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ABSTRACT

Separation of roughly equal volume mixtures of methanol and gasoline into two phases at low temperature may cause problems for vehicles that are designed to operate on these mixtures. Cosolvent alcohols (C_2-C_{12}) and surfactants were evaluated as additives for enhancing phase stability at -25°C of a blend containing 50 volume percent methanol, 40 percent isooctane, and 10 percent toluene (simulating a 50/50 methanol/gasoline mixture).

For alcohol cosolvents, the amount required decreased with increasing carbon number (number of carbon atoms per molecule) from about 50 percent with C_2 to about 6 percent for C_8 through C_{12}. A simple cost analysis indicated that decanol (C_{10}) provided the minimum treatment cost for preventing separation at -25°C: $0.13/gallon. Of the various commercial nonionic surfactants and various anionic fatty acid surfactants evaluated, only palmitic acid (C_{16}) showed good effectiveness.

METHANOL, A LEADING ALTERNATIVE fuel candidate for vehicles (1, 2),* can be made from non-petroleum resources and some consider it to have potential for improving ambient air quality (3,4). Neglecting economic considerations, three of the major problems associated with the introduction of methanol fuel are: cold starting, lack of flame luminosity and the logistics of having a widespread fuel distribution system as soon as vehicles are available (the so-called "chicken and egg" problem). Likely near-term solutions to the first two of these involve addition of hydrocarbons to methanol (5,6), and one of the proposed solution to the latter involves the production of "variable-fuel vehicles" which

* Numbers in parentheses designate references at the end of the paper.

operate on methanol, gasoline, or any mixture of the two (7).

Other studies have suggested that roughly equal blends of methanol and gasoline could provide optimum engine (8) and vehicle (9) performance. In a single-cylinder engine study comparing, gasoline, M35 (35% methanol in gasoline), M50, M70, and M100, Sapre (8) found that M50 provided nearly all of the octane quality, lean limit, thermal efficiency, and NO_x emissions benefits observed with M100. Furthermore, some of the undesirable effects of methanol (high formaldehyde and unburned methanol emissions) were less severe with M50 than with M100.

A serious potential problem with mixtures of hydrocarbons and methanol, however, is phase separation at low temperatures. Figure 1, constructed based on correlations developed in a previous study of methanol-gasoline solubility (10), shows cloud point as a function of methanol concentration at various levels of water contamination. The cloud point is the temperature at
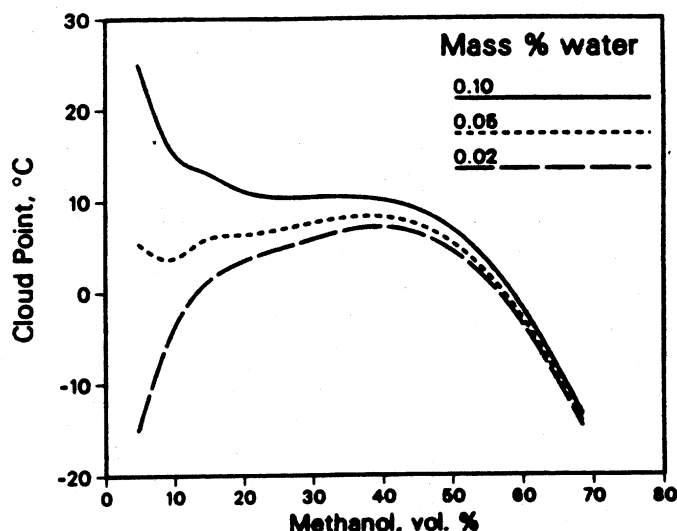

Figure 1. Effect of Methanol Concentration in Gasoline and Water Content on Cloud Point (From Reference 10).

2

which two phases become visible, giving a hazy appearance to the solution. At a low (0.02%) water level, the cloud point temperature is maximum near 40% methanol, and decreases for higher and lower methanol concentrations. Figure 1 also shows that increasing water content causes a large increase in cloud point at low methanol concentrations (less than 20%), but has little effect at higher methanol levels. Even at low (0.02%) water contents, blends of 30-50% methanol in gasoline can separate into two phases at temperatures in the vicinity of 5°C.

There have been various studies of cosolvents to enhance the solubility of low level (5-20%) methanol gasoline blends (11-17), but we are not aware of any work at higher methanol concentrations. In addition, these studies generally involved only a narrow range of cosolvent additives. This study was initiated to investigate additives for improving low-temperature phase stability of mid-range (50/50) methanol/hydrocarbon blends using a variety of cosolvent alcohols and surfactants. The major impetus for this work was the potential for vehicles dedicated to operation on a 50/50 methanol/gasoline mixture. The results may also be relevant to variable-fueled vehicles.

EXPERIMENTAL

METHANOL-HYDROCARBON BLEND SELECTION - The base fuel for these studies was:

        50 vol. % methanol
        40 vol. % isooctane
        10 vol. % toluene

A 50% methanol concentration was chosen because 50/50 methanol/gasoline blends showed the the best promise in single-cylinder engine studies (8).

Pure hydrocarbons were selected to represent gasoline in this study, since variation in gasoline composition can affect its solubility with methanol (10-13, 16-17). This allowed the exploratory work to be done with a fluid of known composition, permitting the experiments to be easily duplicated or extended by others. In a study of low methanol concentrations, Eccleston and Cox (10) found that a blend of 4 parts isooctane to 1 part toluene provided solubility characteristics similar to that of a commercial gasoline. Our preliminary experiments showed that the phase separation temperature of the selected methanol-isooctane-toluene blend (about 0°C) was similar to that of a fuel we blended to contain 50% methanol and 50% of a commercial gasoline containing about 25% aromatics.

MATERIALS - A detailed description of the materials used, including source, purity, water content, and structure, are given in Appendix Table A-1. Cosolvents investigated were alcohols ranging 2 to 12 carbon atoms per molecule. Several surfactants were also investigated; these will be described later.

TEMPERATURE BATH - A mechanical temperature-controlled bath was not available, so techniques for preparing chemical baths were reviewed (18). A bath of dry ice and carbon tetrachloride was selected as being the most suitable for this study. Initially, solid lumps of dry ice were placed in a Dewar flask containing carbon tetrachloride to lower the temperature to near the control point. Then a small amount of crushed dry ice was continually added and agitated until a slush was formed giving the desired temperature of -25°C. The bath could be maintained in the range of -23°C to -26°C by intermittent agitation, as long as only a small excess of dry ice had been used.

The temperature of the sample was measured by an alcohol thermometer, which was periodically checked by comparison to a thermocouple probe.

PHASE EQUILIBRIA - Phase equilibria were studied by placing graduated tubes containing the samples into the temperature bath. The base solution for each sample consisted of 5 mL methanol, 4 mL isooctane, and 1 mL toluene, all at room temperature. In different tubes, varying amounts of cosolvent alcohols were added to the 10 mL base solution. The amount of cosolvent added varied in 0.10 mL steps for the C_2-C_5 alcohols, giving a resolution of about 1% in the phase stability studies. For the C_6-C_{12} alcohols, the grid size was halved to provide about 0.5% resolution. In each case, the amounts of added cosolvent bracketed the required amounts to achieve a single phase. After 30 minutes in the temperature bath (sufficient time for the samples to reach -25°C), each sample was checked to see if it was one or two phases. When two phases were observed, the volume ratio of the upper to lower phase was recorded based on the tube graduations.

RESULTS AND DISCUSSION

The amounts of various additives required to maintain phase stability of a mixture consisting of 50% methanol, 40% isooctane, and 10% toluene at -25°C were measured in a study consisting of two parts. The first part involved investigation of a wide range of higher alcohols as cosolvents, and the second part consisted of evaluation of several surfactants. A simple cost analysis of the additives was also made.

COSOLVENCY OF HIGHER ALCOHOLS - The effect of addition of n-propanol on the phase stability of the 50/50 methanol/hydrocarbon blend is shown in Figure 2, which presents the volume ratio of the upper to lower phase. With no additive, the volume of the upper phase was 0.54 times that of the lower phase. Compositions of the phases were not analyzed, but based on previous studies (12, 13, 17), the bulk of the methanol would be expected to be in the lower phase. As n-propanol was added, the volume of the upper phase decreased until, at 9.9% n-propanol, the upper phase disappeared. The value of 9.9% n-propanol was then defined as the minimum concentration for one phase. Similar studies were performed for other cosolvents, and the resulting minimum concentrations for one phase are summarized in Table 1. Although the minimum concentrations are reported to the nearest 0.1%, the resolution of the measurements was only about 1% for the C_2-C_5 alcohols and about 0.5% for the C_6-C_{12} alcohols.
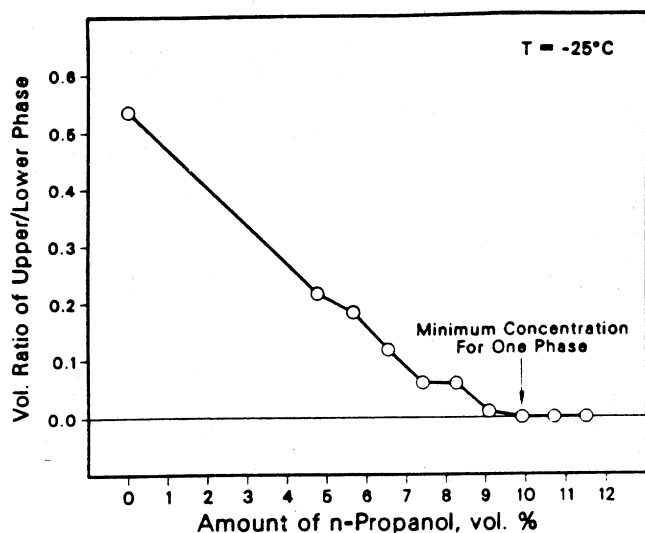
Figure 2. Effect of N-Propanol Cosolvent on Volume Ratio of Phases

Table 1. Cosolvent Effectiveness of Various Alcohols at -25°C

(Base Material: 50% methanol, 40% isooctane, 10% toluene)

Alcohol	Minimum Concentration For One Phase vol. %	Carbon Number
Ethanol	50	2
n-Propanol	9.9	3
2-Propanol	12.3	3
n-Butanol	9.1	4
i-Butanol	8.3	4
2-Butanol	8.3	4
n-Pentanol	7.4	5
3-Pentanol	7.4	5
i-Amyl Alcohol	8.3	5
t-Amyl Alcohol	8.3	5
n-Hexanol	6.5	6
2-Hexanol	6.5	6
n-Heptanol	6.1	7
4-Heptanol	6.5	7
n-Octanol	5.7	8
2-Octanol	6.5	8
n-Nonanol	5.7	9
n-Decanol	5.2	10
n-Undecanol	5.7	11
n-Dodecanol	5.2	12

The data from Table 1 are plotted as a function of the number of carbon atoms (carbon number) in Figure 3. The required additive concentration decreased as the carbon number in the additive increased up to about 9 carbons per molecule, and was fairly constant for C_9 through C_{12} at 5 to 6 percent. The different alcohol structures, identified by different symbols in Figure 3, did not generally have a large effect on required additive concentration. With the

exception of the butanols (C_4), the required concentration for primary straight chain alcohols was equal to or lower than that for primary branched chain, secondary, or tertiary alcohols. Previous studies (11-13) of C_3-C_8 cosolvents for 10-15% methanol-hydrocarbon blends have indicated optimum cosolvent performance in the C_5-C_6 range, with primary alcohols somewhat more effective than secondary or tertiary alcohols. Effects of variations in water content were not explored but results in Figure 1 suggest that effects will be small with 50% or more methanol.
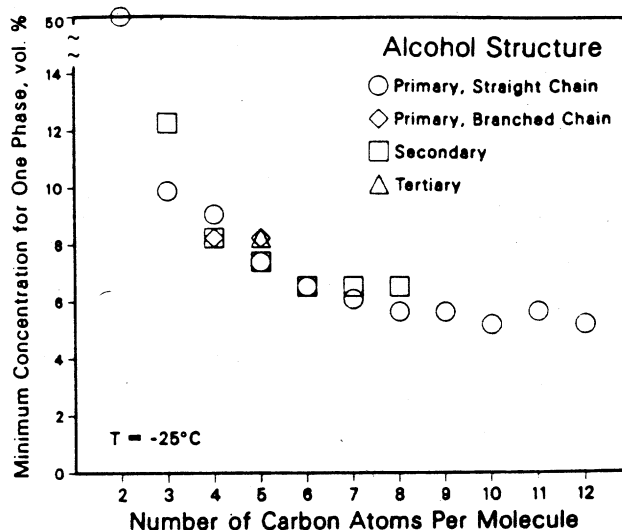

Figure 3. Cosolvent Alcohol Additive Requirement as a Function of Chain Length and Structure

The mechanism of cosolvency of the higher alcohols can be postulated based on a study of the effect of cosolvents on the interaction of methanol with elastomers (19). This study reported the use of nuclear magnetic resonance spectroscopy to identify associations in methanol/n-butanol solutions. In the absence of butanol, methanol was found to exist as a cyclic tetramer. Addition of n-butanol results in the replacement by n-butanol molecules of one or two of the methanol molecules on the cyclic tetramer. The hydrocarbon chain of the n-butanol is likely to enhance the solubility of the tetramer in hydrocarbons. Longer chain hydrocarbons probably form similar tetramers with enhanced solubility because of the longer chain length.

We also compared cosolvency properties of the various alcohols by analyzing the (upper/lower) phase volume ratio data at subcritical cosolvent concentrations (concentrations below the minimum required for one phase). To compare these ratios for different cosolvents, it was necessary to define a normalized cosolvent quantity by dividing each cosolvent concentration by the minimum required for one phase:

Normalized Amount of Cosolvent =

$$\frac{\text{Cosolvent Concentration}}{\text{Minimum Concentration for One Phase}}$$

The ratio of upper-to-lower phase ratio is plotted in Figure 4 as a function of the normalized amount of cosolvent. Although there was some scatter in the 0.2 to 0.4 normalized cosolvent range, phase ratio data for the various alcohols generally clustered about the same line. The results also suggest that the mechanism of two-phase formation for the subcritical concentrations of alcohols is the same for all alcohols.

anionic and nonionic surfactants, which are listed in Table 2.

A preliminary experiment with oleic acid showed that its maximum effectiveness for decreasing the volume of the upper phase occurred at a concentration of about 1 vol. %, and decreased sharply at higher concentrations. Based on this result, all surfactants were added to the base blend (methanol-isooctane-toluene) at a concentration of 10 grams surfactant per liter of blend (about 1 vol. %). For these tests, n-pentanol was arbitrarily selected as the cosolvent. Keeping the surfactant concentration constant, the n-pentanol concentration was varied to determine the minimum required to achieve a single phase.

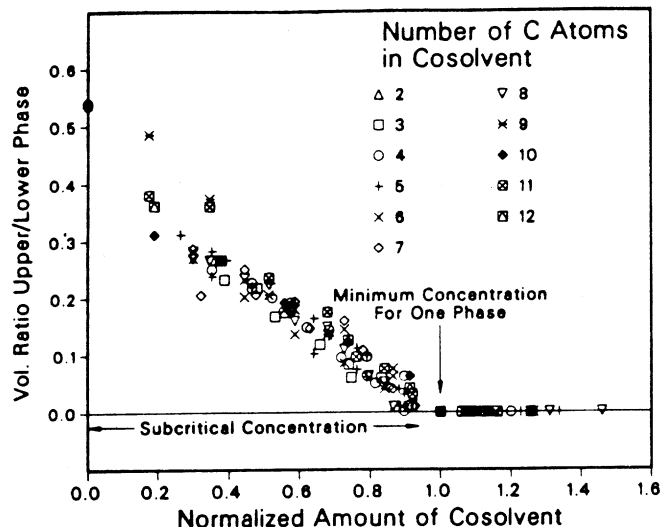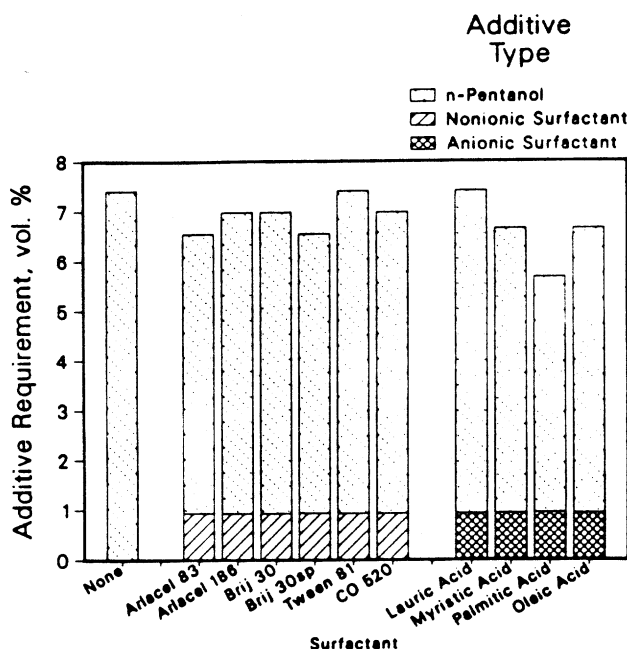Figure 5 shows data on the amount of surfactant and cosolvent required. The shading

Figure 4. Volume Ratio of Upper to Lower Phase as a Function of Normalized Additive Content

This work has shown the higher alcohols to be effective cosolvents. However, the minimum concentrations required are sufficiently high to warrant additional investigation to reduce the amount of additive. Hence, additional studies were made with surfactants in combination with alcohol cosolvent.

COSOLVENT-SURFACTANT COMBINATIONS - To explore the potential benefit of surfactants, screening tests were run with a variety of

Figure 5. Comparison of Effectiveness of Various Various Surfactants

Table 2. Listing of Surfactants Evaluated

Type	Name	Supplier	Structure
Nonionic	Arlacel 83	ICI	Sorbitan Sesquoleate
Nonionic	Arlacel 186	ICI	Mono- and di-glycerides
Nonionic	Brij 30	ICI	Polyoxyethylene[4] lauryl ether
Nonionic	Brij 30sp	ICI	Brij 30 + 0.01% BHA + 0.01% citric acid
Nonionic	Tween 81	ICI	Polyoxyethene[5] Sorbitan Monooleate
Nonionic	CO 520	GAF	$CH_3(CH_2)_8C_6H_4O(CH_2CH_2O)_4(CH_2)_2OH$
Anionic	Lauric Acid	Baker	$CH_3(CH_2)_{10}COOH$
Anionic	Myristic Acid	K&K	$CH_3(CH_2)_{12}COOH$
Anionic	Palmitic Acid	Baker	$CH_3(CH_2)_{14}COOH$
Anionic	Oleic Acid	Fisher	$CH_3(CH_2)_7CHCH(CH_2)_7COOH$

indicates the portion of the total which was
surfactant and that which was n-pentanol
cosolvent. All of the nonionic surfactants
tested caused either no change, or only a slight
(less than one percentage point) reduction in the
total amount of additive required. Keller et al.
(12) had also found nonionic surfactants to be
ineffective at lower methanol concentrations.

The effect of the fatty acid (anionic)
surfactants appeared to be related to structure.
The lowest additive requirement was with the
saturated acid with the longest chain length
(palmitic acid, C_{16}). Palmitic acid in
combination with n-pentanol provided a stable
system at a combined concentration of 5.7%,
significantly less than the 7.4% required for n-
pentanol alone.** Although oleic acid (C_{18}) had
a larger chain length, the presence of the double
bond apparently reduced its effectiveness.

The methanol-isooctane-toluene mixtures with
small amounts of surfactant and higher alcohol
cosolvent may have formed microemulsions in these
experiments. Although no evidence was sought in
this study, the existence of an isooctane-in-
methanol microemulsion at -25°C cannot be ruled
out based on the following:

- a mixed fuel consisting of aqueous ethanol
  and hydrocarbon fuels including a vegetable
  oil has been shown to form a hydrocarbon
  fuel-aqueous ethanol microemulsion upon
  addition of a surfactant even with as little
  as 0.05 % water (20, 21);

- a waterless microemulsion can be prepared
  using methanol as well as other solvents
  such as glycerol, formamide, glycol, etc. in
  place of water (22);

- the solubility of oil in the microemulsion
  increases considerably if light organic
  solvents, especially aromatics such as
  toluene and benzene, are added to the system
  (23, 28);

- the lower phase, which is expected to be
  rich in methanol (12, 13, 17), grows as the
  amount of additives increase.

COST ANALYSIS - From a practical standpoint,
the most important aspect influencing the
selection of cosolvents and/or surfactants is one
of economics. A good economic analysis, one that
would consider effects on markets and plant
construction, is beyond the scope of this report.
Instead the additives were compared based on
current prices published in the Chemical
Marketing Reporter (25). Reference 25 listed
prices for most of the cosolvents and the anionic
surfactants, but not the nonionic surfactants.
(No additional cost data was sought for the
nonionic surfactants because they were not
effective.) When a range of prices was listed,

**An interesting observation made with palmitic
acid surfactant at N-pentanol concentrations of
2% and less was the formation of three phases.
The middle phase was milky and turbid,
apparently a macroemulsion.

the midpoint of the range was used. Table 3
gives a summary of the cost data.

Table 3. Costs of Cosolvents and Surfactants

Material	Cost, $/gal.	Treatment Cost,* $/gal.
Ethanol	1.17	0.58
n-Propanol	3.13	0.31
2-Propanol	1.51	0.19
n-Butanol	2.56	0.23
2-Butanol	2.46	0.20
i-Butanol	2.50	0.21
n-Pentanol	3.15	0.23
n-Hexanol	2.17	0.14
n-Octanol	4.84	0.27
n-Decanol	2.49	0.13
n-Dodecanol	5.29	0.27
Lauric Acid	4.05	0.24
Myristic Acid	6.36	0.24
Palmitic Acid	3.91	0.18
Oleic acid	4.05	0.22

* Cost ($/gallon fuel blend) to prevent
  separation at -25°C

For each additive, a treatment cost was computed
based on the selling price and the concentration
required for one phase at -25°C. (If used
commercially, higher concentrations may be
required to maintain one phase in the presence of
water contamination and lower temperatures.)
Figure 6 shows the treatment cost plotted as a
function of carbon number for the alcohol
cosolvents. The minimum cost was $0.13/gallon
for n-decanol (C_{10}), one of the alcohols having
the minimum concentration requirement. The C_8
and C_{12} alcohols, which had similar required
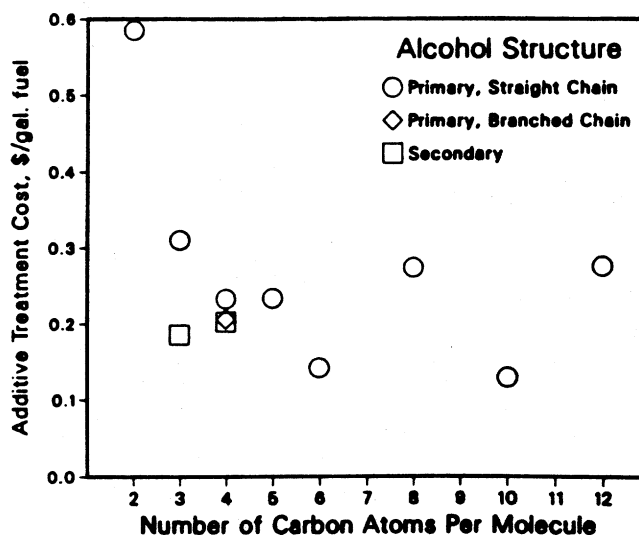concentrations, had much higher treatment costs

Figure 6. Treatment Cost of Required Alcohol
Additive as a Function of Chain
Length and Structure

because of their higher prices. The treatment cost for n-hexanol (C_6) was only slightly higher ($0.14/gallon) than that of n-decanol.

Additive treatment costs for the anionic surfactants in combination with n-pentanol are shown in Figure 7. The first bar shows the cost of n-pentanol alone ($0.23/gallon), which was relatively high (see Figure 6). Two of the surfactants (lauric acid and myristic acid) had essentially the same treatment cost relative to n-pentanol alone, and one (oleic acid) provided only a slight ($0.02/gallon) decrease. The most effective surfactant, palmitic acid, gave a $0.05/gallon decrease in treatment cost, compared to n-pentanol alone. However, the combined cost for palmitic acid and n-pentanol was $0.18/gallon, which was higher than of n-hexanol or n-decanol. Unfortunately, we have no data available to determine whether addition of palmitic acid in combination with the C_6 or C_{10} alcohols would provide a reduced treatment cost.
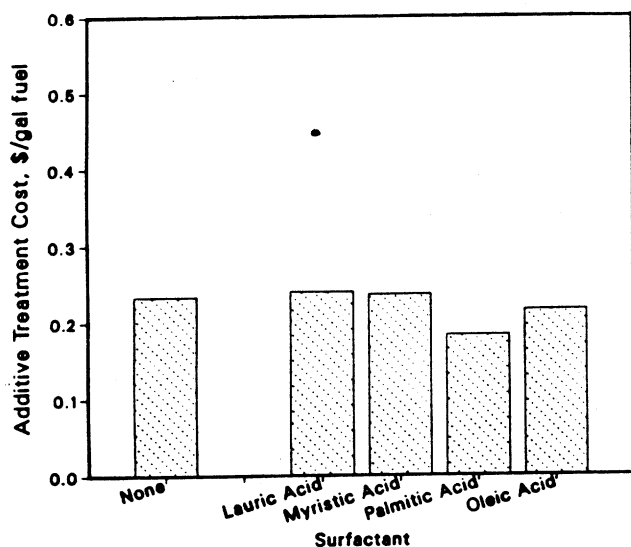

Figure 7.   Comparison of Cost Effectiveness of Various Anionic Surfactants Used in Combination with n-Pentanol Cosolvent

CLOSURE - This study presented results of screening tests to evaluate additives for solubilizing 50/50 methanol/hydrocarbon blends at low temperatures. The results have shown that neither the cost nor the quantity of additives required is trivial. Perhaps more effective cosolvents can be found, but it is questionable whether large reductions in required concentrations can be achieved. The most cost-effective treatment may be to alter the methanol synthesis process to coproduce higher alcohols (26) as required to maintain phase stability in mixtures with gasoline.

Blending higher molecular weight alcohols into methanol will affect properties; however, the effects will be minor if the higher alcohol concentrations are kept below 10 percent. On the positive side, heating values will increase about 5 percent with the addition of alcohol cosolvents at the minimum concentration required for one

phase, and heats of vaporization will decrease about 5 percent. Vapor pressures would be expected to decrease a little, but the effects on engine performance would probably not be significant. One noticeable property effect may be the 3-4 percent reduction in stoichiometric fuel-air ratio. Although variable-fueled vehicles and vehicles with closed-loop fuel control systems would probably not be greatly affected, open-loop fuel control vehicles calibrated for a particular methanol concentration without cosolvents may show some adverse emissions effects of this 3-4 percent change in stoichiometry.

This study was primarily concerned with potential vehicles dedicated to operation on a 50/50 methanol/gasoline blend, however, effects on variable fueled vehicles should also be considered. The relatively mild temperature (0°C) at which mid-range mixtures of methanol and gasoline will separate suggests that phase separation may be frequently experienced in variable-fuel vehicles which are alternately fueled with gasoline and methanol. Ideally, the in-line fuel sensors in these vehicles will correctly measure the methanol composition of the separated phase being picked up in the tank, and select the proper air-fuel ratio. However, it is not clear if the sensor would respond properly to a macro- or micro-emulsion of both phases. It is also not clear whether the methanol-rich phase would have the sufficient quantity of hydrocarbons for good starting and driveabilty. Tests of variable-fuel vehicles on phase-separated fuels are recommended.

SUMMARY

A blend containing 50 volume percent methanol, 40 percent isooctane, and 10 percent toluene (simulating a 50/50 methanol/gasoline mixture) was found to separate into two phases at temperatures below 0°C. The effectiveness of additives to enhance low-temperature (-25°C) phase stability was measured using C_2 through C_{12} alcohols, and various anionic and nonionic surfactants in combination with n-pentanol.

For alcohol cosolvents, the amount required decreased with increasing carbon number (number of carbon atoms per molecule) from about 50 percent with C_2 to about 6 percent for C_8 through C_{12}. Alcohol structure (branching or location of the OH group) had little effect on the concentration required. Of the various commercial nonionic surfactants and various anionic fatty acid surfactants evaluated, only palmitic acid (C_{16}) showed good effectiveness. With 1 percent palmitic acid added to the base blend, the amount of n-pentanol required for one phase decreased from 7.4 to 4.7 percent.

Using current market prices, a simple cost analysis was performed based on the minimum additive concentrations required for one phase at -25°C. For cosolvent alcohols, the minimum treatment cost was $0.13/gallon fuel for n-decanol. The palmitic acid surfactant also was cost effective when used with n-pentanol, reducing the treatment cost from $0.23/gallon to $0.18 per gallon. It is not known whether the

palmitic acid would be cost effective if used with n-decanol or other alcohol cosolvents.

If vehicles are developed and marketed to operate on mid-range methanol-gasoline blends, blending agents for phase stability will be necessary for low-temperature operation. Variable-fueled vehicles are also likely to encounter mid-range mixtures of methanol and gasoline due to fuel switching, so blending agents may also be required to prevent operation problems in these vehicles at low temperatures.

REFERENCES

1. N. E. Gallopoulos, "Alcohols for Use as Motors Fuels and Motor Fuel Components," General Motors Research Laboratories Paper # GMR-4933, Presented at the Coordinating European Council, Second International Symposium, Wolfsburg, West Germany, June 6, 1985.

2. U.S. General Accounting Office, "Alternative Fuels - Status of Methanol Vehicle Development," GAO/RCED-87-10BR, October, 1986.

3. K. W. Wilson and M. C. McCormack, "Methanol as an Ozone Control Strategy in the Los Angeles Area," Paper B-10, Presented at VI International Symposium on Alcohol Fuels Technology, Ottawa, Canada, May 21-25, 1984.

4. R. K. Pefley, B. Pullman, and G. Whitten, "The Impact of Alcohol Fuels on Urban Air Pollution: Methanol Photochemistry Study," U.S. Department of Energy Report DOE/CE/50036-1, November, 1984.

5. M. J. Denham, G. J. Lang, and F. H. Palmer, "The Effects of Hydrocarbon in Methanol Automotive Fuels," Presented at the VII International Symposium on Alcohol Fuels, Paris, October 20-23, 1986.

6. E. R. Fanick, L. R. Smith, and T. M. Baines, "Safety Related Additives for Methanol Fuel," Society of Automotive Engineers Paper No. 841378, Baltimore, Maryland, October 8-11, 1984.

7. J. V. D. Weide and R. J. Wineland, "Vehicle Operation with Variable Methanol/Gasoline Mixtures," Paper A-71 Presented at the VI International Symposium on Alcohol Fuel Technology, Ottawa, May 21-25, 1984.

8. A. R. Sapre, "Properties, Performance, and Emissions of Medium Concentration Methanol-Gasoline Blends in a Single-Cylinder, Spark-Ignition Engine," Society of Automotive Engineers Paper No. 881679, Portland, Oregon, October 13, 1988.

9. R. J. Nichols, D. S. Moulton, N. R. Sefer, and E. Ecklund, "Options for the Introduction of Methanol as a Transportation Fuel," SAE Paper No. 872166, Toronto, Ontario, November 2-5, 1987.

10. B. H. Eccleston and F. W. Cox, "Physical Properties of Gasoline/Methanol Mixtures," U. S. Department of Energy Bartlesville Energy Technology Center Report BETC/RI-76/12, January, 1977.

11. Cavit Aydemir, "Properties of Methanol/Gasoline Fuels and Suggested Fuel Handling Procedures," Paper A-2 Presented at the VI International Symposium on Alcohol Fuels Technology, Ottawa, Canada, May 21-25, 1984.

12. J. L. Keller, G. M. Nakaguchi, and J. C. Ware, "Methanol Fuel Modification For Highway Vehicle Use," U.S. Department of Energy Publication HCP/W3683-18, July, 1978.

13. G. Terzoni, R. Pea, F. Ancillotti, "Improvement of the Water Tolerability of Methanol-Gasoline Blends," Paper I-11 Presented at the Third International Symposium on Alcohol Fuels Technology, Asilomar, California, May, 1979.

14. E. J. Smith and D. R. Jordan, "The Use of Surfactants in Preventing Phase Separation of Alcohol Petroleum Fuel Mixtures," Society of Automotive Engineers Paper 830385, February-March, 1983.

15. B. C. Davis and W. H. Douthit, "The Use of Alcohol Mixtures as Gasoline Additives," Paper AM-80-47 Presented at the 1980 National Petroleum Refiners Association Meeting, New Orleans, Louisiana, March, 1980.

16. Coordinating Research Council, "Performance Evaluation of Alcohol-Gasoline Blends in 1980 Model Automobiles Phase II--Methanol-Gasoline Blends," CRC Report No. 536, Atlanta, Georgia, January, 1984.

17. F. W. Cox, "Component Relationships Within Two-Phase Gasoline/Methanol/Water Systems," U. S. Department of Energy Bartlesville Energy Technology Center Report BETC/RI-78/6, February, 1979.

18. J. Nassler, "Experimental Techniques For Low Boiling Solvents," The Chemistry of Non-Aqueous Solvents, Vol. 1, edited by J. J. Lagowski, Academic Press, New York, New York, 1966, p. 213.

19. M. E. Myers and I. A. Abu-Isa, "Elastomer Solvent Interactions III-Effects of Methanol Mixtures on Fluorocarbon Elastomers," Journal of Applied Polymer Science, Vol. 32, pp. 3515-3539, 1986.

20. A. W. Schwab, "Diesel Fuel-Aqueous Alcohol Microemulsions," U.S. Patent No. 4451265, May 29, 1984.

21. A. W. Schwab and E. H. Pryde, "Microemulsions from Vegetable Oil and Aqueous Alcohol with Trualdylamine Surfactant as Alternative Fuel for Diesel Engines," U.S. Patent No. 4451267, May 29, 1984.

22. I. Rico, de Savingnas, A. Ahmadzadej and A. Lattes, "Waterless Microemulsions," International Workshop on Microemulsions, Chemical Center, University of Lund, Lund, Sweden, June 6-8, 1984.

23. J. E. Desnoyers, M. Sarbar and Lemieux, "Tar Sand Extractions with Microemulsion II: The Dispersion of Bitumen in Microemulsions," Can. J. Chem. Eng., Vol. 61, p. 680, 1983.

24. M. Sarbar, C. Brochu, M. Voisvert and J. E. Desnoyers, "Tar Sand Extractions with Microemulsions and Emulsions," Can. J. Chem. Eng., Vol. 62, p. 267, 1984.

25. Chemical Marketing Reporter, Schnell Publishing Co., April 4, 1988.

26. The Texas Methanol Corporation, "Application for a Waiver Under Section 211(f)(4) of the Clean Air Act," Submitted to the U.S. Environmental Protection Agency, August, 1987.

APPENDIX

Table A-1. Description of Materials (Surfactants Described in Table 2)

Material	Manufacturer	Grade	Water,* mg H_2O/ml	Structure
Isooctane	Phillips	Spectro	0.028	$(CH_3)_3CCH_3CH(CH_3)_2$
Toluene	Fisher	Certified	0.180	$C_6H_5CH_3$
Methanol	Fisher	Certified	0.158	CH_3OH
Ethanol	Fisher	Denatured	4.863	CH_3CH_2OH
n-Propanol	Fisher	Certified	1.157	$CH_3(CH_2)_2OH$
2-Propanol	Fisher	Certified	0.492	$CH_3CHOHCH_3$
n-Butanol	Fisher	Certified	0.692	$CH_3(CH_2)_3OH$
i-Butanol	Fisher	Certified	0.667	$(CH_3)_2CHCH_2OH$
2-Butanol	Mallincrodt	Organic	1.282	$CH_3CH_2CHOHCH_3$
n-Pentanol	Fisher	Certified	1.208	$CH_3(CH_2)_4OH$
3-Pentanol	Kodak	Reagent	1.400	$CH_3CH_2CHOHCH_2CH_3$
i-Amyl alcohol	J.T.Baker	Analyzed	0.020	$(CH_3)_2CH(CH_2)_2OH$
t-Amyl alcohol	Fisher	Reagent	1.388	$(CH_3)_2C(OH)CH_2CH_3$
n-Hexanol	Kodak		0.775	$CH_3(CH_2)_5OH$
2-Hexanol	Kodak		2.967	$CH_3CHOH(CH_2)_3CH_3$
n-Heptanol	Fisher	Certified	1.379	$CH_3(CH_2)_6OH$
4-Heptanol	Kodak		2.000	$CH_3(CH_2)_2CHOH(CH_2)_2CH_3$
n-Octanol	Fisher	Certified	1.088	$CH_3(CH_2)_7OH$
2-Octanol	Kodak		1.975	$CH_3CHOH(CH_2)_5CH_3$
n-Nonanol	Kodak		0.800	$CH_3(CH_2)_8OH$
n-Decanol	Aldrich	99%	0.492	$CH_3(CH_2)_9OH$
n-Undecanol	Sigma	99%	1.800	$CH_3(CH_2)_{10}OH$
n-Dodecanol	Kodak		0.625	$CH_3(CH_2)_{11}OH$

*Determined by Karl Fisher method