

# Volumetric and Transport Properties of Binary Liquid Mixtures of Aliphatic Ketones with Phenylacetonitrile at $T = 308.15$ K

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Measurement of densities,  $\rho$ , viscosities,  $\eta$ , and ultrasonic speeds,  $u$ , have been carried out for binary mixtures of phenylacetonitrile (PAN) with methylethylketone (MEK), methylpropylketone (MPK), methylisobutylketone (MIBK), and diethylketone (DEK) and their pure liquids at  $T = 308.15$  K over the entire composition range. From these experimental data, excess molar volumes,  $V^E$ , deviations in viscosity,  $\Delta\eta$ , and isentropic compressibility,  $\Delta\kappa_s$ , of aliphatic ketones with phenylacetonitrile have been calculated. The variation of these properties with composition of the mixture suggests dipole–dipole interactions and charge transfer complex formation between associated phenylacetonitrile molecules and dipolar ketones. The magnitude of the property is found to depend on the chain length of the ketone molecule. These results have been fitted to the Redlich–Kister polynomial using multiparametric nonlinear regression analysis to estimate the binary coefficients and standard errors. The experimental data are used to test the applicability of empirical relations of Grunberg and Nissan, Tamura and Kurata and Hind, and McLaughlin and Ubbelohde for the system studied.

## Introduction

Thermophysical properties of binary liquid mixtures have been very useful in obtaining information on the intermolecular interactions and geometrical effects in the systems. The data of thermophysical properties of the investigated liquids and their mixtures are required for the design of mixing, storage, and process equipment. The data measured reflect the interactions between the molecules of the mixtures and can serve for testing theories of the liquid state. Furthermore, thermodynamic properties of binary mixtures, containing components capable of undergoing specific interactions, exhibit significant deviations from ideality not only arising from a difference in molecular size and shape but also due to structural changes. Research activities of our laboratory comprise the systematic measurement of volumetric and transport properties of mixtures of compounds.<sup>1–6</sup> Our current project is devoted to the systematic study of liquid systems containing aliphatic ketones with respect to their environmental importance.

In recent years, several studies have been advanced to study thermodynamic and transport properties of binary liquid mixtures containing aliphatic ketones.<sup>7–18</sup> A perusal of the literature reveals that the thermophysical property studies on the binary mixtures containing phenylacetonitrile are not yet reported. This paper presents the data on density, viscosity, and speed of sound measurements in systems of phenylacetonitrile with four aliphatic ketones at  $T = 308.15$  K and at atmospheric pressure.

The experimental values of densities,  $\rho$ , viscosities,  $\eta$ , and ultrasonic speeds,  $u$ , of pure phenylacetonitrile, methylethylketone, methylpropylketone, methylisobutylketone, and diethylketone and their binary mixtures over the whole composition range have been measured at  $T = 308.15$  K. Using these experimental data, excess molar volume,  $V^E$ , deviation in viscosity  $\Delta\eta$ , and deviation in isentropic compressibility  $\Delta\kappa_s$  are calculated. These

Table 1. Densities ( $\rho$ ) of the Pure Components at  $T = 298.15$  K

component	$\rho$ g·cm <sup>-3</sup>	
	this work	literature
phenylacetonitrile	1.01532	1.01500 <sup>a</sup>
methylethylketone	0.80078	0.80097 <sup>7</sup>
diethylketone	0.81009	0.80977 <sup>12</sup>
methylpropylketone	0.80153	0.80163 <sup>18</sup>
methylisobutylketone	0.79712	0.79633 <sup>17</sup>

<sup>a</sup> Handbook of Fine Chemicals, Sigma-Aldrich, India.

results have been fitted to the Redlich–Kister polynomial equation<sup>19</sup> to derive the binary coefficients and estimate the standard deviation between experimental and calculated data. Results have been used to explain the nature of intermolecular interactions between mixing components.

## Experimental

**Materials.** High purity analytical grade phenylacetonitrile (98.0 % GC Assay) was procured from SD. Fine Chemicals Ltd., India. It was dried with 3A × 1.5 mm molecular sieves from Merck.<sup>20</sup> Methylethylketone with 99.0 % (GC Assay) purity was purchased from Merck, India, and methylpropylketone ( $\geq 99$  %) (GC) and diethylketone (98 %) were purchased from Sigma-Aldrich Chemicals Pvt Ltd., Germany. Methylisobutylketone 99.0 % (GC Assay) was procured from Finar Chemicals Pvt. Ltd., India. All the ketones were used without further purification. The densities of pure substances and their comparison with literature values are shown in Table 1.

**Apparatus and Procedure.** Binary mixtures were prepared by mass in airtight bottles. The mass measurements were performed on a Dhona 100 DS, India, single-pan analytical balance with a resolution of  $0.01 \cdot 10^{-6}$  kg. The required properties of the mixture were measured on the same day. The uncertainty in mole fraction was estimated to be less than  $\pm 1 \cdot 10^{-4}$ .

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Densities of pure liquids and their mixtures were determined by using a  $1 \cdot 10^{-5} \text{ m}^3$  double arm pycnometer as described in our previous paper.<sup>4</sup> The density values from triplicate replication at the temperature of 308.15 K were reproducible within  $\pm 2 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$ . The uncertainty in density and excess molar volume values was found to be  $\pm 4 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$  and  $\pm 1 \cdot 10^{-3} \text{ cm}^3 \cdot \text{mol}^{-1}$ .

An Ubbelohde viscometer<sup>21</sup> having a capacity of about 15 mL and the capillary having a length of about 90 mm and 0.5 mm internal diameter has been used to measure the flow times of pure liquids and liquid mixtures, and it was calibrated with benzene and doubly distilled water (water conductivity less than  $1 \cdot 10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$  with (0.9970 and 0.9940)  $\text{g} \cdot \text{cm}^{-3}$  as its density at (298.15 and 308.15) K, respectively, and the density of benzene (0.87381 and 0.87341)  $\text{g} \cdot \text{cm}^{-3}$  at (298.15 and 308.15) K, respectively). The detailed experimental procedure with the viscometer was discussed in our previous paper.<sup>4</sup> Viscosity values ( $\eta$ ) of pure liquids and mixtures are calculated using the relation

$$\eta = (at - b/t)\rho \quad (1)$$

where  $a$  and  $b$  are the characteristic constants of the viscometer;  $\rho$  is the density; and  $t$  represents the flow time. The flow times of pure liquids and liquid mixtures were repeated 5 times. The uncertainty of viscosity was  $\pm 0.005 \text{ mPa} \cdot \text{s}$ .

Speed of sound was determined by using an ultrasonic interferometer [model M-82, Mittal Enterprises, India], working at 2 MHz frequency. The working principle used in the measurement of speed of sound through medium was based on the accurate determination of the wavelength of ultrasonic waves of known frequency produced by a quartz crystal in the measuring cell.<sup>22,23</sup> The temperature of the solution was controlled by circulating water at a desired temperature through the jacket of the double-walled cell. The speed of sound was measured with relative uncertainty of  $\pm 0.3 \%$ .

In all the property measurements, the temperature was controlled within  $\pm 0.01 \text{ K}$  using a constant temperature bath [INSREF model IRI - 016 C, India], and the temperature was monitored with a platinum resistance thermometer with an accuracy of  $\pm 0.001 \text{ K}$  and an uncertainty of  $\pm 0.004 \text{ K}$ .

## Results and Discussion

The values of density  $\rho$ , viscosity  $\eta$ , ultrasonic speed  $u$ , excess molar volume  $V^E$ , deviation in viscosity  $\Delta\eta$ , and deviation in isentropic compressibility  $\Delta\kappa_s$  for the binary mixtures of phenylacetonitrile (1) with methylethylketone (2), methylpropylketone (2), methylisobutylketone (2), and diethylketone (2) at  $T = 308.15 \text{ K}$  along with the mole fraction are given in Table 2. Due to the extreme irritating effect of phenylacetonitrile, special precautions were taken when handling the substance. Even so, the number of points measured had to be limited to only nine mixtures.

The excess molar volumes  $V^E$  have been evaluated from density using

$$V^E = (x_1M_1 + x_2M_2)/\rho_m - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \quad (2)$$

where  $\rho_m$  is the density of the mixture;  $x_1$ ,  $M_1$ ,  $\rho_1$ , and  $x_2$ ,  $M_2$ , and  $\rho_2$  are the mole fraction, molar mass, and density of pure components 1 and 2, respectively. The deviation in viscosity is calculated using the relation

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \quad (3)$$

where  $\eta_m$ ,  $\eta_1$ , and  $\eta_2$  are viscosities of the liquid mixture and of the pure components 1 and 2, respectively, and  $x_1$  and  $x_2$  are

**Table 2.** Densities,  $\rho$ , Viscosities,  $\eta$ , Speed of Sound,  $u$ , Excess Molar Volume  $V^E$ , Deviation in Viscosity,  $\Delta\eta$ , and Deviation in Isentropic Compressibility,  $\Delta\kappa_s$ , of the Binary Mixtures of Phenylacetonitrile (1) with Methylethylketone (2), Methylpropylketone (2), Methylisobutylketone (2), and Diethylketone (2) at  $T = 308.15 \text{ K}$

$x_1$	$\rho \cdot 10^{-3}$ $\text{kg} \cdot \text{m}^{-3}$	$\eta \cdot 10^3$ $\text{mPa} \cdot \text{s}$	$u$ $\text{m} \cdot \text{s}^{-1}$	$V^E \cdot 10^6$ $\text{m}^3 \cdot \text{mol}^{-1}$	$\Delta\eta$ $\text{mPa} \cdot \text{s}$	$\Delta\kappa_s \cdot 10^{11}$ $\text{m}^2 \cdot \text{N}^{-1}$
phenylacetonitrile + methylethylketone (2)						
0.0000	0.7892	0.316	1157	0.0000	0.000	0.00
0.0205	0.7961	0.334	1167	-0.1552	-0.008	-1.04
0.1218	0.8259	0.412	1208	-0.5109	-0.059	-3.97
0.2283	0.8540	0.497	1265	-0.6989	-0.109	-7.35
0.3188	0.8768	0.583	1308	-0.8601	-0.138	-8.80
0.4403	0.9055	0.720	1356	-1.0232	-0.1544	-8.84
0.5655	0.9313	0.868	1397	-0.9604	-0.165	-7.52
0.6706	0.9507	1.015	1421	-0.7960	-0.153	-5.41
0.8086	0.9741	1.228	1454	-0.5049	-0.114	-2.75
0.9657	0.9981	1.498	1497	-0.0856	-0.043	0.05
1.0000	1.0032	1.585	1518	0.0000	0.000	0.00
phenylacetonitrile + diethylketone (2)						
0.0000	0.8000	0.371	1185	0.0000	0.000	0.00
0.0235	0.8060	0.388	1199	-0.1113	-0.012	-1.65
0.1407	0.8354	0.474	1237	-0.6144	-0.068	-3.91
0.2569	0.8615	0.567	1278	-0.7671	-0.117	-5.46
0.358	0.8833	0.665	1314	-0.8384	-0.140	-6.27
0.4803	0.9090	0.790	1354	-0.8892	-0.164	-6.18
0.6048	0.9337	0.936	1397	-0.8288	-0.169	-5.61
0.6943	0.9512	1.064	1421	-0.7957	-0.150	-4.46
0.8378	0.9767	1.281	1471	-0.5059	-0.107	-2.86
0.9722	0.9989	1.528	1496	-0.1117	-0.023	0.30
1.0000	1.0032	1.585	1518	0.0000	0.000	0.00
phenylacetonitrile + methylpropylketone (2)						
0.0000	0.7908	0.394	1179	0.0000	0.000	0.00
0.0221	0.7970	0.410	1189	-0.1650	-0.010	-1.15
0.1416	0.8268	0.495	1228	-0.5431	-0.067	-3.61
0.2622	0.8560	0.600	1271	-0.8570	-0.106	-5.52
0.3564	0.8775	0.685	1313	-0.9683	-0.133	-7.10
0.4811	0.9042	0.819	1363	-0.9398	-0.148	-7.66
0.6125	0.9315	0.976	1394	-0.8762	-0.147	-5.75
0.7133	0.9509	1.100	1418	-0.6745	-0.143	-3.98
0.8389	0.9748	1.290	1456	-0.4612	-0.102	-2.12
0.9736	0.9986	1.509	1499	-0.0758	-0.045	0.13
1.0000	1.0032	1.585	1518	0.0000	0.000	0.00
phenylacetonitrile + methylisobutylketone (2)						
0.0000	0.7868	0.455	1150	0.0000	0.000	0.00
0.0271	0.7925	0.475	1166	-0.0543	-0.011	-1.87
0.1600	0.8233	0.573	1212	-0.6540	-0.063	-5.51
0.2926	0.8522	0.679	1261	-0.8561	-0.107	-7.67
0.3931	0.8746	0.775	1298	-1.0005	-0.124	-8.47
0.5217	0.9028	0.910	1340	-1.0420	-0.134	-7.99
0.6436	0.9289	1.049	1382	-0.9279	-0.133	-6.77
0.7407	0.9498	1.164	1414	-0.8044	-0.128	-5.19
0.8599	0.9760	1.338	1459	-0.6606	-0.089	-3.06
0.9758	0.9981	1.523	1498	-0.0769	-0.035	0.01
1.0000	1.0032	1.585	1518	0.0000	0.000	0.00

the mole fractions of the pure components 1 and 2 in the liquid state.

The deviations in isentropic compressibility have been evaluated using the equation

$$\Delta\kappa_s = \kappa_s - (\Phi_1\kappa_{s1} + \Phi_2\kappa_{s2}) \quad (4)$$

where  $\Phi_i$  is the volume fraction of pure components and is calculated from the individual pure molar volumes,  $V_i$ , using the relation

$$\Phi_i = x_iV_i/(\sum x_iV_i) \quad (5)$$

and  $\kappa_{s1}$ ,  $\kappa_{s2}$ , and  $\kappa_s$  are the isentropic compressibility of the pure components and observed isentropic compressibility of the liquid mixture, respectively.

**Table 3.** Various Parameters Calculated from Equations 8 to 10 and the Corresponding Standard Deviations ( $\sigma$ )

$G_{12}$	$\sigma$ mPa·S	$T_{12}$	$\sigma$ mPa·S	$H_{12}$	$\sigma$ mPa·S
-0.0306	phenylacetonitrile (1) + methylethylketone (2) 0.0368	0.0045	0.1126	0.2983	0.0673
0.1418	phenylacetonitrile (1) + diethyl ketone (2) 0.0705	0.0134	0.1244	0.5511	0.0676
-0.4822	phenylacetonitrile (1) + methylpropylketone (2) 0.0613	0.0019	0.1374	0.1222	0.1169
-0.4097	phenylacetonitrile (1) + methylisobutylketone (2) 0.0506	0.0086	0.1555	0.2878	0.0948

The excess or deviation properties  $\Delta Y$  are fitted by the method of nonlinear least-squares to the fourth-order Redlich–Kister-type polynomial equation.<sup>19</sup>

$$\Delta Y = x_1 x_2 \sum A_i (x_1 - x_2)^i \quad (6)$$

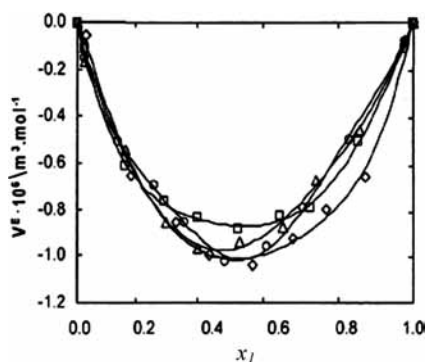
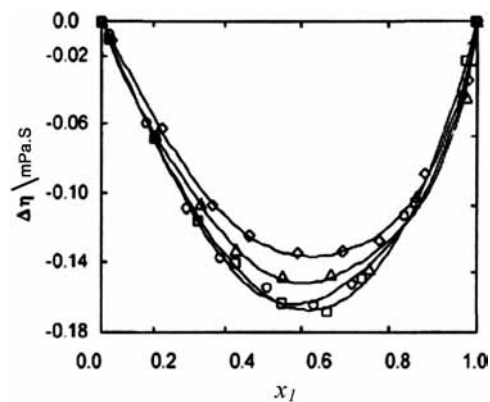
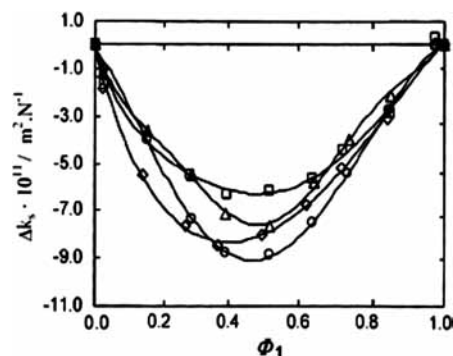
where  $A_0$ ,  $A_1$ , and  $A_2$  are adjustable binary coefficients. The coefficients  $A_i$  were estimated using multiparametric regression analysis based on a least-squares method. The number of  $A_i$  parameters was optimized using the  $F$ -test and is found to be five ( $m = 5$ ). In each case, the optimum number of coefficients  $A_i$  is determined from an examination of the variation of standard deviation ( $\sigma$ ) as calculated by

$$\sigma(Y^E) = [\sum (\Delta Y_{\text{obs}} - \Delta Y_{\text{cal}})^2 / (n - m)]^{1/2} \quad (7)$$

where  $n$  represents the number of experimental points and  $m$  is the number of coefficients used in fitting the data. The coefficients  $A_i$  and standard deviations  $\sigma$  ( $V^E$ ,  $\Delta\eta$ , and  $\Delta\kappa_s$ ) of the fit are summarized in Table 4.

**Excess Molar Volume.** The excess molar volume curves are negative and almost symmetric for all the systems. The isotherms drawn in Figure 1 are parabolic in nature indicating that the interactions are maximum at equimolar composition. Further, it can be observed from the experimental results in Figure 1 that  $V^E$  curves are shifted in a regular way with increasing chain length, viz.,  $V^E$  becomes less negative at higher chain length. The minimum value of each isotherm falls around the mole fraction (PAN)  $x_1 = 0.5$  indicating the possibility of formation of 1:1 adducts<sup>24</sup> (complexes) in all the systems.

All ketones are dipolar aprotic solvents. Similarly, phenylacetonitrile is also a dipolar aprotic solvent. Phenylacetonitrile, due to its high dipole moment ( $1.532 \cdot 10^{-30}$  C·m),<sup>25</sup> favors dipole–dipole interactions.<sup>20</sup> Hence, there will be a dipole–dipole

**Figure 1.** Plots of excess molar volume  $V^E$  versus mole fraction  $x_1$  of phenylacetonitrile (1) with  $\circ$ , methylethylketone (2);  $\Delta$ , methylpropylketone (2);  $\diamond$ , methylisobutylketone (2); and  $\square$ , diethylketone (2) at  $T = 308.15$  K.**Figure 2.** Plots of deviation in viscosity  $\Delta\eta$  versus mole fraction  $x_1$  of phenylacetonitrile (1) with  $\circ$ , methylethylketone (2);  $\Delta$ , methylpropylketone (2);  $\diamond$ , methylisobutylketone (2); and  $\square$ , diethylketone (2) at  $T = 308.15$  K.**Figure 3.** Plots of deviation in isentropic compressibility  $\Delta\kappa_s$  versus volume fraction  $\Phi_1$  of phenylacetonitrile (1) with  $\circ$ , methylethylketone (2);  $\Delta$ , methylpropylketone (2);  $\diamond$ , methylisobutylketone (2); and  $\square$ , diethylketone (2) at  $T = 308.15$  K.

interaction between unlike molecules of all the systems, contributing to the reduction in the volume.

In addition to the strong dipole–dipole interactions, there may be a possibility of charge transfer complex formation between ketones and cyano group solvents. Nitrogen atoms are the best donors<sup>26</sup> possessing lone pairs of electrons on them. Hence, phenylacetonitrile is a good electron pair donor to exhibit specific interactions with ketones. The order of interaction for these four ketones would be: MIBK > MEK > MPK > DEK with increasing molar volumes of liquids.

**Viscosity Deviation.** Results of the plots of  $\Delta\eta$  against  $x_1$  at  $T = 308.15$  K are displayed in Figure 2. The deviation in viscosity ( $\Delta\eta$ ) from the linear dependence on mole fraction reveals that it is negative for all the four binary mixtures investigated.

The  $\Delta\eta$  values at  $x_1 = 0.5$  (equimolar composition) show the following descending order: DEK > MEK > MPK > MIBK.

Several semiempirical models (relations) have been proposed to estimate the dynamic viscosities,  $\eta$ , of the binary liquid mixtures in terms of pure component data.<sup>27,28</sup> We examined our results with some models as follows.

**Grunberg and Nissan.** On the basis of Arrhenius' equation, Grunberg and Nissan<sup>29</sup> have suggested the following logarithmic relation between the viscosity of binary liquid mixtures and of pure components

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \quad (8)$$

where  $\eta$  is the dynamic viscosity of the mixture;  $x_1$  and  $x_2$  are the mole fractions of pure components;  $\eta_1$  and  $\eta_2$  are the



**Table 4. Binary Coefficients ( $A_i$ ) and Standard Deviation ( $\sigma$ ) for the Binary Mixtures of Phenylacetonitrile (1) + Aliphatic Ketones (2) at  $T = 308.15$  K**

binary system	function	binary coefficients					
		$A_0$	$A_1$	$A_2$	$A_3$	$A_4$	$\sigma$
phenylacetonitrile (1) + methylethylketone (2)	$V^E \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	-4.0883	-0.2786	2.9848	3.1110	-4.5108	0.222
	$\Delta\eta \cdot 10^3/\text{mPa} \cdot \text{s}$	-0.6551	0.0826	0.0615	-0.6255	-0.3498	0.042
	$\Delta\kappa_s \cdot 10^{11}/\text{m}^2 \cdot \text{N}^{-1}$	-36.0337	2.4536	23.1299	21.1791	-4.9533	3.277
phenylacetonitrile (1) + diethylketone (2)	$V^E \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	-3.4428	0.5849	-2.5935	-0.1216	1.5631	0.271
	$\Delta\eta \cdot 10^3/\text{mPa} \cdot \text{s}$	-0.6595	-0.1278	-0.0546	-0.0614	0.0332	0.0142
	$\Delta\kappa_s \cdot 10^{11}/\text{m}^2 \cdot \text{N}^{-1}$	-24.5785	-12.8120	-2.7814	57.6385	-0.5149	6.119
phenylacetonitrile (1) + methylpropylketone (2)	$V^E \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	-3.9376	0.1935	1.5506	2.3021	-3.2925	0.422
	$\Delta\eta \cdot 10^3/\text{mPa} \cdot \text{s}$	-0.6166	0.1287	0.2649	-0.8698	-0.8765	0.086
	$\Delta\kappa_s \cdot 10^{11}/\text{m}^2 \cdot \text{N}^{-1}$	-29.3749	-2.0940	25.8454	33.0291	-19.8183	3.85
phenylacetonitrile (1) + methylisobutylketone(2)	$V^E \cdot 10^6/\text{m}^3 \cdot \text{mol}^{-1}$	-3.7547	0.2289	-6.0417	-1.0699	7.9731	0.505
	$\Delta\eta \cdot 10^3/\text{mPa} \cdot \text{s}$	-0.5647	0.0440	0.2663	-0.6237	-0.7515	0.069
	$\Delta\kappa_s \cdot 10^{11}/\text{m}^2 \cdot \text{N}^{-1}$	-32.2991	-0.3547	1.8089	43.6171	-9.0927	4.643

dynamic viscosities of pure components 1 and 2, respectively; and  $G_{12}$  is a parameter, proportional to interchange energy and is a measure of nonideal behavior of the system. It may be regarded as an approximate measure of the strength of molecular interactions between the mixing components.

**Tamura and Kurata.** Tamura and Kurata<sup>30</sup> put forward the following equation for the viscosity of binary liquid mixtures

$$\eta = x_1\Phi_1\eta_1 + x_2\Phi_2\eta_2 + 2(x_1x_2\Phi_1\Phi_2)0.5 \cdot T_{12} \quad (9)$$

where  $T_{12}$  is the interaction parameter which depends on temperature and composition of the mixture and  $\Phi_1$  [ $\Phi_1 = x_1V_1/(x_1V_1 + x_2V_2)$ ] and  $\Phi_2$  [ $\Phi_2 = 1 - \Phi_1$ ] are the volume fractions of pure components 1 and 2, respectively.

**Hind, McLaughlin, and Ubbelohde.** Hind et. al.<sup>31</sup> suggested the following equation for the viscosity of the binary liquid mixtures

$$\eta = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2H_{12} \quad (10)$$

where  $H_{12}$  is the Hind interaction parameter related to unlike pair interactions.<sup>32</sup>

The evaluated values of various interaction parameters  $G_{12}$ ,  $T_{12}$  and  $H_{12}$  and standard deviation  $\sigma$  are presented in Table 3. A perusal of Table 3 shows that a reasonable fit is given by Grunberg and Nissan empirical relation for all binary systems. In comparison, the empirical equation of Hind et al. gave the best fit for the mixtures of phenylacetonitrile with diethyl ketone system.

**Deviation in Isentropic Compressibility.** All the systems of phenylacetonitrile + ketones show negative deviations through  $\Delta\kappa_s$  isotherms over the entire range of volume fractions (Figure 3) and exhibiting a clear minima at the volume fraction around  $x_1 = 0.5$ , indicating that the maximum interactions are at that volume fraction range in every system. From Table 2, it is observed that  $\Delta u$  values are positive while  $\Delta\kappa_s$  values are negative. Such a trend of positive deviation in speed of sound and negative deviation in isentropic compressibility is quite common.<sup>33,34</sup>

Generally, the deviation parameters are considered to be the reflecting agents of the magnitude of polarity at the site of interactions in the molecules. The negative  $\Delta\kappa_s$  values for aliphatic ketones decrease in the absolute value following the sequence: MEK > MIBK > MPK > DEK.

This appears to be a correlation between the sign of  $V^E$  and  $\Delta\kappa_s$ . This tendency is also found in the present study, where both  $V^E$  and  $\Delta\kappa_s$  have negative values and are of the same order. This similarity in both the properties lends support to the existence of specific interactions between unlike components which leads to volume reduction of the system.

## Conclusions

This paper reports experimental data for density, viscosity, and speed of sound at  $T = 308.15$  K for four binary mixtures of phenylacetonitrile and aliphatic ketones. From this data, excess molar volumes  $V^E$ , deviations in viscosity  $\Delta\eta$ , and deviations in isentropic compressibility  $\Delta\kappa_s$  have been evaluated. The results are analyzed in the light of molecular interactions between the components. The viscosity data are correlated with the Grunberg–Nissan, Tamura and Kurata and Hind, and the McLaughlin and Ubbelohde model in which the Grunberg and Nissan empirical relation gave the best fit for all binary systems.

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