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Excess Viscosity and Compressibility of Binary Mixtures of Methanol with Acetonitrile and Dimethyl Formamide at Different Temperatures

Neeta Sharma, Seema Rana and Anunidhi Sharma

Department of Chemical Engineering and Technology, Panjab University, Chandigarh, 160014, India

Abstract: The densities, viscosities and ultrasonic velocities of binary mixtures of methanol with acetonitrile and dimethyl formamide have been determined at 298.15, 303.15, 308.15 and 313.15 K over the whole composition range. From the experimental data the values of compressibility (K_s), excess compressibility (K_s^e) and excess viscosity (η_e) have been calculated. The results are discussed and interpreted in terms of molecular package and specific interaction predominated by hydrogen bonding. The data at various temperatures also provide an opportunity to study the effect of temperature on the sign and magnitude of the deviation in viscosity and compressibility. Results show that excess properties are found to be either negative or positive depending on the molecular interactions and the nature of liquid mixtures.

Key words: Binary solvent system · Ultrasonic velocity · Excess viscosity · Temperature effect

INTRODUCTION

The study of molecular interactions in binary liquid mixtures has attracted the attention of scientific community for more than a century. The study finds direct applications in chemical and biological industry [1]. Mixed solvents rather than single pure liquids are of utmost practical importance in most of chemical and industrial processes as they provide a wide range of mixtures of two or more components in varying proportions so as to permit continuous adjustment of desired properties of the medium [2-5].

In recent years the measurement of ultrasonic velocity has been adequately employed in understanding the nature of molecular interactions in pure liquids and liquid mixtures. Velocity of sound waves in a medium is fundamentally related to the binding forces between the atoms or the molecules. The variation of ultrasonic velocity and related parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components as well as strongly interacting components. The composition dependence of ultrasonic properties of binary liquid mixtures has proved to be a useful tool to investigate the interaction between the components of binary liquid mixtures. The ultrasonic speed and thermodynamic data derived from it has been widely used for this purpose [6-10].

In the present work, densities (ρ), viscosities (η) and ultrasonic velocities (u) of binary mixtures of methanol (MeOH) with acetonitrile (AN) and dimethylformamide (DMF) covering the entire composition range (expressed by the mole fraction of MeOH) at 298.15, 303.15, 308.15 and 313.15 K are reported. From the experimental value of ρ, η and u, the excess viscosity (η_e), compressibility (K_s) and excess compressibility (K_s^e) have been calculated. The present study is expected to reveal the nature and extent of interaction between the component molecules in these binary mixtures. The dependence of these thermodynamic parameters on composition and temperature has also been discussed.

MATERIALS AND MATHODS

The spectral grade acetonitrile (E. Merck, 99.5%) and dimethylformamide (E. Merck, 99.5 %) were used as such without further purification. Methanol (E. Merck) was refluxed over calcium oxide (CaO) and distilled at atmospheric pressure. Methanol obtained is then stored over 4 A° type molecular sieve [11, 12]. The purity of the chemicals was checked by comparing their measured densities (ρ), viscosities (η) and ultrasonic velocities (u) with those reported in the literature [1-8, 13, 14]. All the mixtures were prepared by mixing known masses of

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Corresponding Author: Neeta Sharma, Department of Chemical Engineering and Technology, Panjab University,
Chandigarh, 160014, India. E-mail neetachem@hotmail.com & neetapu@gmail.com.

Table 1: The observed and literature values of Density,Viscosity and Ultrasonic Velocity for Methanol, Acetonitrile and Dimethyl Formamide at 298.15 K

	Observed Values	Literature Values
Density (g/cc)		
Methanol	0.77664	0.7866
Acetonitrile	0.7765	0.7762
Dimethyl formamide	0.9487	0.9444
Viscosity (cP)		
Methanol	0.553	0.545
Acetonitrile	0.341	0.342
Dimethyl formamide	0.86	0.825
Ultrasonic Velocity (m/s)		
Methanol	1266	Not available
Acetonitrile	1250	1280.8
Dimethyl formamide	1431	1456.7

pure liquids. The weighing were done on electronic balance (Afcoset ER-120A) with a precision of $\pm 1 \times 10^{-4}$ gm. The probable error in mole fraction was estimated to be less than $\pm$ 0.0001.

The densities of pure liquids and their binary mixtures were measured by using bicapillary pyknometer. The accuracy in density measurements was found to be 0.0001g/cc. The viscosities of pure liquids and their binary mixture were measured by using a modified Ubbelohde capillary type viscometer. The viscometer was calibrated with pure water. The viscometer

containing the test liquid was allowed to stand for about 30 minutes in a thermostatic water bath so that the thermal fluctuations in viscometer were minimized. The accuracy in viscosity data was $\pm$ 0.002 mPa.s.

The ultrasonic velocity of pure liquids and their binary mixtures was measured using ultrasonic time intervalometer model UTI-101 purchased from Innovative Instrument (Hyderabad).

The temperature of the test liquids during the measurement was maintained at an accuracy of $\pm$ 0.02 K in an electronically controlled thermostatic water bath.

The reliability of the experimental measurements of ρ, η and u was checked by comparing the observed values of these properties for pure liquids (Table 1) with the corresponding literature values[1-8, 13, 14].

RESULTS AND DISCUSSION

The experimental values of densities (ρ), viscosities (η) and ultrasonic velocities (u) of pure MeOH, AN, DMF and binary mixtures of methanol(MeOH) with acetonitrile (AN) and dimethyl formamide(DMF) covering the entire composition range(expressed by the mole fraction of MeOH) at 298.15, 303.15, 308.15 and 313.15 K are reported in Tables 2 and 3.

Table 2: Densities, viscosities, ultrasonic velocities, compressibilities, excess viscosities and excess compressibilities for AN + MeOH(X_2) system at 298.15, 303.15, 308.15 and 313.15 K

T (K)	X_2	$\rho \times 10^3$ (kg/m³)	η (mPa.s)	u (m/s)	$K_s \times 10^{-12}$ (m²/N)	η_e (mPa.s)	$Ks^e \times 10^{-12}$ (m²/N)
298.15	0.0000	0.9640	0.7960	1430.8	506.7166	0.00000	0.000000
	0.2022	0.9362	0.7700	1411.2	536.3573	0.02313	-25.498675
	0.3632	0.9143	0.7450	1392.3	564.2163	0.03725	-41.543988
	0.4944	0.9000	0.7270	1373.8	588.7223	0.05113	-52.815921
	0.6033	0.8852	0.7160	1357.2	613.2971	0.06660	-57.939503
	0.6952	0.8677	0.6745	1338.6	643.1744	0.04744	-53.132323
	0.7739	0.8415	0.6391	1322.3	679.6509	0.03115	-38.106237
	0.8418	0.8240	0.6037	1307.8	709.5616	0.01227	-26.725276
	0.9012	0.8271	0.5668	1282.7	734.7939	-0.01020	-17.688514
	0.9535	0.8050	0.5320	1274.0	765.3591	-0.03228	-1.390809
	1.0000	0.8000	0.5530	1266.4	779.4140	0.00000	0.000000
303.15	0.0000	0.9650	0.7900	1445.2	496.1543	0.00000	0.000000
	0.2022	0.9430	0.7650	1428.8	519.4520	0.02373	-33.035865
	0.3632	0.9186	0.7420	1396.6	558.1224	0.03953	-39.220543
	0.4944	0.8842	0.7250	1380.9	593.0960	0.05415	-40.799674
	0.6033	0.8773	0.7000	1360.2	616.0931	0.05539	-48.144203
	0.6952	0.8621	0.6700	1343.3	642.8303	0.04755	-47.020109
	0.7739	0.8565	0.6300	1322.0	668.0512	0.02651	-43.714156
	0.8418	0.8498	0.5980	1298.0	698.4477	0.01088	-32.248709
	0.9012	0.8252	0.5620	1292.6	725.2913	-0.01080	-21.951332
	0.9535	0.8100	0.5300	1280.5	752.9321	-0.03019	-8.887062
	1.0000	0.8000	0.5490	1270.2	774.7575	0.00000	0.000000

Table 2: Continued

308.15	0.0000	0.9440	0.7850	1450.3	503.6308	0.00000	0.000000
	0.2022	0.9089	0.7600	1435.5	533.9216	0.02454	-26.941814
	0.3632	0.8992	0.7380	1408.0	560.9684	0.04198	-45.466021
	0.4944	0.8804	0.7200	1391.7	586.4469	0.05612	-57.123599
	0.6033	0.8698	0.6940	1368.2	614.1599	0.05681	-60.236467
	0.6952	0.8522	0.6850	1350.1	643.7639	0.07033	-56.654339
	0.7739	0.842	0.6250	1335.0	666.3853	0.02960	-56.297633
	0.8418	0.8264	0.5920	1328.2	685.9346	0.01325	-55.981459
	0.9012	0.8152	0.5590	1296.0	730.3412	-0.00520	-28.385179
	0.9535	0.7994	0.5500	1285.3	757.2283	-0.00138	-16.307268
	1.0000	0.7854	0.5400	1272.2	786.6804	0.00000	0.000000
313.15	0.0000	0.9094	0.7850	1455.2	519.2777	0.00000	0.000000
	0.2022	0.8952	0.7600	1438.1	540.1343	0.02453	-29.867396
	0.3632	0.8864	0.7380	1410.3	567.2144	0.04198	-43.175842
	0.4944	0.8779	0.7330	1409.0	573.7636	0.06912	-69.539568
	0.6033	0.8586	0.6940	1370.7	619.9038	0.05681	-50.719556
	0.6952	0.8471	0.6850	1356.3	641.6867	0.07033	-51.999258
	0.7739	0.8323	0.6250	1342.2	666.9383	0.02960	-46.480374
	0.8418	0.8136	0.5920	1330.3	694.5282	0.01325	-35.936422
	0.9012	0.8024	0.5590	1302.2	734.9431	-0.00520	-10.420149
	0.9535	0.8000	0.5500	1290.5	750.5748	-0.00138	-7.913410
	1.0000	0.7849	0.5400	1286.2	770.1382	0.00000	0.000000

Table 3: Densities, viscosities, ultrasonic velocities, compressibilities, excess viscosities and excess compressibilities for DMF+MeOH (X_2) system at 298.15, 303.15, 308.15 and 313.15 K

T (K)	X_2	$\rho \times 10^3$ (kg/m³)	η (mPa.s)	u (m/s)	$K_s \times 10^{-12}$ (m²/N)	η_e (mPa.s)	$Ks^e \times 10^{-12}$ (m²/N)
298.15	0.0000	0.7765	0.3341	1250.8	823.1572	0.00000	0.000000
	0.1246	0.7775	0.3584	1232.4	846.8300	-.00297	-9.416348
	0.2426	0.7785	0.3824	1210.0	877.3455	0.00481	-10.237256
	0.3545	0.7795	0.4065	1190.0	905.9202	-0.0052	-11.378983
	0.4607	0.7805	0.4290	1173.0	931.1745	0.00595	-14.327494
	0.5617	0.7815	0.4470	1165.7	941.6672	0.01006	-30.656665
	0.6578	0.7825	0.4520	1143.6	977.1638	0.02609	-20.680630
	0.7497	0.7835	0.4760	1126.2	1006.3060	0.02221	-15.943883
	0.8367	0.7845	0.4931	1110.0	1034.5730	0.02415	-10.780703
	0.9202	0.7855	0.5345	1096.4	1059.0480	0.00103	-8.479814
	1.0000	0.7866	0.5530	1080.6	1088.7200	0.00000	0.000000
303.15	0.0000	0.7758	0.3380	1278.7	788.3388	0.00000	0.000000
	0.1246	0.7767	0.3600	1260.0	810.9715	0.00392	-9.885534
	0.2426	0.7778	0.3790	1245.0	829.4560	0.00916	-22.196829
	0.3545	0.7787	0.4020	1224.0	857.1210	0.00974	-23.735601
	0.4607	0.7797	0.4190	1205.0	883.2799	0.01483	-25.292889
	0.5617	0.7803	0.4380	1189.9	905.1283	0.01683	-29.803597
	0.6578	0.7818	0.4450	1171.7	931.5788	0.02982	-28.433460
	0.7497	0.7828	0.4650	1150.0	965.9475	0.02894	-18.048951
	0.8367	0.7839	0.4940	1130.0	998.9718	0.01803	-7.729944
	0.9202	0.7843	0.5270	1115.3	1024.8810	0.00150	-3.612240
	1.0000	0.7860	0.5460	1101.1	1049.3200	0.00000	0.000000

Table 3: Continued

308.15	0.0000	0.7752	0.3350	1298.5	765.072	0.00000	0.000000
	0.1246	0.7763	0.3550	1279.4	786.9692	-0.00554	-1.081745
	0.2426	0.7772	0.3750	1269.8	797.9884	-0.00973	-11.824284
	0.3545	0.7782	0.3940	1255.0	815.8707	-0.01367	-14.578749
	0.4607	0.7794	0.4150	1242.2	831.4891	-0.01444	-18.545907
	0.5617	0.7802	0.4300	1228.2	849.6117	-0.02015	-19.049809
	0.6578	0.7812	0.4450	1200.3	888.5015	-0.02485	2.117012
	0.7497	0.7822	0.4600	1186.4	908.2803	-0.02869	4.947538
	0.8367	0.7834	0.4890	1173.8	926.4633	-0.01752	7.085835
	0.9202	0.7844	0.5250	1167.0	936.0967	0.001359	1.320011
	1.0000	0.7854	0.5400	1158.0	949.4935	0.000000	0.000000
313.15	0.0000	0.7745	0.3300	1326.4	733.8876	0.00000	0.000000
	0.1246	0.7756	0.3488	1308.0	753.6101	-0.00687	-1.960539
	0.2426	0.7766	0.3700	1290.9	772.7116	-0.00998	-3.393578
	0.3545	0.7777	0.3880	1275.8	789.9920	-0.01503	-5.586093
	0.4607	0.7787	0.4090	1260.8	807.8625	-0.01590	-6.196711
	0.5617	0.7797	0.4230	1255.5	813.6526	-0.02271	-17.982679
	0.6578	0.7805	0.4400	1235.8	838.9396	-0.02551	-9.419114
	0.7497	0.7815	0.4550	1220.0	859.6383	-0.02944	-4.712988
	0.8367	0.7826	0.4820	1201.8	884.6994	-0.02036	5.208311
	0.9202	0.7838	0.5178	1193.8	895.2237	-0.00176	1.201834
	1.0000	0.7849	0.5360	1184.6	907.9088	0.00000	0.000000

Excess Viscosities Were Obtained by Using the Relation:

$$\eta_{e} = \eta - (x_1\,\eta_1 + x_2\,\eta_2) \qquad (1)$$

Where x_1, x_2 are the mole fraction of components 1 and 2 respectively and η_1, η_2 the viscosities of pure components 1 and 2 and η is the viscosity of the mixture.

Compressibilities (K_s) were calculated from the values of density (ρ) and ultrasonic velocity (u) from the equation given as:

$$K_s = 1/u^2\rho \qquad (2)$$

Excess compressibilities (K_s^e) were obtained by using the relation:

$$K_s^e = K_s - (x_1\,K_{s\,1} + x_2\,K_{s\,2}) \qquad (3)$$

Where K_s is the compressibility of the mixture and K_{s1} and K_{s2} the compressibilities of pure component 1 and 2. The calculated values of η_e, K_s, K_s^e using equation 1,2 and 3 are given in Tables 2 and 3.

For both AN+MeOH and DMF+MeOH mixtures the values of ultrasonic velocity at different temperature were plotted as a function of mixture composition (Figures 1 and 1A). All the curves show a decrease in ultrasonic velocity with increase in mole fraction of MeOH. Increasing the temperature for a particular mole fraction causes an increase in velocity. It is significant here to compare density and ultrasonic velocity as density decreases the ultrasonic velocity increases [15] (Tables 2, 3).

The variation of compressibility with mole fraction for AN+MeOH and DMF+MeOH is shown in Figure 2 and 2A. It has been observed that the value of compressibility increases with increase in mole fraction of MeOH at a constant temperature this indicates that as the mole fraction of MeOH increases the intermolecular interactions between the molecules increases [7, 8] because of formation of hydrogen bonds in MeOH.

The excess viscosity η_e are negative for AN+MeOH system under study over the whole composition range at all investigated temperatures as derived from Fig. 3. The negative η_e values indicate that the dispersion forces are dominant in these systems. It has been reported [7, 8, 16, 17] that dispersion forces are dominant in the systems where the component molecules have different molecular size as in the present case. However, the DMF+MeOH system (Fig. 3A) shows positive deviation in viscosity which indicates the presence of significant interactions between the component molecules [7, 8, 18, 19].
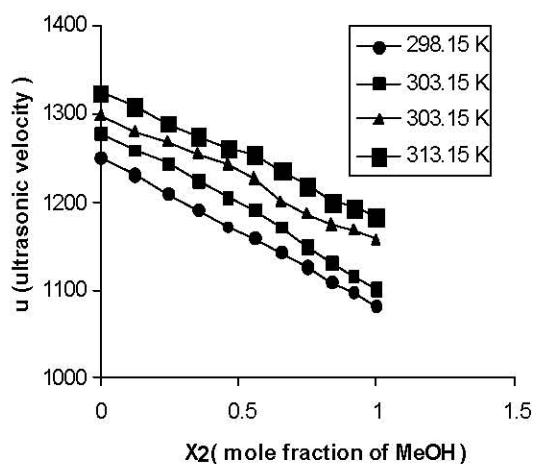
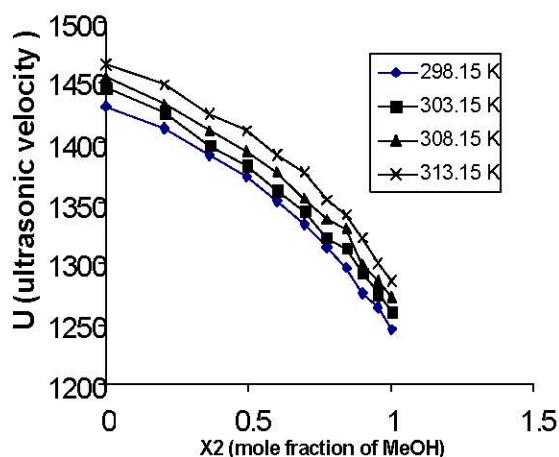Fig. 1: Ultrasonic velocity versus mole fraction of MeOH in AN-MeOH System

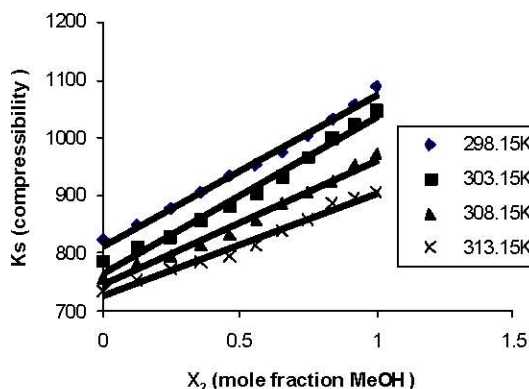Fig. 1A: Ultrasonic velocity versus mole fraction of MeOH in DMF-MeOH system

Fig. 2: Compressibility versus mole fraction of MeOH in AN + MeOH systeml
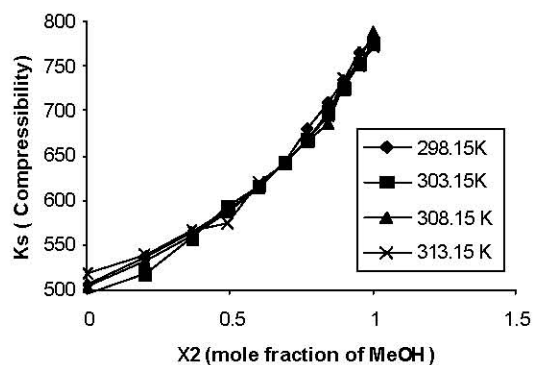

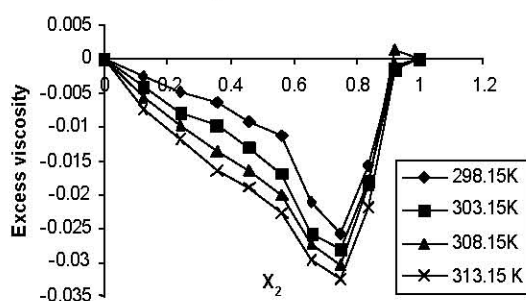Fig. 2A: Compressibility versus mole fraction of MeOH for DMF+ MeOH system

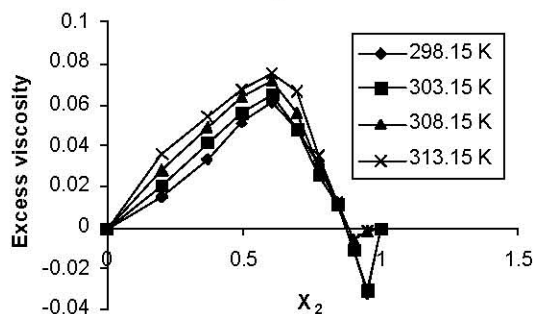Fig. 3: Excess viscosity versus mole fraction of MeOH for AN+MeOH

Fig. 3A: Excess viscosity versus mole fraction of MeOH for DMF + MeOH system

Variation of excess compressibility K_s^e plotted against the composition of MeOH in the binary system for different temperatures of study is shown in Fig. 4 and 4A. It can be seen that the excess compressibility for AN+MeOH system the curve reaches negative maxima at 0.5617 mole fraction of MeOH at all the temperatures studied. The results show that the variation in excess compressibility exhibit inversion in sign with increasing mole fraction of MeOH at higher temperatures (308.15 and 313.15 K) for AN+MeOH system. More specifically, a positive excess compressibility in
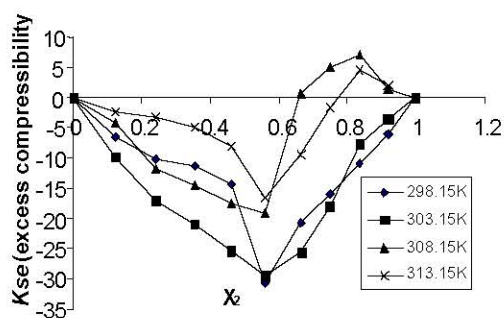
Fig. 4: Excess compressibility versus mole fraction of MeOH for AN + MeOH system

Fig. 4A: Excess compressibility versus mole fraction of MeOH for DMF +MeOH system

binary mixtures is related to repulsive interactions between unlike species which gives rise to a less rigid local structure [20] and to the ability of one or both components to develop dynamical networks,whose properties explicitly depend on concentration.

In case of DMF+MeOH system excess compressibility K_s^e is negative over the entire range and the negative maxima of all the curves are shifting towards right (higher mole fraction of MeOH) with increase in temperature from 298.15 to 313.15 K. Negative values of K_s^e are indicative of strong interaction between the component molecules due to hydrogen bonding as well as interstitial accommodation of molecules. Mixing of AN or DMF with MeOH will induce the dissociation of MeOH- MeOH associates with subsequent interstitial accommodation of AN or DMF molecules in alcohol aggregates. This leads to decrease in intermolecular free space and formation of closer molecular aggregates [17]. The effect of increase in the temperature appears to increase the excess properties suggesting the presence of specific molecular interactions. As the temperature increases the values of K_s^e becomes more negative which may be due to thermal dissociation of hetero-aggregates in liquid mixtures and more interstitial accommodation of one component into another [21].

More specifically, a negative _positive_ excess compressibility1,2,4–14 in binary mixtures is related to attractive _repulsive_ interactions between unlike species which gives rise to a more _less_ rigid local structure. Moreover, more complicated behaviors can be ascribed to the ability of one or both components to develop dynamical networks, whose properties explicitly depend on concentration.

CONCLUSION

It is clear from all the curves and observations that close packed structure in the intermediate composition range of the binary system is formed. The temperature
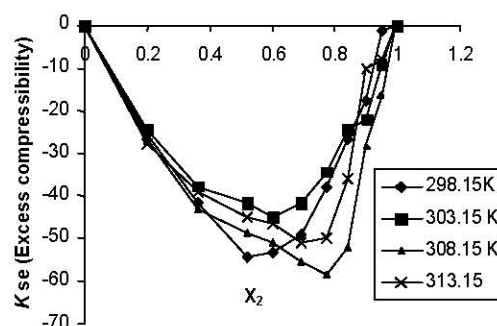
dependence of the different parameters suggests that the degree of deviation from ideality is strongly temperature sensitive and is influenced by the weakening of hydrogen bonds.

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