RP571

THE EFFECT OF GASOLINE VOLATILITY ON THE MISCIBILITY WITH ETHYL ALCOHOL

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ABSTRACT

Data are presented on the effect of the volatility of gasoline on its miscibility with ethyl alcohol containing various amounts of water. Samples of gasoline having different volatilities were obtained by two methods—first, fractional distillation of an original gasoline and second, blending of refinery and natural gasolines. The more volatile gasolines were found to be more miscible with alcohol, in that they produced mixtures having lower critical solution temperatures than similar mixtures containing less volatile gasoline. Comparatively small differences were found in the miscibility with ethyl alcohol of gasolines having the same volatility but different composition.

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I. INTRODUCTION

In a previous paper[1] data were presented on the critical solution temperatures of mixtures, in various proportions, of eight different gasolines with ethyl alcohol containing various percentages of water. The experimental results were suggestive in indicating that differences in the volatility of various gasolines might account for most of the differences found in the critical solution temperatures of mixtures of ethyl alcohol and these gasolines. Differences in the crude from which the gasoline was refined, or differences in composition of cracked and straight-run gasolines of about the same volatility, appeared to have comparatively little effect on the critical solution temperatures. In order to obtain more direct experimental evidence regarding the effect of the volatility of gasoline on its miscibility with ethyl alcohol, the investigation described in the present paper was undertaken.

II. DESCRIPTION OF GASOLINE SAMPLES

Three of the gasolines used in the previous investigation were "topped", so as to reduce the temperature at 90 percent evaporated to approximately the same value in the three cases. This "topping" process was accomplished by distilling the gasoline in a laboratory

[1] Bridgeman and Querfeld, Critical Solution Temperatures of Mixtures of Gasoline, Ethyl Alcohol and Water, B.S. Jour. Research, vol. 10 (RP560), p. 693, May 1933.

still, stopping the distillation at an appropriate stage, and discarding the residue left in the distillation flask. Distillation of the product thus obtained, employing A.S.T.M. standard method D86–30, was used to determine when a sufficient percentage of the distillate had been collected. By the above procedure, the 90 percent temperatures of gasolines nos. 1, 7, and 8 were reduced by 46°, 38°, and 41° C., respectively, to a value which was close to 152° C. in all three cases. This particular value of 152° C. was chosen since the volatility of the Pennsylvania straight-run gasoline no. 1, after removal of the heavier fractions, was thereby made almost identical with that of the Rumanian straight-run gasoline no. 2, and permitted a direct comparison of the critical solution temperatures for two gasolines of the same volatility but of widely different chemical characteristics.

In order to evaluate the effect on critical solution temperatures produced by lowering the 10 percent distillation temperature of the gasoline, blends of natural gasoline with gasoline no. 1 were prepared. Two different natural gasolines were employed and the blends contained 10, 20, and 30 volume percent of the respective natural gasoline. These blends were prepared at 0° C. in order to minimize evaporation of the lighter constituents. In addition to the measurements made on the above gasolines and blends, some supplementary data were obtained on six commercial gasolines, presumably mixtures of straight-run and cracked products.

Distillation and specific gravity data are given in table 1 for the various gasolines and blends, and for the two natural gasolines used in blending with gasoline no. 1.

TABLE 1.—*Identification data on gasolines*

No.	Description	Distillation temperatures at stated percentages evaporated			60°/60° specific gravity
		10 percent	50 percent	90 percent	
		° C.	° C.	° C.	
1	Straight-run Pennsylvania	76	135	199	0.738
9	Gasoline no. 1 distillate	69	107	153	.720
2	Straight-run Rumania	70	106	152	.734
7	Cracked gasoline	54	126	188	.754
10	Gasoline no. 7 distillate	53	96	150	.722
8	Cracked gasoline	69	142	194	.773
11	Gasoline no. 8 distillate	60	102	153	.734
18	10 percent natural gasoline A+90 percent no. 1	64	128	197	.731
19	20 percent natural gasoline A+80 percent no. 1	55	119	196	.721
20	30 percent natural gasoline A+70 percent no. 1	42	104	192	.707
21	10 percent natural gasoline B+90 percent no. 1	69	128	197	.736
22	20 percent natural gasoline B+80 percent no. 1	61	120	195	.727
23	30 percent natural gasoline B+70 percent no. 1	57	111	193	.719
12	Commercial gasoline	61	130	180	.742
13	do	58	123	181	.742
14	do	68	127	175	.743
15	do	69	136	186	.752
16	do	65	124	174	.741
17	do	66	131	187	.752
	Natural gasoline A	24	31	52	.632
	Natural gasoline B	43	58	101	.678

III. EXPERIMENTAL DATA

The apparatus and procedure used in the present work were identical with those previously described. A description of the aqueous ethyl alcohol solutions employed is given in table 2.

TABLE 2.—*Concentrations of ethyl alcohol solutions*

No.	60°/60° specific gravity	Volume percent alcohol at 60° F.	Volume percent water at 60° F.	No.	60°/60° specific gravity	Volume percent alcohol at 60° F.	Volume percent water at 60° F.
A	0.79820	99.144	1.110	E	0.81269	95.845	5.178
A1	.79826	99.131	1.127	E1	.81274	95.833	5.193
A2	.79835	99.112	1.151	E2	.81257	95.875	5.143
				E3	.81293	95.787	5.248
B	.80202	98.337	2.133				
B1	.80207	98.325	2.149	F	.81608	94.987	6.196
B2	.80199	98.344	2.124	F1	.81609	94.984	6.201
B3	.80210	98.318	2.157	F2	.81615	94.970	6.218
				F3	.81623	94.948	6.244
C	.80565	97.528	3.139				
C1	.80580	97.492	3.182	G	.81948	94.097	7.243
C2	.80586	97.479	3.199	G1	.81940	94.119	7.217
C3	.80586	97.479	3.199	G2	.81961	94.061	7.285
				G3	.81949	94.094	7.246
D	.80917	96.703	4.145				
D1	.80927	96.679	4.175	H	.82264	93.243	8.237
D2	.80930	96.672	4.184	H1	.82281	93.196	8.291
D3	.80941	96.645	4.216	H2	.82275	93.210	8.275
				H3	.82275	93.210	8.275

With each of the three fractionated gasolines, mixtures containing from 10 to 90 volume percent of gasoline, by even steps of 10 percent, were prepared with the alcohol solution of each concentration, and measurements of the critical solution temperature were made. No measurements were made on those mixtures having critical solution temperatures outside of the approximate range from +65° C. to −65° C. The data on the three gasolines are given in tables 3, 4, and 5 where for comparison the values previously obtained on the gasolines before fractionation are also included. It is seen that the decrease in the 90 percent distillation temperatures of the gasolines has produced a marked lowering in the critical solution temperatures. This lowering is shown graphically in figure 1 for fuels nos. 9 and 1, the latter being the original gasoline. The lowering in critical solution temperature as the result of removing the heavier fractions of the gasoline becomes less (*a*) as the percentage of gasoline in the mixture increases and (*b*) as the percentage of water in the alcohol solution increases. For mixtures with the alcohol solution of the C series (97.5 percent alcohol), the lowering in critical solution temperature resulting from the average decrease of 42° C. in 90 percent distillation temperature was on the average 18° C. for mixtures containing 50 percent gasoline and 7° C. for mixtures containing 90 percent gasoline.

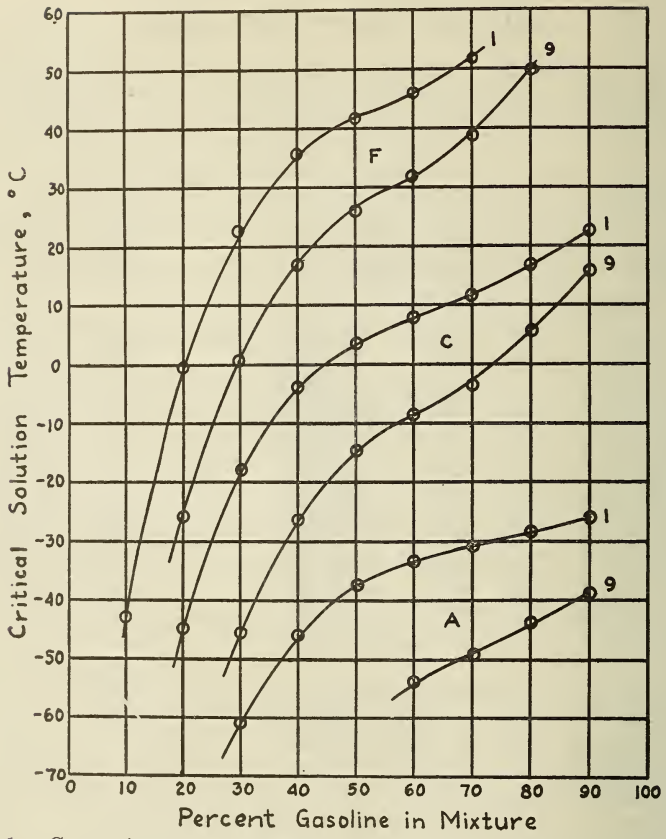

FIGURE 1.—*Comparison of data on the critical solution temperatures of mixtures in various proportions of ethyl alcohol and gasolines nos. 1 and 9*

Gasoline no. 9 is the more volatile fraction of gasoline no. 1 and the differences between the curves represent the effect of change in volatility. The letters between each pair of curves indicate the alcohol solutions used, the concentrations of which are recorded in table 2.

TABLE 3.—*Critical solution temperatures in ° C. of alcohol mixtures with gasolines nos. 9 and 1*

No.	Alcohol solution	Volume percent gasoline in mixture								
		10	20	30	40	50	60	70	80	90
9	A	--------	--------	--------	--------	--------	−54.0	−49.1	−43.9	−39.0
1	A	--------	--------	−61.0	−46.2	−37.4	−33.4	−31.0	−28.3	−26.4
9	B1	--------	--------	--------	−47.1	−35.2	−28.1	−23.9	−17.0	−9.3
1	B	--------	−60.0	−36.8	−24.0	−15.1	−10.3	−7.4	−2.5	.8
9	C	--------	--------	−45.4	−26.8	−15.0	−8.9	−3.9	5.2	15.3
1	C	--------	−45.0	−18.0	−4.1	3.7	7.7	11.3	16.6	22.3
9	D	--------	--------	−28.5	−9.9	1.0	7.5	12.1	20.9	31.0
1	D	−60.6	−26.2	−3.2	11.5	18.7	22.4	26.6	33.1	39.4
9	E	--------	−39.6	−12.3	5.5	14.5	20.3	26.1	35.6	47.9
1	E	−54.7	−12.7	11.3	24.3	30.8	34.4	39.5	47.7	52.9
9	F	--------	−25.0	1.5	17.4	26.2	31.6	38.8	49.6	--------
1	F	−43.2	.3	22.5	35.3	41.6	45.7	51.6	--------	--------
9	G	--------	−12.6	13.6	28.2	36.7	42.3	50.3	--------	--------
1	G	−30.2	12.6	33.7	45.0	--------	--------	--------	--------	--------
9	H	−49.2	−1.4	24.1	38.3	46.1	--------	--------	--------	--------
1	H	−19.3	23.2	43.2	--------	--------	--------	--------	--------	--------

TABLE 4.—*Critical solution temperatures in ° C. for alcohol mixtures with gasolines nos. 10 and 7*

No.	Alcohol solution	Volume percent gasoline in mixture								
		10	20	30	40	50	60	70	80	90
10	A1	--------	--------	--------	--------	--------	--------	--------	--------	--------
7	A1	--------	--------	--------	--------	--------	--------	--------	--------	−53.1
10	B2	--------	--------	--------	--------	--------	−56.4	−49.0	−41.2	−28.9
7	B1	--------	--------	--------	--------	−49.8	−44.8	−40.1	−30.9	−19.9
10	C2	--------	--------	--------	−55.6	−41.3	−31.3	−24.9	−16.5	−.1
7	C1	--------	--------	−59.9	−40.0	−26.8	−19.3	−15.9	−9.3	2.8
10	D2	--------	--------	−56.4	−35.4	−22.6	−14.2	−8.1	1.9	18.3
7	D1	--------	--------	−38.8	−21.6	−10.9	−4.6	.7	9.6	24.5
10	E2	--------	--------	−41.0	−19.7	−6.8	−.3	6.4	18.0	37.5
7	E1	--------	−50.2	−23.7	−6.5	3.5	8.6	14.8	24.4	42.6
10	F2	--------	−55.9	−25.2	−5.7	5.6	12.1	19.6	32.6	--------
7	F1	--------	−37.0	−9.1	6.2	14.7	20.2	27.0	39.0	--------
10	G2	--------	−41.6	−11.3	6.7	17.0	23.3	31.8	46.8	--------
7	G1	--------	−23.6	4.0	18.0	25.8	32.0	39.4	51.4	--------
10	H2	--------	−28.7	.3	17.3	26.9	34.0	43.0	54.4	--------
7	H1	−58.1	−11.6	14.5	27.4	35.5	41.1	50.5	--------	--------

TABLE 5.—*Critical solution temperatures in ° C. for alcohol mixtures with gasolines nos. 11 and 8*

No.	Alcohol solution	Volume percent gasoline in mixture								
		10	20	30	40	50	60	70	80	90
11	A2	--------	--------	--------	--------	--------	--------	--------	--------	−57.6
8	A1	--------	--------	--------	--------	--------	--------	--------	−51.7	−45.6
11	B3	--------	--------	--------	--------	--------	−52.7	−47.3	−40.0	−27.7
8	B1	--------	--------	--------	−50.9	−40.9	−34.9	−28.2	−22.7	−13.9
11	C3	--------	--------	--------	−52.8	−39.6	−30.4	−24.7	−15.9	−2.0
8	C1	--------	--------	−48.8	−30.0	−18.5	−13.3	−9.2	−.8	9.8
11	D3	--------	--------	−56.1	−34.7	−21.0	−13.1	−6.9	3.9	20.1
8	D1	--------	−56.8	−28.2	−12.0	−1.5	2.1	8.2	15.9	27.4
11	E3	--------	--------	−38.0	−17.4	−4.7	1.2	8.4	19.2	39.0
8	E1	--------	[1]−42.3	[1]−14.1	1.9	11.2	15.5	21.9	31.5	45.9
11	F3	--------	−53.8	−23.1	−3.8	7.1	13.3	20.0	33.9	--------
8	F1	--------	−27.2	−.7	14.1	21.8	26.6	33.3	44.3	--------
11	G3	--------	−39.4	−9.5	7.9	18.2	24.2	31.0	47.7	--------
8	G1	--------	−13.6	13.3	25.4	33.1	37.6	45.8	--------	--------
11	H3	--------	−26.4	2.0	18.4	27.9	36.0	43.8	57.8	--------
8	H1	−49.8	−2.0	22.0	34.6	41.8	--------	--------	--------	--------

[1] Solution E2.

For the blends of gasoline no. 1 with the two natural gasolines, measurements of the critical solution temperature were made only on alcohol mixtures containing 50 and 75 percent of the blend, since the primary object of the research was to investigate this range. The results obtained are given in tables 6 and 7. The slight differences in alcohol content of the different solutions used are not sufficient to vitiate the comparison, being equivalent to less than 1° C. difference in critical solution temperature. The data for the mixtures containing 75 percent of gasoline are shown graphically in figures 2 and 3, where the volume percent of water in the mixture is plotted against the critical solution temperature. Decrease in the 10 percent distillation temperature of the gasoline by addition of natural gasoline results in a lowering of the critical solution temperature, which on

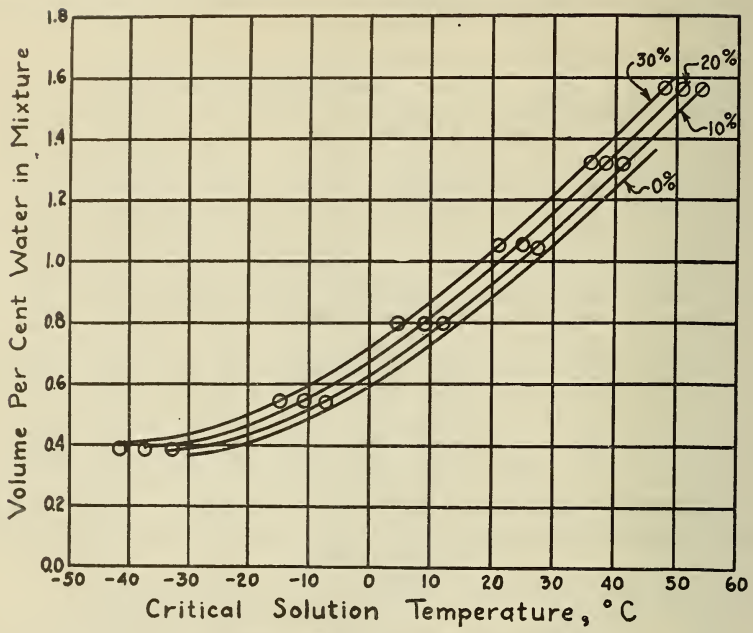

FIGURE 2.—*Data on the critical solution temperatures of mixtures containing 25 percent of ethyl alcohol of various water contents and 75 percent of blends of gasoline no. 1 with natural gasoline A in the proportions indicated on the curves.*

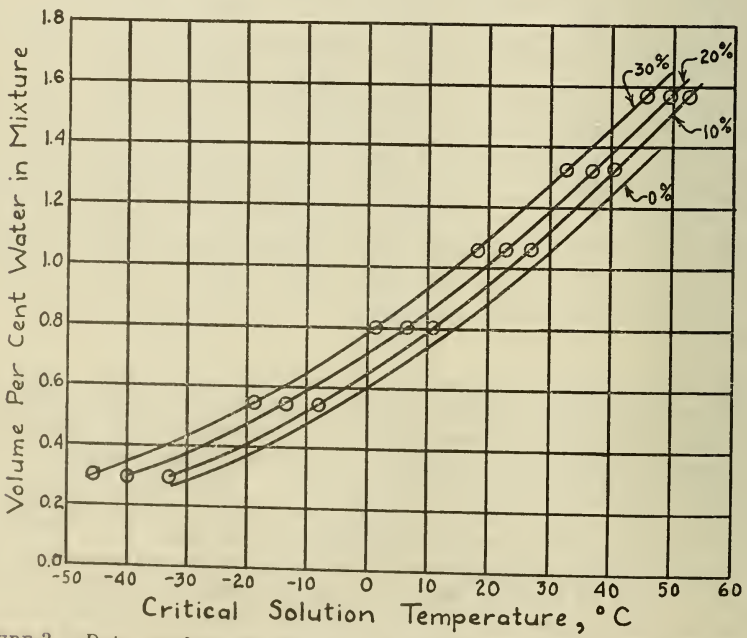

FIGURE 3.—*Data on the critical solution temperatures of mixtures containing 25 percent of ethyl alcohol of various water contents and 75 percent of blends of gasoline no. 1 with natural gasoline B in the proportions indicated on the curves.*

the average is 4° C. for each 10 percent addition of natural gasoline A and 3° C. for each 10 percent addition of natural gasoline B. For mixtures with the alcohol solution of the C series (97.5 percent alcohol), the lowering in critical solution temperature resulting from a decrease in the 10 percent distillation temperature of 20° C. was about 8° C. on the average, being only slightly different in the case of the two natural gasolines.

TABLE 6.—*Critical solution temperatures in ° C. for alcohol mixtures with gasolines containing various added percentages of natural gasoline A*

Gasoline no.	Amount of natural gasoline A	50 percent gasoline in mixture		75 percent gasoline in mixture	
		Alcohol solution	Critical solution temperature	Alcohol solution	Critical solution temperature
	Percent		*° C.*		*° C.*
1	0	A	−37.4	A	−30.1
18	10	A1	−41.2	A2	−33.6
19	20	A1	−46.2	A2	−40.1
20	30	A1	−53.3	A2	−46.2
1	0	B	−15.1	B	−5.0
18	10	B1	−16.8	B3	−8.4
19	20	B1	−20.4	B3	−13.9
20	30	B1	−29.5	B3	−19.0
1	0	C	3.7	C	13.7
18	10	C1	.7	C3	10.7
19	20	C1	−3.5	C3	6.3
20	30	C1	−10.5	C3	1.5
1	0	D	18.7	D	29.9
18	10	D1	15.9	D3	26.5
19	20	D1	11.2	D3	22.5
20	30	D1	5.3	D3	18.0
1	0	E	30.8	E	43.0
18	10	E1	27.9	E3	40.3
19	20	E1	23.9	E3	36.4
20	30	E1	18.5	E3	32.3
1	0	F	41.6	F	----------
18	10	F1	38.6	F3	52.8
19	20	F1	35.0	F3	49.2
20	30	F1	29.7	F3	45.7
1	0	G	----------	----------	----------
18	10	G1	49.0	----------	----------
19	20	G1	45.2	----------	----------
20	30	G1	39.5	----------	----------

TABLE 7.—*Critical solution temperatures in ° C. for alcohol mixtures with gasolines containing various added percentages of natural gasoline B*

Gasoline no.	Amount of natural gasoline B	50 percent gasoline in mixture		75 percent gasoline in mixture	
		Alcohol solution	Critical solution temperature	Alcohol solution	Critical solution temperature
	Percent		° *C.*		° *C.*
1	0	A	−37.4	A	−30.1
21	10	A1	−39.9	A2	−32.7
22	20	A1	−44.3	A2	−37.2
23	30	A1	−49.2	A2	−41.4
1	0	B	−15.1	B	−5.0
21	10	B2	−16.9	B3	−7.1
22	20	B2	−21.3	B3	−10.7
23	30	B2	−26.1	B3	−15.0
1	0	C	3.7	C	13.7
21	10	C2	2.1	C3	12.5
22	20	C2	−1.7	C3	9.4
23	30	C2	−6.2	C3	4.8
1	0	D	18.7	D	29.9
21	10	D2	16.9	D3	28.2
22	20	D2	13.1	D3	24.8
23	30	D2	9.1	D3	21.5
1	0	E	30.8	E	43.0
21	10	E2	28.6	E3	41.5
22	20	E2	25.3	E3	38.4
23	30	E2	21.7	E3	36.1
1	0	F	41.6	F	----------
21	10	F2	39.4	F3	53.9
22	20	F2	36.4	F3	51.0
23	30	F2	33.0	F3	48.2
1	0	G	----------	----------	----------
21	10	G2	49.3	----------	----------
22	20	G2	46.4	----------	----------
23	30	G2	43.2	----------	----------

Since the Pennsylvania gasoline no. 9, produced by topping gasoline no. 1, has the same volatility as the Rumania gasoline no. 2, within experimental error, a direct comparison is possible between the critical solution temperatures of two gasolines of equal volatility but of widely different chemical characteristics. Data on these two gasolines are given in table 8, and it is seen that gasoline no. 2 has somewhat lower critical solution temperatures. The difference is almost constant, being on the average 6.7° C. This difference represents about the maximum which is likely to be found between any two straight-run gasolines of the same volatility refined from different crude oils. Greater differences might be found, however, between a straight-run and a 100 percent cracked gasoline of equal volatility.

TABLE 8.—*Comparison of critical solution temperatures in ° C. for mixtures with alcohol of the Pennsylvania gasoline no. 9 and of the Rumania gasoline no. 2 of equal volatility*

No.	Alcohol solution	Volume percent gasoline in mixture								
		10	20	30	40	50	60	70	80	90
9	A	--------	--------	--------	--------	--------	−54.0	−49.1	−43.9	−39.0
2	A	--------	--------	--------	--------	−67.0	−60.7	−55.6	−52.3	−47.9
9	B	--------	--------	--------	−47.1	−35.2	−28.1	−23.9	−17.0	−9.3
2	B	--------	--------	--------	−56.5	−43.6	−35.3	−30.4	−24.2	−16.2
9	C	--------	--------	−45.4	−26.8	−15.0	−8.9	−3.9	5.2	15.3
2	C	--------	--------	−53.5	−34.5	−21.5	−15.0	−10.8	−3.0	7.6
9	D	--------	--------	−28.5	−9.9	1.0	7.5	12.1	20.9	31.0
2	D	--------	−59.9	−35.4	−16.5	−5.4	−.2	5.8	14.5	27.0
9	E	--------	−39.6	−12.3	5.5	14.5	20.3	26.1	35.6	47.9
2	E	--------	−47.9	−18.5	−1.3	8.5	14.0	19.7	29.4	41.9
9	F	--------	−25.0	1.5	17.4	26.2	31.6	38.8	49.6	--------
2	F	--------	−33.2	−1.5	11.1	20.1	25.6	32.4	44.4	--------
9	G	--------	−12.6	13.6	28.2	36.7	42.3	50.3	--------	--------
2	G	--------	−20.4	7.3	22.2	30.7	36.5	44.4	--------	--------
9	H	−49.2	−1.4	24.1	38.3	46.1	--------	--------	--------	--------
2	H	−57.0	−7.8	17.7	32.2	40.7	46.4	--------	--------	--------

As a supplement to the information presented in this paper and the previous one, some data were obtained on six branded gasolines purchased on the open market, and are given in table 9. The differences in the critical solution temperatures of comparable mixtures containing any of the six commercial gasolines are very small.

TABLE 9.—*Critical solution temperatures in °C. for alcohol mixtures with various commercial gasolines*

(*a*) 50 PERCENT GASOLINE IN MIXTURE

Alcohol solution	Gasoline no.					
	12	13	14	15	16	17
A1	−58.8	−59.5	−60.6	−56.2	−58.8	−58.3
B1	−33.5	−34.1	−36.9	−29.5	−36.7	−34.1
C1	−13.3	−15.1	−16.5	−10.9	−17.1	−15.1
D1	1.5	−.1	−.5	4.1	−.6	1.5
E1	14.9	12.7	13.1	17.3	12.8	14.7
F1	26.5	24.4	24.6	28.6	24.2	25.9
G1	37.0	34.5	34.9	39.8	34.7	36.3
H1	47.3	44.1	44.4	47.9	44.3	45.6

(*b*) 75 PERCENT GASOLINE IN MIXTURE

A2	−49.4	−52.3	−51.0	−47.1	−52.6	−51.1
B3	−22.0	−24.0	−22.6	−18.9	−23.8	−22.7
C3	−.8	−3.2	−1.5	1.8	−2.9	−1.7
D3	15.3	13.7	14.9	18.1	14.0	15.3
E3	29.5	27.9	29.5	32.3	28.4	29.0
F3	42.8	41.0	42.2	44.9	41.6	42.0
G3	54.3	52.7	54.3	55.8	53.3	53.8

IV. CONCLUSIONS

The present work indicates that an increase in the volatility of a gasoline produces a marked lowering in the critical solution temperatures of its mixtures with ethyl alcohol. Differences in the critical solution temperatures of mixtures containing gasolines of the same volatility but of different composition were found to be comparatively small.

WASHINGTON, April 15, 1933.