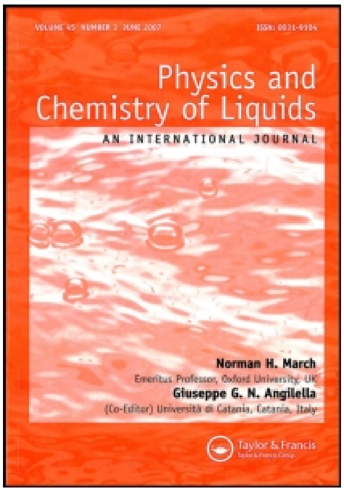

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Volumetric, viscometric and acoustic properties of binary mixtures of 2-propanol with <i>n</i>-alkanes (C_6, C_8, C_{10}) at 298.15 and 308.15 K

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Volumetric, viscometric and acoustic properties of binary mixtures of 2-propanol with *n*-alkanes (C_6, C_8, C_{10}) at 298.15 and 308.15 K

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Densities (ρ), viscosities (η), and speeds of sound, (u) of the binary mixtures of 2-propanol with *n*-alkanes (*n*-hexane, *n*-octane, and *n*-decane) were measured over the entire composition range at 298.15 and 308.15 K and at atmospheric pressure. Using the experimental values of density, viscosity and speed of sound, the excess molar volumes (V^E), viscosity deviations ($\Delta\eta$), deviations in speed of sound (Δu), isentropic compressibility (κ_s), deviations in isentropic compressibility ($\Delta\kappa_s$), and excess Gibbs energies of activation of viscous flow (ΔG^{*E}) were calculated. These results were fitted to the Redlich–Kister type polynomial equation. The variations of these excess parameters with composition were discussed from the viewpoint of intermolecular interactions in these mixtures. The excess properties are found to be either positive or negative depending on the molecular interactions and the nature of liquid mixtures.

Keywords: densities; viscosities; excess molar volume; viscosity deviation; excess Gibbs energy of activation of viscous flow; speeds of sound; isentropic compressibility

1. Introduction

During the last few years the thermodynamic properties of binary mixtures of alcohol + alkane have been studied extensively [1–3]. The mixtures of alcohol with alkane are interesting for a number of scientific reasons, mostly connected to the formulation and testing of models to predict the properties of associating fluids, since the binary systems are composed of an associating liquid, the alcohol and a nonassociating one, the alkane [4]. Alcohol molecules associate mainly by building up linear chains. The extent of this association depends in a specific way on the concentration of the alcohol in the liquid state and on temperature [5]. On the other hand, alkanes are an important series of homologous, nonpolar organic solvents. They have often been used in the study of solute dynamics because their physico-chemical properties as a function of chain length are well-known [6]. The temperature dependence of the thermodynamic properties of these mixtures is also important, from the viewpoint of understanding the extent of self-association of alkanol molecules. The alkane + alkanol mixtures are also used as additives to petrol and in rectification processes for binary azeotropes [7].

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2-Propanol is widely used as coupling and dispersing agent in the chemical, pharmaceutical and household industries and as carrier and extraction solvent for natural products. The particular alkanes were chosen in view of their importance in hydrocarbon processing industries. The main purpose of our study is to characterize the molecular interactions in these systems and subsequently predict the effect of increasing chain length of alkanes and temperature on the molecular interactions.

The present article reports the experimental data for the densities, ρ, viscosities, η, and speeds of sound, u of 2-propanol with *n*-hexane, *n*-octane, and *n*-decane over the entire composition range at $T = (298.15$ and $308.15)$ K and at atmospheric pressure. Using the experimental values of ρ, η, and u, the excess molar volumes (V^E), viscosity deviations ($\Delta\eta$), deviations in speed of sound (Δu), isentropic compressibility (κ_s), deviations in isentropic compressibility ($\Delta\kappa_s$), and excess Gibb's energies of activation of viscous flow (ΔG^{*E}) were calculated. These results were fitted to the Redlich–Kister type polynomial equation [8]. An attempt is also made to rationalise the results by collecting the data on 2-propanol + *n*-alkane mixtures.

2. Experimental

2.1. *Materials*

2-Propanol was supplied by Qualigens Fine Chemicals Pvt. Ltd. (Mumbai, India). The analytical grade *n*-hexane, *n*-octane and *n*-decane were supplied by S.D. Fine Chemicals Ltd. The purities of these reagents are >99% in mass. Before use, all the chemicals were degassed by vacuum pump. The experimentally measured values of ρ, η, u, and κ_s of all the pure components at 298.15 and 308.15 K with their corresponding literature values [9–23] are listed in Table 1. These comparisons indicated good consistency between these results and those presented in the literature.

2.2. *Apparatus and procedure*

The binary mixtures were prepared by mass in special air-tight bottles. The weighing was done on an electronic balance with a precision of ±0.1 mg. The densities were measured using a bicapillary pycnometer of about 10 cm^3 volume and a capillary bore with an internal diameter of 1 mm. The pycnometer was calibrated by using double- distilled, deionized, and degassed water with 997.05 and 994.03 kg m^{-3} with densities at 298.15 and 308.15 K, respectively. The accuracy in density measurements was estimated as $\pm 0.0003 \times 10^3\ \text{kg m}^{-3}$.

The kinematic viscosities, ν, were measured by means of a suspended-level Ubbelohde viscometer. The time of flow was measured with a stopwatch capable of recording to 0.01 s. For each mixture, at least four flow time measurements were performed and the results were averaged. The viscometer was calibrated at the experimental temperatures using the relation $\nu (= \eta/\rho) = (C_1 t - C_2)/t$, where ν is the kinematic viscosity, η is the absolute viscosity, ρ is the density, and t is the flow time of calibration liquid. C_1 and C_2 are calibration constants of the viscometer. The estimated accuracy in η measurements is within ±0.003 mPa s.

The speeds of sound were measured using ultrasonic interferometer (Model MX-3) provided by Mittal Enterprises, New Delhi. The instrument was calibrated by measuring the speeds of sound in standard liquids e.g., water, acetone, cyclohexane, ethanol, etc.

Table 1. Comparison of experimental densities ρ, viscosities η, speeds of sound u, and isentropic compressibility κ_s, with literature data for pure liquids.

	$\rho \times 10^{-3}$ (kg m^{-3})		η (mPa s)		u (m s^{-1})		κ_s (T Pa^{-1})	
Pure liquid	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
298.15 K								
n-Hexane	0.6549	0.65489 [9]	0.313	0.300 [11]	1078.50	1078.0 [12] 1078.1 [13]	1312.8	1314 [12] 1318 [10]
n-Octane	0.6986	0.69862 [10]	0.518	0.519 [14]	1170.88	1172.02 [15]	1044.1	1042.5 [10]
n-Decane	0.7269	0.72635 [10]	0.852	0.845 [16]	1235.50	1234.7 [17]	902.6	903 [16]
2-Propanol	0.7815	0.7813 [18]	2.061	2.052 [15]	1141.39	1141.0 [19]	982.2	–
308.15 K								
n-Hexane	0.6458	0.64586 [2]	0.267	0.271 [20]	1032.80	1032 [21] 1032.4 [22]	1451.7	1452.3 [22]
n-Octane	0.6903	0.6906 [20]	0.450	0.450 [20]	1131.52	1132.9 [22]	1131.5	1128.6 [22]
n-Decane	0.7189	0.7186 [20]	0.740	0.733 [20]	1192.80	–	977.7	–
2-Propanol	0.7731	0.77306 [10]	1.573	1.5673 [23]	1110.08	1097 [19]	1049.7	–

The temperature of the test liquids and their binary mixtures, during the measurements, was maintained to an accuracy of ±0.01 K by using an electronically controlled thermostatic water bath.

3. Results and discussion

The values of density, ρ, viscosity, η, speed of sound, u, excess molar volumes, V^{E}, viscosity deviation, $\Delta\eta$, deviation in speed of sound, Δu, isentropic compressibility, κ_{s}, deviation in isentropic compressibility, $\Delta\kappa_{\mathrm{s}}$, and excess Gibbs energy of activation of viscous flow, $\Delta G^{*\mathrm{E}}$ for the binary mixtures at 298.15 and 308.15 K are recorded in Tables 2 and 3, respectively.

The excess functions, which are a measure of deviation from ideal behaviour, are found to be highly sensitive to intermolecular interactions between component molecules of the mixture. The sign and magnitude of these functions depend on the strength of interaction between dissimilar molecules in the mixture. The excess functions such as V^{E}, $\Delta\eta$, Δu, $\Delta\kappa_{\mathrm{s}}$, and $\Delta G^{*\mathrm{E}}$ were calculated by using the following equations:

$$V^{\mathrm{E}}\ (\mathrm{m^3\,mol^{-1}}) = \frac{(M_1x_1 + M_2x_2)}{\rho_{\mathrm{m}}} - \left(\frac{M_1x_1}{\rho_1} + \frac{M_2x_2}{\rho_2}\right), \tag{1}$$

$$\Delta\eta\ (\mathrm{mPa\,s}) = \eta_{\mathrm{m}} - (x_1\eta_1 + x_2\eta_2), \tag{2}$$

$$\Delta u\ (\mathrm{m\,s^{-1}}) = u_{\mathrm{m}} - (x_1u_1 + x_2u_2), \tag{3}$$

$$\Delta\kappa_{\mathrm{s}} = \kappa_{\mathrm{s}}^{\mathrm{mix}} - (\varphi_1\kappa_{\mathrm{s},1} + \varphi_2\kappa_{\mathrm{s},2}). \tag{4}$$

Volume fraction, φ_i is defined by the relation:

$$\varphi_i = \frac{x_iV_i}{\sum_{i=1}^{2} x_iV_i}, \tag{5}$$

$$\Delta G^{*\mathrm{E}} = RT[\ln(\eta_{\mathrm{m}}V) - x_1\ln(\eta_1V_1) - x_2\ln(\eta_2V_2)], \tag{6}$$

where ρ_{m}, η_{m}, u_{m}, $\kappa_{\mathrm{s}}^{\mathrm{mix}}$, and V denote the density, viscosity, speed of sound, isentropic compressibility, and molar volume of the mixtures, respectively. ρ_i, η_i, u_i, $\kappa_{\mathrm{s},i}$, V_i, and M_i ($i = 1$ and 2) denote, respectively, the density, viscosity, speed of sound, isentropic compressibility, molar volume, and molecular weight of i-th component.

Isentropic compressibility, κ_{s}, and molar volume, V, were calculated using the relation:

$$\kappa_{\mathrm{s}} = (\rho u^2)^{-1}, \tag{7}$$

$$V = \frac{M_1x_1 + M_2x_2}{\rho_{\mathrm{m}}}. \tag{8}$$

The values of V^{E}, $\Delta\eta$, Δu, and $\Delta G^{*\mathrm{E}}$ were fitted to Redlich–Kister type polynomial equation:

$$Y = x_1x_2\sum_{i=1}^{k} A_i(x_1 - x_2)^{i-1}, \tag{9}$$

Table 2. Experimental densities ρ, viscosities η, speeds of sound u, isentropic compressibility κ_s, excess molar volume V^E, viscosity deviation $\Delta\eta$, deviation in speeds of sound Δu, and deviation in isentropic compressibility $\Delta\kappa_s$ and excess Gibbs energies of activation of viscous flow, ΔG^{*E} for the binary mixtures at 298.15 K.

x_1	$\rho \times 10^{-3}$ (kg m^{-3})	η (mPa s)	u (m s^{-1})	κ_s (T Pa^{-1})	$V^E \times 10^6$ (m^3 mol^{-1})	$\Delta\eta$ (mPa s)	Δu (m s^{-1})	$\Delta\kappa_s$ (T Pa^{-1})	ΔG^{*E} (J mol^{-1})
2-Propanol + *n*-Hexane									
0.0000	0.6549	0.313	1078.50	1312.8	0.000	0.000	0.0	0.0	0
0.0486	0.6577	0.318	1074.88	1316.0	0.171	−0.080	−6.7	12.8	−172
0.1046	0.6614	0.326	1070.50	1319.4	0.303	−0.170	−14.6	27.7	−351
0.1633	0.6657	0.334	1067.60	1318.0	0.398	−0.264	−21.2	39.1	−548
0.2720	0.6748	0.364	1065.63	1305.0	0.482	−0.424	−30.0	51.4	−823
0.3138	0.6787	0.377	1065.60	1297.6	0.489	−0.484	−32.6	54.5	−920
0.3636	0.6836	0.399	1066.94	1285.0	0.488	−0.550	−34.4	54.9	−1005
0.4036	0.6878	0.420	1068.24	1274.1	0.474	−0.598	−35.6	55.0	−1063
0.5026	0.6990	0.496	1073.75	1240.8	0.432	−0.696	−36.4	50.9	−1110
0.5630	0.7065	0.557	1078.60	1216.7	0.396	−0.740	−35.3	45.9	−1101
0.6074	0.7124	0.613	1082.90	1197.0	0.361	−0.762	−33.8	41.2	−1075
0.6996	0.7256	0.763	1094.04	1151.4	0.293	−0.773	−28.5	29.2	−971
0.8182	0.7450	1.060	1110.69	1088.1	0.189	−0.687	−19.3	14.8	−734
0.9038	0.7611	1.400	1124.27	1039.5	0.097	−0.493	−11.1	6.4	−478
0.9566	0.7719	1.723	1133.86	1007.7	0.049	−0.262	−4.8	1.7	−221
1.0000	0.7815	2.061	1141.39	982.2	0.000	0.000	0.0	0.0	0
2-Propanol + *n*-Octane									
0.0000	0.6986	0.518	1170.88	1044.1	0.000	0.000	0.0	0.0	0
0.0569	0.7000	0.515	1168.49	1046.3	0.201	−0.091	−0.7	3.9	−176
0.1093	0.7016	0.518	1166.27	1047.9	0.334	−0.169	−1.4	7.2	−314
0.1441	0.7028	0.524	1163.68	1050.8	0.404	−0.216	−3.0	11.2	−386
0.2343	0.7065	0.542	1156.94	1057.5	0.513	−0.338	−7.0	21.2	−570

0.3228	0.7108	0.568	1151.36	1061.3	0.568	−0.448	−10.0	28.5	−728
0.3517	0.7123	0.579	1149.49	1062.5	0.589	−0.482	−11.0	31.0	−771
0.4196	0.7163	0.611	1145.31	1064.3	0.592	−0.554	−13.2	35.9	−852
0.5016	0.7217	0.665	1141.00	1064.3	0.588	−0.627	−15.1	40.1	−913
0.5603	0.7261	0.717	1138.88	1061.8	0.564	−0.666	−15.5	40.9	−925
0.6122	0.7304	0.773	1137.60	1057.9	0.533	−0.690	−15.2	40.2	−919
0.7012	0.7388	0.900	1137.12	1046.8	0.458	−0.700	−13.1	35.2	−861
0.7937	0.7492	1.088	1138.08	1030.5	0.353	−0.655	−9.4	26.3	−737
0.9122	0.7660	1.496	1139.52	1005.4	0.156	−0.430	−4.5	12.7	−420
0.9475	0.7719	1.680	1140.60	995.8	0.091	−0.300	−2.3	7.1	−280
1.0000	0.7815	2.061	1141.39	982.2	0.000	0.000	0.0	0.0	0
2-Propanol (1) + *n*-Decane (2)									
0.0000	0.7269	0.852	1235.50	901.2	0.000	0.000	0.0	0.0	0
0.0571	0.7274	0.839	1230.62	907.8	0.200	−0.082	−0.5	4.7	−116
0.1237	0.7283	0.837	1222.84	908.2	0.365	−0.165	−1.0	12.7	−216
0.1714	0.7291	0.838	1218.23	924.2	0.458	−0.221	−1.1	16.9	−284
0.2709	0.7314	0.851	1210.16	933.6	0.560	−0.329	0.2	22.1	−404
0.3525	0.7336	0.867	1203.68	940.8	0.612	−0.411	1.4	25.3	−499
0.4184	0.7358	0.888	1198.12	946.8	0.621	−0.470	2.0	27.8	−506
0.5253	0.7400	0.945	1189.95	954.4	0.620	−0.542	3.9	28.7	−616
0.5786	0.7425	0.986	1185.52	958.3	0.604	−0.566	4.5	28.7	−625
0.6537	0.7466	1.059	1178.90	963.7	0.561	−0.583	4.9	28.0	−619
0.6971	0.7494	1.113	1175.20	966.2	0.516	−0.582	5.3	26.5	−601
0.7895	0.7565	1.261	1166.39	971.2	0.400	−0.546	5.2	22.1	−531
0.8717	0.7644	1.457	1157.63	976.2	0.268	−0.449	4.2	16.1	−423
0.9099	0.7688	1.583	1154.00	976.7	0.195	−0.369	4.1	10.8	−336
0.9453	0.7734	1.727	1149.92	977.8	0.117	−0.268	3.4	6.0	−240
1.0000	0.7815	2.061	1141.39	982.2	0.000	0.000	0.0	0.0	0

Table 3. Experimental densities ρ, viscosities η, speeds of sound u, isentropic compressibility κ_s, excess molar volume V^E, viscosity deviation $\Delta\eta$, deviation in speeds of sound Δu, and deviation in isentropic compressibility $\Delta\kappa_s$ and excess Gibb's energies of activation of viscous flow, ΔG^{*E} for the binary mixtures at 308.15 K.

x_1	$\rho \times 10^{-3}$ (kg m^{-3})	η (mPa s)	u (m s^{-1})	κ_s (T Pa^{-1})	$V^E \times 10^6$ (m^3 mol^{-1})	$\Delta\eta$ (mPa s)	Δu (m s^{-1})	$\Delta\kappa_s$ (T Pa^{-1})	ΔG^{*E} (J mol^{-1})
2-Propanol + *n*-Hexane									
0.0000	0.6458	0.267	1032.80	1451.7	0.000	0.000	0.0	0.0	0
0.0486	0.6483	0.260	1027.52	1461.0	0.238	−0.070	−9.0	20.9	−259
0.1046	0.6523	0.268	1025.28	1458.4	0.315	−0.136	−15.6	32.3	−415
0.1633	0.6565	0.276	1021.76	1459.0	0.435	−0.204	−23.7	48.3	−579
0.2720	0.6654	0.310	1022.90	1436.3	0.561	−0.312	−30.9	56.4	−751
0.3138	0.6691	0.330	1024.62	1423.6	0.603	−0.347	−32.4	56.5	−772
0.3636	0.6740	0.360	1025.73	1410.2	0.603	−0.382	−35.2	59.2	−768
0.4036	0.6781	0.382	1027.62	1396.5	0.604	−0.412	−36.4	58.4	−787
0.5026	0.6893	0.451	1033.60	1358.0	0.561	−0.472	−38.0	55.2	−810
0.5630	0.6967	0.508	1040.48	1325.8	0.539	−0.494	−35.8	46.4	−780
0.6074	0.7025	0.561	1043.68	1306.8	0.517	−0.499	−36.1	45.6	−727
0.6996	0.7159	0.694	1058.40	1246.9	0.420	−0.487	−28.5	26.6	−617
0.8182	0.7354	0.934	1078.40	1169.3	0.305	−0.402	−17.6	8.6	−425
0.9038	0.7515	1.237	1093.40	1113.0	0.214	−0.210	−9.2	1.2	−129
0.9566	0.7631	1.379	1101.94	1092.2	0.084	−0.137	−4.8	0.4	−115
1.0000	0.7731	1.573	1110.08	1049.7	0.000	0.000	0.0	0.0	0
2-Propanol + *n*-Octane									
0.0000	0.6903	0.450	1131.52	1131.5	0.000	0.000	0.0	0.0	0
0.0569	0.6915	0.446	1125.76	1141.1	0.251	−0.068	−4.5	11.9	−164
0.1093	0.6929	0.450	1120.96	1148.5	0.430	−0.123	−8.2	21.5	−278
0.1441	0.6940	0.451	1119.84	1149.0	0.522	−0.161	−8.6	23.5	−358
0.2343	0.6978	0.466	1114.40	1153.9	0.604	−0.247	−12.1	32.7	−522

0.3228	0.7021	0.486	1110.36	1155.2	0.654	−0.327	−14.2	38.7	−660
0.3517	0.7036	0.497	1107.95	1157.8	0.673	−0.348	−16.0	42.9	−687
0.4196	0.7075	0.523	1106.40	1154.6	0.689	−0.398	−16.1	43.8	−754
0.5016	0.7131	0.561	1104.00	1150.6	0.644	−0.452	−16.8	45.4	−824
0.5603	0.7175	0.601	1102.59	1146.4	0.617	−0.478	−16.9	45.5	−834
0.6122	0.7218	0.643	1101.64	1141.6	0.582	−0.495	−16.8	44.9	−830
0.7012	0.7304	0.732	1100.55	1130.4	0.472	−0.505	−15.9	41.8	−798
0.7937	0.7408	0.877	1099.00	1117.6	0.389	−0.464	−15.5	38.8	−667
0.9122	0.7576	1.177	1104.00	1083.0	0.160	−0.297	−8.0	19.4	−371
0.9475	0.7634	1.315	1104.75	1073.3	0.104	−0.199	−6.5	15.0	−233
1.0000	0.7731	1.573	1110.08	1049.7	0.000	0.000	0.0	0.0	0
2-Propanol + *n*-Decane									
0.0000	0.7189	0.740	1192.80	977.7	0.000	0.000	0.0	0.0	0
0.0571	0.7190	0.757	1187.50	986.3	0.308	−0.031	−0.6	6.9	−3
0.1237	0.7197	0.740	1181.00	996.2	0.521	−0.103	−1.6	14.7	−132
0.1714	0.7204	0.726	1176.50	1002.9	0.633	−0.157	−2.1	19.8	−234
0.2709	0.7227	0.735	1172.20	1007.0	0.710	−0.231	1.8	20.1	−331
0.3525	0.7249	0.746	1166.20	1014.3	0.761	−0.288	2.6	23.9	−407
0.4184	0.7271	0.762	1161.20	1020.0	0.759	−0.327	3.0	26.4	−454
0.5253	0.7314	0.800	1152.24	1029.8	0.722	−0.378	3.2	30.3	−512
0.5786	0.7340	0.824	1148.26	1033.3	0.680	−0.398	3.3	30.4	−535
0.6537	0.7379	0.882	1142.08	1039.0	0.659	−0.403	3.4	30.6	−512
0.6971	0.7410	0.909	1138.60	1041.0	0.559	−0.412	3.5	29.1	−530
0.7895	0.7482	1.013	1130.66	1045.5	0.411	−0.385	3.2	24.9	−477
0.8717	0.7560	1.152	1123.04	1048.8	0.287	−0.314	2.4	18.7	−372
0.9099	0.7608	1.246	1119.20	1049.3	0.161	−0.252	1.7	14.1	−290
0.9453	0.7652	1.350	1116.30	1048.7	0.104	−0.177	1.7	8.2	−199
1.0000	0.7731	1.573	1110.08	1049.7	0.000	0.000	0.0	0.0	0

Table 4. Values of A_i parameters of Equations (9) and (11) along with standard deviations σ for excess properties of the binary mixtures at 298.15 K.

Binary mixture	Excess property	A_0	A_1	A_2	A_3	A_4	σ
2-Propanol + *n*-Hexane	$V^E \times 10^6$ (m^3 mol^{-1})	1.732	−1.110	0.770	−0.330		0.003
	$\Delta\eta$ (mPa s)	−2.776	−1.671	−0.983	−1.059	−0.699	0.003
	Δu (m s^{-1})	−145.4	18.2	9.0			0.3
	$\Delta\kappa_s$ (T Pa^{-1})	152.5	−219.3	118.2	−34.3		0.6
	ΔG^{*E} (J mol^{-1})	−4445.6	−298.6	116.9	−1043.9	−462.4	10.2
2-Propanol + *n*-Octane	$V^E \times 10^6$ (m^3 mol^{-1})	2.341	−0.477	0.612	−0.729		0.004
	$\Delta\eta$ (mPa s)	−2.505	−1.493	−0.843	−1.073	−1.040	0.003
	Δu (m s^{-1})	−59.8	−23.0	39.3			0.3
	$\Delta\kappa_s$ (T Pa^{-1})	146.5	−114.3	11.9	83.4	−67.9	0.6
	ΔG^{*E} (J mol^{-1})	−3645.8	−958.4	−152.8	−437.8	−1067.8	3.5
2-Propanol + *n*-Decane	$V^E \times 10^6$(m^3 mol^{-1})	2.503	−0.295	0.679	−0.672		0.004
	$\Delta\eta$ (mPa s)	−2.117	−1.161	−0.551	−0.978	−1.198	0.004
	Δu (m s^{-1})	14.3	25.9	−13.7	14.8	32.2	0.3
	$\Delta\kappa_s$ (T Pa^{-1})	103.3	−55.1	42.3	−79.8		0.7
	ΔG^{*E} (J mol^{-1})	−2371.6	−959.5	−353.6	−401.9	−1094.6	16.5

where Y is V^E or $\Delta\eta$ or Δu or ΔG^{*E}, k is the number of estimated parameters and A_i represents polynomial coefficients, which were obtained by fitting the equation to the experimental results with least-squares regression method. The corresponding standard deviations $\sigma(Y)$ were calculated using the relation:

$$\sigma(Y) = \left[\frac{\sum (Y_{\text{expt.}} - Y_{\text{calcd}})^2}{(n-k)}\right]^{1/2}, \tag{10}$$

where n is the no. of experimental data points. The $\Delta\kappa_s$ values were correlated with composition data by relation

$$\Delta\kappa_s = \varphi_1\varphi_2 \sum_{i=1}^{k} A_i(\varphi_1 - \varphi_2)^{i-1}. \tag{11}$$

The standard deviations $\sigma(\Delta\kappa_s)$ may be given as

$$\sigma(\Delta\kappa_s) = \left[\frac{\sum (\Delta\kappa_s(\text{exp}) - \Delta\kappa_s(\text{calcd}))^2}{(n-k)}\right]^{1/2}. \tag{12}$$

The parameters of Equations (9) and (11) and standard deviations of Equations (10) and (12) are listed in Tables 4 and 5. The variation of smoothed values of V^E, $\Delta\eta$, Δu, and ΔG^{*E} with mole fraction x_1 and that of $\Delta\kappa_s$ with volume fraction φ_1 of 2-propanol are shown graphically in Figures 1–5, respectively.

Figure 1(a) and (b) display the dependence of V^E on x_1 for all the mixtures at 298.15 and 308.15 K, respectively. It is observed that, for all the mixtures, these values are positive, suggesting the weak dispersive-type intermolecular interactions. This can be

Table 5. Values of A_i parameters of Equations (9) and (11) along with standard deviations σ for excess properties of the binary mixtures at 308.15 K.

Binary mixture	Excess property	A_0	A_1	A_2	A_3	A_4	σ
2-Propanol + *n*-Hexane	$V^{\mathrm{E}} \times 10^6$ (m^3 mol^{-1})	2.274	−0.893	0.978			0.025
	$\Delta\eta$ (mPa s)	−1.887	−0.960	−0.372	0.273		0.014
	Δu (m s^{-1})	−151.1	12.5	43.9	49.4	−49.4	0.9
	$\Delta\kappa_{\mathrm{s}}$ (T Pa^{-1})	159.3	−269.2	−24.9	−65.0	279.5	2.3
	$\Delta G^{*\mathrm{E}}$ (J mol^{-1})	−3202.8	496.9	−404.1	1704.5		33.5
2-Propanol + *n*-Octane	$V^{\mathrm{E}} \times 10^6$ (m^3 mol^{-1})	2.581	−0.819	1.084	−1.003		0.017
	$\Delta\eta$ (mPa s	−1.799	−1.083	−0.731	−0.564	−0.396	0.002
	Δu (m s^{-1})	−66.7	−15.7	−39.9			0.7
	$\Delta\kappa_{\mathrm{s}}$ (T Pa^{-1})	175.3	−53.5	48.5	−97.9	82.3	1.6
	$\Delta G^{*\mathrm{E}}$ (J mol^{-1})	−3259.9	−1010.5	−712.0			6.1
2-Propanol + *n*-Decane	$V^{\mathrm{E}} \times 10^6$ (m^3 mol^{-1})	2.940	−0.730	1.130	−1.698		0.020
	$\Delta\eta$ (mPa s)	−1.465	−0.778	−0.750	−0.858		0.006
	Δu (m s^{-1})	14.0	4.7	−17.1	34.5		0.7
	$\Delta\kappa_{\mathrm{s}}$ (T Pa^{-1})	118.3	−42.8	−46.8	−68.2	163.9	1.8
	$\Delta G^{*\mathrm{E}}$ (J mol^{-1})	−1975.7	−692.9	−1253.1	−1337.2	1318.1	20.4

explained by the fact that 2-propanol is hydrogen bonded self-associated liquid and the addition of alkanes, which are nonpolar and nonassociated, causes the rupture of hydrogen bonds in 2-propanol with resulting volume expansion and V^{E} is positive. The values of V^{E} vary according to the sequence *n*-hexane < *n*-octane < *n*-decane. The nature of V^{E} *versus* x_1 curves for all the mixtures at both the temperatures is almost identical but the V^{E} values show an increase with rise in temperature.

The dependence of $\Delta\eta$ on the mole fraction of 2-propanol at 298.15 and 308.15 K is displayed in Figure 2(a) and (b), respectively. We observe that $\Delta\eta$ values are negative for all the binary mixtures, further supporting the presence of weak intermolecular interactions. With an increase in temperature, the absolute values of $\Delta\eta$ decrease as observed in the present study. This can be explained by the fact that an increment of temperature diminishes the self association in the pure components (2-propanol) and also the hetero-association between unlike molecules, because of the increase in thermal energy. This leads to less negative values of $\Delta\eta$ as temperature is raised.

Figure 3(a) and (b) show the variation of Δu with mole fraction of 2-propanol at 298.15 and 308.15 K, respectively. The Δu values show a negative trend for 2-propanol + *n*-hexane and 2-propanol + *n*-octane binary mixtures over the entire composition range, whereas for 2-propanol + *n*-decane binary mixture, Δu is negative at lower x_1 values of 2-propanol but it shows a positive trend at higher x_1 of 2-propanol. The negative Δu values show the importance of interstitial accommodation of alkane molecules between alcohol aggregates, whereas positive Δu values for 2-propanol + *n*-decane suggest that as the size of the alkane molecule increases, the molecules of the mixing component cannot accommodate easily.

The deviations in isentropic compressibility, $\Delta\kappa_{\mathrm{s}}$, at 298.15 and 308.15 K are positive over the whole range of composition for all the binary mixtures formed by 2-propanol

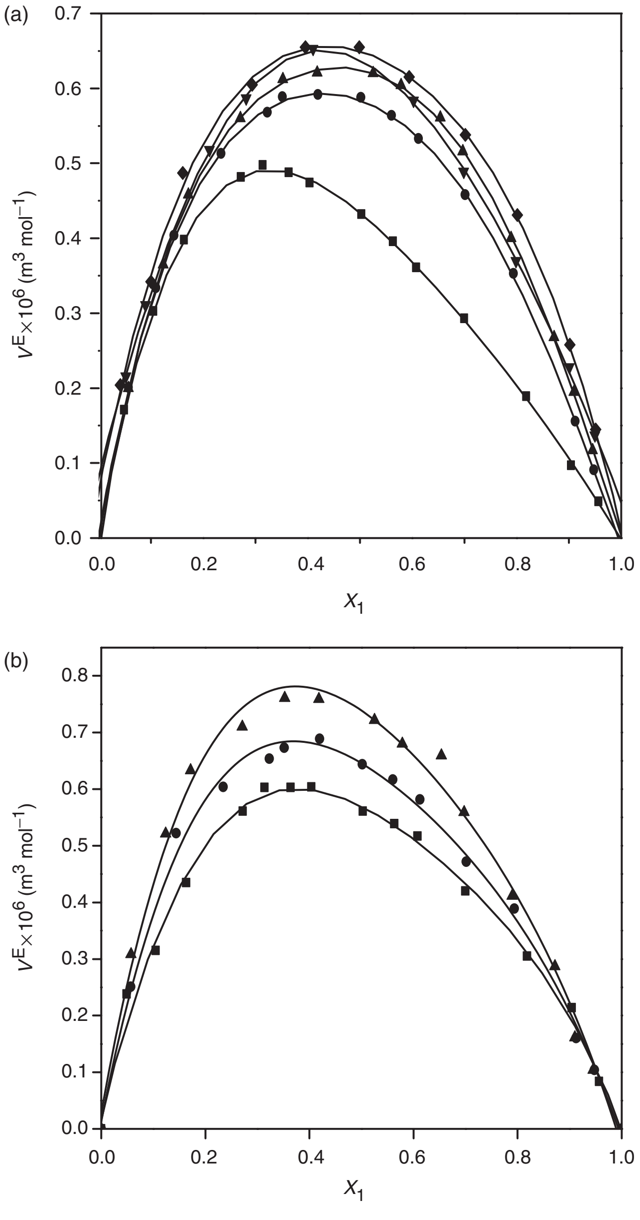

Figure 1. (a) Excess molar volumes V^E at 298.15 K for binary mixtures of 2-propanol (1) with ■, *n*-hexane; ●, *n*-octane; ▲, *n*-decane; (—) for Redlich–Kister Equation (9); ▼represents V^E values for 2-propanol +*n*-octane; and ◆ for 2-propanol + *n*-decane at 298.15 K given by Tojo *et al*. (b) Excess molar volumes V^E at 308.15 K for binary mixtures of 2-propanol (1) with ■, *n*-hexane; ●, *n*-octane; ▲, *n*-decane; and (—) for Redlich–Kister Equation (9).

with *n*-alkanes, as shown in Figure 4(a) and (b), respectively. The positive deviations in $\Delta\kappa_s$ may be attributed to the presence of weak interactions between the component molecules in the mixture, thereby indicating the predominance of long range dispersive forces. The positive $\Delta\kappa_s$ values also suggest that the mixture is more compressible than the

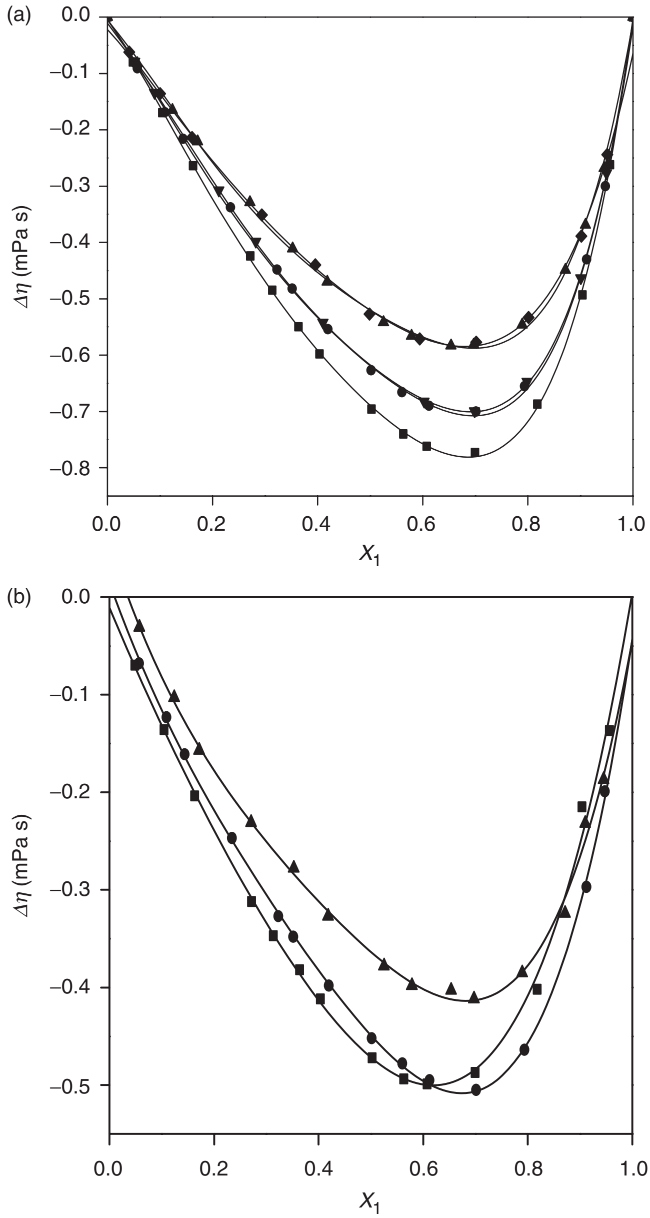

Figure 2. (a) Viscosity deviations $\Delta\eta$ at 298.15 K for binary mixtures of 2-propanol (1) with ■, *n*-hexane; ●, *n*-octane; ▲, *n*-decane; (—) for Redlich–Kister Equation (9); ▼ represents $\Delta\eta$ values for 2-propanol + *n*-octane; and ◆ for 2-propanol + *n*-decane at 298.15 K given by Tojo *et al.* (b) Viscosity deviations $\Delta\eta$ at 308.15 K for binary mixtures of 2-propanol (1) with ■, *n*-hexane; ●, *n*-octane; ▲, *n*-decane; and (—) for Redlich–Kister Equation (9).

corresponding ideal mixture. Therefore, in these binary mixtures, an expansion in free volume is considered to occur, making the mixtures more compressible than the ideal mixture. As the temperature increases, the absolute value of $\Delta\kappa_S$ also increases in all the binary mixtures.

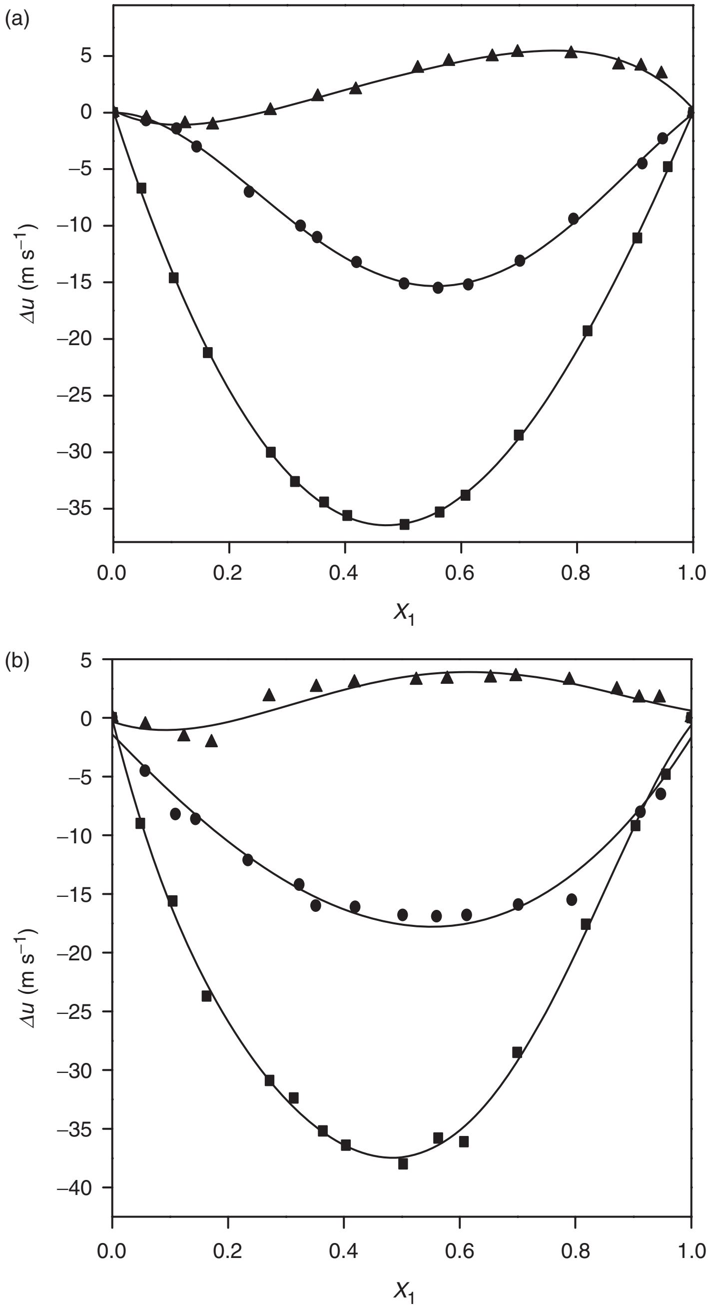

Figure 3. (a) Deviation in speed of sound Δu at 298.15 K for binary mixtures of 2-propanol (1) with ■, *n*-hexane; ●, *n*-octane; ▲, *n*-decane; and (—) for Redlich–Kister Equation (9). (b) Deviation in speed of sound Δu at 308.15 K for binary mixtures of 2-propanol (1) with ■, *n*-hexane; ●, *n*-octane; ▲, *n*-decane; and (—) for Redlich–Kister Equation (9).

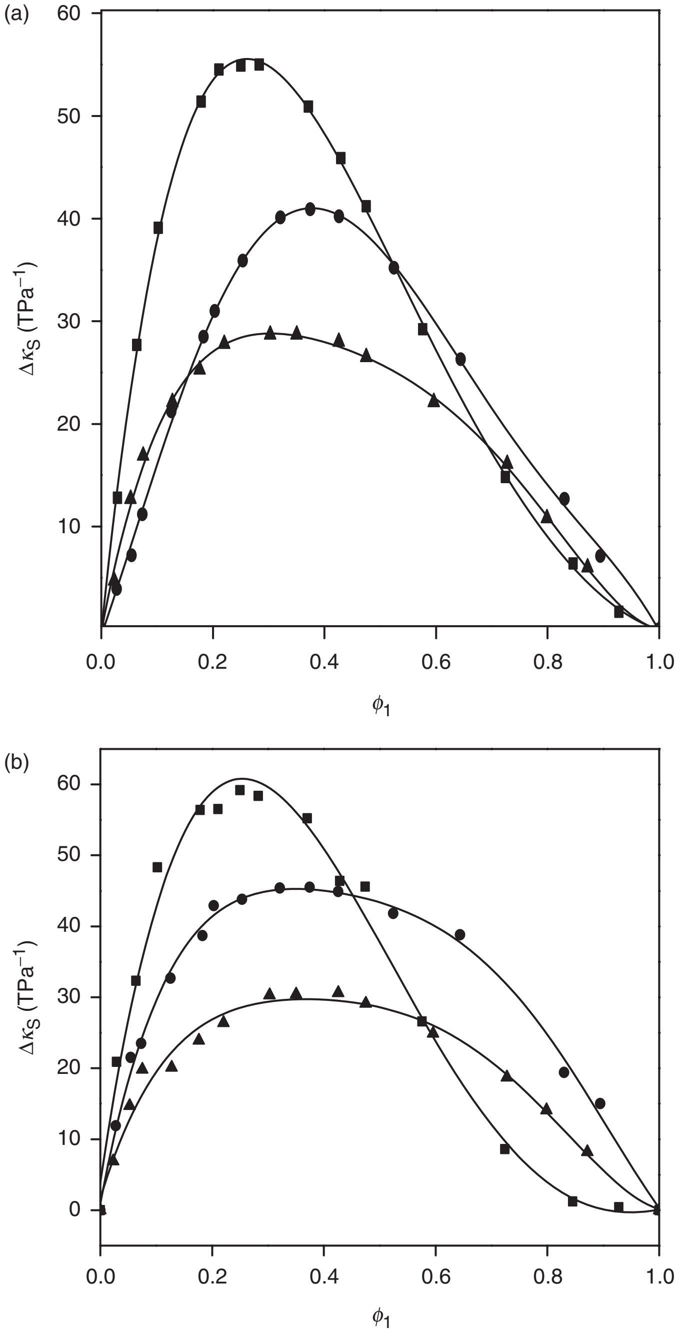

Figure 4. (a) Deviation in isentropic compressibility $\Delta\kappa_s$ at 298.15 K for binary mixtures of 2-propanol (1) with ■, *n*-hexane; ●, *n*-octane; ▲, *n*-decane; and (—) for Redlich–Kister Equation (11). (b) Deviation in isentropic compressibility $\Delta\kappa_s$ at 308.15 K for binary mixtures of 2-propanol (1) with ■, *n*-hexane; ●, *n*-octane; ▲, *n*-decane; and (—) for Redlich–Kister Equation (11).

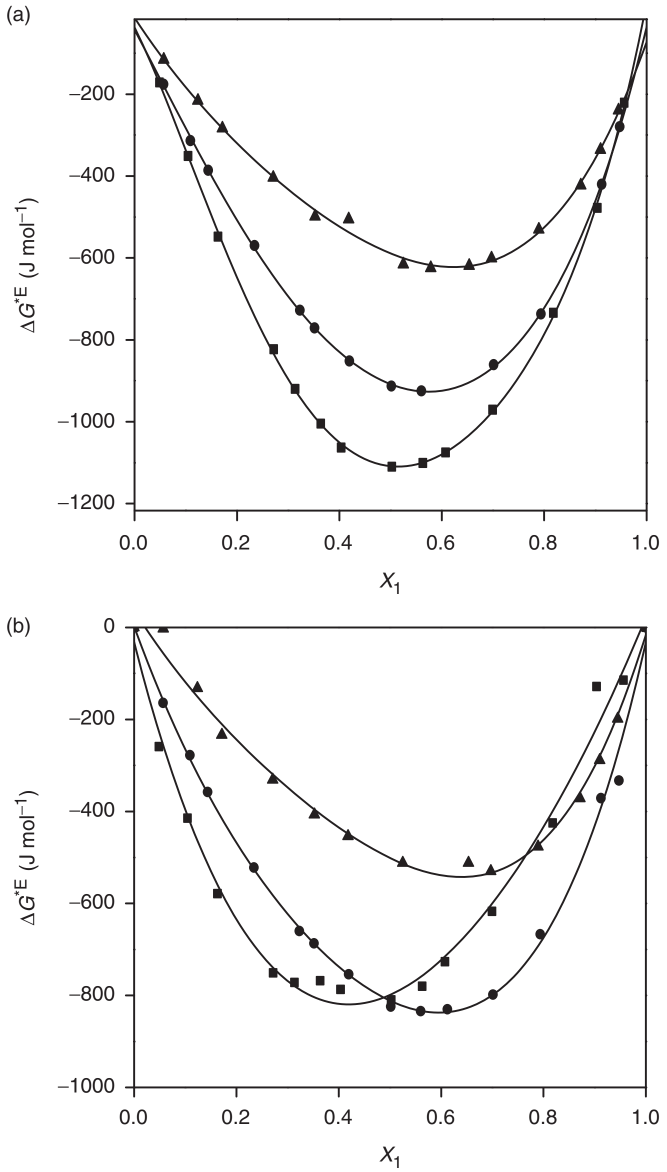

Figure 5. (a) Excess Gibbs energies of activation of viscous flow ΔG^{*E} at 298.15 K for binary mixtures of 2-propanol (1) with ■, *n*-hexane; •, *n*-octane; ▲, *n*-decane; and (—) for Redlich–Kister Equation (9). (b) Excess Gibbs energies of activation of viscous flow ΔG^{*E} at 308.15 K for binary mixtures of 2-propanol (1) with ■, *n*-hexane; •, *n*-octane; ▲, *n*-decane; and (—) for Redlich–Kister Equation (9).

Figure 5(a) and (b) show the variation of excess free energy of activation of viscous flow ΔG^{*E} with the mole fraction x_1 of 2-propanol. The ΔG^{*E} values are negative over the entire composition range for all the binary mixtures but the absolute value of ΔG^{*E} diminishes with increasing chain length of the alkanes. The order it follows is: *n*-hexane > *n*-octane > *n*-decane. The negative values of ΔG^{*E} indicate the presence of weak interactions between the mixing components. This behaviour is also supported by the positive values of V^E. As the temperature increases, the absolute values of ΔG^{*E} decrease for all these binary mixtures.

In the literature, Tojo *et al.* [24] presented the values of V^E and $\Delta\eta$ for the binary mixtures of 2-propanol with *n*-octane and *n*-decane at 298.15 K. Comparison of our V^E and $\Delta\eta$ values at 298.15 K suggest a reasonably good agreement for these systems. The shapes of the curves also remain almost identical to our data. No experimental data of ρ, η, and u on these mixtures are available in the literature at 308.15 K with which we can compare the present results. The V^E values for the binary mixture of 2-propanol + *n*-hexane at 298.15 K and 308.15 K have also been compared with V^E results given by Modarress *et al.* [25]. The shapes of curves also remain almost identical to our data, but our values are lower than those given by Modarress *et al.*

4. Conclusion

The interaction between 2-propanol and *n*-alkane is such that the basic network of intermolecular association in 2-propanol is disrupted. The behaviour of 2-propanol + *n*-alkane mixtures indicates the presence of long dispersive forces among the components. Positive deviations are observed in the case of V^E and $\Delta\kappa_s$, whereas $\Delta\eta$ and ΔG^{*E} show negative deviations for all binary mixtures. Both positive and negative deviations are observed in the case of Δu. The behaviour of all these excess parameters studied here support each other. On the whole, it can be concluded that the strength of bonding is expected to decrease with an increase in the chain length of alkane molecule and also with rise in temperature.

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