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Excess Volumes for Alkanol + Morpholine Systems at 298.15 and 308.15 K

So-Jin Park,* Kai Fischer, and Jürgen Gmehling

Department of Chemical Engineering, College of Engineering, Chungnam National University,
Dae-Jeon 305-764, Republic of Korea, and Universität Oldenburg, Technische Chemie (FB9),
Postfach 2503, D-26111 Oldenburg, Federal Republic of Germany

Excess molar volumes, V^E, were measured at 298.15 and 308.15 K by using a digital vibrating tube densimeter for binary mixtures of alkanol (methanol, ethanol, 1,2-propanol, 1,2-butanol) with morpholine (tetrahydro-1,4-oxazine, C_4H_9NO). The V^E values were found to be negative for all systems and became less negative with increasing carbon chain length of the alkanols. All the experimental values were correlated by using Redlich−Kister polynomials.

Introduction

This paper reports excess molar volumes (V^E) for morpholine with C_1 to C_4 alkanols at two temperatures (298.15 and 308.15 K). Morpholine derivatives are of great interest in the petroleum industry because of their high efficiency for the extraction of aromatic hydrocarbons from petroleum products. There are a few reports (*1*, *2*) for the excess properties of alkanol + morpholine mixtures at 298.15 K, but no V^E data were reported for 1-butanol + morpholine or 2-butanol + morpholine mixtures at this temperature nor any alkanol + morpholine V^E data at 308.15 K. The purpose of this work is not only to report the dependence of V^E values on composition and temperature for binary mixtures of alkanols with morpholine but also to compare these values with those reported for some alkanol + morpholine mixtures at 298.15 K.

Experimental Section

Materials. Morpholine (better than 99.5 mass % by GLC analysis) was obtained from Fluka and used without any further purification because the purity of substances is not a crucial factor in V^E measurements (*3*, *4*). The alkanols, provided by Merck, were carefully stored over molecular sieves (Union Carbide type 3 Å, from Fluka). Methanol and ethanol were distilled in an approximately 20 theoretical plate glass column under reduced pressure. Analysis by GLC showed that the purities of methanol, ethanol, 1-propanol, and 2-butanol were better than 99.9 mass %, and the purities of 2-propanol and 1-butanol were better than 99.5 mass %. The measured densities of the pure chemicals at 298.15 and 308.15 K are given in Table 1 together with the literature values.

Mixture Preparation. All solutions (ca. 3.5 cm³) were prepared by using a Satorius balance (precision 1×10^{-4} g) and air-tight stoppered 4 cm³ glass bottles. The more volatile component was filled directly into the bottle, and then the closed charged bottle was weighed. The second component was injected into the bottle through the stopper by means of a syringe. This method prohibited significant vapor loss and contamination. The possible error in mole fraction using this procedure is estimated to be lower than $\pm 1 \times 10^{-4}$.

Table 1. Experimental Densities (ϱ) of the Pure Components at 298.15 and 308.15 K Together with Literature Data

	ϱ/(g cm^{-3})		
	298.15 K		308.15 K
component	lit.	present study	present study
methanol	0.786 40[a]	0.786 45	0.776 42
ethanol	0.784 93[b]	0.784 96	0.776 91
1-propanol	0.799 57[a]	0.799 48	0.791 44
2-propanol	0.780 82[a]	0.780 89	0.772 32
1-butanol	0.806 00[c]	0.805 83	0.798 12
2-butanol	0.802 60[c]	0.802 45	0.794 04
morpholine	0.995 47[b]	0.995 46	0.985 95

[a] Reference 2. [b] Reference 5. [c] Reference 6.

Density Measurement. Densities of the pure components and binary mixtures were measured with an Anton-Paar digital vibrating glass tube densimeter (model DMA 02D) at 298.15 and 308.15 K with a precision in the densities of 3×10^{-6} g cm^{-3}. For each experimental determination the apparatus constant, *K*, was determined with doubly distilled water (ϱ(298.15 K) = 0.997 047 g cm^{-3}) and dried air. The temperature of the U-shaped tube was checked using a calibrated Hart Scientific digital thermometer with an accuracy of ±0.01 K. The apparatus and measuring method of densities have already been described elsewhere (*7*, *8*).

Results and Discussion

The excess molar volume for the binary mixture V^E (cm³ mol^{-1}) can be calculated by means of eq 1 from the experimental densities of the mixture and the pure components.

$$V^E = \left[\frac{x_1M_1 + x_2M_2}{\varrho_m}\right] - \frac{x_1M_1}{\varrho_1} - \frac{x_2M_2}{\varrho_2} \tag{1}$$

x_i, M_i, and ϱ_i are the mole fraction, the molecular weight, and the density of component *i* and ϱ_m is the density of the binary mixture.

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* To whom correspondence should be addressed at the Chungnam National University.

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Table 2. Excess Molar Volumes for Alkanol (1) + Morpholine (2) at 298.15 K

x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})
Methanol (1) + Morpholine (2)									
0.0522	−0.1848	0.2620	−0.8030	0.4497	−1.1743	0.6484	−1.2551	0.8478	−0.8197
0.0972	−0.3297	0.3007	−0.8977	0.5003	−1.2330	0.7000	−1.2016	0.9011	−0.5882
0.1469	−0.4830	0.3496	−1.0030	0.5495	−1.2653	0.7500	−1.1135	0.9442	−0.3606
0.2170	−0.6835	0.4104	−1.1163	0.5992	−1.2751	0.7995	−0.9859		
Ethanol (1) + Morpholine (2)									
0.0523	−0.1486	0.2493	−0.6197	0.4507	−0.9403	0.6508	−0.9821	0.8485	−0.6282
0.1024	−0.2800	0.3080	−0.7348	0.5009	−0.9830	0.6996	−0.9365	0.8999	−0.4613
0.1498	−0.4001	0.3500	−0.8067	0.5484	−0.9996	0.7510	−0.8627	0.9481	−0.2717
0.1980	−0.5124	0.3990	−0.8796	0.6095	−1.0027	0.7997	−0.7591		
1-Propanol (1) + Morpholine (2)									
0.0508	−0.1267	0.2560	−0.5497	0.4491	−0.8025	0.6511	−0.8247	0.8516	−0.4966
0.1026	−0.2464	0.3034	−0.6267	0.5007	−0.8366	0.6966	−0.7836	0.9002	−0.3615
0.1517	−0.3473	0.3516	−0.6931	0.5459	−0.8505	0.7494	−0.7127	0.9520	−0.1872
0.2001	−0.4504	0.4011	−0.7595	0.5979	−0.8489	0.7984	−0.6249		
2-Propanol (1) + Morpholine (2)									
0.0732	−0.1709	0.2603	−0.4740	0.4837	−0.6930	0.7022	−0.6241	0.8980	−0.2719
0.0994	−0.2018	0.3038	−0.5560	0.5443	−0.6984	0.7486	−0.5689	0.9501	−0.1327
0.1415	−0.2776	0.3728	−0.6100	0.6132	−0.6865	0.8126	−0.4622		
0.1873	−0.3590	0.4406	−0.6693	0.6574	−0.6624	0.8713	−0.3359		
1-Butanol (1) + Morpholine (2)									
0.0477	−0.1095	0.2496	−0.4609	0.4530	−0.6895	0.6495	−0.6931	0.8476	−0.4236
0.1001	−0.2101	0.2999	−0.5308	0.4997	−0.7071	0.6941	−0.6567	0.8978	−0.3020
0.1511	−0.3034	0.3507	−0.5932	0.5485	−0.7197	0.7496	−0.5981	0.9522	−0.1521
0.1994	−0.3822	0.3995	−0.6421	0.6037	−0.7149	0.7996	−0.5142		
2-Butanol (1) + Morpholine (2)									
0.0290	−0.0569	0.2552	−0.3319	0.4467	−0.4647	0.6476	−0.4624	0.8450	−0.2748
0.0830	−0.1351	0.2971	−0.3677	0.4985	−0.4808	0.6895	−0.4387	0.9014	−0.1927
0.1414	−0.2108	0.3480	−0.4116	0.5486	−0.4842	0.7462	−0.3908	0.9326	−0.1421
0.2021	−0.2759	0.3900	−0.4350	0.6024	−0.4784	0.8017	−0.3352		

Table 3. Excess Molar Volumes for Alkanol (1) + Morpholine (2) at 308.15 K

x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})	x_1	V^E/ (cm^3 mol^{-1})
Methanol (1) + Morpholine (2)									
0.0529	−0.1953	0.2502	−0.7992	0.4522	−1.2136	0.6473	−1.2968	0.8480	−0.8504
0.0968	−0.3430	0.2986	−0.9225	0.5024	−1.2718	0.6990	−1.2429	0.9037	−0.6040
0.1531	−0.5223	0.3474	−1.0317	0.5511	−1.3062	0.7490	−1.1558	0.9499	−0.3478
0.2003	−0.6616	0.3973	−1.1286	0.6046	−1.3155	0.7991	−1.0236		
Ethanol (1) + Morpholine (2)									
0.0523	−0.1505	0.2493	−0.6237	0.4507	−0.9514	0.6508	−0.9991	0.8485	−0.6646
0.1024	−0.2846	0.3080	−0.7428	0.5009	−0.9908	0.6996	−0.9702	0.8999	−0.5005
0.1498	−0.4050	0.3500	−0.8088	0.5484	−1.0118	0.7510	−0.8966	0.9481	−0.2976
0.1980	−0.5153	0.3990	−0.8843	0.6095	−1.0230	0.7997	−0.7923		
1-Propanol (1) + Morpholine (2)									
0.0512	−0.1306	0.2495	−0.5421	0.4500	−0.8027	0.6482	−0.8225	0.8485	−0.5023
0.0983	−0.2360	0.2996	−0.6233	0.4967	−0.8330	0.6911	−0.7852	0.8991	−0.3626
0.1484	−0.3447	0.3472	−0.6938	0.5525	−0.8477	0.7499	−0.7083	0.9430	−0.2147
0.2068	−0.4635	0.3987	−0.7524	0.6026	−0.8436	0.7941	−0.6280		
2-Propanol (1) + Morpholine (2)									
0.0582	−0.1372	0.1874	−0.3804	0.4417	−0.6825	0.6620	−0.6763	0.8642	−0.3835
0.0732	−0.1676	0.2572	−0.4917	0.4948	−0.7061	0.7092	−0.6348	0.9023	−0.2933
0.0991	−0.2187	0.3135	−0.5618	0.5403	−0.7143	0.7486	−0.5866	0.9527	−0.1513
0.1407	−0.3001	0.3741	−0.6259	0.6118	−0.7049	0.8093	−0.4959		
1-Butanol (1) + Morpholine (2)									
0.0314	−0.0796	0.2482	−0.4635	0.4500	−0.6861	0.6486	−0.6944	0.8492	−0.4162
0.0800	−0.1755	0.2980	−0.5312	0.4991	−0.7106	0.6971	−0.6555	0.8987	−0.3030
0.1382	−0.2843	0.3493	−0.5941	0.5491	−0.7248	0.7495	−0.5944	0.9394	−0.1935
0.2004	−0.3875	0.4026	−0.6438	0.5993	−0.7184	0.8015	−0.5115	0.9809	−0.0694
1-Butanol (1) + Morpholine (2)									
0.0572	−0.0974	0.2496	−0.3333	0.4488	−0.4703	0.6490	−0.4674	0.8457	−0.2767
0.0996	−0.1630	0.3004	−0.3826	0.5056	−0.4845	0.7016	−0.4307	0.8963	−0.2060
0.1411	−0.2155	0.3510	−0.4201	0.5557	−0.4889	0.7502	−0.3894	0.9390	−0.1266
0.2014	−0.2868	0.4020	−0.4567	0.5974	−0.4803	0.7932	−0.3496	0.9825	−0.0432

Table 4. Standard Deviations $\sigma_{st}(V^E)$ and Parameters A_i in Eq 2 at 298.15 K

system	A_1	A_2	A_3	A_4	A_5	$\sigma_{st}(V^E)$/(cm^3 mol^{-1})
methanol + morpholine	−4.929 67	−1.843 53	−0.363 88	0.113 00	−0.060 36	0.0012
ethanol + morpholine	−3.928 20	−1.277 48	0.035 51	−0.047 12	−0.463 33	0.0034
1-propanol + morpholine	−3.344 09	−0.975 42	0.056 22	0.205 49	−0.079 16	0.0019
2-propanol + morpholine	−2.782 92	−0.593 98	0.116 02	0.273 59	0.177 07	0.0083
1-butanol + morpholine	−2.837 54	−0.768 48	0.151 09	0.254 36	−0.212 53	0.0022
2-butanol + morpholine	−1.927 03	−0.389 71	0.216 39	0.222 18	−0.464 69	0.0026

Table 5. Standard Deviations $\sigma_{st}(V^E)$ and Parameters A_i in Eq 2 at 308.15 K

system	A_1	A_2	A_3	A_4	A_5	$\sigma_{st}(V^E)/(cm^3\ mol^{-1})$
methanol + morpholine	−5.083 59	−1.892 69	−0.415 31	0.045 28	−0.194 39	0.0020
ethanol + morpholine	−3.965 78	−1.377 06	−0.221 13	−0.220 21	−0.528 30	0.0051
1-propanol + morpholine	−3.334 69	−0.931 59	0.011 77	0.189 30	−0.005 95	0.0015
2-propanol + morpholine	−2.830 25	−0.602 58	−0.005 42	0.113 31	−0.145 61	0.0016
1-butanol + morpholine	−2.848 29	−0.759 27	0.235 22	0.279 89	−0.420 61	0.0024
2-butanol + morpholine	−1.944 52	−0.322 22	0.079 38	0.113 00	−0.251 37	0.0028

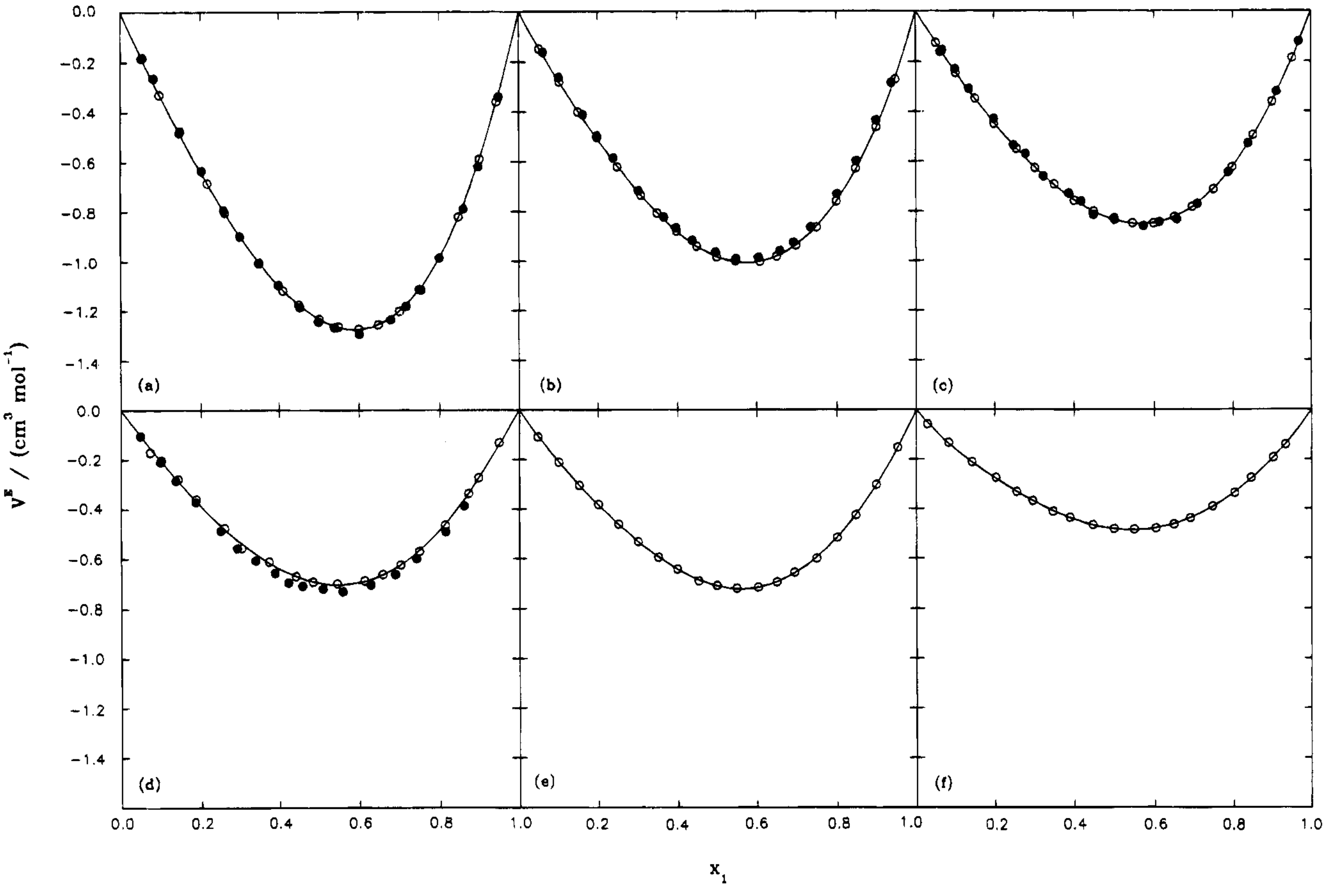

Figure 1. Excess molar volumes at the temperature 298.15 K for (a) methanol (1) + morpholine (2), (b) ethanol (1) + morpholine (2), (c) 1-propanol (1) + morpholine (2), (d) 2-propanol (1) + morpholine (2), (e) 1-butanol (1) + morpholine (2), and (f) 2-butanol (1) + morpholine (2): (○) experimental data, (●) data of Pettenati et al. (*2*).

A Redlich–Kister polynomial was used to describe the composition dependence of the experimental V^E data:

$$V^E = x_1x_2\sum_{i=1}^{n} A_i(x_1 - x_2)^{i-1} \tag{2}$$

where A_i are adjustable parameters. The standard deviations of the fits σ_{st} are defined as

$$\sigma_{st} = \left[\frac{\sum_i (V^E_{calc} - V^E_{exp})_i^2}{(N-n)}\right]^{1/2} \tag{3}$$

where N stand for the number of experimental data points and n the number of fitted parameters A_i (*9*).

The experimental V^E data of the alkanol + morpholine systems at the two temperatures of 298.15 and 308.15 K are presented in Tables 2 and 3, respectively. The values of the fitted parameters A_i and standard deviation σ_{st} are listed in Tables 4 and 5. All data points are weighted equally for each binary mixture. The V^E values at 298.15 K for each binary alkanol + morpholine system investigated in this work and the curves calculated from the Redlich–Kister smoothing equation, along with the literature values at the same temperature, have been plotted in

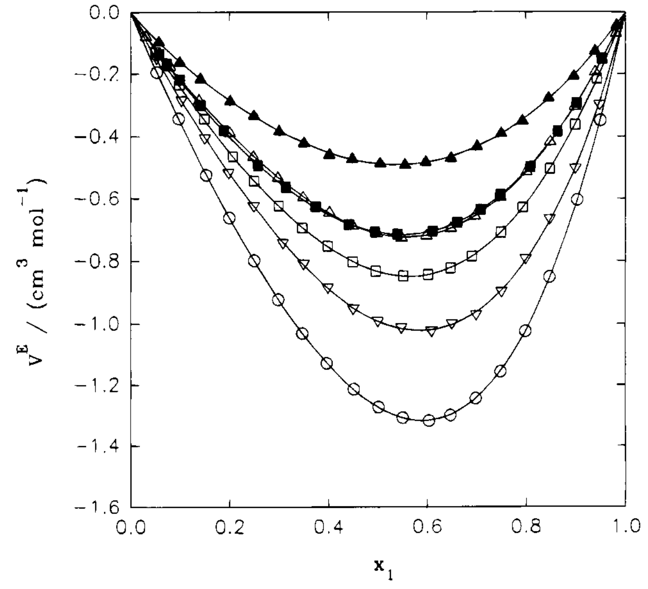

Figure 2. Excess molar volumes at the temperature 308.15 K for alkanol (1) + morpholine (2) systems: (○) methanol (1), (▽) ethanol (1), (□) 1-propanol (1), (■) 2-propanol (1), (△) 1-butanol (1), (▲) 2-butanol (1).

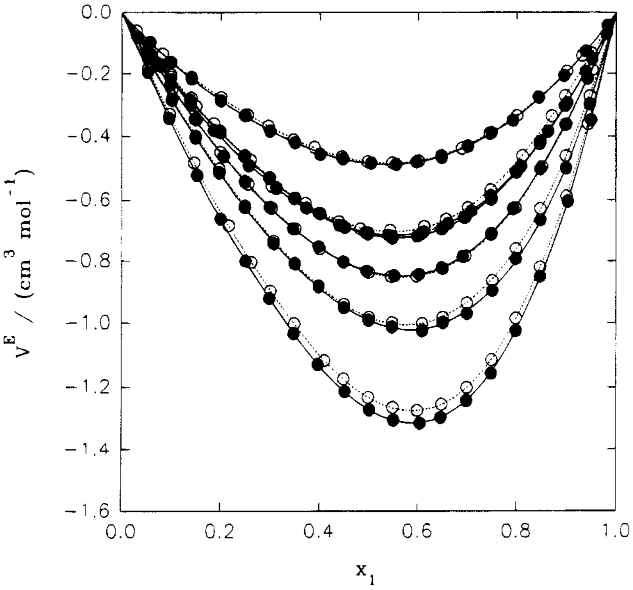

Figure 3. Comparison for excess molar volumes for alkanol (1) + morpholine (2) systems at two different temperatures: (○) 298.15 K, (●) 308.15 K.

Figure 1 for easy comparison. It can be seen that experimental results of this work are in good agreement with the values reported by Pettenati et al. (*2*). The overall agreement assures the reliability of our data, in spite of little deviation in the middle concentration region for the system 2-propanol + morpholine. Figure 2 represents the measured V^E values at 308.15 K for the same binary systems, and Figure 3 shows a comparison of the measured V^E data at two different temperatures: 298.15 and 308.15 K. It shows no significant temperature dependence except for the system of methanol + morpholine because of their small temperature difference. In the figures, the symbols represent the experimental V^E values and the different lines represent the correlation results of eq 2.

The negative deviation from the linear volumetric behavior suggests a strong hydrogen bonding. Morpholine acts as a proton donor, and alkanol acts as a proton acceptor. The methanol + morpholine system shows the largest negative value deviation among the alkanol + morpholine mixtures in this study and their negative V^E values decrease with increasing aliphatic chain length of the alcohol. The alkan-2-ol + morpholine mixture shows smaller V^E values than the corresponding alkan-1-ol + morpholine mixture. Among the measured systems in this study, the 2-butanol + morpholine system has the smallest V^E values.

Literature Cited

(1) Awward, A. M.; Allos, E. I.; Salman, S. R. *J. Chem. Eng. Data* **1988**, *33*, 265.
(2) Pettenati, C.; Alessi, P.; Fermeglia, M.; Kikic, I. *Thermochim. Acta* **1990**, *162*, 203.
(3) Berti, P.; Lepori, L.; Matteoli, E. *Fluid Phase Equilib.* **1989**, *44*, 285.
(4) Spanedda, A.; Lepori, L.; Matteoli, E. *Fluid Phase Equilib.* **1991**, *69*, 209.
(5) Riddick, J. A.; Bunger, E. B. *Organic Solvents. Physical Properties and Methods of Purification*, 4th ed.; Wiley-Interscience: New-York, 1986.
(6) Dean, J. A. *Handbook of Organic Chemistry*; Donnelley & Sons Co.: New York, 1987.
(7) Letcher, T. M. ; Lucas, A. *Fluid Phase Equilib.* **1982**, *8*, 301.
(8) Letcher, T. M.; Schoonbaert, F. E. Z.; Bean, B. *Fluid Phase Equilib.* **1990**, *61*, 111.
(9) Choudary, N. V.; Naldu, P. R. *J. Chem. Eng. Data* **1985**, *30*, 78.

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