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WATER TOLERANCES OF MIXTURES OF GASOLINE WITH ETHYL ALCOHOL

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ABSTRACT

Equations, based on 23 different gasolines, have been developed for calculating the water tolerance of any mixture of gasoline with ethyl alcohol from critical-solution-temperature measurements on a few mixtures with the particular gasoline. Conversely, it is also possible to compute critical solution temperatures of mixtures of known composition. The average deviation between observed and calculated critical solution temperatures of the 23 gasolines studied was 1.4° C and the corresponding average difference between observed and calculated water tolerances was 0.005 percent of the total mixture.

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I. INTRODUCTION

One of the major problems in connection with the use of mixtures of gasoline and ethyl alcohol as motor fuels involves the small water tolerances of such fuels without separation into two layers. In previous papers,[1] data were presented on the critical solution temperatures of mixtures, in various proportions, of 23 different gasolines with ethyl alcohol containing various percentages of water. From these data, it is easily possible to obtain the water tolerance of any of these gasolines at any given temperature within the range investigated. Analysis of the water-tolerance values indicated certain similarities in the trend of water tolerance with composition of the mixtures when comparing the results with different gasolines. This suggested the possibility of deriving a general empirical equation for the water tolerance of mixtures of gasoline and ethyl alcohol, and of assigning to any gasoline a characteristic constant which would be indicative of the water tolerance of all mixtures of this gasoline with ethyl alcohol. The derivation of such an equation and the evaluation of the characteristic constants for the various gasolines are outlined in the present paper.

II. ANALYTICAL TREATMENT OF DATA

The first step in the procedure of analyzing the experimental data consisted in the computation of the water content of each mixture

[1] Oscar C. Bridgeman and Dale Querfeld. *Critical solution temperatures of mixtures of gasoline, ethyl alcohol, and water*, BS J. Research **10,** 693 (1933) RP560; *The effect of gasoline volatility on the miscibility with ethyl alcohol*, BS J. Research **10,** 841 (1933) RP571.

of gasoline and ethyl alcohol investigated. This was accomplished simply by multiplying the volume percentage of water at 60° F in the aqueous alcohol solution employed by the volume percentage of aqueous alcohol solution at 60° F in the mixture with gasoline. The resulting value, expressed as percentage of the total mixture, was designated as the water tolerance of the mixture at the critical solution temperature. On plotting the logarithm of the water tolerance against the reciprocal of the critical solution temperature (absolute) for any given percentage of any one of the gasolines mixed with ethyl alcohol, it was found that a straight line could be put through the plotted points within experimental error. Accordingly,

$$\log S = a - b/T \tag{1}$$

where

S = volume percentage water in mixture at 60° F,
T = temperature in degrees centigrade absolute, and
a and b = constants characteristic of the percentage of gasoline in the mixture and of the particular gasoline employed.

Examples of the linearity of the data are shown in figure 1 for four different percentages of gasoline 2 in mixtures with ethyl alcohol.

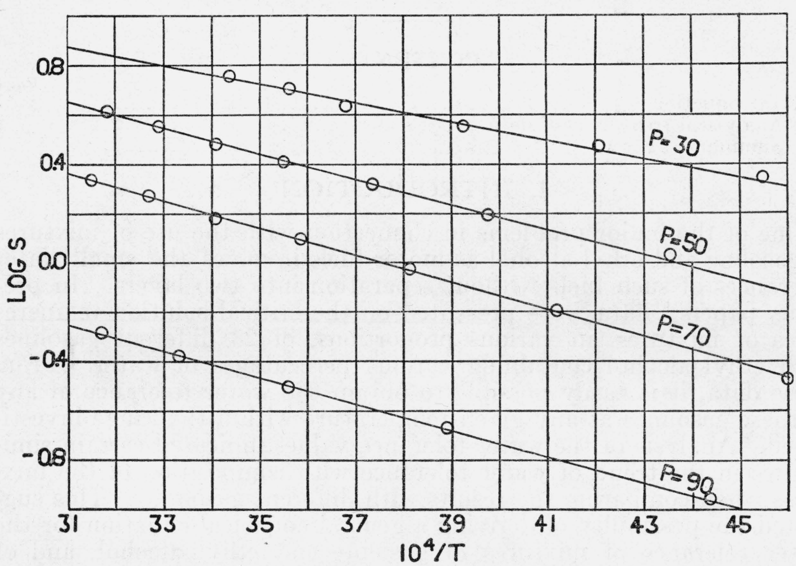

FIGURE 1.—*Log S as a function of temperature for four different percentages of gasoline 2 in mixtures with ethyl alcohol.*

Equations of the type of eq 1 were used to evaluate the parameters a and b for all of the mixtures studied. For any constant percentage P of gasoline in the mixture, it was observed that a plot of all of the b values against the corresponding a values gave a single straight line for all of the gasolines. Different lines were obtained for each value of P, although the slopes were equal within experimental error. Therefore

$$a = m + nb \tag{2}$$

where

$m=f_1(P)$ and
$n=1/410.$

Thus eq 2 becomes

$$a=f_1(P)+b/410 \tag{3}$$

It was found that $f_1(P)$ could be represented by eq 4,

$$f_1(P)=-1.177+1.273 \log (100-P) \tag{4}$$

where P is the volume percentage of gasoline in the mixture.

It follows from eq 3 that the various parallel lines obtained when a is plotted against b may be made to coincide, if the appropriate

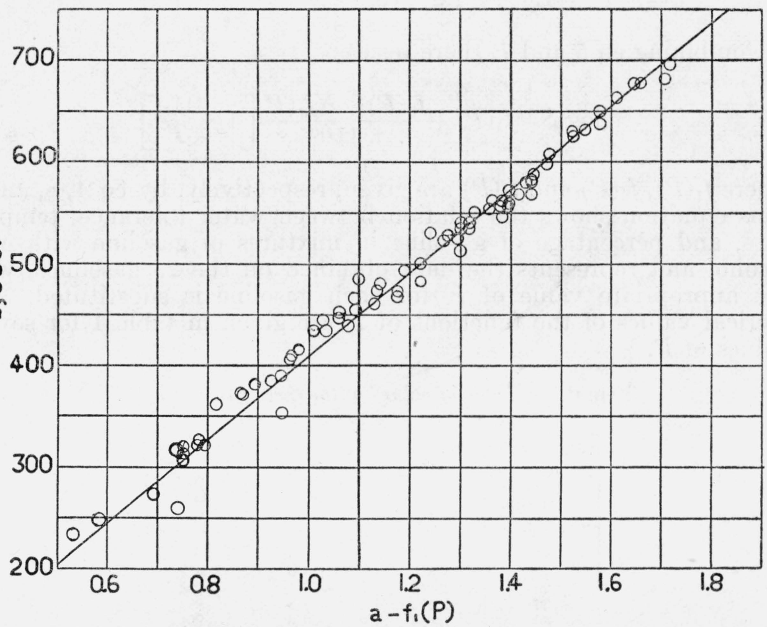

FIGURE 2.—*Comparison of b of equation 1 with b/410 from equation 3.*

value of $f_1(P)$ is subtracted from a, and the resulting values plotted against b. A plot of this nature is shown in figure 2, which indicates the agreement with eq 4.

Combining eq 1 and 3 to eliminate a, there results

$$\log S=f_1(P)+\frac{b}{410}\left[1-\frac{410}{T}\right] \tag{5}$$

In this equation, b depends upon the value of P as well as upon the characteristics of the particular gasoline being considered. The next step in the analysis, therefore, is to evaluate b as a function of P. It was observed that when the values of b for all of the gasolines at any given value of P were plotted against the values of b for $P=50$, a straight line was obtained. Thus

$$b_P=c+db_{50} \tag{6}$$

Different lines were obtained for each value of P, so that the parameters c and d are both functions of P. Since b_{50} is a constant for each gasoline, it may be designated by the symbol K and called the characteristic constant as regards water tolerance in mixtures with ethyl alcohol. Accordingly, eq 6 may be written

$$b_P = f_2(P) + Kf_3(P) \tag{7}$$

It was found that the c and d values could be represented satisfactorily by means of the following equations:

$$c = f_2(P) = -188.3 + 7.64P - 0.119P^2 + 0.00083P^3, \text{ and} \tag{8}$$
$$d = f_3(P) = 1.004 - 1.8 \times 10^{-4}(P-55)^2 \tag{9}$$

Combining eq 5 and 7, there results

$$\log S = f_1(P) + \frac{f_2(P) + Kf_3(P)}{410}\left[1 - \frac{410}{T}\right] \tag{10}$$

where $f_1(P)$, $f_2(P)$ and $f_3(P)$ are given, respectively, by eq 4, 8, and 9. This equation shows the relation between water tolerance, temperature, and percentage of gasoline in mixtures of gasoline with ethyl alcohol and represents the data obtained on the 23 gasolines, when the appropriate value of K for each gasoline is substituted. Numerical values of the functions of P are given in table 1 for several values of P.

TABLE 1.—*Table of values of the three functions of P*

Percentage P of gasoline in mixture	Value of $f_1(P)$	Value of $f_2(P)$	Value of $f_3(P)$
%			
10	1.310	−123.0	0.639
20	1.246	−76.5	.783
30	1.172	−43.8	.892
40	1.086	−20.0	.964
50	0.986	0.0	1.000
60	.862	21.0	1.000
70	.703	48.1	0.964
80	.479	86.3	.892
90	.096	140.5	.783
95	−.287	175.1	.716

It follows from eq 10 that a single measurement of the critical solution temperature of a mixture of known composition is sufficient in principle for determining the value of the characteristic constant K for each gasoline. Accordingly, each observation on the 23 gasolines can be used to compute a value of K and this was done in order to obtain an average value for each of these gasolines. The average values of K together with identification data on the gasolines are shown in table 2. The last column in this table gives the average deviation of individual values of K from the average value of K. It is seen that the values of K vary from 421 to 669, an average commercial gasoline having a value of about 550.

TABLE 2.—*Identification data and values of K for 23 gasolines*

Fuel	Source	Temperature at stated percentages evaporated, °C 10%	50%	90%	Specific gravity 60°/60°	Value of K	Average deviation of K
1	Pennsylvania	76	135	199	0.738	669	14
2	Roumania	70	106	152	.734	505	9
3	California	66	108	154	.730	521	8
4	Oklahoma	72	124	194	.740	603	8
5	California	58	110	156	.732	512	8
6	East Texas	58	110	162	.723	535	9
7	100% cracked	54	126	188	.754	473	12
8	100% cracked	69	142	194	.773	518	11
9	Topped No. 1	69	107	153	.720	546	7
10	Topped No. 7	53	96	150	.722	421	9
11	Topped No. 8	60	102	153	.734	427	9
12	Commercial gasoline	61	130	180	.742	544	8
13	do	58	123	181	.742	532	10
14	do	68	127	175	.743	537	4
15	do	69	136	186	.752	562	7
16	do	65	124	174	.741	531	7
17	do	66	131	187	.752	540	9
18	10% Natural gasoline *A* 90% No. 1	64	128	197	.731	641	10
19	20% Natural gasoline *A* 80% No. 1	55	119	196	.721	607	13
20	30% Natural gasoline *A* 70% No. 1	42	104	192	.707	568	9
21	10% Natural gasoline *B* 90% No. 1	69	128	197	.736	649	8
22	20% Natural gasoline *B* 80% No. 1	61	120	195	.727	620	7
23	30% Natural gasoline *B* 70% No. 1	57	111	193	.719	571	8

As a check on the accuracy of eq 10, all of the critical solution data on each gasoline were computed, using the values of K given in table 2. The agreement between the observed and computed values is illustrated in figures 3 and 4 for gasolines 1 and 2, respectively. A summary of the deviations for all of the gasolines is given in table 3. The grand average deviation is 1.4° C (2.6° F). The deviations are given on a temperature basis, since this greatly magnifies the differences between observed and computed values, for an extremely small difference in water tolerance may correspond to several degrees difference in critical solution temperature. On the average, a temperature deviation of 1.4° C corresponds to a deviation of approximately 0.005 percent in water content and to a difference of about 10 units in the value of K.

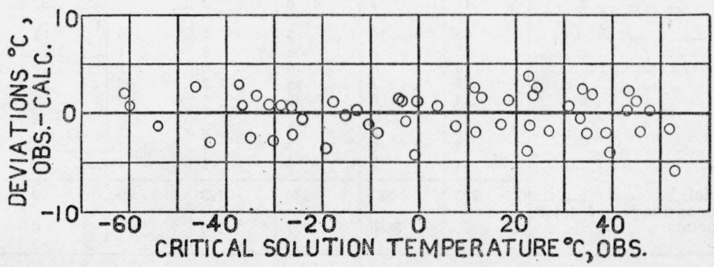

FIGURE 3.—*Comparison of values calculated from equation 10 with observed values of critical solution temperatures of mixtures of gasoline 1 with ethyl alcohol.*

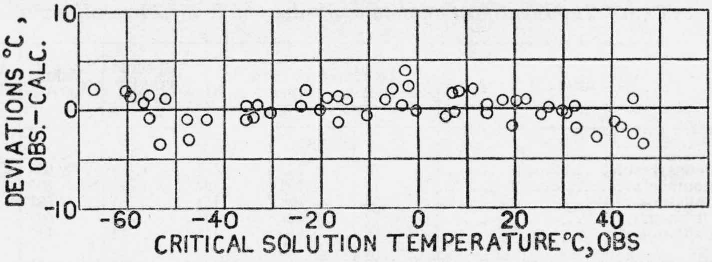

FIGURE 4.—*Comparison of values calculated from equation 10 with observed values of critical solution temperatures of mixtures of gasoline 2 with ethyl alcohol.*

TABLE 3.—*Deviations between observed and calculated critical solution temperatures*

Fuel	Total number of temperatures measured	Number of points for stated ranges of deviations in °C (without regard to sign)					
		0.0 to 1.0	1.0 to 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0	>4.9
1	55	12	17	14	6	3	3
2	53	22	19	9	2	1	
3	54	28	13	11	1	1	
4	54	26	18	8	2		
5	48	19	13	11	2	2	1
6	50	26	11	8	2	1	2
7	49	12	8	10	9	7	3
8	49	17	10	13	7	1	1
9	50	21	18	9	0	2	
10	46	16	16	5	4	3	2
11	46	14	18	6	6	0	2
12	15	6	7	2			
13	15	4	6	5			
14	15	12	2	1			
15	15	7	6	2			
16	15	10	3	1	0	1	
17	15	3	8	3	1		
18	13	6	6	0	1		
19	13	1	8	2	2		
20	14	6	6	1	1		
21	13	5	7	0	1		
22	14	7	5	1	1		
23	14	7	5	1	1		
Total	725	287	230	123	49	22	14
Percentage of total points		39.6	31.7	17.0	6.8	3.0	1.9

Average deviation ---------- 1.4° C (2.6° F)

The major interest at present is in 5- and 10-percent alcohol mixtures (P=95 and 90), and for these mixtures 10 becomes

$$P{=}95\ \log S = -0.287 + \frac{175.1+0.716\,K}{410}\left[1-\frac{410}{T}\right]$$

$$P{=}90\ \log S = 0.096 + \frac{140.5+0.783\,K}{410}\left[1-\frac{410}{T}\right] \qquad (11)$$

Considering an average gasoline for which K=550, and simplifying, there results

$$P{=}95 \quad \log S{=}-0.287+1.388\left[1-\frac{410}{T}\right]$$
$$P{=}90 \quad \log S{=}\ \ 0.096+1.393\left[1-\frac{410}{T}\right] \tag{12}$$

Graphical representation of eq 12 is shown in figure 5. It is seen that the water tolerance for a 5-percent alcohol mixture is less than half

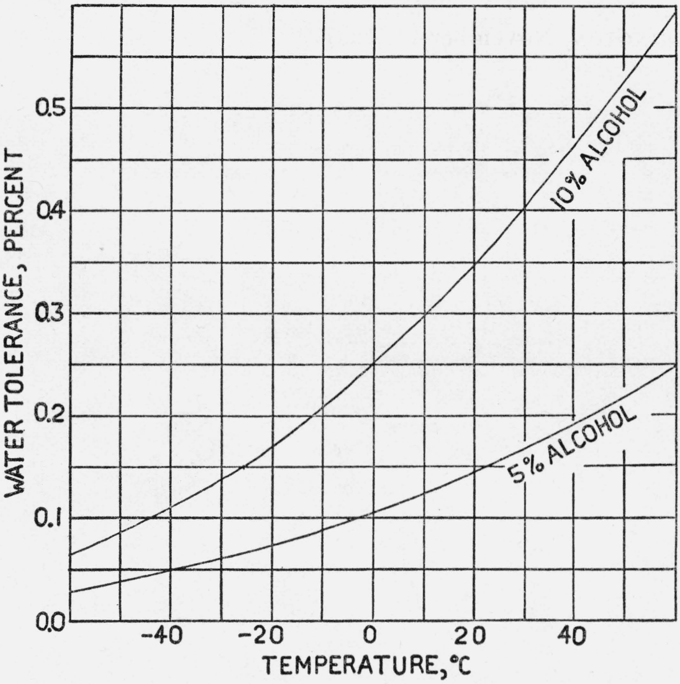

FIGURE 5.—*Water tolerances of mixtures of an average gasoline with 5 and 10 percent of ethyl alcohol at various temperatures.*

the water tolerance for a 10-percent alcohol mixture.

The data on which eq 10 is based cover the range of values of P from 10 to 90, so that the calculation for $P{=}95$ is an extrapolation from the observed data. However, since these calculations were made some additional data on three gasolines included measurements at $P{=}95$ and indicated that the equation is applicable to this percentage.

III. SUMMARY

An analysis of data previously presented, on the solubility of water in mixtures of ethyl alcohol with 23 different gasolines, indicated that it was possible to correlate the results by means of a general empirical equation. This equation contains one constant characteristic of the particular gasoline under consideration, and values of the characteristic constants for the 23 gasolines are given. Evidence is presented regarding the agreement of the equation with the observed data, the difference between the observed and computed critical solution temperatures being 1.4° C, and the difference between the observed and computed water tolerances being about 0.005 percent of the total mixture. Since the characteristic constant may be evaluated from a few solubility experiments with any particular gasoline, the equation can be used with confidence to compute the water tolerances at other temperatures or with other mixtures.

WASHINGTON, November 11, 1937.