction become stronger and stronger. Figure 2 also supports this fact, as sign of C_P^E changes from positive to negative with the increase in temperature.

Figures 3 and 4 represent graphically, the values of V^E and C_P^E for ternary system chlorobenzene + cyclohexane + *n*-heptane at 298.15 K. Both the values of V^E and C_P^E are negative in the entire composition range, indicating strong interaction. Similarly, we can discuss the interaction in other liquid systems investigated in the present work.

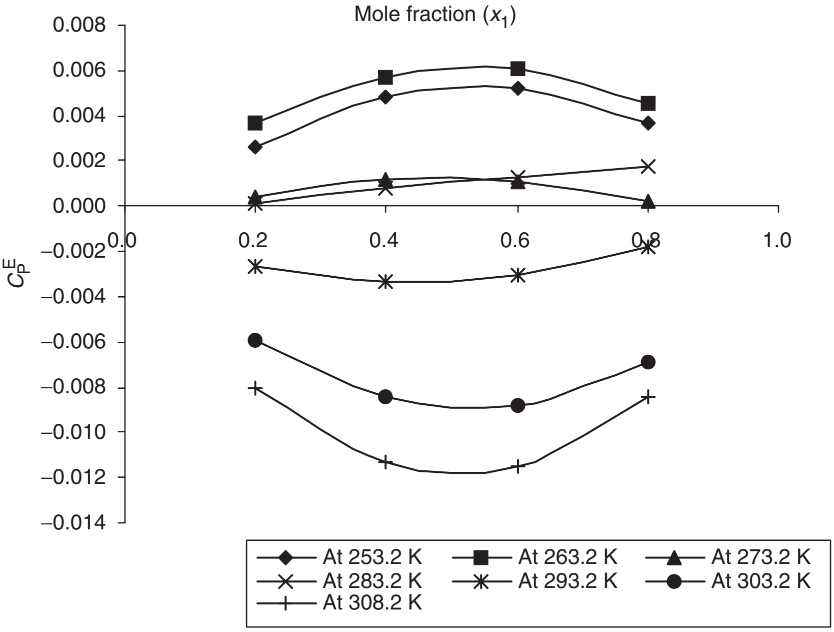

Figure 2. A graph between C_P^E *vs*. mole fraction (x_1) of acetone(x_1) + methyl iodide(x_2) system at different temperatures.

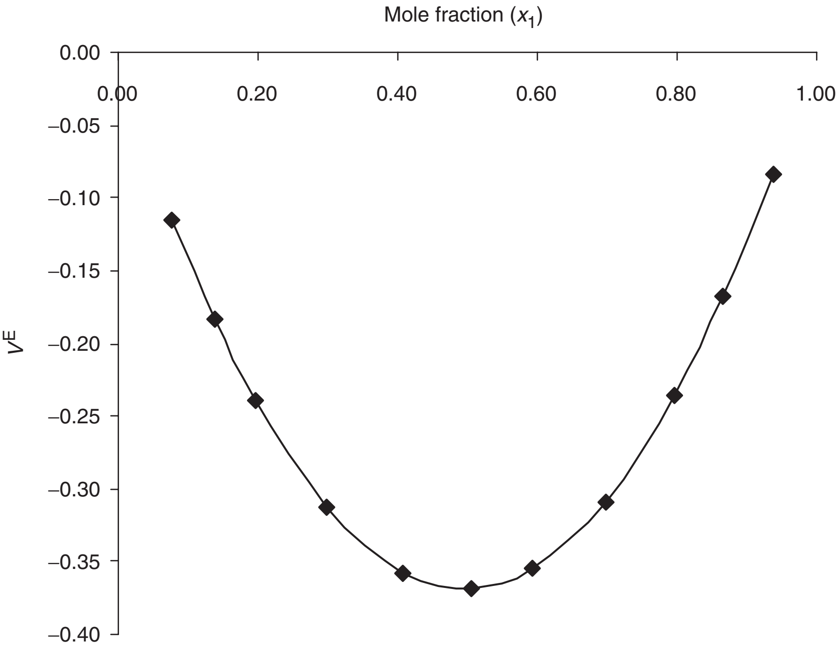

Figure 3. A graph between excess volume *vs*. mole fraction (x_1) of chlorobenzene(x_1) + cyclohexane (x_2) + *n*-heptane(x_3) system at 298.15 K.

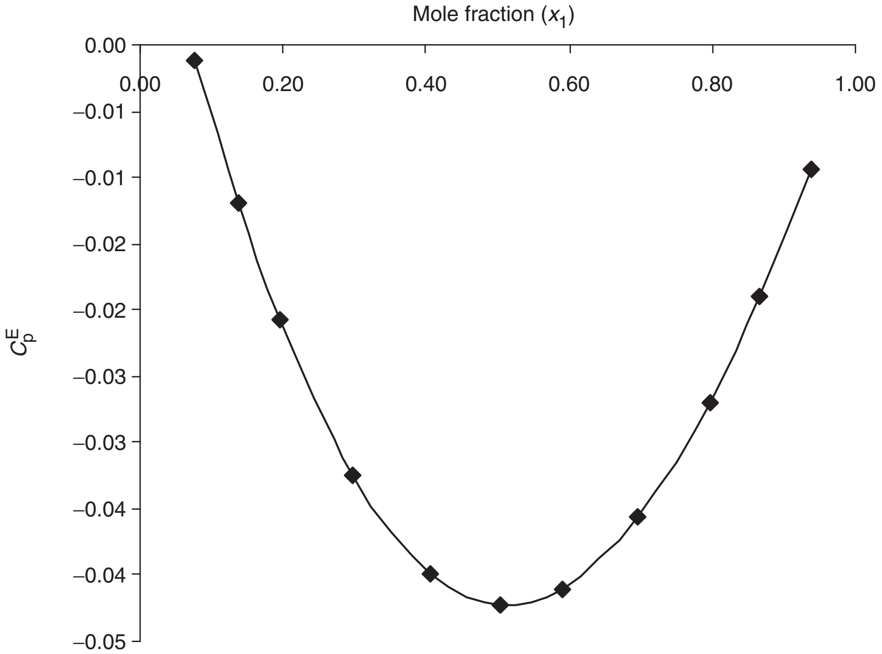

Figure 4. A graph between C_P^E *vs.* mole fraction (x_1) of chlorobenzene(x_1) + cyclohexane(x_2) + *n*-heptane(x_3) system at 298.15 K.

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