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RECIPROCAL SOLUBILITY OF GASOLINE FRACTIONS AND ETHANOL

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Abstract. Reciprocal solubility of gasoline and gasoline fractions in ethanol depending upon the aromatic hydrocarbon content in them has been investigated. Conditionally the ternary system "paraffin-naphthenic hydrocarbons–aromatic hydrocarbon–ethanol" demonstrates a bounded solubility with two pairs of the components. Ethanol solubility in hydrocarbons is only 1–3 %. The hydrocarbons solubility in ethanol depends upon water content in it and the temperature. The curve characterizing the hydrocarbons solubility in ethanol at triangular diagram is atypical: it has the concave shape *versus* the usual convex one.

Keywords: reciprocal solubility, ethanol, gasoline fraction, benzene, toluene, *para*-xylene, pseudocumene.

1. Introduction

Stock of cars extension demands the increase of gasoline quality and decrease of pollutant emissions. One of the ways of solving this problem is the usage of oxygen-containing organic compounds in the gasoline composition. These additives have high octane numbers and increase the completeness of fuel combustion resulting in the decrease of carbon oxide and hydrocarbons content in engine exhausts [1-4].

The spectrum of oxygen-containing organic compounds or so called oxygenates is very wide. Low-molecular ethers of methyl and ethyl alcohols [5, 6] are mainly used. Ethanol is of particular interest because it is less toxic and restoring product [7, 8]. But the usage of ethanol in the mixture with traditional gasoline causes the essential problem – phase stability, homogeneity of gasoline-ethanol composition which is considerably affected by water. Ethanol as itself is a source of water in the composition because it forms the azeotropic solution with 5 mas % of water.

In order to solve this problem two ways are suggested: the water removal from ethanol and micro-emulsion stabilization with different additives [9-11]. The first way is more preferable. This work deals with the establishment of main regularities of gasoline and ethanol reciprocal solubility.

2. Experimental

2.1. Investigation Objects

The main investigation object was straight-run gasoline from which aromatic hydrocarbons were removed by sulfonating. The gasoline was washed by 5 % alkali and water and dried with calcium chloride. Then rectification was carried out at the laboratory plant with 30 theoretical plates and the following fractions were run off: benzene fraction (BF) 343–368 K; toluene fraction (TF) 368–398 K; xylene fraction (XF) 398–423 K and trimethylbenzene fraction (TMBF) 423–453 K. The fractions were conserved over calcium chloride. The fractions were run off in such a way that the boiling temperature of aromatic hydrocarbons would be in the middle of the fraction temperature interval.

Such individual aromatic hydrocarbons as benzene, toluene, *para*-xylene and pseudocumene were used. All of them were dried over calcium chloride. The boiling temperature and refraction index of all components were the same as in the literature.

2.2. Investigation Procedure

To determine the equilibrium state of reciprocal solubility of dearomatic gasoline fraction with different content of one added aromatic hydrocarbon and ethanol the special test tube with a stirrer was used. Water of definite temperature from the thermostat circulated through a tube jacket. The given amount of individual hydrocarbon or hydrocarbon mix of the given composition were sustained in the tube for 5–10 min in order to establish the necessary temperature. Next they were titrated by ethanol with a given content of water: first from a micro-burette till two phases appeared (till turbidity appearance) and then – from the usual burette till two-phase system turned to a single-phase one (till turbidity disappearance). Ethanol discharge at the moment of turbidity appearance determined the

interfacial solubility of ethanol in the hydrocarbon phase and ethanol discharge at the moment of turbidity disappearance – the interfacial solubility of hydrocarbon phase in ethanol.

Hydrocarbon composition of gasoline mixed with ethanol may be divided into two groups by their nature: non-polar hydrocarbons (paraffin-naphthenic) and non-polar but capable of polarization hydrocarbons (aromatic). Taking into account such a division, all multi-component mixture of gasolines may be conventionally reduced to the two-component system. The polar ethanol is the third component. In such a case the system may be described by means of a triangular diagram. Since ethanol contains water, actually we have four-component mixture. But using ethanol with a constant water amount we may describe the system by a triangular diagram [12].

3. Results and Discussion

3.1. Effect of Gasoline Fractional Composition on the Reciprocal Solubility of Ethanol and Gasoline Fraction Depending upon Aromatic Hydrocarbons Content

Dearomatic gasoline fractions with different content of the corresponding aromatic hydrocarbon (benzene, toluene, *p*-xylene or pseudocumene were used. Standard rectified alcohol was the third component. The experimental results of a reciprocal solubility of gasoline fractions and rectified alcohol with 5 mas % of water were processed using the operating diagram and represented in Table 1.

Analyzing the obtained data one can see the increase of hydrocarbons molecular masses by one CH_2-group, *i.e.* by 14 items, decreases their solubility in ethanol by 16–12 %. The solubility of gasoline fractions, which are the boundary points of the main productive part of gasoline, namely toluene and trimethylbenzene, differ approximately in three times. It concerns dearomatic gasoline fractions, first of all. The same tendency is for gasoline fractions containing aromatics. The increase of aromatic hydrocarbon amount in the gasoline fraction increases its solubility in ethanol. Benzene in the benzene fraction considerably increases its solubility in ethanol compared with pseudocumene in the corresponding gasoline fraction. The quantitative solubility of gasoline fraction in ethanol is determined by a minimum amount of ethanol which provides the change of heterogeneous system into the homogeneous one. Thus, for dearomatic fraction BF the necessary amount of ethanol is 24.0 vol % and for TMBF – 71.0 vol % (water content in ethanol is 5 mas %, the temperature is 293 K).

It should be also noted that ethanol has a bad solubility in the gasoline fraction – only 1–2 %. The further addition of ethanol causes the formation of the heterogeneous system. When the ethanol content in the system corresponds to the saturation concentration of ethanol by the gasoline fraction, then the heterogeneous system changes into the homogeneous one. Under above-mentioned conditions such a change takes place at ethanol content of 4.5–5.0 % for BF and 30–38 % for TMBF.

Reciprocal solubility of the system "gasoline fraction–corresponding aromatic hydrocarbon–technical 93 % ethanol" containing esters, aldehyde, ketones and water was studied in a similar way. The experimental results are represented in Table 2.

Table 1

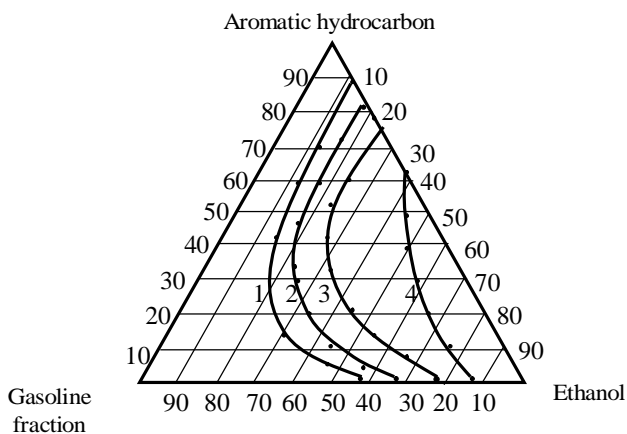**Saturation concentrations of ethanol (95 %) by gasoline depending upon aromatic content in it at 293 K**

Aromatic hydrocarbon content in the gasoline fraction, vol %	BF	TF	XF	TMBF
0	24.0	37.0	51.0	71.0
10	15.0	24.0	40.5	65.0
20	9.0	15.0	30.0	57.5
30	6.0	12.0	21.0	48.0
40	5.0	10.0	16.0	38.0
50	4.5	9.0	11.5	30.0
60	4.0	8.0	10.0	22.0
70	3.0	7.0	9.5	18.0
80	3.0	6.5	8.5	16.0
100	3.0	6.0	8.5	13.0

Table 2

Saturation concentrations of ethanol (93 %) by gasoline depending upon aromatic content in it at 293 K

Aromatic hydrocarbon content in the gasoline fraction, vol %	BF	TF	XF	TMBF
0	59.0	69.0	79.0	88.0
10	42.0	55.0	71.5	85.0
20	31.5	44.5	64.5	83.5
30	24.0	34.5	55.5	81.0
40	19.5	28.0	45.5	78.0
50	17.0	22.5	29.5	73.5
60	15.0	19.5	26.5	66.0
70	13.5	18.0	24.5	57.0
80	12.0	17.5	-	49.5
100	11.5	16.0	24.0	36.0

Insignificant increase of water content in ethanol (2–3 %) does not change the dependence nature (Table 2). There is only the increase of ethanol concentration in the saturation point. The increase of gasoline molecular mass decreases its saturation concentration in ethanol.

For the complete estimation of reciprocal solubility of gasoline fractions and ethanol figures are descriptive. Triangular diagrams represent the system visually and qualitatively (Figs. 1 and 2). The characters of binodal curves are similar for both figures. Every binodal curve divides concentration area of the triangular diagram into two parts: the heterogeneous system – on the left and the homogeneous system – on the right. Actually another part of the complete binodal curve exists, which is non-shown in Fig. 1. It is situated along the side of the triangle which represents the binary mixture "aromatic hydrocarbon–gasoline fraction" at the distance of 1-3 %.
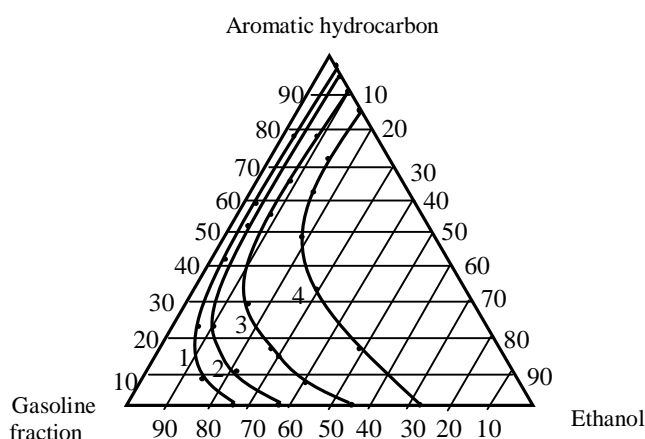
Fig. 1 represents binodal curves of the solubility of the gasoline fraction and 95 % ethanol (standard rectified alcohol). The arrangement of binodal curves at the area of triangular diagram depends upon the gasoline fraction molecular mass. For BF the curve is displaced to the binary system "aromatic hydrocarbon–fraction". In such a case the heterogeneous area is small and starts at 25 % of ethanol in the dearomatic fraction. The addition of benzene to the system (~ 40 %) increases the solvent ability; the curve turns to the left and diminishes the heterogeneous area. The further addition of benzene to the system does not affect the solvent ability – the curve is practically parallel to a triangle side. The increase of gasoline fraction molecular mass and aromatic hydrocarbon, respectively, extends the heterogeneous area and moves the binodal curve to the right cymbately.

The increase of water content (together with ethers, aldehydes and ketones) in ethanol to 7.0 mas % enlarges the heterogeneous area for all gasoline fractions (Fig. 2).

3.2. The Effect of Temperature on the Reciprocal Solubility of Ethanol and Gasoline Fraction Depending upon Aromatic Hydrocarbons Content

Only two gasoline fractions characterizing gasoline were taken for experiments: TF – the beginning of the gasoline working part and TMBF – its end.

The first system is low-molecular gasoline fraction having the greatest ability to solve in ethanol and technical ethanol with considerable amount of water (Table 3).

Fig. 1. Dependence of solubility in 95 % ethanol of the fractions: BF and benzene (1); TF and toluene (2); XF and xylene (3); TMBF and pseudocumene (4). Temperature is 293 K

Fig. 2. Dependence of solubility in 93 % ethanol of the fractions: BF and benzene (1); TF and toluene (2); XF and xylene (3); TMBF and pseudocumene (4). Temperature is 293 K

Table 3

Saturation concentration of ethanol (93 %) by TF at different toluene contents depending upon the temperature

Toluene content in the fraction, vol %	303 K	293 K	283 K	273 K	263 K
0	59.5	69.0	76.0	79.0	80.0
10	45.0	55.0	69.0	76.5	79.0
20	33.0	44.5	61.0	72.0	77.5
30	23.0	34.5	54.0	68.0	75.0
40	16.5	28.0	46.5	62.0	71.0
50	13.0	22.5	37.5	55.0	66.5
60	13.0	19.5	31.5	48.0	60.0
70	13.0	18.0	27.0	40.0	51.0
80	13.0	17.5	23.0	33.5	43.0
100	13.0	16.0	18.5	24.0	34.0

Table 3 represents ethanol concentrations in the point of transition from the heterogeneous to the homogeneous state. The first row of the table characterizes a conditional binary system "TF and ethanol (93 mas %)". The transition of this system into the homogeneous state needs a great amount of ethanol. Moreover, the temperature affects the ethanol necessary concentration. Thus, at the temperature of 303 K the system becomes homogeneous at 59.5 vol % of ethanol. At the decrease of temperature to 293 K it is necessary to use 69 vol % of ethanol already. The further decrease of temperature requires the increase of ethanol concentration but this growth is less. Generally, the effect of temperature on the ethanol concentration in the transition point obeys the damped function.

The second row of Table 3 gives the characteristics of the system with the added third component – 10 vol % of toluene, in BF. The effect of temperature on the ethanol concentration in the transition point is similar to the previous effect but has other quantitative values. The change of ethanol boundary concentrations is more sensitive to the temperature. The increase of toluene concentration in TF improves the solubility in ethanol, *i.e.* ethanol critical concentration decreases in the transition point.

The second investigated system is a high-molecular gasoline fraction "TMBF–pseudocumene–ethanol with the water content of 5 mas %", see Table 4.

Table 4

Saturation concentration of ethanol (95 %) by TMBF at different pseudocumene contents depending upon temperature

Pseudocumene content in the fraction, vol %	293 K	283 K	273 K	263 K	253 K
0	71.0	74.0	79.5	83.0	85.0
10	65.0	69.0	77.0	81.5	84.0
20	57.5	64.5	74.0	79.0	81.5
30	48.0	58.0	70.5	76.0	78.5
40	38.0	53.0	67.0	74.0	77.0
50	30.0	47.0	61.0	68.5	72.0
60	22.0	39.5	54.5	64.0	68.5
70	18.0	33.0	47.5	59.0	66.0
80	16.0	27.5	39.5	53.0	62.0
100	13.0	17.5	24.0	33.5	44.5

Using data from Table 4, right parts of binodal curves (Fig. 3) were drawn. The visual characteristic of the second system is similar to the first one. The difference between the systems is caused by different solubility of toluene and pseudocumene in ethanol. Dearomatic TF and TMBF have almost the same solubility in ethanol with the water content of 7.0 and 5.0 %. The pseudocumene solubility depends upon the temperature in a greater degree. Just this difference changes the form and location of binodal curves at the area of triangular diagram.
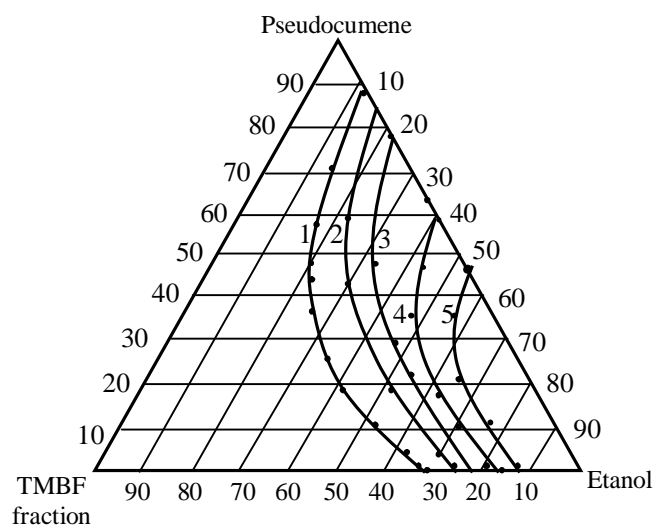

Fig. 3. Dependence of TMBF fraction and pseudocumene solubility in ethanol with water content of 5 mas % at different temperatures: 293 (1); 283 (2); 273 (3); 263 (4) and 253 (5) K

3.3. Effect of Water Content in Ethanol on the Solubility of Gasoline Fraction in it at Low Temperatures

Table 5 represents conditions under which the second phase disappears, *i.e.* the saturation concentration may be determined. The boundary values in such a system are solubility of paraffin-naphthenic and aromatic hydrocarbons. In the first row there are solubility values of paraffin-naphthenic hydrocarbons of TF fraction in ethanol depending upon water content in it. The fraction solubility considerably depends upon water content in ethanol. Thus, at water content of 2 mas % about 63.5 vol % of the fraction is soluble in ethanol and at water content of 5 mas % only 33 vol % of the fraction is soluble. Toluene has the second boundary values. At the water content of 2 mas % it dissolves the unlimited amount of toluene. Ethanol with 5 mas % of water dissolves about 82.5 vol % of toluene to calculate for the mixture. The presence of 50 % of toluene in the toluene fraction actually does not affect the solubility of gasoline fraction in ethanol.

**Saturation concentration of ethanol by TF at different toluene
content depending upon water content in ethanol at 258 K**

Toluene content in the fraction, vol %	Solubility in ethanol at different water content, %					
	2.0	3.0	4.0	5.0	6.0	7.7
0	36.5	48.0	58.0	67.0	74.5	84.0
10	21.5	34.5	48.5	58.5	67.5	74.0
20	10.5	22.0	33.5	45.5	56.0	70.0
30	6.0	13.0	22.5	33.0	47.0	67.0
40	2.5	7.5	15.0	24.0	38.0	62.0
50	1.0	4.5	11.0	19.5	32.0	58.0
60	1.0	3.5	9.5	18.5	29.5	55.0
70	1.0	3.5	9.0	18.0	28.5	51.0
80	1.0	3.5	9.0	17.5	28.0	48.0
100	1.0	3.0	9.0	17.5	28.0	46.0

**Saturation concentration of ethanol (95 %) by dearomatic
gasoline different benzene or pseudocumene contents in it depending upon temperature**

Aromatic hydrocarbon content in gasoline, vol %	293 K		283 K		273 K		263 K		253 K	
	B	PC	B	PC	B	PC	B	PC	B	PC
0	48.0	49.0	61.5	61.5	70.0	70.0	75.0	74.5	80.0	80.0
10	33.0	39.5	45.5	54.6	59.5	64.5	66.5	70.5	72.5	74.0
20	20.0	32.5	26.5	46.5	35.0	57.5	47.5	65.5	61.5	71.0
30	13.0	27.6	15.0	38.0	17.6	48.0	22.6	57.5	34.0	65.5
40	8.5	24.5	10.0	33.5	12.0	41.5	15.0	51.5	17.5	60.5
50	5.4	22.0	7.0	27.6	8.6	34.0	10.0	44.6	13.0	56.0
60	4.5	20.0	6.0	23.5	7.5	29.5	8.5	39.5	10.0	51.0
70	4.0	18.0	5.0	21.0	6.5	26.5	7.0	35.5	8.0	46.5
80	3.5	16.0	4.0	19.5	5.5	25.0	6.0	33.5	6.5	44.5
100	3.0	13.0	3.5	17.5	4.5	24.0	5.0	33.5	6.0	44.5

The mixtures of TF paraffin-naphthenic hydrocarbons and toluene originally dissolve in toluene. TF with the toluene content over 40 % dissolves in ethanol with the water content of 2.0 mas % without limits. The decrease of toluene to 40 % decreases the solubility. The analogous phenomena takes place in ethanol with the water content of 3.0; 4.0; 5.0 mas % and more compared with toluene solubility. The difference between paraffin-naphthenic fraction and toluene is within the range of 36–50 % by ethanol concentration in the mixture.
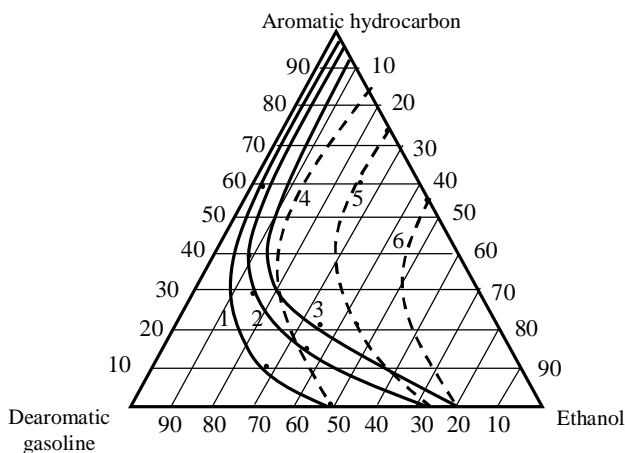
3.4. Solubility of Gasoline in Ethanol Depending upon Temperature

Taking into account previous results we studied gasoline solubility in ethanol. Two series of investigations were carried out. In one case we added about 80 vol % of benzene (B) to dearomatic gasoline, and pseudocumene (PC) – in other case. The saturation concentration of ethanol by dearomatic gasoline was determined at different contents of aromatic hydrocarbon (benzene and pseudocumene) at 293, 283, 273, 263 and 253 K (Table 6).

Data presented in Table 6 were used for plotting the reciprocal solubility of the system "dearomatic gasoline–benzene (or pseudocumene)–ethanol" at 293, 273 and 253 K (Fig. 4).

One can see from Fig. 4 that the first portions of aromatic hydrocarbons in gasoline considerably increase its solubility in ethanol. The increase of aromatics concentration above 40 % leads to the negligible change of solubility.

Fig. 4. Solubility of dearomatic gasoline and benzene (firm line) and pseudocumene (dotted line) in ethanol with the water content of 5 mas % at different temperatures: 293 (1, 4); 273 (2, 5) and 253 (3, 6) K

4. Conclusions

Ethanol slightly dissolves in hydrocarbons of gasoline fraction (1–3 vol %). Therefore while mixing gasoline and ethanol it should be considered that gasoline dissolves in ethanol but not *vice versa*. The gasoline–ethanol system may be represented as the ternary one and described by the triangular diagram "paraffin-naphthenic hydrocarbons–aromatic hydrocarbons–ethanol". The reciprocal solubility is represented by the part of binodal curve characterizing the hydrocarbons solubility in ethanol. The curve is not convex but concave inside; it divides the concentration area by the homogeneous and heterogeneous part. The heterogeneous part decreases with the increase of temperature and the decrease of water content in ethanol.

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ВЗАЄМНА РОЗЧИННІСТЬ БЕНЗИНОВИХ ФРАКЦІЙ Й ЕТАНОЛУ

Анотація. *Досліджено взаємну розчинність бензину і бензинових фракцій в етанолі залежно від вмісту в них ароматичного вуглеводню. Показано, що умовно трикомпонентна система "парафіно-нафтенові вуглеводні–ароматичний вуглеводень–етанол" дає обмежену розчинність з двома парами компонентів. Розчинність етанолу у вуглеводнях становить всього 1–3 %. Розчинність вуглеводнів в етанолі залежить від вмісту в ньому води і температури. На трикутній діаграмі крива, що характеризує розчинність вуглеводнів в етанолі, має нетиповий вигляд: не опукла, як звичайно, а ввігнута.*

Ключові слова: *взаємна розчинність, етанол, бензинова фракція, бензол, толуол, пара-ксилол, псевдокумол.*