

A Comparison Study on Molecular Interaction of an Acidic Organophosphoric Extractant with Substituted Aromatic Hydrocarbon (*p*-xylene/toluene) at 303.15K

Biswajit Dalai^{1,*}, Prativa Kar², Sarat Kumar Dash³, Saroj Kumar Singh⁴

¹ Department of Physics, School of Science, GIET University, Gunupur, Odisha – 765022, India; biswajit@giet.edu (B.D.)

² Department of Chemistry, School of Science, GIET University, Gunupur, Odisha – 765022, India; pravivakar@giet.edu (P.K.);

³ Department of Physics, Regional Institute of Education (NCERT), Bhubaneswar, Odisha– 751022, India; skdash@yahoo.com (S.K.D.);

⁴ Institute of Minerals and Materials Technology (CSIR), Bhubaneswar, Odisha – 751013, India; sarojksingh@gmail.com (S.K.S.);

* Correspondence: biswajit@giet.edu;

Scopus Author ID 35368227700

Received: 15.09.2020; Revised: 7.10.2020; Accepted: 8.10.2020; Published: 12.10.2020

Abstract: In the present study, the excess molar volume (V^E) and the deviations in intermolecular free length (ΔL_f), isentropic compressibility ($\Delta\beta_s$), acoustic impedance (ΔZ), and ultrasonic velocity (ΔU) were calculated using the experimentally measured values of density (ρ) and ultrasonic velocity (U) of binary mixtures of an acidic organophosphoric extractant (DEHPA) with two substituted aromatic hydrocarbons, i.e., *p*-xylene and toluene at 303.15K and atmospheric pressure, 0.1MPa over the entire composition range of DEHPA. The results of both binary mixtures have been presented graphically and compared in terms of molecular interaction between unlike molecules of the mixtures, which outcome may be applied in the solvent extraction process.

Keywords: density; ultrasonic velocity; excess/deviation properties; molecular interactions.

© 2020 by the authors. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

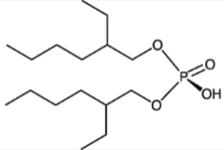
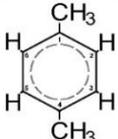
Ultrasonic and volumetric properties of binary organic liquid mixtures have been investigated by a number of researchers [1-3] over the last several decades. Such studies have great relevance in many areas of theoretical and applied fields on solvent extraction. The interaction parameters such as excess molar volume (V^E) and the deviations in isentropic compressibility ($\Delta\beta_s$), intermolecular free length (ΔL_f), acoustic impedance (ΔZ), and ultrasonic velocity (ΔU) were calculated using the experimentally measured values of density (ρ) and ultrasonic velocity (U), are of considerable interest in understanding the inter- and intramolecular interactions in liquid mixtures [4-6]. The acidic organophosphoric extractant, di-(2-ethyl hexyl) phosphoric acid (DEHPA) is widely used as an extractant [7, 8] for the extraction of actinides, lanthanides, and other valuable metals, viz. zinc, cobalt, copper, lead, beryllium, etc. In continuation of our earlier work [9-11], we propose to extend our investigation to make a comparison study on molecular interaction between two substituted aromatic hydrocarbons (*p*-xylene and toluene) with DEHPA, which could be used as a better modifier with DEHPA for solvent extraction process.

2. Materials and Methods

2.1. Materials.

The samples DEHPA, toluene, and *p*-xylene, used in this investigation were of AR grade and presented in Table 1.

Table 1. Specification of the pure compounds used in this work.

Chemicals used	Provenance	Mass fraction purity	CAS number	Molecular mass (g mol ⁻¹)	Structure
DEHPA (C ₁₆ H ₃₅ O ₄ P)	Spectrum	0.98	298-07-7	322.43	
Toluene (C ₇ H ₈)	Sigma-Aldrich	0.99	108-88-3	92.14	
<i>p</i> -Xylene (C ₈ H ₁₀)	Merck	0.99	106-42-3	106.17	

2.2. Properties measurements.

The procedure of measurements of ρ and U are the same as reported earlier [9, 10]. All samples were kept in airtight bottles, and adequate precautions were taken to avoid contamination and evaporation. The measurements of ρ and U for each sample were measured thrice at 303.15K and 0.1 Mpa, and average values were taken. The temperature during the measurement of samples was maintained within ± 0.1 K by an electronically controlled thermostatic water bath. The measured values of ultrasonic velocity (U) and density (ρ) of the pure samples were checked by comparing with data available in the literature [9, 12-15] and shown fairly well with literature data, summarized in Table 2.

Table 2. Values of ultrasonic velocity (U) and density (ρ) of pure samples vs. literature values at 303.15K.

Sample	Ultrasonic velocity, U (ms ⁻¹)		Density, ρ (kg m ⁻³)	
	Experimental	Literature	Experimental	Literature
<i>p</i> - Xylene	1289.2	1291.0 ^a	852.4	852.24 ^a
Toluene	1282.6	1282.81 ^b	856.2	857.55 ^{b, c}
DEHPA	1293.0	1293.0 ^d	961.3	965.3 ^e

^a [12], ^b [13], ^c [14], ^d [9], ^e [15]

3. Results and Discussion

In continuation of our earlier work of toluene + DEHPA [9], the experimental values of density (ρ) and ultrasonic velocity (U) and derived parameters of *p*-xylene + DEHPA over the entire mole fraction range of DEHPA at 303.15K under atmospheric pressure and are reported in Table 3. Excess molar volume (V^E) and deviation in intermolecular free length (ΔL_f) isentropic compressibility ($\Delta\beta_s$), acoustic impedance (ΔZ), ultrasonic velocity (ΔU) of *p*-xylene + DEHPA were computed from the experimental values of density (ρ), ultrasonic velocity (U) over the entire mole fraction range of DEHPA by following standard relations [16-18] and then compared with toluene + DEHPA graphically displayed in Figure 1-5.

Excess volume (V^E) is computed from density data by following the relation:

$$V^E = \{(x_1M_1 + x_2M_2) / \rho\} - \{(x_1M_1 / \rho_1) + (x_2M_2 / \rho_2)\} \tag{1}$$

where, x_1, M_1, ρ_1 and x_2, M_2, ρ_2 are the mole fraction, molecular mass, and density of pure components 1 and 2, respectively, and ρ is the density of the binary mixtures.

The deviation functions, viz. $\Delta L_f, \Delta \beta_s, \Delta Z, \Delta U$ were calculated using the expression [16-18]:

$$\Delta Y = Y_{exp} - Y_{ideal} = Y_{exp} - [(1-X_2)Y_1 + X_2 Y_2] \tag{2}$$

Where, Y represents the parameters L_f, β_s, U, Z , and X_2 is the mole fraction of DEHPA. Subscript 1 and 2 refer to *p*-xylene / toluene and DEHPA, respectively.

Table 3. Variation of density, ultrasonic velocity, and deviation functions, viz. molar volume, intermolecular free length, isentropic compressibility, the acoustic impedance in binary mixtures, *p*-xylene + DEHPA over entire mole fraction of DEHPA at 303.15K.

Mole fraction (X ₂)	ρ (kg m ⁻³)	U (m s ⁻¹)	$V \times 10^4$ (m ³ mol ⁻¹)	$L_f \times 10^{11}$ (m)	$\beta_s \times 10^{10}$ (m ² N ⁻¹)	$Z \times 10^{-6}$ (kg m ⁻² s ⁻¹)
0	852.4	1289.2	1.246	5.515	7.059	1.099
0.0601	868.7	1289.5	1.372	5.495	6.923	1.120
0.1212	882.5	1289.8	1.500	5.474	6.811	1.138
0.2004	898.8	1290.2	1.663	5.447	6.684	1.160
0.2802	912.3	1290.5	1.828	5.420	6.582	1.177
0.3407	922.2	1290.8	1.950	5.400	6.508	1.190
0.4118	930.4	1291.2	2.098	5.376	6.447	1.201
0.4924	937.9	1291.5	2.267	5.349	6.392	1.211
0.5502	943.2	1291.7	2.387	5.329	6.354	1.218
0.6128	947.7	1291.9	2.519	5.308	6.322	1.224
0.6713	952.5	1292.1	2.639	5.288	6.288	1.231
0.7441	955.1	1292.3	2.796	5.263	6.269	1.234
0.8372	957.5	1292.6	3.000	5.232	6.251	1.238
0.9305	960.5	1292.8	3.200	5.200	6.229	1.242
1	961.3	1293	3.354	5.177	6.222	1.243

From Table 3, both isentropic compressibility (β_s) and intermolecular free length (L_f) decrease whereas specific acoustic impedance (Z) increases with an increase in DEHPA concentration (X_2) suggest that (i) there is a significant interaction between components of binary mixtures and (ii) a structure promoting behavior [19-20].

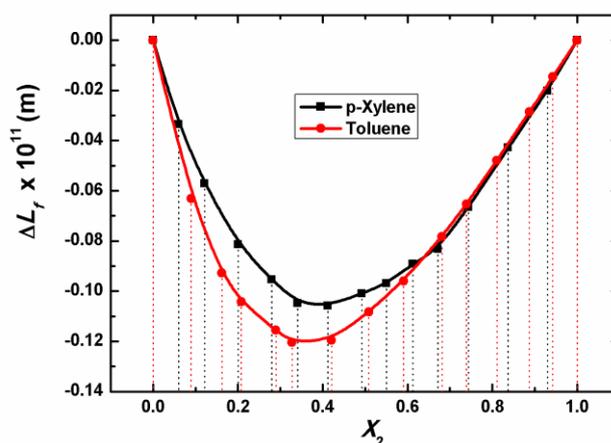


Figure 1. Deviation in intermolecular free length (ΔL_f) versus mole fraction (X_2) of DEHPA.

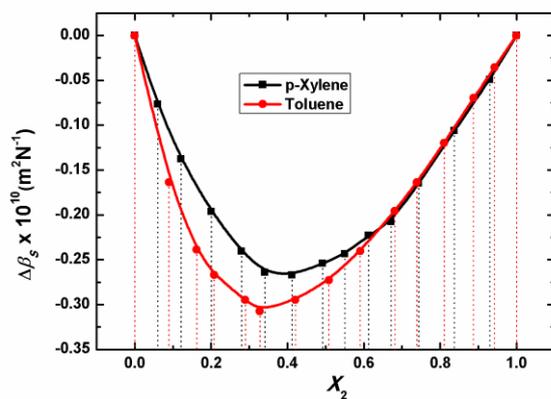


Figure 2. Deviation in isentropic c compressibility ($\Delta\beta_s$) vs. mole fraction (X_2) of DEHPA.

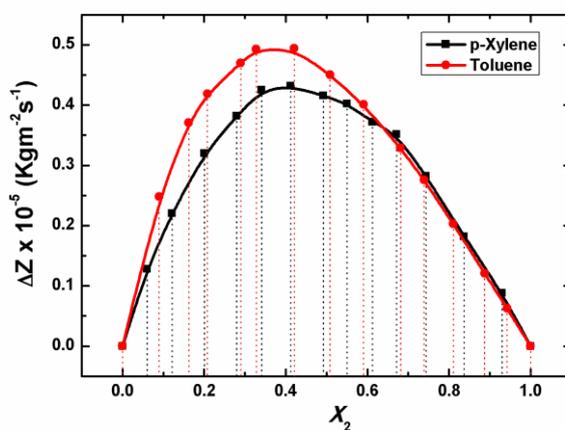


Figure 3. Deviation in acoustic impedance (ΔZ) vs. mole fraction (X_2) of DEHPA.

In Figure 1-3, the negative values of deviation of intermolecular free length (ΔL_f), isentropic compressibility ($\Delta\beta_s$), and positive values of specific acoustic impedance (ΔZ) of both binary mixtures, i.e., *p*-xylene / toluene + DEHPA indicate strong specific interactions between component molecules. Interstitial accommodation of smaller molecules (toluene / *p*-xylene) in the voids created by bigger molecules (DEHPA), probably lead to compact structure [12-15, 19, 20].

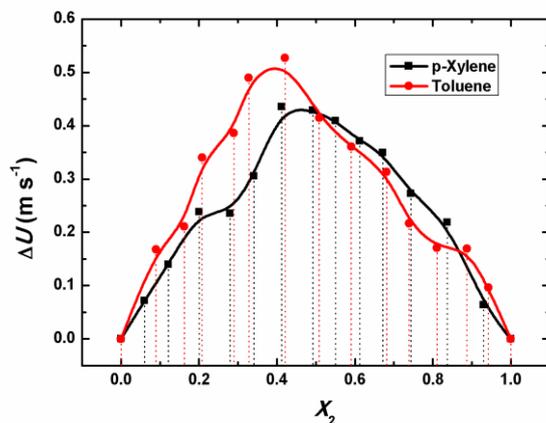


Figure 4. Deviation in ultrasonic velocity (ΔU) vs. mole fraction (X_2) of DEHPA.

The variation of ΔU (Figure 4) has been observed positive over the entire mole fraction range of DEHPA. The positive ΔU values corroborate the result of ΔL_f , $\Delta\beta_s$ and ΔZ predict strong force between the unlike molecules [17-19]. The trend of intermolecular free length (ΔL_f), isentropic compressibility ($\Delta\beta_s$), excess volume (V^E) are negative, whereas acoustic impedance (ΔZ), ultrasonic velocity (ΔU) is positive for both systems under study over the whole composition range specifies that the liquid mixture is less compressible than the pure liquids, forming the complex and the unlike molecules in the mixture are more tightly bound than in pure liquids. It confirms the presence of relatively strong molecular interaction [17-19], and the strength of the interaction between the component molecules follows toluene + DEHPA > *p*-xylene+ DEHPA.

The values of dielectric constant (ϵ) and dipole moment (μ) of all pure components [9, 12, 19]:

$$\text{DEHPA } (\epsilon_D \sim 4.46) > \text{toluene } (\epsilon_T \sim 2.354) > \textit{p}\text{-xylene } (\epsilon_X \sim 2.245)$$

$$\text{DEHPA } (\mu_D \sim 2.74 \text{ D}) > \text{toluene } (\mu_T \sim 0.36 \text{ D}) > \textit{p}\text{-xylene } (\mu_X \sim 0 \text{ D})$$

Due to slightly high values in dielectric constant (ϵ) and dipole moment (μ) values of toluene than *p*-xylene may imply stronger molecular interaction in the toluene mixture.

The excess molar volume, V^E (Figure 5) is negative for both binary mixtures, and the magnitude of the maximum value of V^E is slightly more in toluene + DEHPA than *p*-xylene + DEHPA. This also suggests that the unlike molecules are more closely packed in the mixture than in the pure stage and further indicates attractive molecular interaction between component molecules, i.e., strong interactions between unlike molecules [19-21].

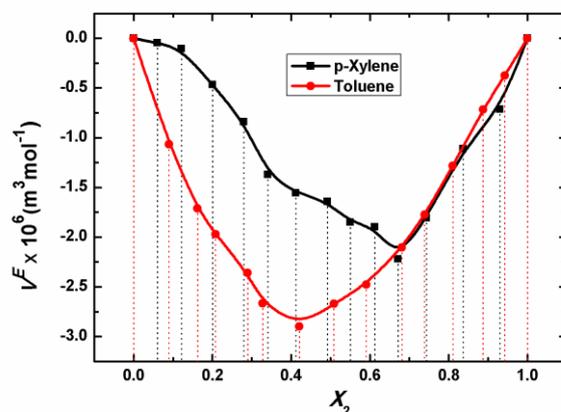


Figure 5. Excess molar volume (V^E) vs. mole fraction (X_2) of DEHPA.

A plausible explanation to above results on molecular interaction can be drawn in two ways (i) because of possible hydrogen bonding ($\pi \cdots \cdots \text{OH}$) between $\text{H}^{\delta+}$ of the hydroxyl group of DEHPA and a π -electron cloud of an aromatic ring, through the electron donor-acceptor type of interaction and (ii) it may also be presumed of hydrogen bonding ($\text{P}=\text{O} \cdots \cdots \text{H}-$) between unlike molecules due to hydrogen bonding through lone pair $\text{O}^{\delta-}$ of $\text{P}=\text{O}$ group of D2EHPA and $\text{H}^{\delta+}$ of CH_3 group of *p*-xylene/ toluene, resulting in negative values of V^E in both toluene + DEHPA and *p*-xylene + DEHPA mixtures. This may lead to volume contraction, means negative V^E , and the strength of the interaction between the component molecules, which corroborates with the results of ΔL_f , $\Delta\beta_s$, ΔZ , ΔU , that follows the same relation, i.e., toluene + DEHPA > *p*-xylene + DEHPA. Again, due to the presence of an additional methyl group ($-\text{CH}_3$) in *p*-xylene, the molecular interaction decreases with DEHPA in comparison to toluene.

This reveals that the additional methyl group in *p*-xylene has influenced the sign and magnitude of excess/ deviation functions that result in a decrease in interaction in the *p*-xylene case in comparison to toluene due to structural effect. The degree of interaction is relatively stronger in toluene may be due to its single methyl group. Interstitial accommodation due to the size effect of unlike molecules along with the van der Waals dispersion force may not be ignored in the computation of resultant effect. The strength of interaction between the component molecules: toluene + DEHPA > *p*-xylene+ DEHPA.

4. Conclusions

In the present comparison study, the molecular interaction between *p*-xylene / toluene + DEHPA has been displayed graphically, and intermolecular interactions are analyzed through the nature of negative trends in intermolecular free length (ΔL_f), isentropic compressibility ($\Delta\beta_s$), excess volume (V^E), and positive trends in acoustic impedance (ΔZ), ultrasonic velocity (ΔU). The variation of excess/ deviation functions of liquid mixtures over the entire composition of DEHPA indicates the presence of molecular interaction in the binary mixture of *p*-xylene/ toluene and DEHPA. The degree of interaction is relatively stronger in toluene as a comparison to *p*-xylene. This study may be useful in the solvent extraction process.

Funding

This research received no external funding.

Acknowledgments

The authors are thankful to the Director, Institute of Minerals and Materials Technology (IMMT), Bhubaneswar, for providing necessary facilities to carry out the research work. The authors are grateful to the President, Vice President, and Registrar of GIET University, Gunupur, for motivation and support.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Prasad, G.; Reddy, K.M.; Padamasuvarna, R.; Mohan, T.M.; Krishna, T.V.; Rao, S.G.; Investigations of Molecular Interactions in the Binary Mixtures of 1-Butyl-3-methylimidazolium bis(Trifluoromethanesulfonyl) Amide and 2-Propoxyethanol from T = (298.15 to 323.15) K at Atmospheric Pressure. *J. Sol. Chem.* **2018**, *47*, 1980–2006, <https://doi.org/10.1007/s10953-018-0833-x>.
2. Santos, A.; Moita, M.-L.; Nobre, L.; Lampreia, I. A volumetric and acoustic study of pseudo-binary mixtures of (water+ 1,3- propanediol + 3-butoxy propan-1-amine) from T=(283.15 to 303.15) K. *J. Chem. Thermodyn.* **2019**, *128*, 344-351, <https://doi.org/10.1016/j.jct.2018.08.033>.
3. Kurdakova, S.V.; Zapolskih, T.V.; Kovalenko, N.A.; Uspenskaya, I.A. Volumetric Properties of the D2EHPA–o-Xylene–Neodymium (Samarium, Europium, Gadolinium, Terbium, Dysprosium) Di(2-ethylhexyl)phosphate Systems at 298.15 K. *J. Chem. Eng. Data.* **2018**, *63*, 3839–3845, <https://doi.org/10.1021/acs.jced.8b00487>.
4. Ankita; Chand, D.; Nain, A.K. Molecular interactions of drug semicarbazide hydrochloride in aqueous-D-xylose/L-arabinose solutions at different temperatures: Volumetric, acoustic and viscometric study. *J. Chem. Thermodynamics* **2020**, *146*, <https://doi.org/10.1016/j.jct.2020.106106>.
5. Wagh, P.S.; Bhumkar, A.N.; Rathnam, M.V. Excess Volume, Viscosity, and Isentropic Compressibility of Methyl Acrylate+Alkane Binary Mixtures. *J. Chem. Eng. Data.* **2020**, *65*, 2343-2350, <https://dx.doi.org/10.1021/acs.jced.9b00924>.

6. Bhanuprakash, P.; Gardas, R.L.; Prathibha, R.; Sivakumar, K.; Jyothi, N.V.V. Insights into non-ideal behaviour of benzyl alcohol with (C2-C4) carboxylic acids through volumetric, ultrasonic and ATR-FTIR spectroscopic studies. *Phy. Chem. Liq.* **2020**, <https://doi.org/10.1080/00319104.2020.1808654>.
7. Das, D.; Juvekar, V.A.; Rupawate, V.H.; Ramprasad, K.; Bhattacharya, R. Effect of the nature of organophosphorous acid moiety on co-extraction of U(VI) and mineral acid from aqueous solutions using D2EHPA, PC88A and Cyanex 272. *Hydrometallurgy* **2015**, *152*, 129–138, <http://dx.doi.org/10.1016/j.hydromet.2014.12.018>.
8. Kumar, N.; Binnemans, B.K. Effect of the diluent on the solvent extraction of neodymium (III) by bis(2-ethylhexyl)phosphoric acid (D2EHPA). *Hydrometallurgy* **2018**, *177*, 146–151, <https://doi.org/10.1016/j.hydromet.2018.03.012>.
9. Dalai, B.; Dash, S.K.; Singh, S.K.; Swain, N.; Swain, B.B. Ultrasonic and ³¹P NMR investigations of an acidic nuclear extractant with some monosubstituted benzenes. *J. Chem. Thermodyn.* **2016**, *93*, 143–150, <https://doi.org/10.1016/j.jct.2015.09.036>.
10. Dalai, B.; Dash, S.K.; Singh, S.K.; Swain, B.B. H NMR and acoustic response of binary mixtures of an organophosphorous extractant with 1-alkanols (C1–C4, C8). *J. Mol. Liq.* **2015**, *208*, 151–159, <https://doi.org/10.1016/j.molliq.2015.04.026>.
11. Dalai, B.; Dash, S.K.; Singh, S.K. Viscometric, volumetric and acoustic properties of binary mixtures of a nuclear extractant with monocarboxylic acids (C₁–C₃) at 303.15 K. *Indian J. pure Appl. Phys.* **2014**, *52*, 24–29.
12. Losetty, V.; Chittluri, N.R.; Gardas, R.I.; Kumar, K.S. FT-IR study of excess thermodynamic properties of binary liquid mixtures of p-xylene with 1-alkanols at 303.15K. *J. Mol. Liq.* **2015**, *207*, 171–176, <http://dx.doi.org/10.1016/j.molliq.2015.03.031>.
13. Keshapolla, D.; Ijadar, S.P.; Gardas, R.L. Temperature dependent apparent molar properties of trihexylammonium carboxylate based protic ionic liquids in toluene and dodecane. *J. Mol. Liq.* **2018**, *272*, 1058–1069, <https://doi.org/10.1016/j.molliq.2018.10.114>.
14. Moncayo-Riascos, I.; Taborda, E.; Hoyos, B.A.; Franco, C.A.; Cortés, F.B. Theoretical-experimental evaluation of rheological behavior of asphaltene solutions in toluene and p-xylene: Effect of the additional methyl group. *J. Mol. Liq.* **2020**, *303*, <https://doi.org/10.1016/j.molliq.2020.112664>.
15. Srirachat, W.; Wannachod, T.; Pancharoen, U.; Kheawhom, S. Effect of polarity and temperature on the binary interaction between D2EHPA extractant and organic solvents (kerosene, n-heptane, chlorobenzene and 1-octanol): Experimental and thermodynamics. *Fluid Phase Equilib.* **2017**, *434*, 117–129, <https://doi.org/10.1016/j.fluid.2016.11.029>.
16. Savitha Jyostna, T.; Satheesh, B.; Sreenu, D.; Ramesh, G.; Jayanthi Rani, E. The study of thermo-physical properties of binary liquid mixtures of isoamyl alcohol with amines at 298.15–308.15 K. *Phy. Chem. Liq.* **2019**, *58*, 349–363, <https://doi.org/10.1080/00319104.2019.1594226>.
17. Sharma, V.K.; Malik, S.; Solanki, S. Thermodynamic Studies of Molecular Interactions in Mixtures Containing Tetrahydropyran, 1,4-Dioxane, and Cyclic Ketones. *J. Chem. Eng. Data* **2017**, *62*, 623–632, <https://doi.org/10.1021/acs.jced.6b00606>.
18. Shakila, A.; Ravikumar, S.; Raveendra, M.; Sivakumar, K.; Raju, R.; Pandiyan, V. Thermodynamic and FT-IR study on molecular interactions between ethyl lactate with alkyl amines at different temperatures. *Phy. Chem. Liq.* **2019**, *57*, 117–136, <https://doi.org/10.1080/00319104.2018.1432047>.
19. Rajalakshmi, R.; Ravikumar, S.; Gaba, R.; Pandiyan, V. Thermodynamic properties and IR studies of binary mixtures of benzyl amine with alkyl esters at different temperatures. *Chem. Data Collect.* **2019**, *24*, <https://doi.org/10.1016/j.cdc.2019.100278>.
20. Vuksanovic, J.; Soldatovic, D.; Radovic, I.; Visak, Z.; Kijevcanin, M. Thermodynamic characterization of binary mixtures of poly(propylene glycol) 425 with toluene and o-, m- and p-xylenes. *J. Chem. Therm.* **2019**, *131*, 393–403, <https://doi.org/10.1016/j.jct.2018.11.020>.
21. Gahlyan, S.; Rani, M.; Devi, R.; Park, S.-J.; Maken, S. Volumetric, acoustic and optical studies of ternary mixture of diisopropyl ether, n-heptane and n-octane. *J. Mol. Liq.* **2020**, *306*, <https://doi.org/10.1016/j.molliq.2020.112605>.