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CRITICAL SOLUTION TEMPERATURES OF SOME HYDROCARBONS IN SULPHUR DIOXIDE[1]

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ABSTRACT

The variation with composition of the solution temperatures in sulphur dioxide of 17 paraffin and naphthene hydrocarbons of the naphtha fraction of petroleum has been determined. These data have been correlated with the boiling points of the hydrocarbons to determine the possibility of separating nearly constant-boiling mixtures of these hydrocarbons by extraction with sulphur dioxide. A few critical solution temperatures in aniline have been determined to complete a series for comparison with the data for sulphur dioxide. Some experiments on the behavior of the hydrocarbons in ammonia were also made.

It is concluded that sulphur dioxide and ammonia offer little promise as extraction agents to supplement distillation. Aniline shows greater difference than ammonia or sulphur dioxide in its behavior towards 3 classes of hydrocarbons, normal paraffin, iso-paraffin, and naphthene.

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I. INTRODUCTION

The difficulties encountered in the separation by distillation alone of a complex mixture of hydrocarbons, such as that occurring in petroleum can frequently be solved by resort to methods depending upon other physical properties than boiling point. Extraction, which depends on differences in solubilities, is a convenient method and has frequently proved useful, notably for separating nearly constant-boiling mixtures containing olefin and aromatic compounds. It is therefore desirable to obtain information which will aid in predetermining the feasibility of using the process and in selecting the best solvent. To predict the behavior of a distillation fraction on extraction, it would be necessary to determine the phase relations of the solvent and all the constituents, since the hydrocarbons mutually affect one another's solubilities. The critical solution temperatures are, how-

[1] Financial assistance has been received from the research fund of the American Petroleum Institute. This work is part of Project No. 6, The Separation, Identification, and Determination of the Constituents of Petroleum.

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ever, an easily determinable property on the basis of which qualitative indication of the behavior of hydrocarbons on extraction can be obtained. Since extraction will be of greatest value where compounds which boil close together have considerable differences in critical solution temperatures and since structure has an important influence on the solution temperature, it is to be expected that constant-boiling mixtures containing members of different structural classes (paraffin, naphthene, iso-paraffin, and aromatic compounds) would be more likely to yield to separation by the method than members of a homologous series.

The results presented herein for sulphur dioxide and ammonia are a part of an investigation into the possible use of some extracting agents, boiling at approximately 0° C or below, for the separation of compounds of the naphtha fraction of petroleum. Low-boiling solvents are of particular interest because they can be removed from the hydrocarbon with the minimum amount of manipulation and consequent loss. Since aromatic compounds are known to be extremely soluble in sulphur dioxide, they were not further investigated. Some of the work of other investigators was repeated in order to compare the methods of measurement, but the chief object was to supplement the data which were already available.

The values for the critical solution temperatures of the hydrocarbons in aniline were used for reference because the different classes of compounds were known to display considerable differences in solution temperatures in it. Most of these data were available in the literature, but a few were determined in this work to complete the series.

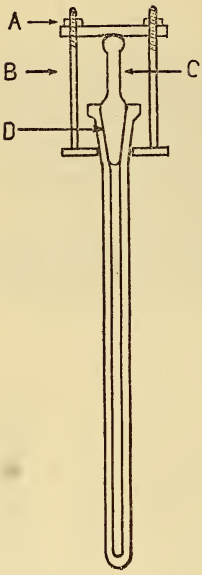

FIGURE 1.—*Tube for observation of solution temperatures.*

A, nuts for clamping tube in frame; B, aluminum frame; C, ground stopper; D, waxed joint.

II. METHOD OF STUDY

Weighed amounts of hydrocarbon and solvent were mixed and the solution cooled until the second liquid phase appeared. The stoppered tubes shown in figure 1 were used instead of sealed tubes usually employed. A chlorinated paraffin with a melting point of 70° C, sold as "Opal-wax", was used to seal the stoppers. Care was taken to keep the liquid from coming in contact with the wax. With the stoppered tubes it was possible to obtain a series of points by adding successive quantities of solvent to a given quantity of hydrocarbon. The tubes were of about 3 mm bore and 3 mm wall. This is unnecessarily thick-walled for sulphur dioxide and is sufficient for studies with ammonia.

The experiments with aniline were done in a well-stirred water bath. The temperature at which turbidity was observed, following the first opalescence, was recorded. A mixture of carbon tetrachloride and chloroform cooled with solid carbon dioxide and contained in an unsilvered dewar tube was used for the measurements with sulphur dioxide. The temperatures of separation were much more

definite near the critical points than at lower ones. The bath was cooled rapidly at first to find the approximate solution temperature. It was then reheated and a more careful determination made. No attempt to determine the temperature of disappearance of the 2 liquid phases was made. The points could generally be checked to less than half a degree with different samples but occasional deviations occurred. Most of these were evidently caused by contamination with moisture or other substances, errors in weighing, or nonuniform cooling and the values were discarded.

III. MATERIALS USED

The sources of most of the hydrocarbons are listed in the footnotes to table 1. The journal articles there referred to give methods of preparation and the properties from which the purity can be estimated. None was less than 95 mole percent pure, except for the possible presence of isomers.

The samples of ethylcyclohexane and hexahydromesitylene were supplied by J. D. White and F. W. Rose of this laboratory. Both materials were prepared by the hydrogenation of the corresponding aromatic compounds in acetic acid solution in the presence of platinum black. After hydrogenation, the products were washed with concentrated sulphuric acid and then sodium carbonate solution, and distilled from solid sodium hydroxide. The properties of the ethylbenzene from which ethylcyclohexane was prepared are reported by White and Rose.[3] The hydrogenation product had the following physical constants: n_D^{25} 1.4306; bp 131.6° C, cst in aniline 44° C. The constants reported by Garner and Evans [4] for ethylcyclohexane are n_D^{25} 1.4298; bp 131.6; and cst in aniline 43.8° C. The properties of the mesitylene which was used in the preparation of hexahydromesitylene are reported by Mair and Shicktanz.[5] The hexahydromesitylene had the following constants: n_D^{25} 1.4248; fp −50.7° C, and bp 138.9° C. Properties of cis- and trans-modifications have been reported by Eisenlohr,[6] but it was not determined whether the product used in this work was a pure modification or a mixture.

The hydrocarbons and the aniline were distilled from sodium and kept over the same metal until they were pipetted into the tubes. Sulphur dioxide was condensed from a cylinder of the commercial product and was redistilled into the tubes through a glass capillary.

III. RESULTS

The curves from which the critical solution temperatures in sulphur dioxide were obtained are shown in figures 2, 3, and 4. These curves are probably not as flat as drawn, but the curvature is within the limit of error of the determinations. Only a sufficient part of each of the solubility curves with aniline was determined to fix the critical temperature, and the curves are not reproduced.

[3] BS J.Research 10,643(1933). footnote 10.
[4] J. Inst. Pet. Techn. 18,751(1932).
[5] BS J.Research 11,665(1933).
[6] Fortsch. Chem. 18,652(1925).

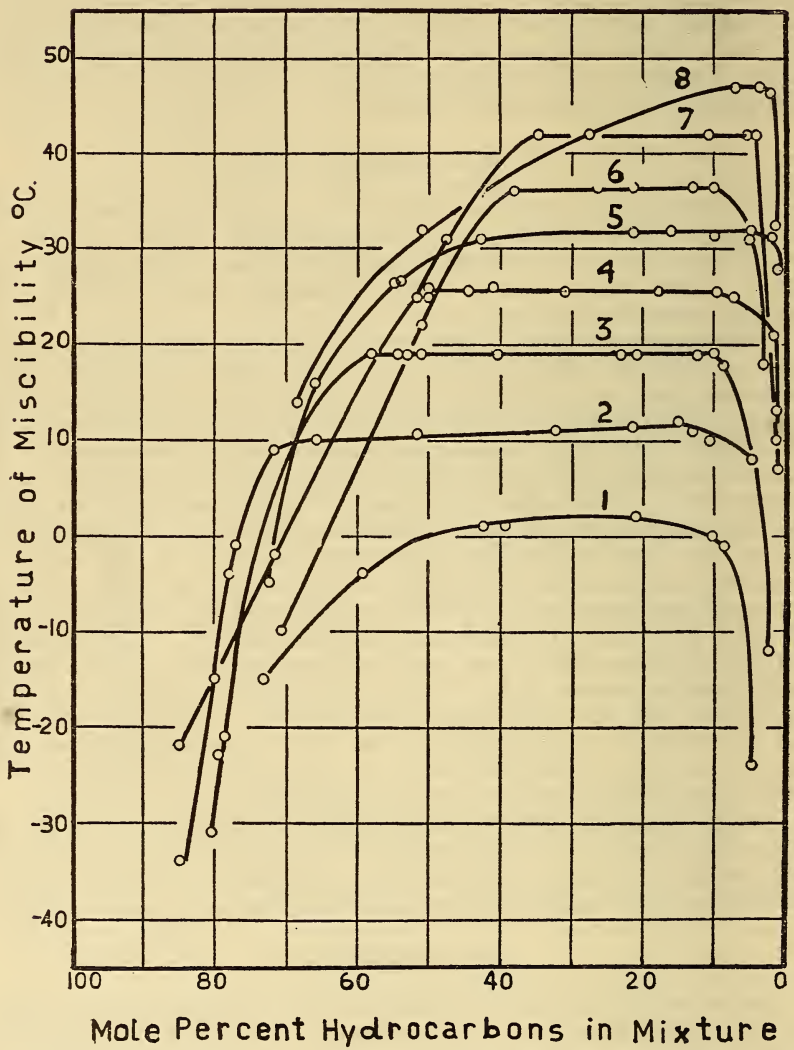

FIGURE 2.—*Solution temperature curves of normal hydrocarbons in sulphur dioxide.*

1. Pentane
2. Hexane
3. Heptane
4. Octane
5. Nonane
6. Decane
7. Undecane
8. Dodecane

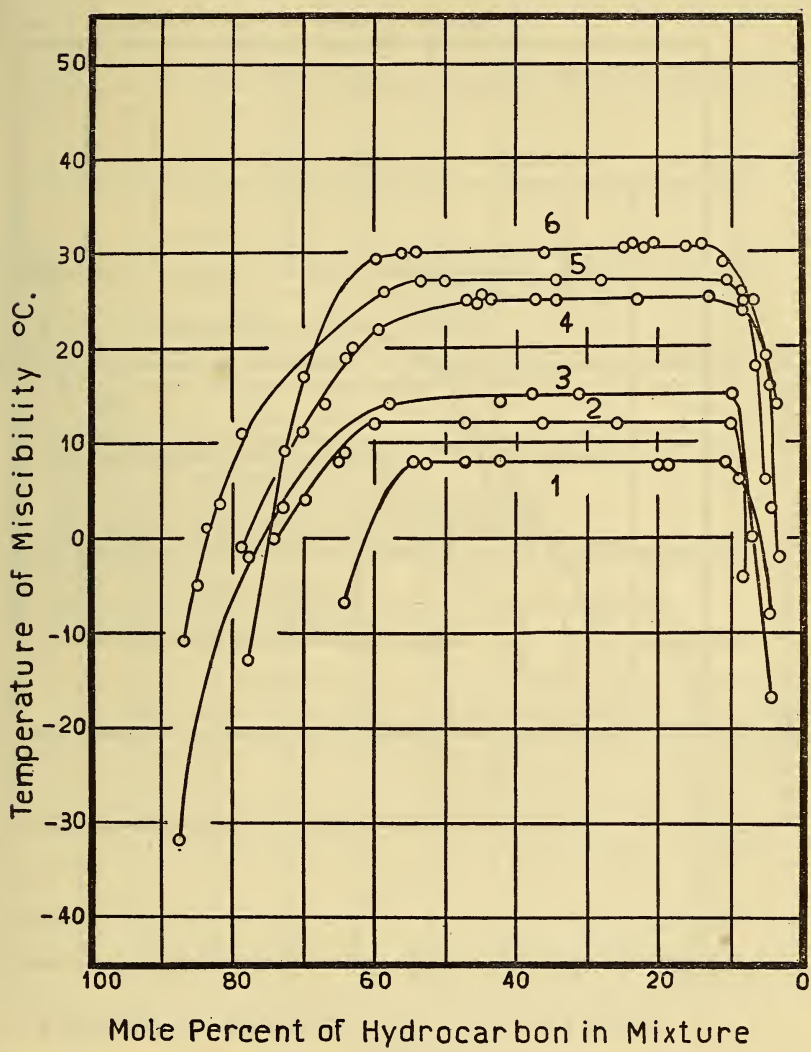

FIGURE 3.—*Solution temperature curves of cyclic hydrocarbons in sulphur dioxide.*

1. Methylcyclopentane
2. Cyclohexane
3. Methylcyclohexane
4. Ethylcyclohexane
5. Nonanaphthene
6. Hexahydromesitylene

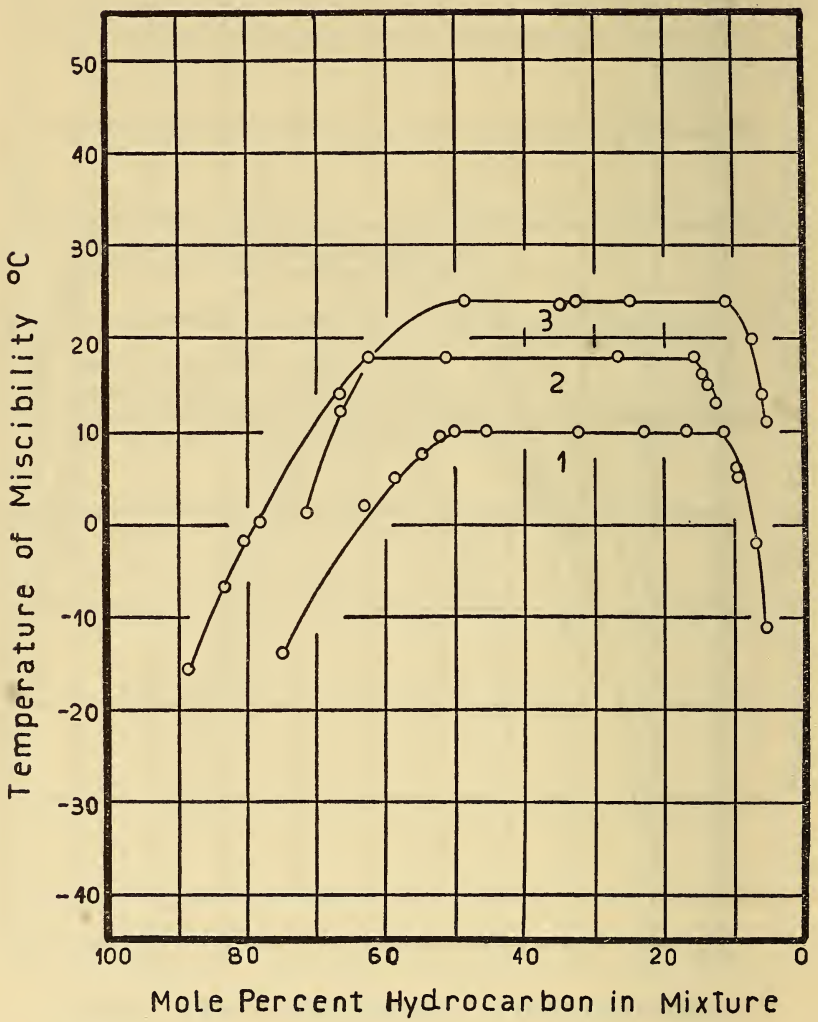

FIGURE 4.—*Solution temperature curves of iso-paraffin hydrocarbons in sulphur dioxide.*

1. 2-Methylpentane
2. 2-Methylhexane
3. 2-Methylheptane

The critical solution temperatures in sulphur dioxide are listed in table 1 together with those found by Seyer and Todd.[7] The maximum difference in the results obtained is approximately 2 degrees, which may have been caused by differences in the method and materials used. All the results reported in this work were obtained by one observer, using a uniform procedure.

TABLE 1.—*Critical solution temperatures of hydrocarbons in sulphur dioxide*

Hydrocarbon [a]	cst (This work)	cst (Seyer and Todd)	Hydrocarbon [a]	cst (This work)	cst (Seyer and Todd)
	°C	°C		°C	°C
Butane [1]	--------	−4.7	Ethylcyclohexane [9]	25	--------
Pentane [2]	2	--------	Octane [8]	25.5	26.9
2-Methylpentane [3]	10	--------	Nonanaphthene [10]	27	--------
Hexane [2]	12	10.2	Hexahydromesitylene [9]	30.5	--------
Methylcyclopentane [4]	8	--------	Nonane [11]	32	--------
Cyclohexane [5]	12	--------	Decane [2]	36.5	37.3
2-Methylhexane [6]	18	--------	Undecane [2]	42	--------
Heptane [2]	19	--------	Dodecane [2]	47	47.3
Methylcyclohexane [7]	15	--------	Dotriacontane [1]	--------	110.0
2-Methylheptane [8]	24	--------			

[a] Superior numbers refer to following literature describing properties of hydrocarbons used:
[1] F. Seyer and E. Todd, Ind. Eng. Chem. **23**, 325(1931).
[2] B. J. Mair, BS J.Research, **9**, 457(1932).
[3] J. H. Bruun and M. M. Hicks-Bruun, BS J.Research **5**, 933(1930).
[4] M. M. Hicks-Bruun and J. H. Bruun, BS J.Research **7**, 799(1931).
[5] J. H. Bruun and M. M. Hicks-Bruun, BS J.Research **7**, 607(1931).
[6] J. H. Bruun and M. M. Hicks-Bruun, BS J.Research **10**, 465(1933).
[7] J. Timmermans and F. Martin. For properties see reference M. M. Hicks-Bruun and J. H. Bruun, BS J.Research **8**, 536(1932).
[8] R. T. Leslie, BS J.Research **10**, 609(1933).
[9] J. D. White and F. W. Rose. Preparation and properties reported in this paper.
[10] J. D. White and F. W. Rose, BS J.Research.
[11] J. D. White and F. W. Rose, BS J.Research **7**, 907(1931).

The 4 critical temperatures in aniline which were determined in this work were included in figure 5 and are designated by numbers alone without letters. The footnotes to the figure give the sources of the data which were taken from the results of other investigators. A determination for iso-octane was made because the value of 74° C given by Chavanne and Simon [8] was only estimated from observations on iso-hexane and iso-heptane. The critical solution temperature in aniline of the same material which was used in the work with sulphur dioxide was found to be 75° C. The values of 56.9° C for hexahydromesitylene and of 57° C for the nonanaphthene have not previously been reported. The cst of ethylcyclohexane was determined to compare it with that found by Garner and Evans,[9] since insufficient material was at hand to establish its purity by determining its freezing point.

IV. DISCUSSION

In figure 5 the data on critical solution temperatures have been correlated with the boiling points to show the possibilities of supplementing distillation by extraction. For the normal and iso-hydrocarbons from hexane to tetradecane the relation is nearly linear. Seyer and Todd[10] plotted the relationships between molecular weight and critical solution temperatures for some hydrocarbons, from bu-

[7] Ind. Eng. Chem. **23**, 325(1931).
[8] Compt. rend. **168**, 1111(1919).
[9] See footnote 4.
[10] See footnote 7.

tane to dotriacontane, against the molecular weight and obtained a smooth curve.

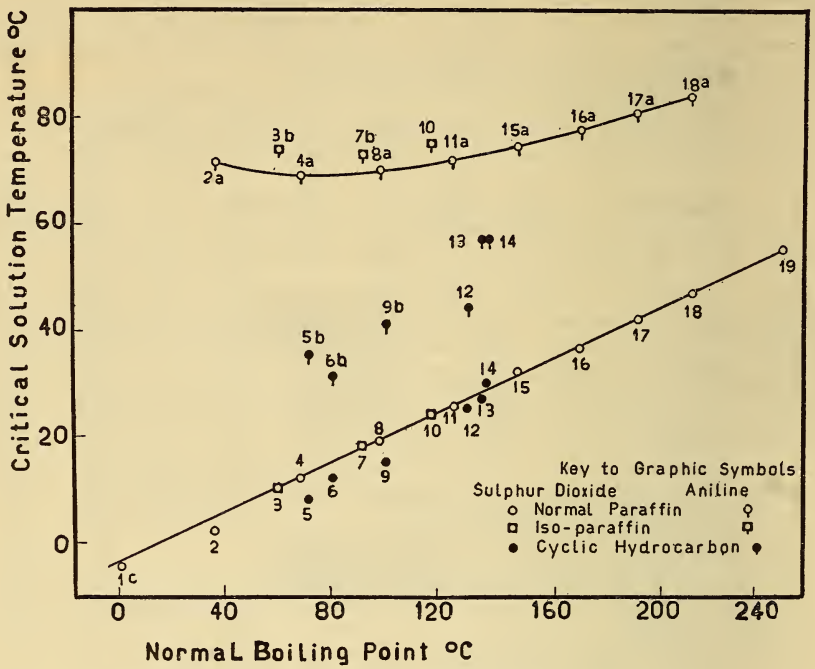

FIGURE 5.—*Relation of critical solution temperature of some hydrocarbons in sulphur dioxide and aniline to the normal boiling points*

1. Butane.
2. Pentane.
3. 2-Methylpentane.
4. Hexane.
5. Methylcyclopentane.
6. Cyclohexane.
7. 2-Methylhexane.
8. Heptane.
9. Methylcyclohexane.
10. 2-Methylheptane.
11. Octane.
12. Ethylcyclohexane.
13. Nonanaphthene.
14. Hexahydromesitylene.
15. Nonane.
16. Decane.
17. Undecane.
18. Dodecane.
19. Tetradecane.

Letters following numbers refer to sources of information taken from other investigators as follows:
a. A. F. Shepard, A. L. Henne and T. Midgley, J.Am.Chem.Soc. **53**, 1948(1931).
b. C. Chavanne and L. J. Simon, Compt. rend. **168**, 1111(1919).
c. W. F. Seyer and E. Todd, Ind. Eng. Chem. **23**, 325(1931).

The critical solution temperatures in sulphur dioxide of all the cyclic hydrocarbons which were examined, with the exception of hexahydromesitylene, fell below the boiling point-critical solution temperature line of the paraffin and iso-paraffins but there appears to be no marked regularity. The lack of regularities of the values may be the result of different influences of ring and side-chain structures.

The critical solution temperatures in aniline are plotted in figure 5 for comparison with the values in sulphur dioxide. There is a uniformity in the relationship for paraffin and iso-paraffin hydrocarbons, but the cyclic compounds again display irregularities. It is apparent that there is a much greater difference in the solution temperature of paraffin, iso-paraffin and naphthene hydrocarbons in aniline than in sulphur dioxide.

A cursory investigation with ammonia, using about equal volumes of hydrocarbon and solvent, indicated that the solution temperatures for normal and iso-paraffins from hexane to dodecane vary more or less linearly with the boiling points between 60 and 80° C. The cyclics lie, in general, a few degrees below the normal compounds, while ethylbenzene, *o*-, *m*-, and *p*-xylene become completely miscible in the neighborhood of 15° C.

V. CONCLUSIONS

The slight differences in critical solution temperatures offer little promise for the use of extraction with sulphur dioxide and probably ammonia to separate paraffin, iso-paraffin, and naphthene hydrocarbons in the naphtha faction of petroleum whose boiling points lie close together. Aniline appears to be more promising for the purpose than sulphur dioxide and ammonia.

WASHINGTON, August 14, 1934.

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