EXPERIMENTAL VAPOR-LIQUID EQUILIBRIA DATA FOR BINARY MIXTURES OF XYLENE ISOMERS

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Abstract - Separation of aromatic C8 compounds by distillation is a difficult task due to the low relative volatilities of the compounds and to the high degree of purity required of the final commercial products. For rigorous simulation and optimization of this separation, the use of a model capable of describing vapor-liquid equilibria accurately is necessary. Nevertheless, experimental data are not available for all binaries at atmospheric pressure. Vapor-liquid equilibria data for binary mixtures were isobarically obtained with a modified Fischer cell at 100.65 kPa. The vapor and liquid phase compositions were analyzed with a gas chromatograph. The methodology was initially tested for cyclo-hexane+n-heptane data; results obtained are similar to other data in the literature. Data for xylene binary mixtures were then obtained, and after testing, were considered to be thermodynamically consistent. Experimental data were regressed with Aspen Plus® 10.1 and binary interaction parameters were reported for the most frequently used activity coefficient models and for the classic mixing rules of two cubic equations of state.
Keywords: Xylenes; Liquid-vapor equilibrium; Experimental data.

INTRODUCTION

Xylene isomers are of great importance to petrochemical industries, since these substances are bases for the synthesis of many organic compounds. For example, p-xylene is oxidized to teraphtalic or dimethylteraphtalic acid as the first stage in polyester production. Xylenes are normally produced as a mixed stream which contains mainly p-xylene, m-xylene, o-xylene and ethylbenzene. Separation of C8 aromatic compounds by distillation is a difficult task and the columns, in general, have more than 200 stages and a high reflux ratio due to the low relative volatilities of the compounds and to the high degree of purity required of the final commercial products.

For the rigorous simulation and optimization of this separation, an accurate description of vapor-liquid equilibria (VLE) is required. Nevertheless, there is little data in the literature on binary systems of xylene isomers. Gmehling et al. (1980) present isobaric data obtained at 101.3 kPa on p-xylene(1) + meta-xilene(1). Llopis and Montón (1994) obtained isobaric data at 6.66 and 26.66 kPa on ethylbenzene + m-xylene, p-xylene + o-xylene and m-xylene + o-xylene. In this paper, experimental data on vapor-liquid equilibria for binary systems of xylene isomers at local atmospheric pressure (100.65 kPa) are presented. Fischer equipment modified by Castro (1996) was used. The compositions of liquid and vapor phases were analyzed by gas chromatography

(GC). Experimental data were regressed with Aspen Plus® 10.1 and binary interaction parameters were reported for the most frequently used activity coefficient models and for classic mixing rules of two cubic equations of state (Peng and Robinson (1976) and Soave-Redlich-Kwong (Soave, 1972) modified by Mathias et al. (1984)).

EXPERIMENTAL SECTION

Material

The xylenes used in this work were supplied by BRASKEM Unidade de Insumos Básicos. Cyclohexane was supplied by Nitrocarbono S/A and n-heptane was obtained from Merck. All compounds were used without any additional purification. The m-xylene and the o-xylene used were purified with equipment refered to as the Spinning Band Distillation System from BR Instrument Corporation (Figure 1). This equipment is used for purification of solvents and preparation of chromatographic

patterns; the process basically consists of distillation with a high reflux ratio (> 200). P-xylene was purified in many crystallization stages: the solution was initially refrigerated at 283.15 K and after crystals formed, it was maintained at room temperature for 30 minutes and then filtered; after refiltering the solid was then remelted and the process was repeated until the required purity was achieved. All the compounds used were passed through a molecular sieve with a 0.3 nm pore diameter, manufactured by UNION CARBIDE, in order to remove any free water. The normal boiling point (at 100.65 kPa) was determined with the equilibrium cell and relative density was measured in a digital Anton Paar DMA45 by German Weber S.A. Table 1 shows that the normal boiling point and relative density for the compounds used are quite close to the values found in the literature, although local atmospheric pressure is slightly lower than 101.3 kPa. The chromatographic analyses showed a minimum purity of 99.93% for p-xylene, of 99.75% for m-xylene, of 99.85% for o-xylene, of 99.82% for cyclohexane and of 99.37% for n-heptane.
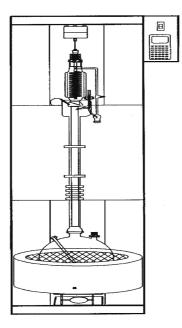

Figure 1: Spinning band distilllation System

Table 1: Normal boiling points (T_{eb}) and relative densities (r) of pure compounds

Substance	T_{eb} (K)		r (kg/m³) 20⁰C	
	Experimental (at P=100.65 kPa)	Literature[1] (at P=101.3 kPa)	Experimental	Literature[1]
p-xylene	411.500	411.509	861.20	860.98
m-xylene	412.333	412.270	864.20	864.36
o-xylene	417.549	417.579	879.80	880.14
cyclo-hexane	353.780	353.880	778.70	864.36
n-heptane	371.431	371.574	684.20	880.14

[1] Riddick et al.(1986)

Apparatus and Procedure

In this work, isobaric data on vapor-liquid equilibria were obtained in a modified Fischer ebuliometer (Figure 2) with recirculation of both liquid and vapor phases. Equilibrium was normally reached after 15 minutes. Heating of the mixture was regulated in order to achieve a mean speed of 30 drops per minute. Samples of 0.02 μl were taken from the condensed vapor and liquid and analyzed with a Shimadzu gas chromatograph equipped with a flame ionization detector (FID). A 60 m × 0.32 mm × 0.5 μm capillary column (type LM100) of polyethylene glycol was used and the area of the peaks was integrated by a Hewlett-Packard 3390A. Data points were the average of three injections of each phase; the standard deviation of the mole fraction was less than 0.001.

The equilibrium temperature was measured with a digital thermometer from Systemteknik with a 0.001 K resolution using a Pt 100 sensor positioned at the Cottrell pump (2), shown in Figure 2. Pressure was measured with a 0.01 kPa resolution. The equipment operates at pressures ranging from 0.25 to 300 kPa (absolute) and temperatures up to 523.15 K. Pressure and temperature sensors were calibrated using the same method described by Castro (1996).
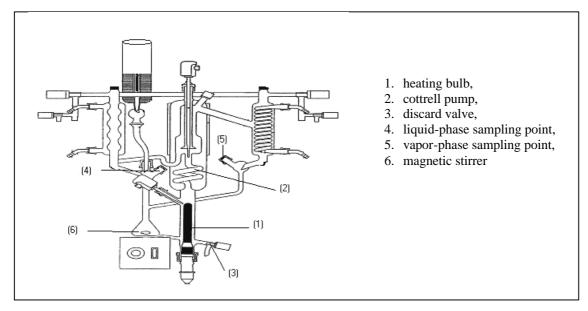

1. heating bulb,
2. cottrell pump,
3. discard valve,
4. liquid-phase sampling point,
5. vapor-phase sampling point,
6. magnetic stirrer

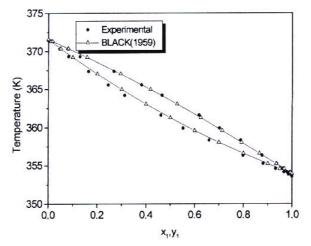**Figure 2:** Modified Fischer cell.

RESULTS

Experimental Data

In order to test the method, data for cyclohexane(1)+n-heptane(2) were obtained and are shown in Table 2. This system, on which a great deal of consistent thermodynamic data have been published in the literature, is used as reference. Data were compared to those presented by Black (1959) [published in Gmehling et al. (1980)]; the results obtained in this work are similar to data in the literature as can be seen in Figure 3, and the experimental procedure was considered satisfactory.

In Tables 3 to 5 VLE experimental data obtained for the p-xylene(1) + m-xylene(2), p-xylene(1) + o-xylene(2) and m-xylene(1) + o-xylene(2) systems are presented. All experimental data were obtained twice as both sets of results were always very close, the mean values were reported. Gas chromatographic analysis of each phase was repeated three times, and again as the three results are very close, the mean results were reported.

Figure 4 shows that the p-xylene + m-xylene experimental data obtained in this work are similar to data published by Gmehling et al. (1980), although they were obtained at a slightly different pressure (in this work P=100.65 kPa and in Gmehling et al. (1980) P= 101.3 kPa).

**Table 2: Experimental VLE data for the cyclohexane(1) + n-heptane(2)
system at pressure 100.65 kPa**

T(K)	x_1	y_1
371.424	0.0000	0.0000
370.332	0.0423	0.0687
369.292	0.0847	0.1356
368.295	0.1247	0.1936
367.423	0.1542	0.2430
365.777	0.2348	0.3409
364.366	0.3047	0.4357
363.173	0.3541	0.4831
360.597	0.5148	0.6447
357.894	0.6061	0.7159
357.008	0.6785	0.7880
355.862	0.7417	0.8433
355.156	0.8777	0.8931
354.523	0.9525	0.9625
354.144	0.9763	0.9809
353.953	0.9899	0.9899
353.780	1.0000	1.0000

Figure 3: Comparison between data obtained in this work and data from Black (1959)
[published by Gmehling et al. (1980)] for the cyclohexane (1) + n-heptane(2) system.

**Table 3: Experimental VLE data for the p-xylene(1) + m-xylene(2)
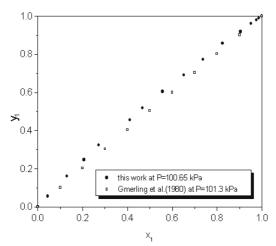system at pressure 100.65 kPa**

T	x_1	y_1
412.333	0.0000	0.0000
412.273	0.0435	0.0445
412.155	0.1276	0.1365
412.112	0.2149	0.2208
411.952	0.4277	0.4309
411.909	0.5352	0.5457
411.806	0.6266	0.6312
411.744	0.7151	0.7170
411.695	0.7944	0.7975
411.630	0.8469	0.8506
411.550	0.9130	0.9136
411.527	0.9989	0.9993
411.500	1.0000	1.0000

Table 4: Experimental VLE data for the p-xylene(1) + o-xylene(2) systems at pressure 100.65 kPa

T	x_1	y_1
417.593	0.0000	0.0000
417.175	0.0438	0.0557
416.627	0.1298	0.1611
416.139	0.2063	0.2469
415.762	0.2719	0.3235
414.920	0.4116	0.4567
414.544	0.4666	0.5176
414.041	0.5578	0.6047
413.636	0.6518	0.6914
413.091	0.7368	0.7724
412.427	0.8243	0.8568
412.053	0.9053	0.9186
411.729	0.9519	0.9606
411.667	0.9751	0.9793
411.623	0.9874	0.9899
411.500	1.0000	1.0000

Table 5: Experimental VLE data for the m-xylene(1) + o-xylene(2) systems at pressure 100.65 kPa

T	x_1	y_1
417.593	0.0000	0.0000
417.337	0.0426	0.0479
416.806	0.1315	0.1511
416.440	0.2033	0.2342
415.754	0.3368	0.3649
415.175	0.4259	0.4746
414.819	0.5027	0.5477
414.333	0.5967	0.6431
413.939	0.6778	0.7184
413.417	0.7757	0.8061
412.827	0.8832	0.9061
412.533	0.9450	0.9527
412.333	1.0000	1.0000

Figure 4: Comparison between data obtained in this work and data from Gmehling et al. (1980) for the p-xylene(1) + m-xylene(2) system.

Thermodynamic Consistency Test

In order to verify the quality of the data obtained, it is necessary to verify whether they are thermodynamically consistent. In this work, the test proposed by Van Ness et al. (1973) and modified by Fredenslund et al. (1977) was used. This method consists of generating values for a variable, usually pressure or composition of the vapor phase, based on the measures of other variables; the dependence on temperature was modeled with a fourth-order Legendre polynomial. Thus, there is an objective function to be minimized, which was the quadratic sum of the difference between experimental and calculated pressures. The data are considered to be consistent if the absolute mean deviation between composition of the experimental and the calculated vapor phases is lower than 0.01.
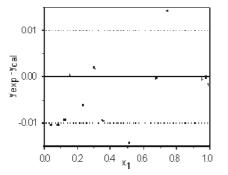
Table 6 reports the calculated values for vapor composition pressure in the thermodynamic consistency test. As all calculated deviations in composition were less than 0.01, all systems were considered thermodynamically consistent. As a further consistency test, the residuals obtained at each point for the entire composition range were analyzed, as suggested by Wisniak (1999). The residuals should be well distributed within both limits (±0.01, marked as a dotted line in the figures). Figures 5 to 8 show the residuals calculated for the four systems studied. For the cyclo-hexane+n-heptane (Figure 5), p-xylene+m-xylene (Figure 6) and m-xylene-o-xylene (Figure 8) systems the residuals were always well distributed within the limits and only a few points fell slightly outside of the range. However, for the p-xylene + o-xylene system (Figure 7), the majority of the points obtained had positive errors and four of them were outside of the range. This indicates that there is probably a systematic error, and thus this system fails the consistency test proposed by Wisniak (1999), although the absolute mean deviation for vapor-phase composition was less than 0.01 and the system was considered consistent by the test proposed by Fredenslund et al. (1977).
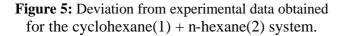
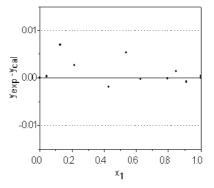**Table 6: Results of the thermodynamic consistency test of experimental data**

System	$^1\sigma\,(y)$	$^1\sigma\,(P)$
cyclohexane+n-heptane	0.0069	0.0085
p-xylene + m-xylene	0.0019	0.0008
p-xylene + o-xylene	0.0084	0.0024
m-xylene + o-xylene	0.0073	0.0031

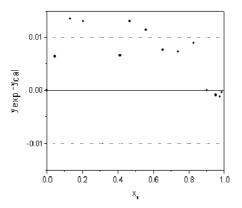$$^1\sigma(M) = \frac{1}{N}\sum_i \left|M_{exp} - M_{cal}\right|_i ,$$

where $M = y$ or P and $N =$ number of experimental points

Figure 5: Deviation from experimental data obtained for the cyclohexane(1) + n-hexane(2) system.

Figure 6: Deviation from experimental data obtained for the p-xylene(1) + m-xylene(2) system.

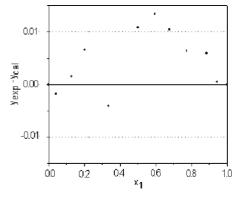**Figure 7:** Deviation from experimental data obtained for the system p-xylene(1) + o-xylene(2).

Figure 8: Deviation from experimental data obtained for the m-xylene(1) + o-xylene(2) system.

Data Regression

Data were regressed to obtain binary interaction parameters for the most frequently used activity coefficient models (NRTL (Renon and Prausnitz, 1968), UNIQUAC (Abrams and Prausnitz, 1975) and Wilson (1964)). In this case, the vapor phase was modeled by using the virial equation with the second virial coefficients calculated by Hayden and O'Connell (1975).

However, as the systems studied are nonpolar,

isomers should only have small deviations of ideality. Both phases of the system should be well represented by a cubic equation of state, and then the Peng-Robinson EOS (Peng and Robinson, 1976) binary interaction parameters (k_{ij}) were also generated for the classic mixing rules. Parameter fitting were performed by the data regression system (DRS) included in the Aspen Plus®10.1 simulator that uses Britt and Luecke's (1973) method, which is based on the maximum-likelihood principle. The objective function, which was minimized, is given by

$$F = \sum_{i=1}^{N} \left[\frac{\left(P_{i,\text{cal}} - P_{i,\text{exp}}\right)^2}{\upsilon_P^2} + \frac{\left(T_{i,\text{cal}} - T_{i,\text{exp}}\right)^2}{\upsilon_T^2} + \frac{\left(x_{i,\text{cal}} - x_{i,\text{exp}}\right)^2}{\upsilon_x^2} + \frac{\left(y_{i,\text{cal}} - y_{i,\text{exp}}\right)^2}{\upsilon_y^2} \right] \qquad (1)$$

where υ are all variances, pressure and temperature variances were estimated from the equipment resolutions (0.001K and 0.01kPa, respectively) and the variances of liquid- and vapor-phase compositions were calculated from the experimental data, since each point was analyzed three times (the deviation was usually less than 0.001 in mole fraction). Bubble pressure and composition are calculated, but deviation in all properties is included in the objective function, as proposed in the maximum-likelihood principle, in order to include experimental uncertainties (for further details see Britt and Luecke (1973)).

Table 7 contains the values of the interaction parameters for the activity coefficient models and mean deviations between experimental and calculated pressure and vapor-phase composition. In Table 8 binary interaction parameters and the absolute mean deviation between experimental and predicted values for each variable for the Peng-Robinson EOS are presented. All deviations are quite small and suggest that these systems could be well represented by any of these models.

Nevertheless, since the relative volatiles of xylene isomers are quite close to one, pure properties should be quite accurately predicted. For example, the Peng-Robinson EOS predicts the pure normal boiling point for xylene isomers (at 100.65 kPa) with less than 0.08 % error (p-xylene 0.016%, m-xylene 0.074%, o-xylene 0.053%). However, as the boiling temperatures of the binaries are too close, this prediction is not good enough, and because the equation is not able to describe the pure normal boiling point accurately, Txy plots are not well represented. For the p-xylene + m-xylene system (Figure 9) a quite unusual Txy plot is obtained; even though the absolute mean deviation for each variable is quite small (as shown in Table 8), these two isomers have similar physicochemical properties and the boiling temperature of both pure compounds differs by only 0.7 K. An unusual Txy plot such as this does not occur when the asymmetric representation is used (vapor phase modelled by virial EOS and liquid phase modelled by Wilson, NRTL or UNIQUAC), since vapor pressure is better reproduced. For the p-xylene+o-xylene system

(Figure 10), the Txy plot is not quite well represented, since a small deviation in pure boiling temperatures could be noted.

In order to improve these predictions, another cubic equation of state was used; the Soave-Redlich-Kwong EOS (Soave, 1972) modified by Mathias et al. (1984) was chosen, since this EOS normally represents pure vapor pressures very accurately and is available in the Aspen Plus®10.1 software.

Classic mixing rule interaction parameters were also fitted to experimental data and results are also reported in Table 8. Figures 11 and 12 show Txy plots for p-xylene+m-xylene and p-xylene-o-xylene, and it could be observed that although there is a difference in the pure boiling points for the p-xylene+m-xylene system, an unusual plot is no longer obtained and the p-xylene+o-xylene system is well represented.

Table 7: Binary interaction parameters of the activity coefficients models, relative mean deviation in the pressure and absolute mean deviation in the vapor-phase composition
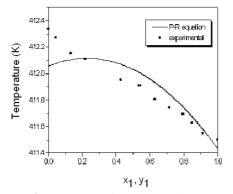
Model	Parameters				
	A_{ij} (J/mol)	A_{ji} (J/mol)	C_{ij}	$^1\delta(P)$ (%)	$^2\sigma(y)$
	n-heptane + cyclohexane				
NRTL UNIQUAC WILSON	4743.2	-533.40	0.30	0.086	0.0009
	-3089.6	1534.7		0.081	0.0010
	3204.9	-9800.4		0.079	0.0010
	p-xylene + m-xylene				
NRTL UNIQUAC WILSON	127.82	-133.51	0.30	0.096	0.0006
	-10.801	15.631		0.094	0.0006
	49.833	-34.144		0.102	0.0006
	p-xylene + o-xylene				
NRTL UNIQUAC WILSON	-315.73	395.04	0.30	0.061	0.0085
	166.10	-203.80		0.077	0.0086
	-335.69	246.45		0.061	0.0085
	m-xylene + o-xylene				
NRTL UNIQUAC WILSON	-159.18	160.27	0.30	0.047	0.0076
	77.716	-80.429		0.043	0.0076
	-133.23	-129.54		0.042	0.0075

$$^1\delta(P) = \frac{100}{N}\sum_i \left|\frac{P_{exp} - P_{cal}}{P_{exp}}\right|_i \; ; \; ^2\sigma(M) = \frac{1}{N}\sum_i \left|y_{exp} - y_{cal}\right|_i,$$
where N = number of experimental points

Table 8: Binary interaction parameters of the classic mixing rules of cubic EOS (Peng-Robinson and Soave-Redlich-Kwong modified by Boston-Mathias) and absolute mean deviation in the systems

System	k_{ij}	$^1\sigma(y)$	$^1\sigma(x)$	$^1\sigma(P)$	$^1\sigma(T)$
Results with Peng and Robinson (1976)					
cyclo-hexane+n-heptane	0.00851	0.0004	3.5×10^{-6}	0.0035	0.0047
p-xylene + m-xylene	-0.0024	0.0017	1.7×10^{-5}	0.0005	0.0005
p-xylene + o-xylene	-0.0019	0.0083	0.0061	0.0017	0.0014
m-xylene + o-xylene	-0.0030	0.0073	6.7×10^{-5}	0.0006	0.0006
Results with SRK modified by Mathias et al. (1984)					
cyclo-hexane+n-heptane	0.00851	0.0004	2.0×10^{-6}	0.0042	0.0038
p-xylene + m-xylene	-0.00053	0.0012	1.4×10^{-5}	0.0005	0.0048
p-xylene + o-xylene	-0.00016	0.0078	8.1×10^{-5}	0.0017	0.0017
m-xylene + o-xylene	-0.00095	0.0071	0.0001	0.0006	8.1×10^{-5}

$$^1\sigma(M) = \frac{1}{N}\sum_i \left|M_{exp} - M_{cal}\right|_i,$$
where M = y, x, P or T and N = number of experimental points

Figure 9: Txy curve for the p-xylene(1) + m-xylene(2) system at P=100.65 kPa for the Peng-Robinson correlation results.
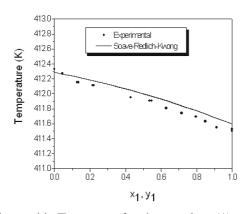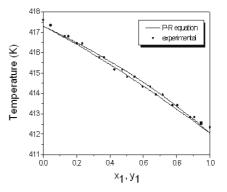

Figure 10: Txy curve for the p-xylene(1) + o-xylene(2) system at P=100.65 kPa for the Peng-Robinson correlation results.

Figure 11: Txy curve for the p-xylene(1) + m-xylene(2) system at P=100.65 kPa for the SRK modified by Mathias et al. (1984) correlation results.

Figure 12: Txy curve for the p-xylene(1) + o-xylene(2) system at P=100.65 kPa for the SRK modified by Mathias et al. (1984) correlation results.
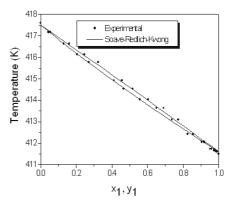
CONCLUSIONS

In this work, VLE experimental isobaric data on three binary systems of xylene isomers were obtained at 100.65 kPa. The systems have low relative volatility and there is a maximum difference of 6 K in the normal boiling point of the pure compounds for all three systems studied. Data were obtained in a modified Fischer cell, where equilibrium was normally reached after 15 minutes, and samples for vapor and liquid phases were analyzed by gas chromatography. The method was initially tested using the cyclo-hexane+n-pentane system as reference and the data obtained is similar to those in the literature.

The data were considered thermodynamically consistent in agreement with the point test of Van Ness et al. (1973), modified by Fredenslund et al. (1977). As a further consistency test, the residuals obtained at each point for the entire composition range were also analyzed as suggested by Wisniak (1999); residuals presented for the majority of the systems were always well distributed within the limits and only a few points were slightly out of range.

Binary interaction parameters were reported for the NRTL, UNIQUAC and Wilson models, as well for the classic mixing rules for the Peng-Robinson and the Soave-Redlich-Kwong (modified by Mathias et al. (1984)) cubic equations of state. Deviations are quite small for all of these models. However, since the relative volatilities of these systems are quite close to one, pure properties should be very accurately represented. Although, the Peng-Robinson EOS predicts a deviation in the normal boiling point less than 0.08%, this is not satisfactory for xylene isomers and the EOS is not able to satisfactorily describe Txy plots for these systems. If an equation of state is preferred, these systems are more accurately described by the Soave-Redlich-Kwong

EOS (modified by Mathias et al. (1984)), since pure normal boiling points are better predicted.

NOMENCLATURE

A,C	Binary interaction parameters of activity coefficients models
F	Objective function
k	Binary interaction parameters of cubic equations of state
P	Pressure (kPa)
T	Temperature (K)
N	Number of points
x	Liquid-phase mole fraction
y	Vapor-phase mole fraction

Subscripts

cal	Calculated
Eb	Normal boiling point
exp	Experimental
1	More volatile component
i, j	Chemical species

Greek Letters

δ	Relative mean deviation
ρ	Relative density
σ	Absolute mean deviation

ACKNOWLEDGMENTS

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