

Thermodynamic and Acoustic Properties of Binary Mixtures of Diisopropyl ether or oxolane with N, N-dimethylaniline or N, N-diethylaniline at different Temperatures

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Abstract: The thermodynamic, acoustic and transport properties of non-electrolyte liquid-liquid mixtures provide information about type and extent of molecular interactions and can be used for the development of molecular models for describing the behaviour of solutions. We are engaged in systematic investigations of binary mixtures of aromatic amine with ether at different temperatures. We found speeds of sound, isentropic compressibilities, excess molar volumes and various other related properties of binary mixtures of diisopropyl ether (DIPE) or oxolane with aniline, N-methylaniline, N-ethylaniline, o-toluidine and m-toluidine (primary and secondary arylamines) at 303.15, 313.15 and 323.15 K. It was observed that there exist specific interactions through hydrogen bonding and dipole-dipole interactions between primary/secondary arylamine and ether molecules. Our studies to the binary mixtures formed from DIPE or oxolane with N,N-dimethylaniline (DMA) or N,N-diethylaniline (DEA). Speeds of sound at different temperatures in the investigated binary mixtures have also been estimated through Nomoto model (NM), Van Dael model (VM), Ernst model (EM), impedance model (IM), Schaaffs' collision factor theory (CFT), Jacobson's free length theory (FLT), and Prigogine-Flory-Patterson-Oswal theory (PFPO).

Keywords: Speeds of sound, Isentropic compressibilities, Excess molar volumes Diisopropyl ether, Oxolane, Aniline, N-methylaniline, N-ethylaniline

1. Results and Discussion

The results for the densities, speeds of sound, isentropic compressibilities, Rao's molar sound functions, specific acoustic impedances and intermolecular free lengths, excess molar volumes, and excess isentropic compressibilities for four binary mixtures of DIPE or oxolane with DMA or DEA at 303.15, 313.15, and 323.15 KF.

The isentropic compressibilities κ_s , Rao's molar sound functions R , specific acoustic impedances Z and intermolecular free lengths L_f were obtained from the experimental densities ρ and speeds of sound u using the following relations

$$\kappa_s = (\rho u^2)^{-1} \quad (1)$$

$$R = u^{1/3} V \quad (2)$$

$$Z = u\rho \quad (3)$$

$$L_f = K_{Jac} / u\rho^{1/2} = K_{Jac} \kappa_s^{1/2} \quad (4)$$

where molar volume $V = \Sigma(x_i M_i) / \rho$, in which x_i and M_i are the mole fraction and molecular mass of component i . $K_{Jac} = (91.368 + 0.3565T) \times 10^{-8}$ is temperature dependent Jacobson's constant. The values of κ_s , R , and Z were uncertain within $\pm 0.2\%$ while L_f within 1% . Excess molar volume V_m^E , excess isentropic compressibility κ_s^E , excess intermolecular free length L_f^E and excess specific acoustic impedance Z^E in each mixture were calculated with following expressions

$$Y^E = Y - Y^{id} \quad (5)$$

where, Y represent either V , κ_s , L_f and Z . The V_m^{id} for an ideal mixture was calculated from usual relation

$$V_m^{id} = \Sigma x_i V_i^o = \Sigma x_i M_i / \rho_i \quad (6)$$

κ_s^{id} for an ideal mixture were calculated from the relation recommended by Benson and Kiyohara.

$$\kappa_s^{id} = \Sigma \phi_i \{ \kappa_{s,i}^o + TV_i^o (\alpha_i^o)^2 / C_{p,i}^o \} - T (\Sigma x_i V_i^o) (\Sigma \phi_i \alpha_i^o)^2 / (\Sigma x_i C_{p,i}^o) \quad (7)$$

L_f^{id} and Z^{id} for an ideal mixture were obtained as

$$L_f^{id} = K_{Jac} (\kappa_s^{id})^{1/2} \quad (8)$$

$$Z^{id} = \rho^{id} u^{id} = (\rho^{id} / \kappa_s^{id})^{1/2} \quad (9)$$

in which the M_i , V_i^o , α_i^o and $C_{p,i}^o$ are respectively, the molar mass, molar volume, isobaric thermal expansion coefficient and molar isobaric heat capacity of pure component i , $\phi_i = x_i V_i^o / \Sigma x_j V_j^o$ is the volume fraction of i in the mixture, stated in terms of the unmixed components and $\rho^{id} = \Sigma \phi_i \rho_i^o$. The values of α^o and C_p^o used for these calculations.

For compact and smooth representation, the values of u and κ_s were fitted to a polynomial equation of the form

$$u \text{ or } \kappa_s \text{ or } R = \sum_{i=0}^m A_i X_1^i \quad (10)$$

The V_m^E , κ_s^E , L_f^E and Z^E were correlated by Redlich-Kister polynomial equation

$$Y^E = x_1 (1 - x_1) \sum_{i=0}^n B_i (1 - 2x_1)^i \quad (11)$$

where $Y^E = V_m^E$, κ_s^E , L_f^E , and Z^E

The coefficients A_i of Eq. (10) and B_i of Eq. (11) and corresponding standard deviations σ obtained from a least-squares fit with equal weights assigned.

It is observed from the values of speeds of sound, specific acoustic impedances decrease with mole fraction of DIPE or oxolane and also with the rise in temperature for all the mixtures studied. The values of isentropic compressibility and intermolecular free length increase with the mole fraction of DIPE or oxolane and with the rise in temperature from 303.15 to 323.15 K. The Figs. 1-4 show the dependence of V_m^E , κ_S^E , L_f^E and Z^E on composition. The V_m^E , κ_S^E , and L_f^E are negative for all the four studied mixtures over the entire mole fraction range, and their magnitude increases with the rise in temperature from 303.15 to 323.15 K. Further, the values of V_m^E for both the DIPE mixtures are much more negative compared to both oxolane mixtures. Other very large negative values of V_m^E reported in the literature include 2-methoxyethanol + tert-butylamine (-2.4 to -2.6 $\times 10^{-6}$ m³ mol⁻¹) and DMSO + cyclohexylamine (-3.4 $\times 10^{-6}$ m³ mol⁻¹).

The observed values of V_m^E for presently investigated DIPE + DMA and + DEA mixtures are less negative than DIPE + aniline, + toluidines. Similarly, V_m^E for presently investigated oxolane + DMA and + DEA mixtures are less negative than oxolane + aniline + monoalkylaniline, + toluidines. This clearly indicates influence of tertiary amine over primary and secondary amines.

The over all behaviour of V_m^E and κ_S^E for the present mixtures can be envisaged as a resultant of opposite effects: (i) disruption of ether-ether interactions (ii) break down of dipolar order in ether and tertiary arylamine, (iii) dipole-dipole interactions in tertiary aryl amine and ether, (iv) free volume effect, and (v) characteristic pressure P^* effect [45,46]. The free volume (V_{fv}^E), characteristic pressure ($V_{p^*}^E$) and interaction (V_{int}^E) contributions to the total V_{total}^E can be estimated from the Prigogine-Flory-Patterson (PFP) theory summarizes these contributions at equimolar composition for the present mixtures. The estimated sum of free volume and P^* contributions ($V_{fv}^E + V_{p^*}^E$) to the V_{total}^E as per the PFP theory is in the range from -1.821 to -2.291 $\times 10^{-6}$ m³ mol⁻¹ DIPE + DMA or DEA and -0.152 to -0.296 $\times 10^{-6}$ m³ mol⁻¹ oxolane + DMA or DEA, while interaction contribution is in the range from -0.114 to -0.968 $\times 10^{-6}$ m³ mol⁻¹ DIPE + DMA or DEA and -0.213 to -0.536 $\times 10^{-6}$ m³ mol⁻¹ oxolane + DMA or DEA. This points to the fact that in very large negative values of V_m^E for DIPE + DMA or DEA the major contribution is because of the free volume and P^* effects, which include size, shape and conformation of the molecules involved. In case of oxolane mixtures, the combined contribution due to the free volume and P^* effects is much smaller as compared to the DIPE mixtures. This difference can be explained by considering the difference in thermal expansion coefficient α or Flory's

reduced volume \tilde{V} and characteristic pressure P^* of unlike components. The free volume (V_{fv}^E) term is proportional to $-(\tilde{V}_1 - \tilde{V}_2)^2$ i.e. $-(\alpha_1 - \alpha_2)^2$ and is always negative and its magnitude depends upon difference in thermal expansion coefficients or Flory's reduced volumes of involved components. The difference between α or \tilde{V} of DIPE and DMA/DEA is relatively very large as compared to the α or \tilde{V} of oxolane and DMA/DEA, that is the reason free volume (V_{fv}^E) term for DIPE+DMA/MEA is very large negative compared to the oxolane + DMA/DEA mixtures. The characteristic pressure ($V_{p^*}^E$) term is proportional to $(P_1^* - P_2^*)(\tilde{V}_1 - \tilde{V}_2)$ and can have either sign depending upon the magnitude of P^* and α (or \tilde{V}) of unlike components. For DIPE+DMA/MEA the $(P_1^* - P_2^*)$ is large negative while $(\tilde{V}_1 - \tilde{V}_2)$ large positive, making ($V_{p^*}^E$) term large and negative. For oxolane + DMA, $(P_1^* - P_2^*)$ is small negative and $(\tilde{V}_1 - \tilde{V}_2)$ positive, with product $(P_1^* - P_2^*)(\tilde{V}_1 - \tilde{V}_2)$ i.e. ($V_{p^*}^E$) term for oxolane + DMA is small negative. Contrary to this for oxolane + DEA, $(P_1^* - P_2^*)$ is small positive and $(\tilde{V}_1 - \tilde{V}_2)$ positive, as a result $V_{p^*}^E$ is small and positive.

The negative values of interactional contribution (V_{int}^E) to V_m^E for the present mixtures suggest that dipole-dipole interactions (μ for DIPE/oxolane = 1.34/1.75 D, and for DMA/DEA \approx 1.61 D), between unlike molecules dominate over the dispersive ether-ether interactions, breaking of dipolar order of aromatic amines as well as of DIPE/oxolane. The negative V_m^E and κ_S^E values at equimolar compositions for common amine follow the order: DIPE > oxolane, while there is a marginal difference between the values of DMA or DEA.

As expected, the trend of negative L_f^E values (Fig. 3) is similar to κ_S^E in the studied mixtures. The negative values of L_f^E are generally observed in the mixtures with specific interactions between unlike molecules. The negative L_f^E values at equimolar compositions for common amine follow the order: DIPE > oxolane. Fig. 4 shows that Z^E is positive for all the studied mixtures. Positive trends in Z^E have also been reported for binary mixtures of methanol + piperidine. Specific acoustic impedance is a quantity, which depends on the molecular packing of the systems. The positive values of Z^E are in accordance with the presence of structural effect and specific interactions between the unlike molecules.

The dependence of Rao's molar sound functions R on mole fractions x_1 is shown in Fig. 5. It is observed that there are slight negative deviations from the linear dependence on x_1

for DIPE binary mixtures while almost linear for oxolane mixtures. As expected the R are independent of temperature. According to Rao's approach, the speed of sound is directly related to the strength of intermolecular energy. If the intermolecular energy were simply a consequence of additive non-bonding interaction, the Rao's molar sound function should predict additive behaviour. The fact that is not so implies some additional interactions in the mixtures compared with those in the simple liquids.

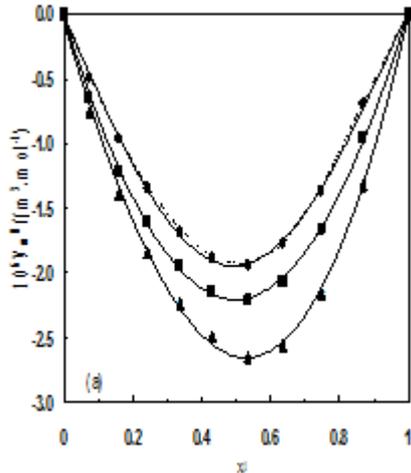


Figure 1 (a)

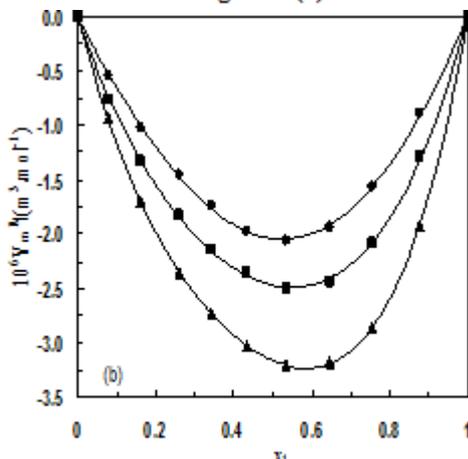


Figure 1 (b)

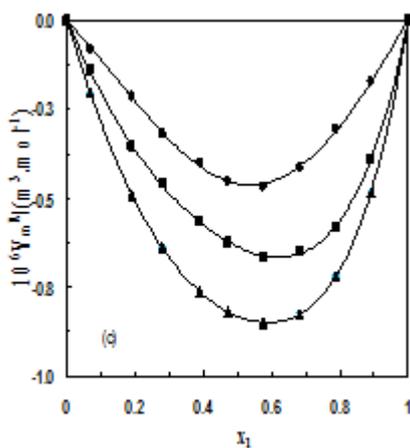


Figure 1 (c)

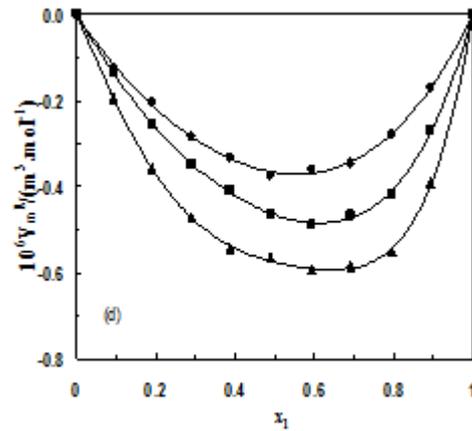


Figure 1 (d)

Figure 1 Dependence of excess molar volumes on mole fraction of DIPE or oxolane, (a) DIPE + DMA, (b) DIPE + DEA, (c) oxolane + DMA and (d) oxolane + DEA at T = 303.15 K (●), 313.15 K (■), 323.15 K (▲). Solid lines have been drawn from Eq. (11) using coefficient.

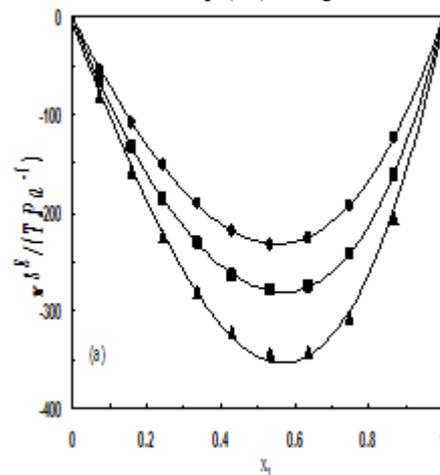


Figure 2 (a)

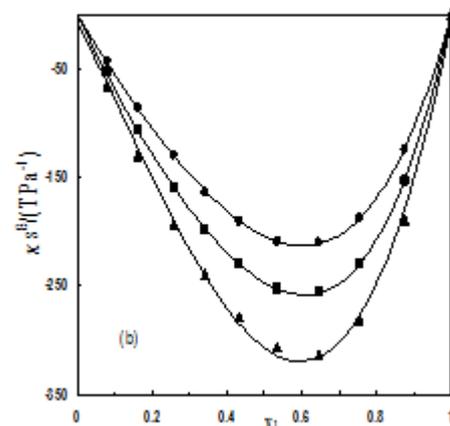


Figure 2 (b)

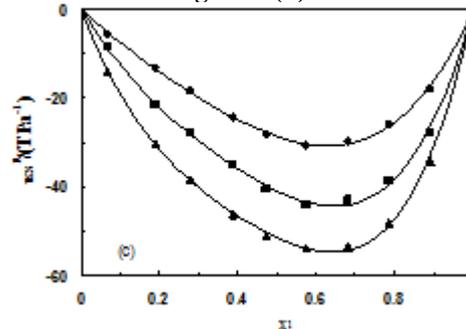


Figure 2 (c)

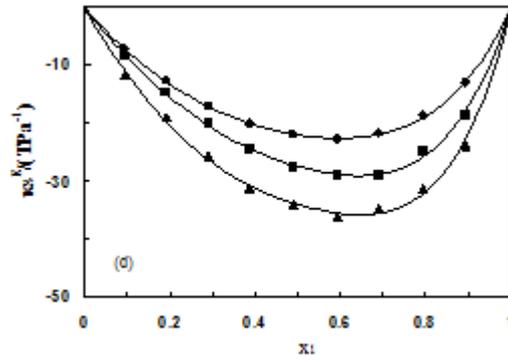


Figure 2 (d)

Figure 2 Dependence of excess isentropic compressibilities on mole fraction of DIPE or oxolane, (a) DIPE + DMA, (b) DIPE + DEA, (c) oxolane + DMA and (d) oxolane + DEA at $T = 303.15\text{ K}$ (●), 313.15 K (■), 323.15 K (▲). Solid lines have been drawn from Eq. (11) using coefficient.

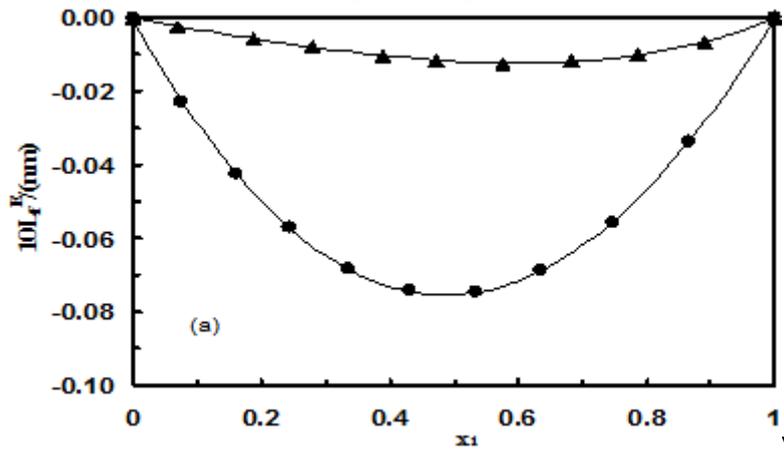


Figure 3 (a)

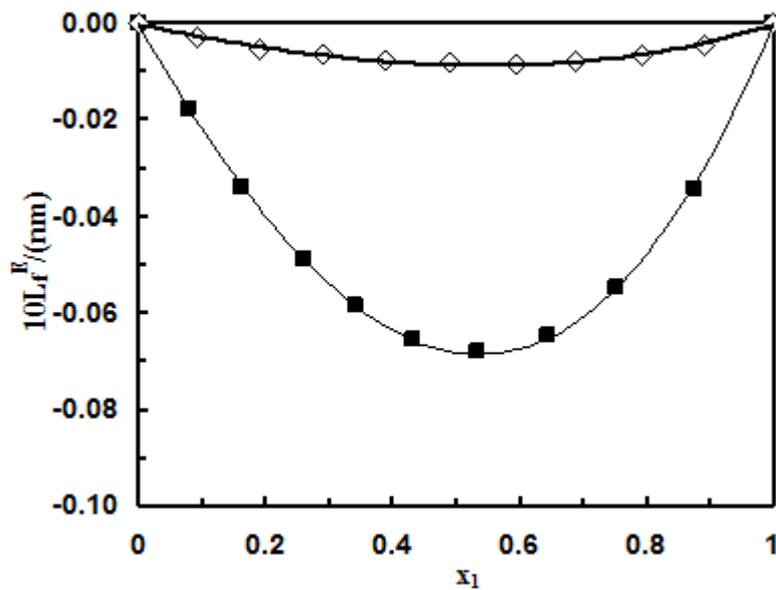


Figure 3 (b)

Figure 3 Dependence of excess intermolecular free length on mole fraction of DIPE or oxolane at $T = 303.15\text{ K}$. (a) DIPE + DMA (●) and oxolane + DMA (▲). (b) DIPE + DEA (■) and oxolane + DEA (◇). Solid lines have been drawn from Eq. (11) using coefficient.

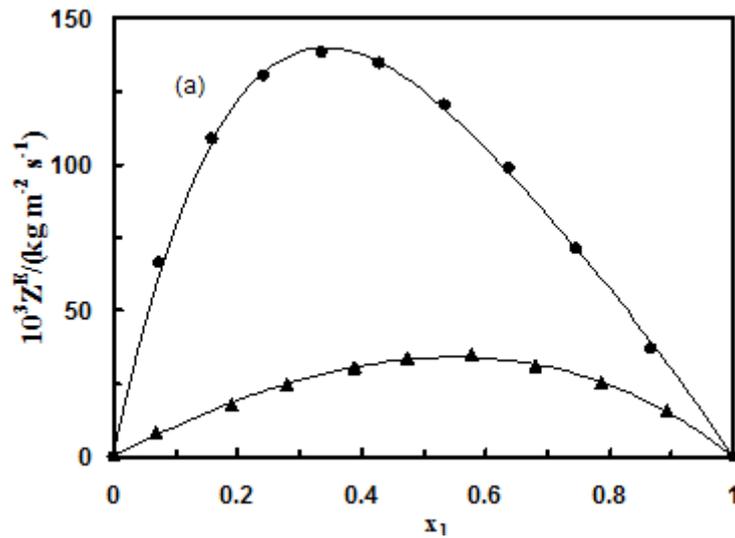


Fig 4(a)

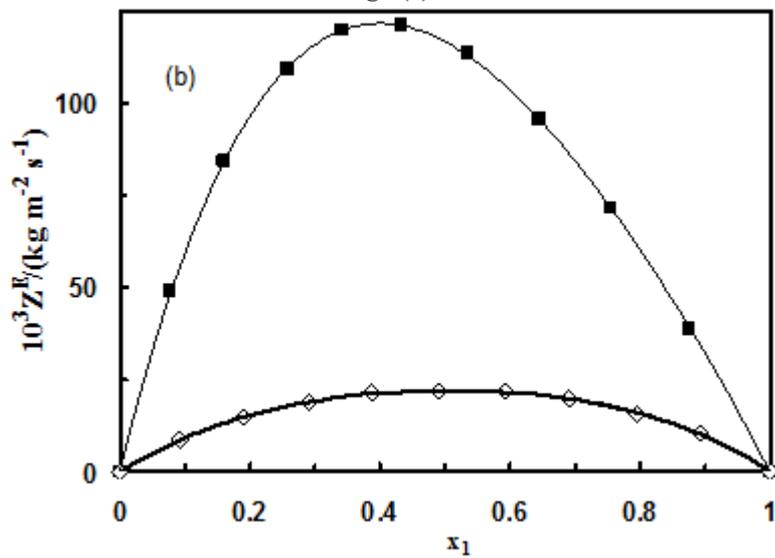


Figure 4(b)

Figure 4 Dependence of excess specific acoustic impedance on mole fraction of DIPE or oxolane at T= 303.15 K. (a) DIPE + DMA (●) and oxolane + DMA (▲). (b) DIPE + DEA (■) and oxolane + DEA (◇), Solid lines have been drawn from Eq. (11) using coefficient.

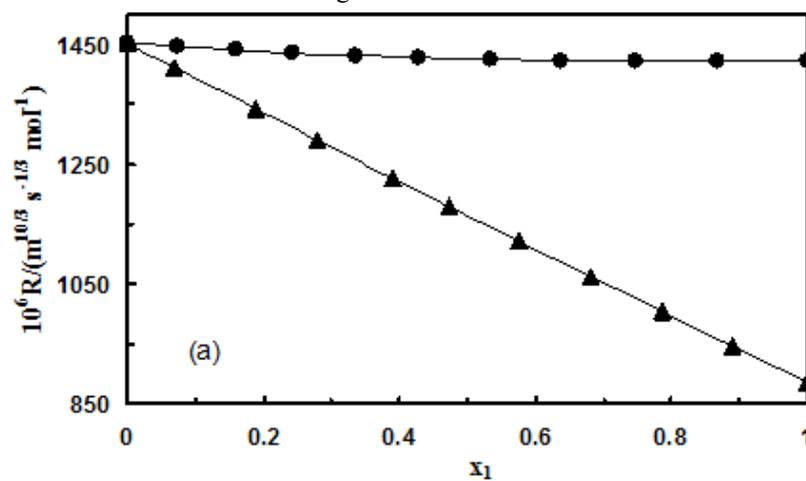


Figure 5 (a)

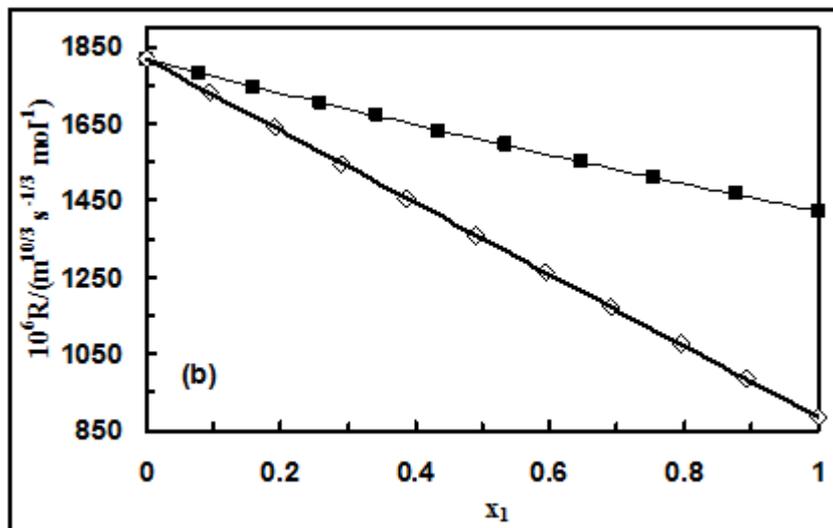


Figure 5 (b)

Figure 5 Dependence of Rao's molar sound function on mole fraction of DIPE or oxolane at $T = 303.15$ K. (a) DIPE + DMA (\bullet) and oxolane + DMA (\blacktriangle). (b) DIPE + DEA (\blacksquare) and oxolane + DEA (\diamond).

2. Conclusions

The magnitude of negative values of V_m^E , κ_S^E , and L_f^E and positive values of Z^E for binary mixtures of DIPE with DMA or DEA is much larger than that observed for oxolane mixtures at 303.15, 313.15, and 323.15 K. This difference is attributed to the effect due to the difference in free volume and internal pressure of involved components. The specific interactions between unlike molecules through dipole-dipole interactions exist and dominate over the dispersion interactions. The overall estimation ability of speed of sound in presently investigated mixtures follows the sequence: PF POT > CFT > \square NM > FLT \cong IM > EM > VM.

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