



SHORT COMMUNICATION

Density, viscosity, ultrasonic velocity and excess thermodynamic parameters of ternary liquid mixtures of morpholine + 1,4-dioxane + toluene or nitrobenzene at 308.15 K

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Abstract: Densities, viscosities and ultrasonic velocities were measured for the two ternary liquid mixtures containing morpholine (1) + 1,4-dioxane (2) + nitrobenzene (3) or + toluene (3) at 308.15 K over the entire range of mole fractions. Thermodynamic parameters, such as excess volume (V^E), deviations in adiabatic compressibility (ΔK_S), free length (ΔL_F), isothermal compressibility ($\Delta\beta_T$), free volume (ΔV_F) and viscosity ($\Delta\eta$) were calculated and applied to the Redlich–Kister polynomial equation to determine the appropriate coefficients. The deviations of the ternary liquid mixtures from their ideal behaviour were determined from the measured and calculated thermodynamic properties. In addition, an insight into the molecular structure and possible interactions for the investigated mixtures was attempted.

Keywords: ternary mixture; thermodynamic properties; Redlich–Kister equation; excess values; molecular interactions.

INTRODUCTION

Currently, many engineering fields require information regarding thermodynamic and transport properties of liquid mixtures. The study of transport fluid phenomena requires knowledge of density and viscosity of the system.^{1,2} Other than density and viscosity,³ an ultrasonic study provides enormous information regarding molecular interactions and the structural behaviour of the molecules in a mixture.

The effectiveness of operations in chemical and engineering processes can be tuned from the investigation of physical properties of the employed liquids

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and their mixtures. Binary mixtures provide molecular interactions prevalent in such operations, but are of limited applicability. Ternary liquid mixtures formed from the corresponding binary mixtures present more intricate interactions encountered frequently in real time applications. Morpholine, a self-associated amino ether⁴ has a wide range of applications in synthetic and industrial processes, in general for extraction processes, extractive distillation and as a solvent. Another compound, *p*-dioxane, is commonly used in polymerizations and other chemical reactions, in the cleaning of polymer surfaces, electronic materials^{5,6} and is an additives to gasoline due to its octane enhancing and pollution reducing properties.^{7,8} Nitrobenzene is a versatile solvent used in synthetic and electrochemical research. It is an important raw material for the synthesis of explosives. Toluene is mainly used as a precursor to benzene via hydro dealkylation. In addition to the synthesis of benzene and xylene, toluene is a feedstock for toluene diisocyanate production (used in the manufacture of polyurethane foam), trinitrotoluene (the explosive, TNT) and a number of synthetic drugs.⁹

The chemicals considered in the current investigation, morpholine, 1,4-dioxane, toluene and nitrobenzene, have applications in different fields, such as pharmaceutical, metallurgy, polymer, petrochemical and electronic industries. The thermodynamic behaviour of the liquid mixtures of non-aromatic cyclic ethers and derivatives of benzene hence constitute an important area of investigations. The molecular interactions influence densities, velocities, ultrasonic velocities and other thermodynamic properties. The investigation of their ternary mixtures assumes greater significance as it mimics real time intricate molecular interactions much better. Hence, the measurement of densities, viscosities, ultrasonic velocities and other calculated excess thermodynamic properties of ternary mixtures of morpholine (1) + 1,4-dioxane (2) with toluene (3) and nitrobenzene (3) warrants immediate attention. The investigated properties, such as excess volume, adiabatic and isothermal compressibility, free length, free volume and viscosity, could be used to parameterize and optimize mass and energy transfer processes and flow operations associated with the applications of the two ternary mixtures. Therefore a detailed study of the thermodynamic and transport properties of ternary mixtures of morpholine (1) + 1,4-dioxane(2) with toluene (3) or nitrobenzene (3) at 308.15 K form the main scope of the present work.

EXPERIMENTAL

Morpholine and 1,4-dioxane (Merck, Mumbai, India), toluene (Loba, Mumbai, India), Nitrobenzene (Fine chemicals, Mumbai, India) were all of Analar grades with 99 % purity. The purchased chemicals were purified by the double distillation method. Hence, techniques to ascertain purity were not attempted but the measured densities, viscosities and ultrasonic velocities were confirmed by comparing with earlier literature reports (Table I). Ternary liquid mixtures were prepared by weight volume in airtight stoppered bottles using an analytical balance with an accuracy of ± 0.0001 g. The densities of the pure liquids and their mix-

tures were measured using the relative density method. Relative density bottle of 10 mL capacity was cleaned successively with chromic acid, distilled water and acetone and then dried and used for the density measurements.¹⁰ An electronic balance was used to measure the density.¹¹ The accuracy of the measurement of density by relative density method depends on the accuracy of measurement of weight. Density values were accurate to $\pm 0.0002 \text{ g cm}^{-3}$.

TABLE I. Densities (ρ), viscosities (η) and ultrasonic velocities (U) of pure morpholine, nitrobenzene, 1,4-dioxane and toluene; $T = 308.15 \text{ K}$

Compound	$\rho \text{ } 10^{-3} / \text{kg m}^{-3}$		η / cP		$U / \text{m s}^{-1}$	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Morpholine ^{19,20}	0.9869	0.9863, 0.9925	2.0977	2.0955	1420	1410
Nitrobenzene ²¹	1.1877	1.1911	1.5678	1.5543	1375	1379
1,4-Dioxane ^{22,23}	1.0167	1.0166, 1.0165	1.025	1.028, 1.014	1300	1300.3
Toluene ^{24,25}	0.8378	0.8566 ^a	0.5099	0.527 ^a	1250	–

^aRefers to values at 303.15 K

Viscosities were measured using an Ostwald viscometer. The viscometer was thoroughly cleaned with chromic acid. It comprises a U-tube the left hand limb of which is essentially a pipette with two defining marks. An electronic digital stopwatch with readability of $\pm 0.01 \text{ s}$ was used to measure the flow time of a liquid between the marks. The ultrasonic velocity values were obtained using an ultrasonic interferometer (Pico, Chennai, India) with a frequency of 2 MHz that was calibrated using water and nitrobenzene. The overall accuracy in the measurement was $\pm 0.2 \%$. All the measurements were realized using a digital thermostat with display accuracy $\pm 0.01 \text{ K}$. The details of the methods and techniques of the measurements have been described earlier.^{12,13}

RESULTS AND DISCUSSION

1,4-Dioxane could be classified as a non-polar solvent, but the distribution of electric charge gives a large quadrupole moment to 1,4-dioxane.^{14,15} The presence of a substituent in the aromatic hydrocarbon should modulate its electron-acceptor ability.^{16,17} The cyclic ethers morpholine and 1,4-dioxane (*p*-dioxane) are hexa cyclic compounds with similar shapes. Morpholine is a non-aromatic cyclic ether containing a secondary amine ($-\text{NH}$) group, which can serve as a site for possible hydrogen bonding. 1,4-Dioxane is a diether and an excellent aprotic solvent with an electron donating ability toward the aromatic ring and has a zero dipole moment.¹⁸ Cyclic ethers have a very small polarity, similar to those of linear ethers that do not have a self-associating nature. Hence no self-interaction or association is possible in 1,4-dioxane.

Nitrobenzene is an aromatic hydrocarbon containing an NO_2 as a functional group. The electron withdrawing $-\text{NO}_2$ group draws π -electrons from the aromatic electron cloud of benzene generating a δ^+ charge in it. Hence, the mode of self-interaction in nitrobenzene is a potential anionic π stacking interaction possible through the nucleophilic oxygen atom of the $-\text{NO}_2$ group with the generated δ^+ charge of the aromatic π -electron cloud of benzene moiety. Toluene is a

methyl carrying benzene ring in which the methyl releases an electron to the benzene moiety. Two different ternary liquid solutions were prepared by mixing morpholine (1) + 1,4-dioxane (2) + nitrobenzene (3) as well as morpholine (1) + 1,4-dioxane (2) + toluene (3) by varying their mole fractions. Experimental densities, viscosity, ultrasonic velocities of the pure components of the liquid mixture were compared with literature values and are reported in Table I. Also their excess thermodynamic parameters were calculated and tabulated at a temperature of 308.15 K to understand the possible interactions between them.

The excess volume values for the ternary mixtures were calculated using the relation:

$$V^E = \left(\frac{X_1 M_1 + X_2 M_2 + X_3 M_3}{\rho_{\text{mix}}} \right) - \left(\frac{X_1 M_1}{\rho_1} \right) - \left(\frac{X_2 M_2}{\rho_2} \right) - \left(\frac{X_3 M_3}{\rho_3} \right) \quad (1)$$

where X_1 , X_2 and X_3 , M_1 , M_2 and M_3 and ρ_1 , ρ_2 and ρ_3 are the mole fractions, molar masses and densities of pure components 1, 2 and 3, respectively.

The adiabatic compressibility (K_S) was calculated from the Laplace equation:²⁶

$$K_S = \frac{1}{\rho U^2} \quad (2)$$

where ρ and U are the density and ultrasonic velocity of the liquid mixtures, respectively. From the above equation, the excess adiabatic compressibility (ΔK_S) was calculated by:

$$\Delta K_S = K_S - \phi_1 K_{S1} - \phi_2 K_{S2} - \phi_3 K_{S3} \quad (3)$$

where K_{S1} , K_{S2} and K_{S3} are adiabatic compressibility of the pure liquids and ϕ_1 , ϕ_2 and ϕ_3 are, respectively, the volume fractions of pure liquids calculated by the relation:

$$\phi_1 = \frac{\frac{X_1 M_1}{\rho_1}}{\frac{X_1 M_1}{\rho_1} + \frac{X_2 M_2}{\rho_2} + \frac{X_3 M_3}{\rho_3}} \quad (4)$$

The viscosity was calculated using the relation:

$$\eta = \left(At - \frac{B}{t} \right) \rho \quad (5)$$

where A and B are constants characteristics of the viscometer that are calculated using the standard liquids water and nitrobenzene, t is the flow time, ρ is the density.

Excess viscosity values were calculated using the following relation:

$$\Delta\eta = \eta (X_1\eta_1 + X_2\eta_2 + X_3\eta_3) \quad (6)$$

where η_1 and η_2 are the viscosity values of pure components 1 and 2, respectively.

The free length was calculated using the relation:

$$L_F = \frac{K}{u\rho^{1/2}} \quad (7)$$

where K is the Jacobson constant,^{27,28} which is a temperature dependent constant but independent of the nature of the liquid.

The isothermal compressibility was calculated using the relation:

$$\beta_T = \frac{1.71 \times 10^{-3}}{\left(\frac{T^4}{9u^2\rho^{4/3}} \right)} \quad (8)$$

To calculate the free volume, Suriyanarayana²⁹ proposed the relation:

$$V_f = \left(\frac{M_{\text{eff}}u}{K\eta} \right)^{3/2} \quad (9)$$

where K is a temperature independent constant that is equal to 4.28×10^9 for all the liquids and M_{eff} is the effective molecular weight of the mixture, calculated using the relation:

$$M_{\text{eff}} = X_1M_1 + X_2M_2 + X_3M_3 \quad (10)$$

where X_1, X_2, X_3 and M_1, M_2, M_3 are the mole fractions and molar masses of the pure components 1, 2 and 3, respectively.

The excess values of the other parameters were calculated using the relation:

$$\begin{aligned} A^E &= A_{\text{exp}} - A_{\text{id}} \\ A_{\text{id}} &= \sum X_i A_i \end{aligned} \quad (11)$$

where X_i and A_i are the mole fraction and parameters of the i^{th} component.

All the calculated excess parameters were fitted to a Redlich–Kister³⁰ type polynomial equation by the least squares method to derive the adjustable parameters a, b and c .

For binary mixtures:

$$A^E = X_1X_2(a + b(X_1 - X_2) + c(X_1 - X_2)) \quad (12)$$

For ternary mixtures:

$$A^E = X_1X_2X_3(a + bX_1(X_2 - X_3) + cX_1^2(X_2 - X_3)^2) \quad (13)$$

Using the theoretical values, all excess parameters were calculated and the standard deviation values were calculated using the relation:

$$\sigma = \left[\frac{(A_{\text{exp}} - A_{\text{cal}})^2}{(n - m)} \right]^{1/2} \quad (14)$$

where n is the number of measurements and m is the number of adjustable parameters.

The calculated thermodynamic parameters and excess acoustical parameters for the ternary liquid mixtures of morpholine, 1,4-dioxane with nitrobenzene or toluene are represented in Tables II–VII.

TABLE II. Thermodynamic transport properties for the ternary liquid mixtures of morpholine + 1,4-dioxane + nitrobenzene at 308.15 K

X_1	X_2	$\rho \times 10^{-3} / \text{kg m}^{-3}$	$V^E \times 10^6 / \text{m}^3 \text{mol}^{-1}$	$U / \text{m s}^{-1}$	ϕ_1	ϕ_2
0.0563	0.4676	1.1051	-0.0882	1370	0.0524	0.4274
0.0789	0.5073	1.0936	-0.0871	1350	0.0742	0.4687
0.0647	0.5290	1.0929	-0.1000	1360	0.0610	0.4895
0.1742	0.5240	1.0710	-0.1050	1364	0.1671	0.4933
0.1300	0.6545	1.0565	-0.1206	1330	0.1267	0.6265
0.1443	0.5808	1.0670	-0.1087	1334	0.1391	0.5498
0.2481	0.3216	1.0913	-0.0625	1356	0.2321	0.2953
0.1622	0.2727	1.1169	-0.0765	1360	0.1483	0.2449
0.1635	0.7323	1.0332	-0.0486	1328	0.1628	0.7156
0.1860	0.7332	1.0284	-0.0908	1330	0.1859	0.7194
0.2184	0.6593	1.0322	0.2031	1324	0.2164	0.6414
0.2239	0.2655	1.1028	0.1982	1334	0.2066	0.2404
0.2312	0.6790	1.0256	0.1880	1340	0.2304	0.6645
0.2549	0.3633	1.0821	-0.0228	1356	0.2405	0.3365
0.2644	0.6731	1.0202	0.0981	1300	0.2648	0.6618
0.2955	0.3563	1.0749	-0.0236	1350	0.2804	0.3319
0.3286	0.0819	1.1159	-0.0557	1356	0.2985	0.0730
0.3292	0.3365	1.0722	-0.0919	1358	0.3130	0.3140
0.3908	0.1457	1.0929	-0.0627	1364	0.3626	0.1327
0.3703	0.3171	1.0668	-0.0698	1374	0.3532	0.2969
0.3880	0.1855	1.0866	-0.0663	1372	0.3624	0.1701
0.4323	0.2993	1.0568	-0.0667	1372	0.4153	0.2823
0.4503	0.3123	1.0501	-0.0311	1376	0.4148	0.2960
0.4996	0.3390	1.0341	-0.0260	1380	0.4889	0.3257

TABLE III. Thermodynamic transport properties for the ternary liquid mixtures of morpholine + 1,4-dioxane+nitrobenzene at 308.15 K

ΔK_S TPa ⁻¹	η cP	$\Delta \ln(\eta / \text{cP})$	$\Delta L_F \times 10^{-10}$ m	$\Delta \beta_T \times 10^{-12}$ kg ⁻¹ K ⁻¹ m ² s	$\Delta V_F \times 10^{-7}$ m ³ mol ⁻¹
-24.1217	1.2612	-0.0790	-2.0396	-4.6571	-1.6313
-11.9790	1.1985	-0.1306	-1.7098	-2.8968	-1.6010
-21.0593	1.2965	-0.0143	-0.8265	-4.1598	-1.5938
-20.6202	1.2464	-0.1175	-0.5238	-3.9033	-1.5598

TABLE III. Continued

ΔK_S TPa ⁻¹	η cP	$\Delta \ln(\eta / \text{cP})$	$\Delta L_F \times 10^{-10}$ m	$\Delta \beta_T \times 10^{-12}$ kg ⁻¹ K ⁻¹ m ² s	$\Delta V_F \times 10^{-7}$ m ³ mol ⁻¹
-2.4442	1.1048	-0.1680	-0.1092	-1.3684	-1.4998
-1.7110	1.1304	-0.1889	-0.2212	-1.3028	-1.5371
-0.4043	1.3191	-0.1885	-0.5035	-1.1682	-1.6506
-2.4442	1.3750	-0.1195	-0.8807	-1.5255	-1.7073
-1.7110	1.0757	-0.1703	-0.8371	-1.0378	-1.4442
-0.4043	1.0942	-0.1617	-0.7828	-1.0795	-1.4363
-2.7728	1.0604	-0.2504	-0.7085	0.5059	-1.4673
-3.6062	1.3576	-0.1692	-1.4130	-1.6677	-1.6908
-4.4400	1.0772	-0.2289	-0.8055	-1.2732	-1.4519
7.4277	1.1612	-0.3269	-1.4170	-1.4045	-1.6239
19.5153	1.1643	-0.1602	-0.2612	3.7882	-1.4447
5.5176	1.2751	-0.2354	-1.2356	-4.9321	-1.6148
-2.4875	1.3538	-0.3207	-1.5883	1.2305	-1.7601
29.8909	1.4627	-0.0740	-1.2445	-1.0445	-1.6154
3.8725	1.5391	-0.1294	-1.3880	0.1304	-1.7036
15.0459	1.5258	-0.0404	-1.3020	-2.2554	-1.6129
-0.5578	1.3765	-0.2092	-1.4245	-0.9903	-1.6814
-9.5182	1.5808	-0.0235	-1.1065	-1.5260	-1.6023
-0.7945	1.6804	0.0747	-1.0648	-1.8432	-1.5892
-5.0662	1.8288	0.2149	-0.8469	-1.9956	-1.5577

TABLE IV. Thermodynamic transport properties for the ternary liquid mixtures of morpholine + 1,4-dioxane+toluene at 308.15 K

X_1	X_2	$\rho \times 10^{-3} / \text{kg m}^{-3}$	$V^E \times 10^6 / \text{m}^3 \text{mol}^{-1}$	$U / \text{m s}^{-1}$	ϕ_1	ϕ_2
0.0477	0.4578	0.9248	0.0166	1280	0.0469	0.4555
0.0756	0.5013	0.9387	-0.0049	1290	0.0744	0.4995
0.0781	0.5043	0.9407	-0.0168	1280	0.0769	0.5024
0.1146	0.5171	0.9487	-0.0195	1290	0.1130	0.5156
0.1121	0.4735	0.9424	-0.0405	1282	0.1104	0.4719
0.1305	0.4508	0.9403	-0.0321	1284	0.1285	0.4493
0.1572	0.3949	0.9337	-0.0261	1290	0.1549	0.3936
0.1570	0.3537	0.9274	-0.0387	1286	0.1546	0.3524
0.1612	0.3151	0.9203	-0.0354	1280	0.1587	0.3139
0.2186	0.2884	0.9239	-0.0281	1290	0.2155	0.2875
0.2066	0.2503	0.9201	-0.0822	1280	0.2034	0.2494
0.2350	0.2269	0.9144	-0.0184	1290	0.2316	0.2261
0.2409	0.3640	0.9399	-0.0177	1286	0.2378	0.3634
0.2443	0.2782	0.9273	-0.0435	1290	0.2409	0.2775
0.2435	0.0065	0.8825	-0.0916	1274	0.2394	0.0065
0.2802	0.3778	0.9305	0.1780	1280	0.2768	0.3776
0.3172	0.3883	0.9090	0.5081	1290	0.3137	0.3884
0.3044	0.0966	0.9527	-0.5729	1276	0.3000	0.0963
0.3532	0.4173	0.9302	0.3803	1286	0.3497	0.4179
0.3610	0.4471	0.9090	0.7011	1294	0.3576	0.4479

TABLE IV. Continued

X_1	X_2	$\rho \times 10^{-3} / \text{kg m}^{-3}$	$V^E \times 10^6 / \text{m}^3 \text{mol}^{-1}$	$U / \text{m s}^{-1}$	ϕ_1	ϕ_2
0.3978	0.4479	0.8972	0.9091	1292	0.3943	0.4491
0.3867	0.1397	0.9315	-0.1300	1296	0.3819	0.1396
0.3952	0.1046	0.9090	0.0635	1316	0.3902	0.1045
0.3570	0.0949	0.8853	0.2553	1310	0.3522	0.0947

TABLE V. Thermodynamic transport properties for the ternary liquid mixtures of morpholine + 1,4-dioxane+toluene at 308.15 K

$\Delta K_S / \text{TPa}^{-1}$	η / cP	$\Delta \ln(\eta / \text{cP})$	$\Delta L_F \times 10^{-11} / \text{m}$	$\Delta \beta_T \times 10^{-12} / \text{kg}^{-1} \text{K}^{-1} \text{m}^2 \text{s}$	$\Delta V_F \times 10^{-9} / \text{m}^3 \text{mol}^{-1}$
-8.8433	0.5730	-0.2994	8.5711	-1.7429	-6.6011
-12.6698	0.6440	-0.2854	5.9629	-2.4475	-6.3165
-3.4661	0.6548	-0.2793	7.0119	-1.0570	-6.2948
-6.6581	0.6842	-0.3065	5.2522	-1.5440	-6.0352
-3.2808	0.7263	-0.2431	7.1149	-1.1156	-6.1844
-2.6529	0.7015	-0.2846	7.3635	-1.0779	-6.1317
-7.9157	0.6734	-0.3277	7.8463	-1.7450	-6.1220
-6.4852	0.6456	-0.3384	9.2292	-1.6720	-6.2377
-2.4236	0.5942	-0.3801	10.0900	-0.9508	-6.3124
-4.4115	0.6198	-0.4245	10.0110	-1.2576	-6.0373
-1.4974	0.5937	-0.4180	11.8296	-1.0168	-6.2179
-4.3844	0.6134	-0.4289	11.4725	-1.2562	-6.1121
8.2209	0.7931	-0.3134	8.6335	0.6184	-5.7072
-1.5954	0.6918	-0.3845	9.9783	-0.9420	-5.9203
-1.3257	0.9114	-0.0531	18.3356	-0.9221	-6.7381
32.9812	1.0040	-0.1633	10.3046	0.4898	-5.4419
50.5900	1.0018	-0.2220	11.0722	0.8325	-5.1804
-23.1576	0.7577	-0.3294	11.5409	-0.5619	-6.0823
54.3454	0.6940	-0.5924	9.7244	0.8502	-4.8393
67.8794	0.8107	-0.4987	10.3545	1.1543	-4.7204
88.6874	0.7787	-0.5828	11.8775	1.5141	-4.4853
1.1146	1.1744	-0.0461	11.0315	-0.0754	-5.4758
-7.1118	1.2879	0.0069	10.9049	-1.3617	-5.5285
4.1838	1.1953	0.0347	13.5514	0.0885	-5.7907

TABLE VI. Coefficients of the Redlich–Kister equation (Eq. (13)) and standard deviation for the ternary mixture of morpholine + 1,4-dioxane + nitrobenzene at 308.15 K

Parameter	a	b	c	σ
$V^E \times 10^6 / \text{m}^3 \text{mol}^{-1}$	-1.4183	19.8996	211.486	0.0022
$\Delta K_S / \text{TPa}^{-1}$	-1893.438	-910.881	365.991	0.6498
η / cP	46.1904	37.8175	1413.52	0.0166
$\Delta \eta / \text{cP}$	-3.1614	-2.7604	-486.90	0.0006
$\Delta L_F \times 10^{-8} / \text{m}$	-0.4484	1.0761	-7.5793	0.0002
$\Delta \beta_T \times 10^{-11} / \text{kg}^{-1} \text{K}^{-1} \text{m}^2 \text{s}$	-2.1234	-8.4693	613.310	0.0037
$\Delta V_F \times 10^{-7} / \text{m}^3 \text{mol}^{-1}$	-0.4472	-1.1541	-17.881	1.3427

TABLE VII. Coefficients of the Redlich – Kister equation (Eq. (13)) and standard deviation for the ternary mixture of morpholine + 1,4-dioxane + toluene at 308.15 K

Parameter	<i>a</i>	<i>b</i>	<i>c</i>	σ
$V^E \times 10^6 / \text{m}^3 \text{mol}^{-1}$	2.1257	149.639	787.797	0.0016
$\Delta K_S / \text{TPa}^{-1}$	551.687	15015.2	7775.7	0.1439
η / cP	23.4643	-34.7198	972.12	0.0127
$\Delta\eta / \text{cP}$	-12.1066	-42.3119	8.8834	0.0078
$\Delta L_F \times 10^{-8} / \text{m}$	3.0210	-4.0753	0.0104	0.0019
$\Delta\beta_T \times 10^{-11} / \text{kg}^{-1} \text{K}^{-1} \text{m}^2 \text{s}$	2.9982	264.08	1354.2	2.1010
$\Delta V_F \times 10^{-7} / \text{m}^3 \text{mol}^{-1}$	-2.0163	4.4961	-2.0265	0.0022

The sign of the V^E values depends on either expansion or contraction that occurs during the mixing of two liquids. The V^E values are negative for most mole fraction values except for a few at 308.15 K for the ternary mixture containing morpholine + 1,4-dioxane + nitrobenzene. This may be due to the strong molecular interactions between the constituent of liquid mixtures.³¹ The other ternary liquid mixture morpholine + 1,4-dioxane + toluene show positive values for many mole fractions. This may be due to the possibility of weak interactions between the components in the liquid mixtures.

The values of ΔK_S are directly proportional to different size and shape of the components and inversely proportional to the velocity. In addition, ΔK_S varies due to change in the free volume.^{32,33} The negative ΔK_S values for the ternary mixture containing nitrobenzene may be due to the intermolecular interactions between unlike molecules, which may make the system slightly flexible and slightly compressible. The observed positive values of ΔK_S may be due to the weak interaction between the unlike molecules that results in rigidity and less compressibility of the system. The η values also serve as a tool to study the nature of intermolecular interactions. The observation of high magnitude of positive values^{34,35} advocates the possibility for specific strong interactions in the nitrobenzene ternary mixtures. The occurrence of lower magnitude η values for the toluene ternary mixtures suggests the chance for weak and non-specific interactions. The influence of interactions in ternary systems and their deviations from ideal behaviour was studied through excess thermodynamic properties, such as ΔL_F , $\Delta\beta_T$, ΔV_F and $\Delta \ln \eta$.

The analysis and comparison of the excess thermodynamic properties of both ternary systems show more negative deviations were observed for those associated with nitrobenzene than those associated with toluene. Hence, it could be assumed that both the ternary liquid mixture exhibit intermolecular interactions. Furthermore, it indicates the chance for the occurrence of strong intermolecular interactions in ternary mixtures containing nitrobenzene is greater in comparison to those associated with toluene. The presence of a $-\text{NO}_2$ group in nitrobenzene deactivates the electron cloud in the benzene ring, while the $-\text{CH}_3$ group in toluene tends to activate the electron cloud. The examination of the nat-

ure of the functional group attached to the benzene ring aids in analysing the geometrical effects in influencing the possible interactions and also to correlate the observed variations in trends of thermodynamic properties. From the above measured and experimental data, the interactions present between the considered ternary mixtures can be presumed as: morpholine + 1,4-dioxane + nitrobenzene > morpholine + 1,4-dioxane + toluene.

CONCLUSIONS

The densities, ultrasonic velocities, viscosities and other excess thermodynamic properties, such as excess volume, adiabatic compressibility, deviation in viscosity, free length, isothermal compressibility, free volume for the two ternary mixtures of morpholine + 1,4-dioxane + nitrobenzene and morpholine + 1,4-dioxane + toluene were measured at atmospheric pressures and at a temperature of 308.15 K. The relevant values for the pure components of the mixtures are also provided for reference. The corresponding thermodynamic excess parameters were calculated with the formulas reported earlier and fitted to a Redlich–Kister type polynomial equation to determine the variable coefficients. The behaviour of the liquid mixtures and the deviation from ideality has been discussed based on experimental and calculated values. The V^E values suggest the existence of intermolecular interactions between the component molecules in the liquid mixtures. The intermolecular interactions may make the morpholine + 1,4-dioxane + nitrobenzene mixtures slightly flexible and a little compressible indicated as suggested by its ΔK_S values. In contrast, the ΔK_S values of morpholine + 1,4-dioxane + toluene mixtures suggest the possibility for the occurrence of stiffness and a less compressible nature. Both the ternary mixtures exhibit intermolecular interactions between like molecules. The self-interaction may dominate in ternary mixture containing nitrobenzene, and it may become less significant for the ternary mixture associated with toluene. According to the measured and calculated properties, it could be assumed that strong molecular interactions are more possible in morpholine + 1,4-dioxane + nitrobenzene than in morpholine + 1,4-dioxane + toluene. The possibility for activation by the methyl group in toluene and the chance for deactivation by the nitro group in nitrobenzene of the benzene moiety help to rationalize the geometrical effects on the measured and calculated properties.

ИЗВОД

ГУСТИНА, ВИСКОЗНОСТ, УЛТРАЗВУЧНА БРЗИНА И ДРУГИ ТЕРМОДИНАМИЧКИ ПАРАМЕТРИ ТРОЈНИХ ТЕЧНИХ СМЕША МОРФОЛИНА + 1,4-ДИОКСАНА + ТОЛУЕНА ИЛИ НИТРОБЕНЗЕНА НА 308,15 К

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Густине, вискозности и ултразвучне брзине мерене су за две тернарне течне смеше: морфолин (1) + 1,4-диоксан (2) + нитробензен (3) и + толуен (3) на 308,15 К у читавом

распона молских фракција. Израчунати су термодинамички параметри попут вишка запремине (V^E), одступања у адијабатској стишљивости (ΔK_S), слободне дужине (ΔL_F), изотермалне компресибилности ($\Delta\beta_T$), слободне запремине (ΔV_F) и вискозности ($\Delta\eta$) и примењени на Редлих–Кистер (Redlich–Kister) једначину ради одређивања одговарајућих коефицијената. Одступања тројних течних мешавина од њиховог идеалног понашања је одређивано из мерених и израчунатих термодинамичких особина. Такође, покушан је увид у молекуларну структуру и могуће интеракције за испитане смеше.

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