AN ACID-SOLVENT SYSTEM FOR REMOVAL OF DOWNHOLE SKIN DAMAGE

James B. Dobbs and Timothy M. Brown
NL Treating Chemicals

INTRODUCTION

As early as 1895, Herman Frasch recognized a need for acid additives in acid stimulation treatments. His observations and subsequent patent spelled out the need for an acid corrosion inhibitor. During the span of years from the early 1930s to the mid 1960s, much advancement was made in the field of developing additives for hydrochloric acid stimulation. Surfactants, corrosion inhibitors, buffering agents, and reaction time retarders as we know them today, had their beginnings. The one notable factor about these advances is the fact that all were truely additives for the acid. That is, the materials were added to the acid in small quantities to alter the properties of the treating fluid. Seldom were the additives used at concentrations exceeding 1%.

In the mid 1960s, alcoholic acid treating solutions were introduced. This launched an era of more basic changes in the whole nature of the acidizing fluids. This was no longer an additive because a significant portion of the treating fluid might now be termed as a solvent. Later in the decade came the use of chemically stabilized dispersions of aromatic solvents in an acid external emulsion. Then in 1971, the use of mutual solvents was introduced. Each of these advancements offered new possibilities and improved the treatment results by helping the acid past physical barriers so it could perform the job it was intended to do.

During the same decade, much work was directed to enhanced oil recovery through micellar flooding. From this technology came the concept of the micellar acidizing solvent. The following sections will compare the properties and use of the popular and widely used solvent systems to the newest - a micellar acidizing solvent.

SOLVENT SYSTEMS

The advent of the solvent systems instigated new techniques that were especially useful in removing skin damage and near-wellbore plugging problems. Historically, some acid treatments did not show the expected results and the treatment may well have been branded as a failure. Many of these treatments literally did not get to the area where the acid was needed. There were sludges of heavy hydrocarbons in and near the perforations, and the formation face was possibly oil wet. When acid encountered this condition, it never reached the scale or rock surfaces where it was expected to react. The various solvent systems offer mechanisms to overcome this problem.

A. Emulsions

Solvent systems of aromatic solvents dispersed in acid were fairly effective in dissolving the residues and allowing the acid to react. These were, and are still used where troublesome paraffin problems cause restrictions in the well bore. One weakness to the use of these dispersions occurs upon matrix injection. The emulsion particles enter the formation matrix as two phase flow which exhibits mobility problems due to viscosity. This causes restrictions to flow in some pore spaces, and therefore, does not result in even penetration of the zone of interest.

B. Mutual Solvents

The mutual solvents, because of their molecular configuration, are soluble or miscible in either oil phase or water phase. When used in quantity, these unique molecules exhibit solvency. They also possess weak surfactant properties. Ethylene glycol monobutyl ether (EGMBE) is probably the most commonly used of the mutual solvents. It is a weak surfactant, but because of the size of the molecule and the insufficient dissimilarity between the hydrophobic and the hydrophilic functions, it possesses only limited detergency etc. Concentrations of 10% or greater do an effective job in treating some forms of skin damage. Higher concentrations (although economically unattractive) perform better.

Other mutual solvents are available that also seem to perform well, but tend to require higher concentrations to be effective and thus reach an economic restriction.

C. Micellar Solvent

The micellar solvent tends to exhibit the same types of properties as the mutual solvents, but does so through an entirely different scheme of chemistry. Like the mutual solvents, it is totally miscible in acid, but exhibits the properties of a much stronger surfactant, and the solvency of a much stronger organic solvent. The micellar system is structured similarly to the enhanced recovery micellar flood materials. By combining a surfactant, cosurfactant, and a high molecular weight polar organic solvent not normally water soluble, and then adding these to an acidic solution, they are melded into a clear, single phase micellar system. This system then exhibits the properties of a water wetting agent, surfactant, dispersing agent and an organic solvent in a totally miscible treating solution capable of even penetration across the zone being treated.

THE MICELLAR SYSTEM

A. Description of the Micelle

Any good surfactant forms micelles when introduced to water and oil phases in the right proportions. For example, a surfactant molecule having a pronounced molecular dissymetry of the hydrophilic-hydrophobic groups, when placed into water will hydrolyze and form micelles. The hydrophobic groups will aggregate to the interior of a group of the surfactant molecules to form a micelle. As oil is added to this system, it will be solvated to the hydrophobic groups and pulled to the interior of the micelle. This aggregate may then be composed of a few hundred molecules. With the addition of more oil, the interior of the micelle will become saturated, swell, and rupture. Now the particles realign themselves into a larger community and form a dispersed system composed of several thousand molecules. This becomes an emulsion which is opaque and sometimes viscous depending upon the ratio of the two phases.

The micellar acidizing solvent is built by placing a cosurfactant into the micelle where it bonds to the primary surfactant to form a strong flexible wall to that micelle (Exhibit A). Now the micelle has extra capacity to carry a high mole weight polar solvent and to absorb hydrocarbons. Since even the loaded micelles are many orders of magnitude smaller than emulsion droplets, the total system maintains the properties of a single phase fluid. These ordered or extended micelles approach the forms known as lyotropic mesomorphs or liquid crystals, if they are extended far enough.

B. Properties of the Micellar Solvent

When added to acid, the micellar acidizing solvent imparts the following benefits:

1. Detergency and foaming action
2. Solubilization of heavy hydrocarbons
2. Penetrant and solvent properties
4. Demulsifying and non-emulsifying properties
5. Water wetting and suspension of solids

The micellar acidizing solvent is clearly soluble in well treating acids such as 3% to 30% HCl and HF/HCl mud acids. When added to acid at 0.2% to 5% by volume (2 to 50 gallons per 1000 gallons), the micellar solution converts the acid to a more powerful solvent.

The components of the micellar system combine to react with acids by hydrogen bonding and protonation. This reaction creates the micellar structures that allow oil soluble components to remain in clear solution at all proportions in acid. The final chemical system (acid plus micellar acidizing solvent) exhibits miscibility or mutual solubility with heavy oils and oil deposits. The low interfacial tensions reduce capillary forces that trap residual oil in porous media. Reduction of these forces will free the oil, allowing it to be recovered. (Exhibit "B")

1. Surfactant Properties

As can be seen in Table I, the micellar acid solutions have low surface tensions and very low interfacial tensions (IFT). Some surfactants can produce low IFT, and even lower surface tension values. However, many of these surfactants also spontaneously generate viscous emulsions, and often do more harm than good in acid treatment of wells. The micellar acidizing system exhibits surface tensions in a very low range, capable of removing capillary water blocks. When this injected fluid comes in contact with the water held in the capillary, it effectively lowers the surface tension of the water droplet and allows the water to be produced from the pore, thus opening that area to production of formation fluids.

The low interfacial tensions exhibited by the micellar acid system suggests that the treating fluid will be able to readily penetrate, break down, and liquefy sludge deposits and thick emulsions that retard full fluid flow in producing and injection wells (Exhibit B). The very low IFT also indicates the easy uniform penetration of oil wet zones as well as water wet zones. This means opening all the potential pore spaces to production or injection. Table II compares these surface phenomena to the most commonly used mutual solvents.

2. Silt Suspension

The detergency of the micellar acidizing system also performs well as a dispersing and suspending agent for both organic and inorganic solids.

Table III illustrates laboratory testing with a non-swelling clay. These tests were static, but indications are any movement by fluid flow will tend to disperse and extend the time before settling. This action benefits greatly the removal of formation fines loosened during acid treatment.

3. Water Wetting

One of the other key factors in improving productivity and/or injectivity of a well is to water wet the rock in the zone of interest. In the producing well, the relative permeability to oil is increased by water wetting. In the injection well, removal of residual oil around the well bore and water wetting the rock promotes single phase flow for the injected water. This improves total injectivity. Table IV shows angles of contact which were measured on oil wet quartz. It is generally agreed that the rock is basically water wet if the angle of contact is 30° or less. Certainly the micellar system creates lower angles of contact and indicates strong water wetting.

C. APPLICATIONS

Since the micellar acid solvent is miscible across a wide range of concentrations and with all acids used in well stimulation, the concentrations are not critical. At low concentrations (0.2% or 2 gal/1,000), the system serves as an acid emulsion preventer or as a non-emulsifying agent. Most often, the system is applied at approximately 5% by volume to make maximum use of the solvent properties. Used at this concentration in producing wells, good function is achieved for hydrocarbon solubilization, suspension of fines, demulsification or breaking of downhole emulsions, removing water blocks and finally, leaving the rock water wet when the treatment is completed.

For treatment of injection wells, the concentration is frequently raised to 10% by volume or 100 gal/1,000 if the well is known to be severely damaged from injecting poor quality water. Particularly, where oil carry-over and/or oily solids have been a problem, additional micellar acidizing solvent may be necessary to solubilize all of the organic materials.

FIELD EVALUATIONS

Thorough field testing in numerous oil and gas wells and in water injection wells across a broad geographical area has been documented. The examples in Table V show improved productivity or injectivity and the absence of any evidence of well damage. Micellar acidizing solvent concentrations used in the tests ranged from 3 to 5% by volume in acid. Most treatments employed 5% by volume of solvent in inhibited acid for wellbore cleaning and deep penetrating well stimulation of both oil and gas producers. The bottomhole temperature in the treated wells has ranged from 100 to 350°F. The treatments have been equally effective in both sandstone and carbonate reservoirs.

CONCLUSION

Reservoir rocks are composed of a broad variety of minerals and exhibit variations in porosity and permeability. Cementing materials, temperature, pressure, water salinity, hydrocarbon composition, etc. all present an infinite array of variables that must be considered in determining the best stimulation program for a given well. Added to this is the multitude of events that cause the formation of skin damage downhole; such as, accumulations of heavy hydrocarbons, capillary water blocks, oil wet scale deposits, iron sulfide, and oil wetting of the formation face. It has been difficult to design treatments to relieve all of these problems and still be compatible with formation fluids and the individual downhole environment. The micellar acidizing system offers a tool to overcome this difficulty.

Data compiled to date on the micellar acidizing solvent strongly suggests its efficiency in boosting performance of conventional acids for well cleaning and stimulation operations. A substantial record of productivity or injectivity improvements has been seen in producing oil and gas wells, and water disposal or water injection wells treated with the micellar acidizing system. These attest to the treatment of a multiple number of downhole problems with successful removal of the downhole skin damage.

REFERENCES

Williams, B. B., Gidley, J. L., and Schechter, R. S.: Acidizing Fundamentals, Henry L. Doherty Series SPE Monograph Volume 6 (1979).

Gidley, J. L.: "Stimulation of Sandstone Formations with the Acid-Mutual Solvent Method", J. Pet. Tech. (May 1971) pp. 551-558.

McLeod, H. L., McGinty, J. E., and Smith, C. F.: "Alcoholic Acid Speeds Clean-Up in Sandstones", Pet. Engr. (Feb. 1966) 66-70.

Rosen, Milton J., Surfactants and Interfacial Phenomena, John Wiley & Sons (1978).

Table 1
Surfactant Properties of the Micellar Acidizing Solvent

Concentration of Solvent % by Volume(1)	Surface Tension Dynes/Cm(2)
0.0 (untreated)	61.0
0.5	32.7
1.0	28.0
3.0	28.0
5.0	28.0
8.0	19.3
10.0	18.0
15.0	17.0

Concentration of Solvent % by Volume(1)	Surface Tension Dynes/Cm(2)
0.0 (untreated)	27.5
0.005	15.4
0.01	15.0
0.03	11.0
0.05	8.4
0.08	<1.0
0.1	<1.0

(1) In 15% HCl
(2) Surface tension of acid solution in air
(3) IFT of acid solution versus purified kerosene

Table 2
A Micellar Acidizing Solvent Displays Mutual Solvent Properties

Additive	Concentration of Additive in Acid (1)-Volume %	Interfacial Tension (2) Dynes/cm	Surface Tension Dynes/cm
None	0	32.2	72.0
Micellar Acidizing Solvent	5%(3)	<1.0	30.0
Ethylene Glycol Mono Butyl Ether	10%(3) 30%(4)	11.6 5.5	33.0 32.8
Mutual Solvent "A"	35%(3)	1.7	27.5
Isopropyl Alcohol	30%(3)	11.7	28.4
Methyl Alcohol	50%(3)	20.9	45.0

(1) 15% HCl

(2) 15% HCl and purified kerosene

(3) Clear solution

(4) Hazy: not all in solution

Table 3
Silt Suspending Properties of Micellar Acidizing Solvent

Concentration of Micellar Acidizing Solvent % by Volume (1)	Dispersed Clay in Suspension % of Original (Static Test) (2) Time - Minutes 2 Min.	10 Min.	30 Min.	60 Min.
0 (untreated)	45	7	5	5
1	>98	50	20	20
3	>98	65	30	25
5	>98	75	45	35

(1) In 7 ½% HCl

(2) 1 gram of -200 mesh (75 micron) kaolinite clay dispersed in 100 ml of acid solution and allowed to stand quiescent.

Table 4
Water Wetting Properties of Micellar Acidizing Solvent

Concentration of Micellar Acidizing Solvent % by Volume	Static Contact Angle, θ (On Oil Wet Quartz Surface) (2)
0.0 (untreated)	92°
0.1	7
0.2	3
0.5	<1
5.0	<1

(1) In 15% HCl

(2) Static contact angle, after 15 minutes contact, through acid phase surrounded by purified kerosene

Table 5
Micellar Acidizing Solvent Field Tests

East Texas Producing Oil Wells

Formation	Depth	Treatment Vol/Gal 15% HCl	Treatment Vol/Gal MAS*	Production	
				Before BOPD-BWPD	Before BOPD-BWPD
Woodbine	3600'	1000	55	19 28	55 28
Cleechville	4000'	1000	55	11 32	16 70

East Texas Producing Gas Wells

Formation	Depth	Treatment Vol/Gal 15% HCl	Treatment Vol/Gal MAS*	Production	
				Before	After
Travis	8700'	1000	55	0.300 MMCFD @ 600 psi	1.2 MMCFD @ 1700 psi
Rodessa	7000'	3000	165	.010 MMCFD	.710 MMCFD

Oklahoma Water Injection Wells

Formation	Depth	Treatment Vol/Gal 15% HCl	Treatment Vol/Gal MAS*	Injection	
				Before BWPD	After BWPD
Viola Limestone	3000'	1000	110	400@ 2000 psi	1200@ 2000 psi
Healdton Sand	1200'	1000	55	10@ 650 psi	584@ 300 psi

*Micellar Acidizing Solvent

Table 5 (Continued)
Micellar Acidizing Solvent Field Tests

West Texas Producing Oil Wells

Formation	Depth	Treatment Vol/Gal 15% HCl	Treatment Vol/Gal MAS*	Production	
				Before BOPD-BWPD	After BOPD-BWPD
San Andres	3000'	4500	220	4 14	29 129
Leonard	5000'	2000	110	71 0	140 6
Canyon Sand	5400'	3000	165	12 340	47 580
Clearfork	6200'	4000	220	28 12	92 49
Glorietta	3100'	2000	80	4 3	29 1
Wolfcamp	8790'	2000	110	50 600	80 90

West Texas Water Injection Wells

Formation	Depth	Treatment Vol/Gal 15% HCl	Treatment Vol/Gal MAS*	Injection	
				Before BWPD	After BWPD
Sprayberry-Dean	7385'	1000	55	500@ 1300 psi	850@ 1080 psi
Canyon Sand	5400'	3000	165	37@ 2020 psi	212@ 2020 psi
Canyon Reef	6900'	2500	165	700@ 1800 psi	4737@ 1800 psi

*Micellar Acidizing Solvent

Table 5 (Continued)
Wyoming Producing Wells

Formation	Depth	Treatment Volume/gal 15% HCl	Treatment Volume/gal MAS*	Production			
				Before		After	
				BOPD	BWPD	BOPD	BWPD
Shannon	9150	1000	55	5	0	83	11
Shannon	9100	1000	55	30	1	79	4
Shannon	9200	1000	55	2	0	26	4
Shannon	9150	1000	55	28	3	112	12
Shannon	9150	1000	55	0	9	9	26

*Micellar Acidizing Solvent

Table 5 (Continued)
Kansas Producing Wells

FORMATION	Treatment Volume/gal 15% HCl	Treatment Volume/gal MAS*	Production Rates			
			Before		After	
			BOPD	BWPD	BOPD	BWPD
Lansing Kansas City	3000	165	5	trace	60	18
Arbuckle	500	28	1	8	25	144
Cherokee Sand	250	14	4	176	12	180
Arbuckle	250	14	1	20	6.5	29

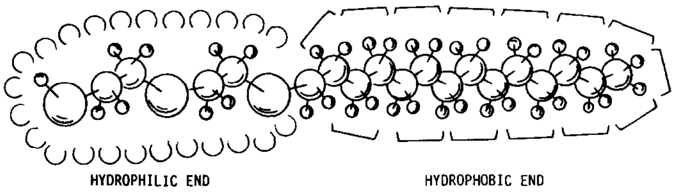
*Micellar Acidizing Solvent

Table 5 (Continued)
Louisiana Off-Shore Gas Wells

Formation	Depth	Treatment Volume/gal 15% HCl	Treatment Volume/gal MAS*	Production			
				Before		After	
				Pressure psi	MCF	Pressure psi	MCF
TA-10 Sand	6610	12,000	600	550	72	690	115
TA-5 Sand	6610	8,250	412	600	86	715	850
TA-11 Stray Sand	7828	6,000	300	540	82	720	2000
TB-4 Sand	9161	23,000	1000	310	23	720	1100
TB-3 Sand	8103	12,000	600	560	715	715	2800

*Micellar Acidizing Solvent

Exhibit A



CROSS SECTION OF MICELLAR WALLS (3 ZONES OF SOLUBILIZATION)

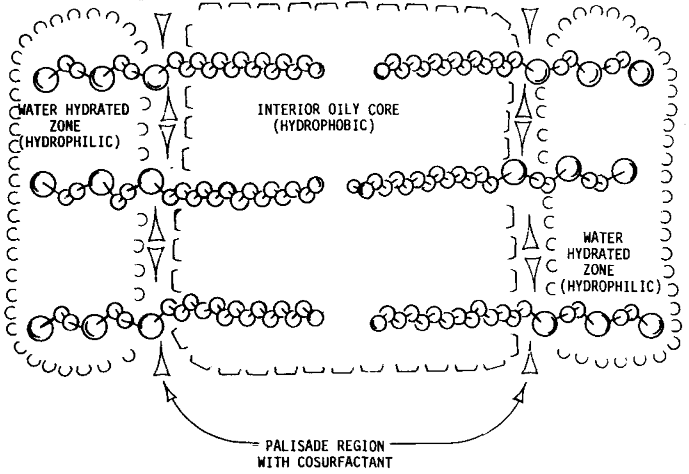


Exhibit B

CORE TESTS

The results of two tests using the Micellar Acidizing Solvent were as follows:

	Test One*	Test Two**
Permeability to water, md	72.2	31.2
Permeability to oil, md	25.1 $(S_{wr} = 30.7\%)$	13.74 $(S_{wr} = 16.4\%)$
Permeability to water, md	22.7 $(S_{or} = 24.8\%)$	24.4 $(S_{or} = 23.3\%)$
Plugged w/oil, psi	350.0	400.0
Acid Treatment with Micellar Acidizing Solvent		
Permeability to water, md	24.9 $(S_{or} = 7.8\%)$	19.2 $(S_{or} = 2.7\%)$

*10% Micellar Acidizing Solvent in 12% HCl and 3% HF

** 5% Micellar Acidizing Solvent in 15% HCl

The results would indicate that following the "effective plugging" of a core with a thick paraffinic oil, permeability can be restored using a "slug" of Micellar Acidizing Solvent in acid solutions, and driving it with a flood water until stable conditions exist.