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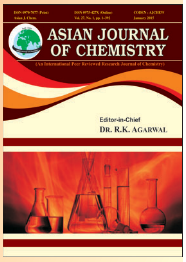

Excess Molar Volumes, Theoretical Viscosities and Ultrasonic Speeds of Binary Mixtures at 298.15 K and 303.15 K

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Excess molar volumes ($V\eta^E$) deviations in entropies (ΔS^*) deviations in enthalpies (ΔH^*) of activation of viscous flow, theoretical viscosities (η_{theo}) and theoretical ultrasonic speeds (υ_{theo}) of the binary mixtures of benzene with methyl acrylate, ethyl acrylate, butyl acrylate and styrene are reported. These parameters were calculated by using experimental viscosity and ultrasonic speed data and different empirical relations and theories were used to calculate the theoretical parameters. The results were discussed in terms of average deviations experimentally and theoretically calculated values. The sign and magnitude of these parameters were found to be sensitive towards intermolecular interactions prevailing in the studied systems. The predicted properties show a good accuracy in comparison with the experimental derived properties.

Keywords: Excess molar volumes, Excess enthalpies, Excess entropies, Theoretical predictions, Binary mixtures, Molecular interactions

INTRODUCTION

The viscosity results of binary mixtures provide information on the structure of individual liquid components in the mixed environment and are needed in the design of industrial processes that involve in mass transfer, fluid flow and viscosity build-up, *etc*. Viscosity is an important non-equilibrium transport property closely associated with self-aggregation in liquids[1]. In recent years, the theoretical and experimental predications of excess and deviation functions are in use as interaction parameters to improve the results[2,3]. Knowledge of viscosity of pure liquids and their binary mixtures plays an essential role in solving chemical engineering problems dealing with heat-transfer, mass transfer, process piping, reactors, stripping columns, deodorizers, liquid-liquid extractors, distillation columns, crystallization equipment and in additional units found in various chemical, oil, paint, clay, dairy and food industry.

The viscosity data of binary mixtures provide a valuable insight into the structure and interactions in mixed solvents and are required to evaluate mass transport and heat transfer[4,5]. In extension of our systematic studies[4,6-9] on thermodynamic and transport behaviour of binary mixtures, here, we present the theoretical excess molar volume of benzene (BNZ) + methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA) and styrene (STY) at 298.15 and 303.15 K. The industrially important chemicals acrylic esters with unsaturated structure along the side of a carbonyl group in the same molecule are mixed with benzene a non-polar, unassociated liquid have received wide attention especially to understand the behaviour in mixed environment.

In this paper, the experimental data of viscosity, ultrasonic speeds and densities reported in literature[9], have been used to estimate the excess molar volumes ($V\eta^E$), deviations in entropies (ΔS^*) and deviations in enthalpies (ΔH^*), of activation of viscous flow have been determined. Theoretical viscosities and ultrasonic speeds of binary mixtures were calculated theoretically from the pure component data by using various empirical and semi-emperical relations and the results were compared with the experimental findings. The results are interpreted in terms of intermolecular interaction occurring in the binary mixtures.

THEORETICAL ANALYSIS

Correlations of excess volumes with viscosity: Thermodynamic excess and deviation properties of binary mixtures correspond to the difference between the actual property and the property if the system behaves ideally and, thus, are useful in the study of molecular interactions and arrangements in the mixtures. In particular, the excess molar volume is a function of several opposing effects which reflect the interactions that take place between solute-solute, solute-solvent and solvent-

solvent species. The effects which are expected to operate between the component molecules under study are (i) The structural effects such as interstitial accommodation (due to differences in size and shape of the components) and changes in the free volume also offer negative contributions to excess molar volume; (ii) the chemical or specific intermolecular interactions (such as hydrogen bond interaction, dipole-dipole/ dipole-induced-dipole interaction, formation of charge transfer complexes, *etc.*) result in a net volume decrease and thus offer negative contributions to excess molar volume and (iii) reorientational effect between component molecules. Therefore, the actual volume change would depend on the relative strength of these effects[10].

The deviation in viscosity data were used to calculate the excess molar volumes ($V\eta^E$), by a correlation proposed by Singh[11]. According to the relation, the deviations in viscosity, and excess molar volumes, are related to each other as:

$$\Delta\eta = KV^E \qquad (1)$$

where K is a fitting parameter. The values of K for the presently investigated mixtures were evaluated by using the $\Delta\eta$ and experimentally reported data[9] at $x_1 = 0.5$ (equimolar fraction). The values of K for BEN + MA/EA/BA and STY at 298.15 and 303.15 K are presented in Table-1. From the experimental $\Delta\eta$ data, the $\Delta\eta^E$ values at various mole fractions were calculated. It is clear from Figs. 1 and 2 the values of $\Delta\eta^E$ become less positive as we move from methyl acrylate to butyl acrylate. The decrease in positive deviations can be explained by considering the order in the pure liquids and in the solution and also by considering the interactions between the component molecules in the mixtures. When benzene is mixed with esters or styrene the order in the mixtures is destroyed which cause an expansion in volume, thereby positive $\Delta\eta^E$ values are expected. But, because of the loss of dipolar association in the esters/styrene molecules and also the n......π type of weak interactions between the lone pair of electrons of oxygen atom of carbonyl group of ester and π-electron cloud of benzene molecule and π....π interaction between π-electrons of benzene rings of styrene and benzene there is expansion in volume of the solution. As the size of alkyl group increases from methyl acrylate to butyl acrylate, the steric hindrance also increases, following the decreased interaction between benzene and esters molecules. The observed values of $\Delta\eta^E$ increase for all the binary mixtures over the entire mole fraction range and, thereby, suggest a decrease in the strength of interaction between the component molecules. The observed small positive $\Delta\eta^E$ values for benzene + styrene mixtures suggest that destruction in order dominates over that of the above mentioned effect in case of acrylates. This decrease in $\Delta\eta^E$ values as we move from methyl acrylate to styrene clearly suggests an increasingly better packing of the component molecules in the mixture than in the pure state. The results of excess molar volumes $\Delta\eta^E$ were compared with the earlier reported V^E values[9], for all the mixtures

TABLE-1
VALUES OF FITTING PARAMETER K, AND MOLAR VOLUMES (V_m) OF BINARY MIXTURES AT DIFFERENT TEMPERATURES

Systems	Temp. (K)	K (10^5 mPa.s.m^{-3})	
BNZ + MA	298.15	-40.96	
	303.15	-24.52	
BNZ + EA	298.15	-88.97	
	303.15	-108.62	
BNZ + BA	298.15	-105.61	
	303.15	-135.50	
BNZ + STY	298.15	-139.96	
	303.15	-146.80	
Compound	Temp. (K)	V_m (10^{-5} m^3 mol^{-1})	[Ref.]
BNZ	298.15	8.92	9
	303.15	8.97	
MA	298.15	9.07	9
	303.15	9.12	
EA	298.15	10.92	9
	303.15	10.99	
BA	298.15	14.33	9
	303.15	14.41	
STY	298.15	11.53	9
	303.15	11.60	

Benzene (BNZ); Methyl acrylate (MA); Ethyl acrylate (EA); Butyl acrylate; (BA) and styrene (STY)

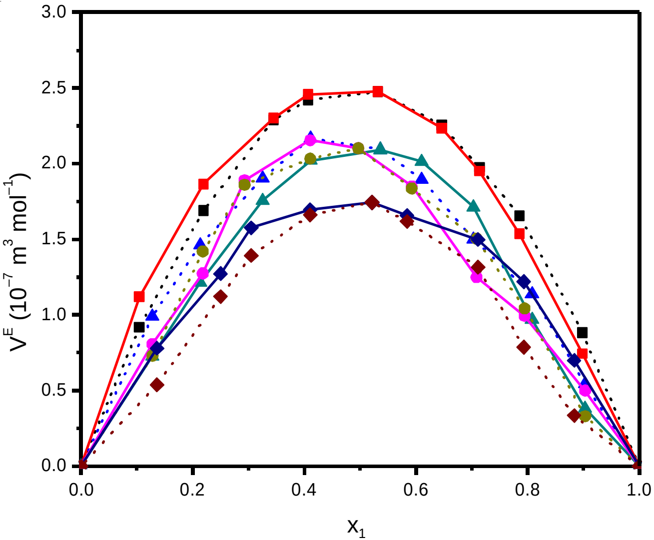

Fig.1. Plots of V^E against x_1 for binary mixtures of methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA) and styrene (STY). Points on solid lines show experimental V^E values [Ref. 8,9] and points on dotted lines show theoretical $V\eta^E$ values calculated using eqn. 1 at 298.15 K

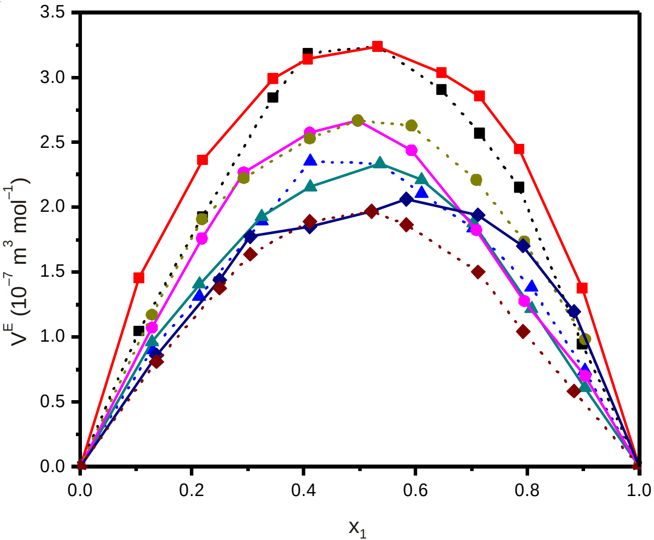

Fig. 2. Plots of V^E against x_1 for binary mixtures of methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA) and styrene (STY). Points on solid lines show experimental V^E values [Ref. 8,9] and points on dotted lines show theoretical $V\eta^E$ values calculated using eqn. 1 at 303.15 K

at 298.15 and 303.15 K and are presented in Figs. 1,2 as dotted lines. A reasonable good agreement has been found between the experimentally calculated and theoretically predicted $\Delta\eta^E$ values. Thereby, it emphasizes the effectiveness of the present approach.

The deviations in entropies (ΔS^*) and deviations in enthalpies (ΔH^*) of activation of viscous flow were calculated. By using the temperature dependence of viscosity data the activation parameters for viscous flow have been investigated. Eyring's viscosity equation[12,13] is given as:

$$\eta = \left(\frac{h\cdot N}{V_m}\right)\exp\left(\frac{\Delta G^*}{R\cdot T}\right) \qquad (2)$$

where h is Planck's constant, N is Avogadro's number, V_m is molar volume of liquid mixtures, ΔG^* is the Gibbs energy of activation of viscous flow. Combining eqn. 2 with $\Delta G^* = \Delta H^* - T\Delta S^*$ gives the equation:

$$R\cdot\ln\left(\frac{\eta\cdot V}{h\cdot N}\right) = \left(\frac{\Delta H^*}{T}\right) - \Delta S^* \qquad (3)$$

Thus the linear regression $R\cdot\ln\left(\frac{\eta\cdot V}{h\cdot N}\right)$ against $\frac{1}{T}$ can give the values of ΔH^* and ΔS^* are the enthalpy and entropy of activation of viscous flow from the slope and intercept respectively. The plots of the left hand side of eqn. 3, *i.e.*, $R\cdot\ln\left(\frac{\eta\cdot V}{h\cdot N}\right)$ against $\frac{1}{T}$ for all the binary mixtures at different compositions were found to show linear trend for each composition of the system under study. This indicates that ΔH^* values are almost constant in the investigated temperature range, *i.e.*, is independent of temperature.

Table-2 reveals the values of ΔH^* and ΔS^* along with the linear correlation factor (r) of eqn. 3. A close perusal of Table-2 indicates that for all the four binary mixtures the values of ΔH^* are positive and opposite negative trend in ΔS^* values with mole fraction x_1 of benzene were observed. The enthalpy of activation of viscous flow may be regarded as a measure of the degree of cooperation between the species taking part in viscous flow suggested earlier[14]. In a highly structured liquid there will be considerable degree of order and, hence, for cooperative movement of entities, a large heat of activation, is needed for the flow process. Therefore, the values in Table-2 indicates that the formation of activated species necessary for viscous flow seems to be easy in butyl acrylate and styrene rich region, owing to the low values of ΔH^* and become difficult in the ethyl acrylate rich region and relatively more difficult in methyl acrylate rich region owing to the high values of ΔH^*, as the mole fraction of benzene in the mixture increases. This is supported by the decreasing value of ΔS^* as the amount of benzene in the mixture increases.

Correlation equations for viscosity: Comparison of theoretical values of viscosities with those obtained experimentally in the present binary liquid mixtures is expected to reveal the nature of interaction between component molecules in the mixture. Such theoretical study is useful in finding the comprehensive theoretical model for the liquid mixtures. Grunberg and Nissan[15] suggested the expression:

TABLE-2
VALUES OF ENTHALPY (ΔH^*) AND ENTROPY (ΔS^*) OF ACTIVATION OF VISCOUS FLOW FOR THE BINARY LIQUID MIXTURES ALONG WITH THE LINEAR CORRELATION FACTOR (r)

x_1	ΔH^* (kJ mol^{-1})	ΔS^* (JK^{-1} mol^{-1})	r
Benzene + Methyl acrylate			
0.0000	12.376	-1.253	0.9991
0.1050	11.758	-1.230	0.9997
0.2191	11.355	-1.215	0.9999
0.3452	11.092	-1.203	1.0000
0.4069	11.030	-1.200	0.9999
0.5314	10.907	-1.193	0.9995
0.6457	10.762	-1.185	0.9989
0.7140	10.653	-1.180	0.9982
0.7852	10.586	-1.176	0.9977
0.8977	10.561	-1.173	0.9970
1.0000	10.811	-1.179	0.9966
Benzene + Ethyl acrylate			
0.0000	11.010	-1.179	0.9867
0.1283	12.043	-1.215	0.9853
0.2137	12.452	-1.230	0.9873
0.3255	12.804	-1.243	0.9902
0.4115	13.100	-1.254	0.9923
0.5361	13.543	-1.269	0.9937
0.6109	13.621	-1.272	0.9936
0.7033	13.286	-1.261	0.9953
0.8074	12.609	-1.239	0.9944
0.9025	12.106	-1.222	0.9947
1.0000	10.706	-1.175	0.9957
Benzene + Butyl acrylate			
0.0000	9.652	-1.074	1.0000
0.1282	12.102	-1.164	0.9977
0.2182	13.436	-1.214	0.9983
0.2926	13.658	-1.227	0.9990
0.4108	14.078	-1.249	0.9994
0.4964	14.070	-1.254	0.9999
0.5923	13.822	-1.252	0.9995
0.7080	13.038	-1.233	0.9987
0.7944	12.201	-1.211	0.9986
0.9032	11.737	-1.203	0.9986
1.0000	10.811	-1.179	0.9966
Benzene + Styrene			
0.0000	9.037	-1.086	0.9965
0.1362	10.259	-1.133	0.9950
0.2498	11.021	-1.163	0.9948
0.3047	11.126	-1.168	0.9960
0.4109	11.404	1.181	0.9961
0.5207	11.746	-1.196	0.9958
0.5834	12.045	-1.209	0.9968
0.7114	12.323	-1.222	0.9969
0.7924	12.445	-1.229	0.9978
0.8831	12.505	-1.233	0.9977
1.0000	10.811	-1.179	0.9966

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \qquad (4)$$

where G_{12} is a parameter proportional to interchange energy, which represents a measure of the strength of interaction between the component molecules in the mixture. It allows for the positive and negative deviations from the addivity rule. x and η are the mole fraction and viscosity; the subscripts 1 and 2 stand for pure components benzene and methyl acrylate/ethyl acrylate/butyl acrylate/styrene, respectively.

Katti and Chaudhri[16] derived the following equation:

$$\ln(\eta V) = x_1\ln(\eta_1 V_1) + x_2\ln(\eta_2 V_2) + x_1x_2W_{visible}/RT \quad (5)$$

where $W_{visible}/RT$ is an interaction term and V is the molar volume for pure components benzene and methyl acrylate/ ethyl acrylate/butyl acrylate/styrene, respectively.

Hind *et al.*[17] proposed the following equation:

$$\eta = x_1\ln\eta_1 + x_2\ln\eta_2 + x_1x_2G_{12} \quad (6)$$

where H_{12} is attributed to unlike pair interactions.

Wilke[18] proposed the viscosity equation:

$$\eta = \frac{x_1\eta_1}{x_1 + x_2\phi_{12}} + \frac{x_2\eta_2}{x_2 + x_1\phi_{21}} \quad (7)$$

where ϕ_{12} and ϕ_{21} are calculated by using the following equations:

$$\phi_{12} = \frac{\left[1+\left(\frac{\eta_1}{\eta_2}\right)^{1/2}\left(M_2/M_1\right)^{1/4}\right]^2}{\left\{8+\left[1+\left(M_1/M_2\right)\right]\right\}^{1/2}} \quad (8)$$

$$\phi_{21} = \phi_{12}\frac{\eta_2}{\eta_1}\frac{M_1}{M_2} \quad (9)$$

ϕ and M are the volume fraction and molar mass and the subscripts 1 and 2 stand for pure components benzene and methyl acrylate, ethyl acrylate, butyl acrylate, respectively. The predicted values of viscosities of the binary mixtures at 298.15 K and 303.15 K were compared with the experimentally measured values and the results are presented in terms of average deviations (AD) in Table-3. A close perusal of Table-3 reveals that all the empirical equations tested show good agreements for all the binary mixtures investigated. The results show that Grunberg and Nissan[15] provide the best results followed by Wilke relation[18] in reproducing the experimental viscosity for the mixtures. However, Katti and Chaudhri[16] and Hind *et al.*[17] show relatively large deviations for the binary mixtures.

Theoretical analysis of ultrasonic speeds: Theoretical equations of ultrasonic speed in binary liquid mixtures by means of different theories and empirical relations and its comparisons with experimental values reveal the extent of

TABLE-3
THEORETICALLY EVALUATED VISCOSITIES BY USING VARIOUS CO- RELATIONS ALONG WITH EXPERIMENTAL VALUES AND AVERAGE DEVIATIONS (AD) FOR THE BINARY MIXTURES AT 298.15 K AND 303.15 K TEMPERATURES

η(mPa.s)		Average deviations (η_{expt}–η_{theo})			
$x_{1\,(BNZ)}$	Exp.	Wileke[18]	$W_{visible}/RT$	Hind *et al.*[17]	Grunberg–Nissan[15]
		Benzene + Methyl acrylate T = 298.15 K			
0.1050	0.4721	0.4731 (-0.0010)	0.4722 (-0.0001)	0.4721 (0.0)	0.4723 (-0.0002)
0.2191	0.4851	0.4869 (-0.0018)	0.4854 (-0.0003)	0.4851 (0.0)	0.4855 (-0.0004)
0.3452	0.5005	0.5029 (-0.0024)	0.5010 (-0.0005)	0.5008 (-0.0003)	0.5010 (-0.0005)
0.4069	0.5087	0.5111 (-0.0024)	0.5090 (-0.0003)	0.5089 (-0.0002)	0.5090 (-0.003)
0.5314	0.5261	0.5283 (-0.0022)	0.5261 (0.0000)	0.5262 (-0.0001)	0.5261 (0.0)
0.6457	0.5432	0.5449 (-0.0017)	0.5430 (0.0002)	0.5432 (0.0)	0.5430 (0.0002)
0.7140	0.5540	0.5553 (-0.0013)	0.5536 (0.0004)	0.5539 (0.0001)	0.5535 (0.0005)
0.7852	0.5654	0.5665 (-0.0011)	0.5651 (0.0003)	0.5654 (0.0)	0.5650 (0.0004)
0.8977	0.5845	0.5849 (-0.0004)	0.5842 (0.0003)	0.5844 (0.0001)	0.5841 (0.0004)
		T = 303.15 K			
0.1050	0.4325	0.4324 (0.0001)	0.4507 (-0.0182)	0.4548 (-0.0223)	0.4324 (0.0001)
0.2191	0.4465	0.4462 (0.0003)	0.4814 (-0.0349)	0.4871 (-0.0406)	0.4463 (0.0002)
0.3452	0.4621	0.4622 (-0.0001)	0.5112 (-0.0491)	0.5165 (-0.0544)	0.4625 (-0.0004)
0.4069	0.4700	0.4704 (-0.0004)	0.5239 (-0.0539)	0.5284 (-0.0584)	0.4707 (-0.0007)
0.5314	0.4875	0.4876 (-0.0001)	0.5449 (-0.0574)	0.5477 (-0.0602)	0.4880 (-0.0005)
0.6457	0.5045	0.5042 (0.0003)	0.5585 (-0.0540)	0.5596 (-0.0551)	0.5047 (0.0002)
0.7140	0.5150	0.5146 (0.0004)	0.5637 (-0.0487)	0.5641 (-0.0491)	0.5150 (0.0)
0.7852	0.5261	0.5258 (0.0003)	0.5668 (-0.0407)	0.5667 (-0.0406)	0.5261 (0.0)
0.8977	0.5450	0.5442 (0.0008)	0.5669 (-0.0219)	0.5666 (-0.0216)	0.5444 (0.0006)

Benzene + Ethyl acrylate					
T = 298.15 K					
0.1283	0.5305	0.5379 (-0.0074)	0.5318 (-0.0013)	0.5313 (-0.0008)	0.5316 (-0.0011)
0.2137	0.5325	0.5433 (-0.0108)	0.5340 (-0.0015)	0.5335 (-0.0010)	0.5339 (-0.0014)
0.3255	0.5367	0.5507 (-0.0140)	0.5383 (-0.0016)	0.5380 (-0.0013)	0.5383 (-0.0016)
0.4115	0.5406	0.5566 (-0.0160)	0.5427 (-0.0021)	0.5426 (-0.0020)	0.5428 (-0.0022)
0.5361	0.5503	0.5655 (-0.0152)	0.5509 (-0.0006)	0.5512 (-0.0009)	0.5511 (-0.0008)
0.6109	0.5575	0.5710 (-0.0135)	0.5569 (0.0006)	0.5574 (0.0001)	0.5572 (0.0003)
0.7033	0.5677	0.5781 (-0.0104)	0.5656 (0.0021)	0.5662 (0.0015)	0.5658 (0.0019)
0.8074	0.5785	0.5863 (-0.0078)	0.5770 (0.0015)	0.5775 (0.0010)	0.5770 (0.0015)
0.9025	0.5907	0.5942 (-0.0035)	0.5889 (0.0018)	0.5892 (0.0015)	0.5889 (0.0018)
T = 303.15 K					
0.1283	0.4995	0.5081 (-0.0086)	0.5220 (-0.0225)	0.5250 (-0.0255)	0.4991 (0.0004)
0.2137	0.5002	0.5126 (-0.0124)	0.5339 (-0.0337)	0.5381 (-0.0379)	0.4990 (0.0012)
0.3255	0.5006	0.5188 (-0.0182)	0.5469 (-0.0463)	0.5520 (-0.0514)	0.5009 (-0.0003)
0.4115	0.5008	0.5236 (-0.0228)	0.5551 (-0.0543)	0.5604 (-0.0596)	0.5038 (-0.0030)
0.5361	0.5085	0.5310 (-0.0225)	0.5636 (-0.0551)	0.5688 (-0.0603)	0.5103 (-0.0018)
0.6109	0.5155	0.5356 (-0.0201)	0.5670 (-0.0515)	0.5717 (-0.0562)	0.5157 (-0.0002)
0.7033	0.5240	0.5415 (-0.0175)	0.5692 (-0.0452)	0.5732 (-0.0492)	0.5238 (0.0002)
0.8074	0.5352	0.5483 (-0.0131)	0.5692 (-0.0340)	0.5720 (-0.0368)	0.5349 (0.0003)
0.9025	0.5479	0.5548 (-0.0069)	0.5668 (-0.0189)	0.5683 (-0.0204)	0.5471 (0.0008)
Benzene + Butyl acrylate					
T = 298.15 K					
0.1282	0.7992	0.8121 (-0.0129)	0.7995 (-0.0003)	0.7990 (0.0002)	0.7983 (0.0009)
0.2182	0.7731	0.7933 (-0.0202)	0.7737 (-0.0006)	0.7732 (-0.0001)	0.7724 (0.0007)
0.2926	0.7491	0.7773 (-0.0282)	0.7533 (-0.0042)	0.7529 (-0.0038)	0.7522 (-0.0031)
0.4108	0.7185	0.7510 (-0.0325)	0.7226 (-0.0041)	0.7223 (-0.0038)	0.7220 (-0.0035)
0.4964	0.6989	0.7313 (-0.0324)	0.7017 (-0.0028)	0.7016 (-0.0027)	0.7017 (-0.0028)
0.5923	0.6790	0.7085 (-0.0295)	0.6797 (-0.0007)	0.6797 (-0.0007)	0.6801 (-0.0011)
0.708	0.6581	0.6799 (-0.0218)	0.6549 (0.0032)	0.6551 (0.0030)	0.6559 (0.0022)
0.7944	0.6405	0.6579 (-0.0174)	0.6380 (0.0025)	0.6382 (0.0023)	0.6391 (0.0014)
0.9032	0.6201	0.6291 (-0.0090)	0.6184 (0.0017)	0.6185 (0.0016)	0.6191 (0.0010)
T = 303.15 K					
0.1282	0.7381	0.7567 (-0.0186)	0.7786 (-0.0405)	0.7767 (-0.0386)	0.7364 (0.0017)
0.2182	0.7091	0.7392 (-0.0301)	0.7713 (-0.0622)	0.7696 (-0.0605)	0.7089 (0.0002)
0.2926	0.6859	0.7243 (-0.0384)	0.7620 (-0.0761)	0.7611 (-0.0752)	0.6881 (-0.0022)
0.4108	0.6559	0.6998 (-0.0439)	0.7412 (-0.0853)	0.7428 (-0.0869)	0.6585 (-0.0026)

0.4964	0.6359	0.6815 (-0.0456)	0.7220 (-0.0861)	0.7258 (-0.0899)	0.6395 (-0.0036)
0.5923	0.6180	0.6603 (-0.0423)	0.6969 (-0.0789)	0.7029 (-0.0849)	0.6204 (-0.0024)
0.708	0.6010	0.6338 (-0.0328)	0.6624 (-0.0614)	0.6701 (-0.0691)	0.6002 (0.0008)
0.7944	0.5895	0.6132 (-0.0237)	0.6342 (-0.0447)	0.6419 (-0.0524)	0.5871 (0.0024)
0.9032	0.5735	0.5865 (-0.0130)	0.5965 (-0.0230)	0.6018 (-0.0283)	0.5727 (0.0008)
Benzene + Styrene					
T = 298.15 K					
0.1362	0.6715	0.6839 (-0.0124)	0.6705 (0.0010)	0.6709 (0.0006)	0.6702 (0.0013)
0.2498	0.6541	0.6744 (-0.0203)	0.6530 (0.0011)	0.6535 (0.0006)	0.6528 (0.0013)
0.3047	0.6448	0.6696 (-0.0248)	0.6455 (-0.0007)	0.6460 (-0.0012)	0.6454 (-0.0006)
0.4109	0.6333	0.6602 (-0.0269)	0.6329 (0.0004)	0.6333 (0.0000)	0.6330 (0.0003)
0.5207	0.6225	0.6502 (-0.0277)	0.6223 (0.0002)	0.6224 (0.0001)	0.6225 (0.0000)
0.5834	0.6179	0.6444 (-0.0265)	0.6173 (0.0006)	0.6172 (0.0007)	0.6175 (0.0004)
0.7114	0.6083	0.6321 (-0.0238)	0.6094 (-0.0011)	0.6091 (-0.0008)	0.6096 (-0.0013)
0.7924	0.6047	0.6241 (-0.0194)	0.6061 (-0.0014)	0.6056 (-0.0009)	0.6062 (-0.0015)
0.8831	0.6036	0.6148 (-0.0112)	0.6037 (-0.0001)	0.6033 (0.0003)	0.6037 (-0.0001)
T = 303.15 K					
0.1362	0.6290	0.6431 (-0.0141)	0.6566 (-0.0276)	0.6575 (-0.0285)	0.6254 (0.0036)
0.2498	0.6100	0.6335 (-0.0235)	0.6547 (-0.0447)	0.6564 (-0.0464)	0.6060 (0.0040)
0.3047	0.6000	0.6287 (-0.0287)	0.6524 (-0.0524)	0.6546 (-0.0546)	0.5979 (0.0021)
0.4109	0.5891	0.6193 (-0.0302)	0.6458 (-0.0567)	0.6489 (-0.0598)	0.5847 (0.0044)
0.5207	0.5772	0.6093 (-0.0321)	0.6359 (-0.0587)	0.6398 (-0.0626)	0.5741 (0.0031)
0.5834	0.5700	0.6035 (-0.0335)	0.6290 (-0.0590)	0.6331 (-0.0631)	0.5694 (0.0006)
0.7114	0.5600	0.5912 (-0.0312)	0.6121 (-0.0521)	0.6162 (-0.0562)	0.5627 (-0.0027)
0.7924	0.5560	0.5832 (-0.0272)	0.5996 (-0.0436)	0.6032 (-0.0472)	0.5605 (-0.0045)
0.8831	0.5550	0.5740 (-0.0190)	0.5840 (-0.0290)	0.5865 (-0.0315)	0.5599 (-0.0049)

molecular interactions in liquid mixtures. Therefore, ultrasonic speeds were evaluated using Nomoto's (NOM) relation[19]:

$$u = \left(\frac{x_1R_1 + x_2R_2}{x_1V_1 + x_2V_2}\right)^3 \qquad (10)$$

Free length theory (FLT)[20] is, represented by:

$$\frac{K'}{Lf_{(theo)}\rho^{1/2}} \qquad (11)$$

$$Lf_{ideal} = Lf_1x_1 + Lf_2x_2 \qquad (12)$$

where K′, Lf and ρ are the Jacobson constant[21], molar free length and density of components, respectively.

The Van Deal and Vangeel[22] ideal mixing relation is:

$$u = u_1u_2\left\{\frac{M_1M_2}{(x_1M_2u_2^2 + x_2M_1u_1^2)(x_1M_1 + x_2M_2)}\right\}^2 \qquad (13)$$

where R_1, R_2, V_1, V_2 and M_1, M_2 are Rao's constants[23], molar volumes and molar masses of methyl acrylate, ethyl acrylate, butyl acrylate and styrene, respectively. The calculated ultrasonic speeds along with the experimental speeds and average deviations in the calculated values from those of experimental values are listed in Table-4. The results indicate that for all the four binary mixtures Nomoto[19] and Van Deal and Vangeel[22] relation provide the best results for the ultrasonic speeds of the systems under study. Thus, the linearity of molar sound speed and additivity of molar volumes, as suggested by Nomoto, Van Deal and Vangeel ideal mixing relation, have been truly

TABLE-4
THEORETICALLY EVALUATED ULTRASONIC SPEEDS FROM NOM, FLT AND VDV RELATIONS ALONG WITH EXPERIMENTAL VALUES AND AVERAGE DEVIATIONS (AD) FOR THE BINARY MIXTURES AT DIFFERENT TEMPERATURES

u (m/s)					Average deviations (u_{expt}- u_{theo})		
$x_{1\,(BNZ)}$	Exp.	NOM	FLT	VDV	NOM	FLT	VDV
Benzene + Methyl acrylate							
T = 298.15 K							
0.1050	1198.1	1205.8	1206.1	1205.3	-7.7	-8.0	-7.2
0.2191	1204.5	1218.1	1218.6	1217.3	-13.6	-14.1	-12.8
0.3452	1212.8	1231.9	1232.5	1230.8	-19.1	-19.7	-18.0
0.4069	1217.6	1238.7	1239.3	1237.5	-21.1	-21.7	-19.9
0.5314	1229.1	1252.5	1253.2	1251.3	-23.4	-24.1	-22.2
0.6457	1241.1	1265.4	1265.9	1264.2	-24.3	-24.8	-23.1
0.7140	1249.6	1273.1	1273.6	1272.0	-23.5	-24.0	-22.4
0.7852	1260.6	1281.2	1281.5	1280.3	-20.6	-20.9	-19.7
0.8977	1281.5	1294.1	1294.3	1293.6	-12.6	-12.8	-12.1
T = 303.15 K							
0.1050	1178.8	1183.3	1183.9	1182.9	-4.5	-5.1	-4.1
0.2191	1185.2	1195.6	1196.5	1194.8	-10.4	-11.3	-9.6
0.3452	1194.5	1209.4	1210.5	1208.3	-14.9	-16.0	-13.8
0.4069	1199.7	1216.2	1217.3	1215.0	-16.5	-17.6	-15.3
0.5314	1210.5	1230.0	1231.2	1228.8	-19.5	-20.7	-18.3
0.6457	1222.4	1242.9	1244.0	1241.7	-20.5	-21.6	-19.4
0.7140	1230.6	1250.6	1251.7	1249.6	-20.0	-21.1	-19.0
0.7852	1241.5	1258.7	1259.7	1257.9	-17.2	-18.2	-16.4
0.8977	1262.6	1271.7	1272.3	1271.2	-9.1	-9.7	-8.6
Benzene + Ethyl acrylate							
T = 298.15 K							
0.1283	1175.2	1181.9	1183.7	1182.5	-6.7	-8.5	-7.3
0.2137	1180.3	1191.9	1194.7	1192.8	-11.6	-14.4	-12.5
0.3255	1189.5	1205.7	1209.5	1206.9	-16.2	-20.0	-17.4
0.4115	1198.5	1216.7	1221.1	1218.1	-18.2	-22.6	-19.6
0.5361	1213.1	1233.5	1238.3	1235.0	-20.4	-25.2	-21.9
0.6109	1222.8	1244.1	1248.8	1245.6	-21.3	-26.0	-22.8
0.7033	1237.2	1257.7	1261.9	1259.1	-20.5	-24.7	-21.9
0.8074	1255.5	1273.8	1276.8	1274.9	-18.3	-21.3	-19.4
0.9025	1278.3	1289.3	1291.0	1289.9	-11.0	-12.7	-11.6
T = 303.15 K							
0.1283	1151.0	1159.5	1161.4	1160.1	-8.5	-10.4	-9.1
0.2137	1156.5	1169.5	1172.4	1170.5	-13.0	-15.9	-14.0
0.3255	1165.8	1183.2	1187.2	1184.5	-17.4	-21.4	-18.7
0.4115	1174.5	1194.3	1198.8	1195.8	-19.8	-24.3	-21.3
0.5361	1188.9	1211.1	1216.0	1212.7	-22.2	-27.1	-23.8
0.6109	1198.9	1221.7	1226.4	1223.2	-22.8	-27.5	-24.3
0.7033	1213.0	1235.3	1239.6	1236.7	-22.3	-26.6	-23.7
0.8074	1230.5	1251.4	1254.6	1252.5	-20.9	-24.1	-22.0
0.9025	1251.2	1266.9	1268.7	1267.5	-15.7	-17.5	-16.3
Benzene + Butyl acrylate							
T = 298.15 K							
0.1282	1210.5	1215.6	1219.1	1208.1	-5.1	-8.6	2.4
0.2182	1213.6	1221.8	1227.5	1210.4	-8.2	-13.9	3.2
0.2926	1216.2	1227.3	1234.6	1213.5	-11.1	-18.4	2.7
0.4108	1224.0	1236.8	1245.8	1220.7	-12.8	-21.8	3.3
0.4964	1230.5	1244.4	1254.1	1227.8	-13.9	-23.6	2.7
0.5923	1240.0	1253.7	1263.5	1237.6	-13.7	-23.5	2.4
0.708	1253.3	1266.2	1275.1	1252.3	-12.9	-21.8	1.0
0.7944	1265.6	1276.6	1284.0	1265.5	-11.0	-18.4	0.1
0.9032	1285.0	1291.2	1295.3	1285.3	-6.2	-10.3	-0.3
T = 303.15 K							
0.1282	1186.5	1193.2	1196.9	1186.0	-6.7	-10.4	0.5
0.2182	1189.0	1199.3	1205.4	1188.5	-10.3	-16.4	0.5
0.2926	1191.5	1204.8	1212.4	1191.6	-13.3	-20.9	-0.1
0.4108	1197.5	1214.4	1223.8	1198.9	-16.9	-26.3	-1.4
0.4964	1203.5	1221.9	1232.1	1206.0	-18.4	-28.6	-2.5

0.5923	1212.5	1231.2	1241.7	1215.8	-18.7	-29.2	-3.3
0.708	1225.7	1243.7	1253.3	1230.4	-18.0	-27.6	-4.7
0.7944	1239.0	1254.1	1262.1	1243.6	-15.1	-23.1	-4.6
0.9032	1258.3	1268.8	1273.4	1263.1	-10.5	-15.1	-4.8
Benzene + Styrene							
T = 298.15 K							
0.1362	1371.0	1374.5	1371.5	1362.0	-3.5	-0.5	9.0
0.2498	1359.5	1367.0	1362.3	1347.4	-7.5	-2.8	12.1
0.3047	1353.9	1363.2	1358.0	1341.3	-9.3	-4.1	12.6
0.4109	1344.7	1355.7	1349.6	1330.9	-11.0	-4.9	13.8
0.5207	1335.9	1347.5	1341.2	1322.2	-11.6	-5.3	13.7
0.5834	1332.0	1342.6	1336.3	1318.1	-10.6	-4.3	13.9
0.7114	1323.8	1332.1	1326.7	1311.6	-8.3	-2.9	12.2
0.7924	1318.6	1325.2	1320.6	1308.8	-6.6	-2.0	9.8
0.8831	1313.1	1317.1	1314.0	1306.8	-4.0	-0.9	6.3
T = 303.15 K							
0.1362	1346.9	1351.6	1348.8	1339.2	-4.7	-1.9	7.7
0.2498	1335.9	1344.1	1339.7	1324.8	-8.2	-3.8	11.1
0.3047	1330.5	1340.4	1335.4	1318.7	-9.9	-4.9	11.8
0.4109	1321.7	1332.9	1327.1	1308.4	-11.2	-5.4	13.3
0.5207	1312.6	1324.8	1318.7	1299.8	-12.2	-6.1	12.8
0.5834	1308.6	1319.9	1313.9	1295.7	-11.3	-5.3	12.9
0.7114	1300.5	1309.6	1304.4	1289.3	-9.1	-3.9	11.2
0.7924	1295.3	1302.7	1298.3	1286.5	-7.4	-3.0	8.8
0.8831	1290.0	1294.6	1291.8	1284.5	-4.6	-1.8	5.5

observed in the present systems. Also the values predicted by Flory relation gives maximum deviations.

Conclusion

In the present study we have measured the theoretical properties based on the viscometric and ultrasonic behaviour of binary mixtures of benzene with methyl acrylate, ethyl acrylate, butyl acrylate and styrene at 298.15 K and 303.15 K. The excess molar volumes ($V\eta^E$) values were calculated from viscosity data. A reasonably good agreement has been found between the experimental excess molar volumes (V^E) and the theoretically predicted excess molar volumes ($V\eta^E$) values. This emphasizes the effectiveness of the present approach. The predicted values of viscosities and ultrasonic speeds were compared with the experimentally measured values, showing good agreement for all the binary mixtures. The positive deviations in $V\eta^E$ values suggest the presence of weak interactions between component molecules at 298.15 K and 303.15 K. The positive contribution of and opposite negative trend in ΔS^* values with mole fraction x_1 of benzene were observed, which indicates that the formation of activated species necessary for viscous flow seems to be easy in the butyl acrylate and styrene rich region, owing to the low values of and become difficult in the ethyl acrylate rich region and relatively more difficult in methyl acrylate rich region owing to the high values of ΔH^*, as the mole fraction of benzene in the mixture increases. This is supported by the decreasing value of ΔS^* as the amount of benzene in the mixture increases. It is found that experimental and predicted viscometric and ultrasonic speeds are in good agreement.

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