International Journal of Thermophysics, Vol. 26, No. 3, May 2005 (© 2005)
DOI: 10.1007/s10765-005-5572-8

Densities, Viscosities, and Refractive Indices of Mixtures of Hexane with Cyclohexane, Decane, Hexadecane, and Squalane at 298.15 K

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Received March 22, 2004

Densities, ρ, viscosities, η, and refractive indices, n_D, have been measured as a function of composition for binary mixtures of cyclohexane, decane, hexadecane, and squalane with hexane at 298.15 K and atmospheric pressure. From these measurements the excess molar volumes, V_m^E, viscosity deviations, $\delta\eta$, and the change in refractive indices on mixing, Δn_D, were calculated. These results were fitted to Redlick–Kister polynomial equations to estimate the binary coefficients and standard errors. The effects of size and shape of the components on excess properties have been discussed.

KEY WORDS: alkanes; binary mixtures; cyclohexane; decane; density; excess volume; hexadecane; hexane; refractive index; squalane; viscosity.

1. INTRODUCTION

Thermophysical properties of liquid mixtures containing alkanes have been studied by several investigators [1–9]. However, there are only a few studies that include the thermophysical properties of mixtures of hydrocarbons with higher alkanes [10–17]. The viscosity and density of mixtures of butane and hexane with squalane, intended to model mixtures of refrigerants and refrigeration oil, were measured by Kumagai and Takahashi [10]. Croucher and Patterson [18] studied excess properties in higher alkanes such as hexadecane and squalane. Since many industrial liquid mixtures contain alkanes as major components, it is important to understand the mechanism of interaction in order to predict its properties in liquid mixtures.

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In continuation of our previous work [13–16] on the thermodynamic properties of binary liquid mixtures with molecules of significantly different size and flow behavior, the present study concerns experimentally measured values of densities, ρ, viscosities, η, and refractive indices, Δn_D, for binary mixtures of cyclohexane, decane, hexadecane, and squalane with hexane at 298.15 K and atmospheric pressure. Furthermore, using these experimental results, excess molar volumes, V_m^E, deviations in viscosity, $\delta\eta$, and changes in refractive indices on mixing, Δn_D, have been calculated in order to gain a better understanding of the intermolecular interactions between the component molecules. These excess properties have been correlated with composition using the Redlich–Kister polynomial equation [19].

2. EXPERIMENTAL

2.1. Materials

Hexane and cyclohexane were Ranbaxy products, whereas decane and hexadecane were obtained from S. D. Fine Chemicals Ltd. The stated label purities of these alkanes ranged from 99 to 99.5% in mass. Squalane was an Acros product with a stated purity >99%. All reagents except squalane were used after purification by fractional distillation. The experimentally measured values of densities, viscosities, and refractive indices of all the pure components at 298.15 K are given in Table I. It can easily be seen that the experimental values of all the measured properties are in close agreement with those reported in the literature [20–23].

Table I. Properties of Pure Liquid Components at 298.15 K and Atmospheric Pressure

	ρ(g·cm^{-3})		η(mPa·s)		n_D	
Component	Observed	Literature	Observed	Literature	Observed	Literature
Cyclohexane	0.7737	0.77389 [20]	0.898	0.8980 [20]	1.4270	1.4235 [20]
Hexane	0.6548	0.65489 [20,21]	0.294	0.2968 [21] 0.2985 [20]	1.3745	1.3723 [20]
Decane	0.7262	0.72625 [20] 0.72614 [21]	0.859	0.8614 [20]	1.4100	1.4097 [20,21]
Hexadecane	0.7706	0.76994 [21] 0.77079 [23]	3.039	3.0320 [22] 3.0520 [21]	1.4340	1.4345 [22] 1.4327 [23] 1.4325 [21]
Squalane	0.8054	0.80600 [21] 0.80500 [10]	31.123	–	1.4474	1.4509 [21]

2.2. Apparatus and Experimental Procedures

Densities, which are accurate to $\pm 0.0003\,\mathrm{g{\cdot}cm^{-3}}$, were measured by a bicapillary pycnometer with a bulb of about $12\,\mathrm{cm}^3$ and a capillary with an internal diameter of about 1 mm. Details of its calibration and operational procedures have been described previously [13]. The pycnometer, filled with the desired liquid, was kept in a transparent walled water bath with a thermal stability of ±0.01°C, as checked by means of a calibrated thermometer, to attain thermal equilibrium. The estimated uncertainty in density measurements was 0.07%.

The kinematic viscosities, $\nu(=\eta/\rho)$ of the binary liquid mixtures and their pure components were measured using a modified suspended level Ubbelohde viscometer [24, 25]. Toluene and doubly distilled water were used to calibrate the viscometer [20, 22]. A thoroughly cleaned and dried viscometer filled with the experimental liquid was placed vertically in a glass-fronted, well-stirred water bath. The flow times of the liquids were recorded with an accurate stop watch precise to ±0.01 s, after thermal stability was attained. The present values of viscosity for the various liquids agree with literature values within a deviation of about ±0.003 mPa·s. The uncertainty of the absolute viscosity is estimated to be ±0.9%.

Refractive indices were measured using an Abbe refractometer (Erma, A-302A). Calibration of the instrument was carried out by measuring the refractive indices of doubly distilled water, toluene, and carbon tetrachloride at known temperatures [20, 22]. Details of the calibration of the refractometer and the experimental procedure of the measurement of refractive index have been given elsewhere [13, 15]. The sample mixtures were directly injected into the prism assembly of the instrument by means of an air-tight hypodermic syringe. An average of four or five measurements was taken for a sample mixture. The estimated uncertainty in refractive index measurement is ±0.2%.

3. RESULTS AND DISCUSSION

Table II summarizes the experimental densities, viscosities, refractive indices, excess molar volumes, viscosity deviations, and changes in refractive indices on mixing for the different binary mixtures at 298.15 K. The excess molar volumes, V_m^E, of the mixture were obtained using the experimental values of density as

$$V_m^E(\mathrm{cm^3\cdot mol^{-1}}) = [xM_1 + (1-x)M_2]/\rho_m - xM_1/\rho_1 - (1-x)M_2/\rho_2 \quad (1)$$

where x is the mole fraction of the first component, ρ_m is the density of the mixture, and M_1, ρ_1 and M_2, ρ_2 are the molar mass and density of

Table II. Densities, Viscosities, Refractive Indices, Excess Molar Volumes, Viscosity Deviations, and Changes in Refractive Index on Mixing for Binary Mixtures at 298.15 K and Atmospheric Pressure

x	ρ(g·cm^{-3})	η(mPa·s)	n_D	V_m^E (cm^3·mol^{-1})	$\delta\eta$(mPa·s)	Δn_D
x Cyclohexane + $(1-x)$ hexane						
0.0000	0.6548	0.294	–	–		
0.0357	0.6582	0.295		0.0202	−0.021	
0.1127	0.6659	0.301		0.0480	−0.062	
0.2000	0.6749	0.312		0.0540	−0.103	
0.3288	0.6886	0.342		0.0860	−0.150	
0.4620	0.7035	0.405		0.1182	−0.169	
0.5424	0.7129	0.451		0.1300	−0.170	
0.5770	0.7170	0.472		0.1362	−0.170	
0.6703	0.7284	0.539		0.1420	−0.160	
0.7543	0.7392	0.603		0.1360	−0.146	
0.8703	0.7549	0.710		0.0982	−0.110	
0.9451	0.7655	0.794		0.0561	−0.071	
0.9740	0.7697	0.842		0.0323	−0.040	
0.9935	0.7727	0.894		0.0062	−0.011	
1.0000	0.7737	0.898		–	–	
x Decane + $(1-x)$ hexane						
0.0000	0.6548	0.294	1.3745	–	–	–
0.0210	0.6571	0.296	1.3755	−0.0251	−0.010	0.0003
0.0659	0.6620	0.307	1.3780	−0.0835	−0.024	0.0012
0.1584	0.6713	0.337	1.3820	−0.1755	−0.047	0.0019
0.2330	0.6781	0.355	1.3854	−0.2156	−0.071	0.0026
0.2761	0.6818	0.377	1.3871	−0.2450	−0.073	0.0028
0.3493	0.6878	0.417	1.3900	−0.2835	−0.075	0.0031
0.4506	0.6953	0.471	1.3940	−0.2712	−0.078	0.0035
0.5410	0.7014	0.518	1.3973	−0.2453	−0.082	0.0036
0.6382	0.7074	0.567	1.4004	−0.2058	−0.088	0.0033
0.7836	0.7156	0.657	1.4045	−0.1350	−0.080	0.0022
0.9095	0.7220	0.772	1.4080	−0.0654	−0.036	0.0012
0.9654	0.7247	0.823	1.4095	−0.0250	−0.016	0.0007
0.9936	0.7260	0.855	1.4099	−0.0055	−0.000	0.0001
1.0000	0.7262	0.859	1.4100	–	–	–
x Hexadecane + $(1-x)$ hexane						
0.0000	0.6548	0.294	1.3745	–	–	–
0.0284	0.6621	0.322	1.3784	−0.0500	−0.051	0.0022
0.0757	0.6733	0.382	1.3860	−0.1300	−0.120	0.0070
0.1349	0.6857	0.473	1.3950	−0.2250	−0.191	0.0125
0.1842	0.6949	0.559	1.4006	−0.3102	−0.241	0.0151
0.2660	0.7084	0.703	1.4087	−0.4452	−0.321	0.0184
0.3427	0.7191	0.864	1.4147	−0.5350	−0.371	0.0198
0.4864	0.7355	1.205	1.4262	−0.6123	−0.424	0.0228
0.5030	0.7371	1.240	1.4266	−0.6085	−0.435	0.0222

Table II. Continued

x	ρ(g·cm^{-3})	η(mPa·s)	n_D	V_m^E (cm^3·mol^{-1})	$\delta\eta$(mPa·s)	Δn_D
0.6779	0.7518	1.735	1.4318	−0.4900	−0.402	0.0170
0.7546	0.7570	2.022	1.4320	−0.4000	−0.344	0.0126
0.8927	0.7651	2.562	1.4322	−0.1753	−0.182	0.0046
0.9468	0.7680	2.805	1.4332	−0.0905	−0.088	0.0024
0.9902	0.7701	3.012	1.4340	−0.0218	−0.0000	0.0006
1.0000	0.7706	3.039	1.4340	–	–	–
x Squalane + $(1-x)$ hexane						
0.0000	0.6548	0.294	1.3745	–	–	–
0.0144	0.6639	0.405	1.3798	−0.1520	−0.334	0.0043
0.0481	0.6821	0.593	1.3904	−0.4450	−1.184	0.0124
0.0748	0.6942	0.727	1.3976	−0.6180	−1.874	0.0176
0.1218	0.7119	0.971	1.4068	−0.8802	−3.076	0.0234
0.1779	0.7285	1.413	1.4153	−1.0812	−4.367	0.0278
0.2858	0.7514	2.923	1.4244	−1.3153	−6.182	0.0291
0.3695	0.7640	4.685	1.4310	−1.3401	−7.002	0.0296
0.4258	0.7707	6.068	1.4349	−1.3210	−7.351	0.0294
0.5661	0.7836	10.154	1.4435	−1.1250	−7.593	0.0277
0.7180	0.7935	15.592	1.4468	−0.8302	−6.836	0.0205
0.8070	0.7980	19.600	1.4468	−0.6301	−5.572	0.0135
0.8939	0.8017	24.318	1.4470	−0.3901	−3.534	0.0073
0.9593	0.8041	28.409	1.4470	−0.1605	−1.461	0.0018
0.9943	0.8052	30.743	1.4472	−0.0225	−0.204	0.0010
1.0000	0.8054	31.123	1.4474	–	–	–

pure components 1 and 2, respectively. The viscosity deviation, $\delta\eta$, and the change in refractive index on mixing, Δn_D, were computed using the equations,

$$\delta\eta(\text{mPa.s}) = \eta_m - [x\eta_1 + (1-x)\eta_2] \tag{2}$$

$$\text{and } \Delta n_D = n_{D_m} - [x n_{D_1} + (1-x)\ n_{D_2}] \tag{3}$$

where η_m and n_{D_m} are the viscosity and refractive index of the mixtures while η_1, n_{D_1} and η_2, n_{D_2}represent the viscosity and refractive index of pure components 1 and 2, respectively. The composition dependence of V_m^E, $\delta\eta$, and Δn_D was represented by a Redlich-Kister type equation [19],

$$Y = x(1-x)\sum_{i=1}^{k} A_i(2x-1)^{i-1} \tag{4}$$

Table III. Values of the Coefficients A_i of Eq. (4) and the Standard Deviations, σ for the Various Mixtures

	A_1	A_2	A_3	A_4	A_5	σ
x Cyclohexane + $(1-x)$ hexane						
V_m^E (cm^3·mol^{-1})	0.4977	0.3104	0.3141	0.0031	–	0.0072
$\delta\eta$(mPa·s)	−0.6959	0.1330	−0.2699	−0.6992	–	0.0091
Δn_D	–	–	–	–	–	–
x Decane + $(1-x)$ hexane						
V_m^E (cm^3·mol^{-1})	−1.0415	0.5378	0.0203	−0.3414	–	0.0072
$\delta\eta$ (mPa·s)	−0.3370	−0.0776	−0.1954	0.0489	–	0.0056
Δn_D	0.0144	0.0000	−0.0065	−0.0019	0.0133	0.0001
x Hexadecane + $(1-x)$ hexane						
V_m^E (cm^3·mol^{-1})	−2.4302	0.1452	0.9192	−0.2171	–	0.0061
$\delta\eta$ (mPa·s)	−1.7285	−0.3298	−0.0503	0.3538	–	0.0075
Δn_D	0.0880	−0.0182	−0.0198	−0.0260	–	0.0007
x Squalane + $(1-x)$ hexane						
V_m^E (cm^3·mol^{-1})	−4.8898	2.6914	−2.2047	0.1309	–	0.0035
$\delta\eta$ (mPa·s)	−30.2836	−3.2373	−11.4308	−3.9222	11.9649	0.0055
Δn_D	0.1137	−0.0288	0.0580	−0.1164	–	0.0006

where k is the number of estimated parameters and A$_i$'s are the polynomial coefficients, which were obtained by fitting the equation to the experimental result with a least-squares regression method. The standard deviation, σ, was defined as

$$\sigma = \left[\sum (Y_{\exp} - Y_{\mathrm{cal}})^2 / \, (n-k)\right]^{\frac{1}{2}} \tag{5}$$

where n is the number of measurements. For all the binary mixtures investigated $\sigma\ \left(V_m^E\right) < 0.0072\,\mathrm{cm}^3\cdot\mathrm{mol}^{-1}, \sigma(\delta\eta) < 0.0091\,\mathrm{mPa}\cdot\mathrm{s}$, and $\sigma(\Delta n_D) <$ 0.0007. The parameters of Eq. (4) and standard deviations, σ, are given in Table III.

The V_m^E values fitted with Eq. (4) are plotted as a function of x in Fig. 1. A close examination of Fig. 1 shows that binary mixtures of decane, hexadecane, and squalane with hexane exhibit negative V_m^E values for the whole range of composition, increasing in magnitude with the length of the hydrocarbon chain. However, V_m^E values for the cyclohexane and hexane mixture show positive values. The maximum negative value is obtained for the squalane + hexane mixture. Squalane (2, 6, 10, 15, 19, 23-hexamethyltetracosane) is branched in molecular structure and has a high molar mass. The negative values of V_m^E can be visualized as being due

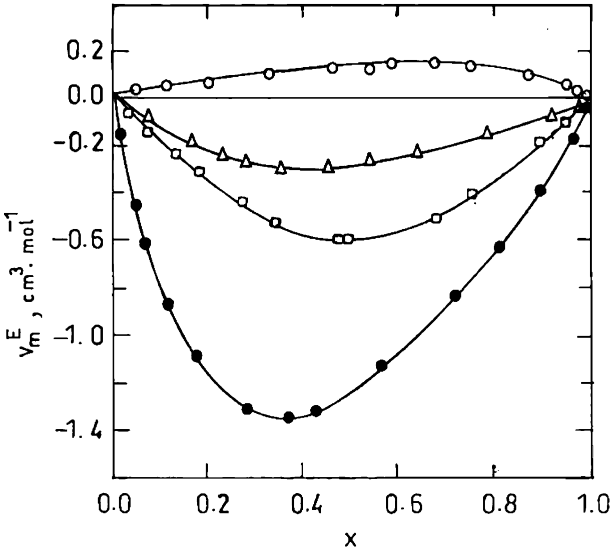

Fig. 1. Excess molar volume, V_m^E, for (O)x cyclohexane, (Δ)x decane, (☐) x hexadecane, and (●)x squalane + $(1-x)$ hexane at 298.15 K. Curves represent Eq. (4) with the coefficients of Table III.

to a closer approach of the unlike molecules having significantly different molecular sizes. It indicates the existence of specific interactions between the liquid components.

The V_m^E values for the binary liquid mixture of cyclohexane + hexane have been compared with V_m^E results given by Ott et al. [26]. The results agree over most of the compositions range ($x = 0.2$, $V_m^E = 0.0540\,cm^3 \cdot mol^{-1}$; $x = 0.5$, $V_m^E = 0.1266\,cm^3 \cdot mol^{-1}$) as given in Table II. For the decane + hexane mixture, density and viscosity values are reported by Cooper and Asfour [2] at 293.15 K. For the case of the hexadecane + hexane liquid mixture, $V_m^E = -0.61\,cm^3 \cdot mol^{-1}$ at the equimolar composition which agrees with the value reported by Van and Patterson [27]. No V_m^E data for the squalane + hexane mixture could be found for comparison. However, density and viscosity values for the above mixture have been reported by Kumagai and Takahashi [10] at 273.15, 293.15, 313.15, and 333.15 K. The measured density of pure squalane has been compared with a literature value [10].

The variations of the viscosity deviations, $\delta\eta$, with the mole fraction of the first component for the binary mixtures are presented in Fig. 2. The $\delta\eta$ values are negative for all four binary mixtures over the whole

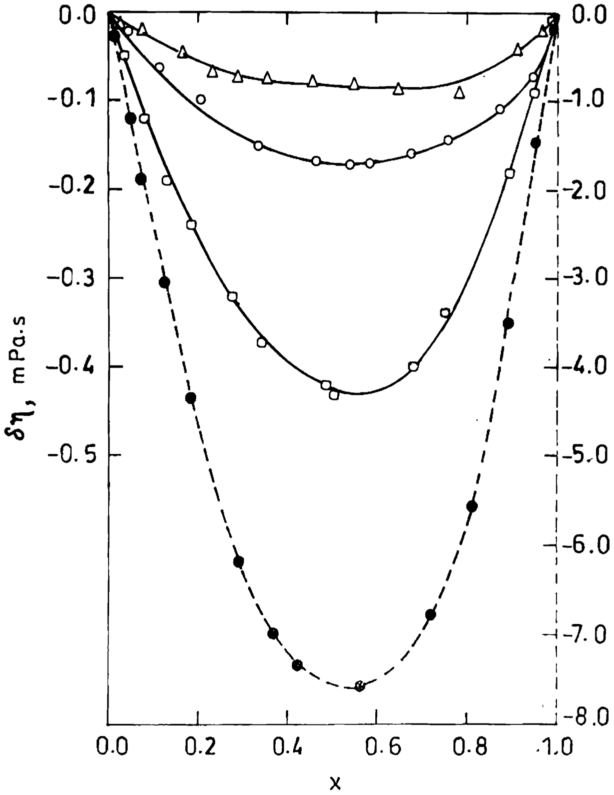

Fig. 2. Viscosity deviation, $\delta\eta$, for (O) x cyclohexane, (Δ)x decane, (☐) x hexadecane, and (●)x squalane + $(1-x)$ hexane at 298.15 K. Curves represent Eq. (4) with the coefficients of Table III. Dashed line for squalane corresponds to y-axis on right-hand side.

composition range. It again shows an increasing trend with an increasing chain length of alkane molecules. The values of viscosities for the cyclohexane + hexane mixture show good agreement at several compositions with those reported in TRC tables [21]. For the hexadecane + hexane mixture, values of viscosities are compared with the data given by Heric and Brewer [28] ($x = 0.2640, \eta = 0.70$ mPa·s; $x = 0.7417, \eta = 2.022$ mPa·s) as well as in TRC tables [21]. Good agreement has been found. The $\delta\eta - x$ curves are almost symmetrical about the equimolar concentration. The negative values of $\delta\eta$ for different binary mixtures vary in the sequence; squalane + hexane > hexadecane + hexane > cyclohexane + hexane > decane + hexane. Squalane is similar in chemical nature to hexadecane [18], but the

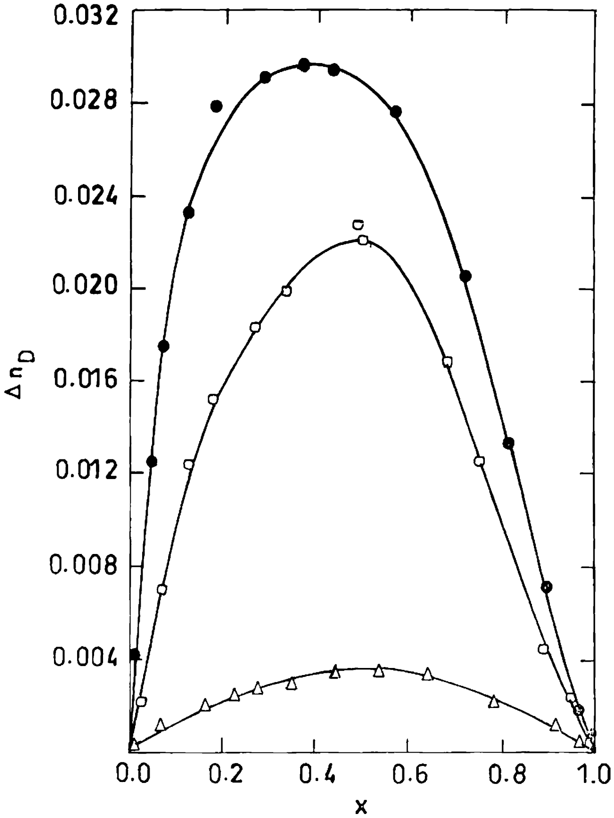

Fig. 3. Change in refractive index on mixing, Δn_D, for (Δ)x decane, (□) x hexadecane, and (•)x squalane + $(1-x)$ hexane at 298.15 K. Curves represent Eq. (4) with the coefficients of Table III.

viscosity of pure squalane is found to be about an order of magnitude larger ($\approx$ 31 mPa·s) than that of hexadecane ($\approx$ 3 mPa·s). For the squalane + hexane mixture, $\delta\eta$ is about seventeen times more negative than that observed for hexadecane + hexane.

The change in refractive index on mixing, Δn_D, for all the binary liquid mixtures except for cyclohexane + hexane at 298.15 K is shown in Fig. 3. The Δn_D values for all three systems are positive for the entire composition range. The Δn_D values also show an increasing trend with increasing chain length, like V_m^E and $\delta\eta$. The values of refractive indices for the hexadecane + hexane mixture have been compared with the values reported by Heric and Brewer [23], and good agreement has been found.

The molecules undertaken for the present investigation have significantly different sizes; hence, their areas of contact will be large. The molar volume of squalane is 525.00 $\text{cm}^3\cdot\text{mol}^{-1}$, which is much larger than for the rest of the components. The possibility of interactions between liquid components increases because of differences in their molecular sizes. The effect of free volume becomes more significant. The strength of specific interaction is not the only factor influencing the V_m^E and $\delta\eta$ of liquid mixtures, the molecular size and shape of the components are equally important factors. The negative values of V_m^E and $\delta\eta$ suggest greater interactions; therefore, it can be concluded that the order of interactions for the studied binary mixtures with hexane follow the sequence: squalane > hexadecane > decane > cyclohexane.

ACKNOWLEDGMENT

Author is thankful to the Council of Scientific and Industrial Research (New Delhi), India for providing financial assistance.

List of Symbols

A_i	polynomial coefficients in Eq. (4) ($\text{cm}^3\cdot\text{mol}^{-1}$)
k	number of estimated parameters in Eq. (4)
n	number of measurements in Eq. (4)
V_m	molar volume ($\text{cm}^3\cdot\text{mol}^{-1}$)
x	mole fraction of the first component
n_D	refractive index

Greek Letters

ρ	density ($\text{g}\cdot\text{cm}^{-3}$)
η	viscosity (mPa·s)
σ	standard deviation ($\text{cm}^3\cdot\text{mol}^{-1}$)

Superscripts

E	excess property

Subscripts

i	index of the coefficients in Eq. (4)

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