Potential Antifreeze Compounds in Present-Day Martian Seepage Groundwater

Jiin-Shuh Jean[1, *], Chieh-Hou Yang[2], Ming-Jer Lee[3], Ming-Kuo Lee[4], and Ming-Hung Chien[5]

[1] *Department of Earth Sciences, National Cheng Kung University, Tainan 701, Taiwan, ROC*
[2] *Presidential Office, Ching Yun University, Chung-Li, Taiwan, ROC*
[3] *Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106-07, Taiwan, ROC*
[4] *Department of Geology and Geography, Auburn University, Auburn, Alabama, 36849, USA*
[5] *Department of Health Care Administration, Chung Hwa Institute of Technology, Tainan 717, Taiwan, ROC*

ABSTRACT

Is the recently found seepage groundwater on Mars pure H_2O, or mixed with salts and other antifreeze compounds? Given the surface conditions of Mars, it is unlikely that pure water could either exist in its liquid state or have shaped Mars' fluid erosional landforms (gullies, channels, and valley networks). More likely is that Mars' seepage groundwater contains antifreeze and salt compounds that resist freezing and suppress evaporation. This model better accounts for Mars' enigmatic surface erosion. This paper suggests 17 antifreeze compounds potentially present in Martian seepage groundwater. Given their liquid state and physical properties, triethylene glycol, diethylene glycol, ethylene glycol, and 1,3-propylene glycol are advanced as the most likely candidate compounds. This paper also explores how a mixing of glycol or glycerol with salts in the Martian seepage groundwater may have lowered water's freezing point and raised its boiling point, with consequences that created fluid gully and channel erosion. Ethylene glycol and related hydrocarbon compounds have been identified in Martian and other interstellar meteorites. We suggest that these compounds and their proportions to water be included for detection in future explorations.

Key words: Mars, Seepage groundwater, Antifreeze compounds, Eroded gully

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1. INTRODUCTION

Malin and Edgett (2000a, b) discovered evidence of recent groundwater seepage and seepage-fed surface runoff in Newton Crater's eroded gullies and sedimentary formations on Mars. These eroded gullies have clearly been formed within the past few million years (Malin and Edgett 2000a, 2001; Edgett et al. 2003). Present-day Martian regions such as the plains of Amazonis, Arabia, Elysium, and the impact basins of Hellas and Argyre possess similar surface features that may have been formed by the action of liquid water (Haberle et al. 2001). Nevertheless, the existence of these hospitable regions does not, in fact, mean that surface liquid water had direct atmospheric origins (Haberle et al. 2001). Moreover, it is unclear whether liquid water or some other liquid was responsible for such fluid erosional landforms.

Superficial seepage from shallow unconfined aquifers (Mellon and Phillips 2001; Heldmann and Mellon 2004), discharge from deep confined aquifers (Gaidos 2001), and geothermal heating (Hartmann 2001, 2002) are the most plausible models for the origins of surface water. Groundwater seepage models suggest a hypothesis whereby Martian subsurface fluids may contain antifreeze constituents or salts that can keep seepage water from freezing on cold surfaces (global mean annual temperature ≈ 217 K) or from boiling under very low Martian atmospheric pressure (6.1 mbar). A water-antifreeze-salt system would allow liquid water to travel substantial distance from the point of discharge before being frozen.

There is increasing evidence from recent interstellar meteorite research that antifreeze compounds may exist on

* *Corresponding author*
  E-mail: jiinshuh@mail.ncku.edu.tw

Mars. Interstellar ethylene glycol has been observed in emissions toward the Galactic center source Sagittarius B_2 (N-LMH); such emissions were detected by means of several millimeter-wave rotational torsional transitions of its lowest energy conformer (Hollis et al. 2002). Ethylene glycol has been identified in both the Murchison and Murray meteorites as the most abundant sugar-related alcohols (Cooper et al. 2001). Polycyclic aromatic hydrocarbons have been also found in three Martian meteorites: ALH 84001 (McKay et al. 1996; Stephan et al. 1998), EETA 79001 (Becker et al. 1997), and Nakhla (Wright et al. 1998; Flynn et al. 1999). Bernstein et al. (2002) simulated ultraviolet photolysis of interstellar ice grains and formed the amino acids, related hydroxy acids, and alcohols-like glycerol that were seen in Martian meteorites. These studies imply that glycerol, ethylene glycol, other glycols (that is, triethylene glycol, diethylene glycol, 1,3-propylene glycol), and other hydrocarbon compounds may naturally occur on Mars or other planets. Additionally, Zolotov and Shock (1999) also pointed out that polycyclic aromatic hydrocarbons and aliphatic hydrocarbons on Mars could be formed from CO_2 and H_2 through Fischer-Tropsch reaction, without the contribution of biogenic carbon. CO_2 and H_2 could also be catalyzed by magnetite to form hydrocarbons. These discoveries motivate us to test the hypothesis that the Martian seepage groundwater may contain antifreeze compounds or salts. We used factor analysis techniques to determine the most likely candidates among 17 selected antifreeze compounds. Examined physical properties include melting point (or freezing point), boiling point, viscosity, solubility in water, and erosiveness.

2. THEORY

2.1 Potential Antifreeze Compounds

The 17 antifreeze candidate compounds (or cases) analyzed in this paper are categorized into: (1) brines with an alcohol base (methanol and ethanol); (2) brines with a glycol base (ethylene glycol, 1,3-propylene glycol, diethylene glycol, and triethylene glycol); (3) brines with low thermal conductivity (methylene chloride or dichloromethane, trichloroethylene, trichlorofluoromethane, and acetone); (4) brines with a salt base (sodium-, calcium-, magnesium-chlorides, and sulfates); and (5) others: 1,1,2-trichlorotrifluoroethane, carbon tetrachloride (or tetrachloromethane), glycerol, and alkanes (hexane, heptane, and octane) (Mark et al. 1985). Ethylene glycol, diethylene glycol, triethylene glycol, and 1,3-propylene glycol have relatively high solubility in water and low vapor pressure. Moreover, other organic compounds known to have come to Mars via meteorites are (1) alkanes, (2) alkylbenzenes, (3) naphthalene and higher polycyclic aromatic hydrocarbons, (4) kerogen, and (5) amino acids and hydroxy acids (Biemann et al. 1976). These organic compounds are most likely to be converted to carboxylic acid derivatives that would not be easily detected

by GC-MS (Benner et al. 2000). In addition, methanol can also depress the freezing point of water (Yung and Pinto 1978). Therefore, these brines with a glycol base and other brines may be locally present on Mars.

Knauth and Burt (2002) indicate that eutectic brines could be present in the shallow mega-regolith at current Martian ground temperatures, and that impact processes probably served to scatter brine, salt, and ice over the planet. Hecht (2002) also demonstrates that surface temperatures may be suppressed a few degrees, perhaps by the incorporation of salts in water. The concentrations of salts in the typical Martian regolith of Viking Lander 1 samples are apparently high (8 - 25%), in which $(Mg,Na)SO_4$ (8 - 15%), NaCl (0.5 - 1.5%), and $(Mg,Ca)CO_3$ and nitrates (0 - 10%) are dominant (Clark and Baird 1979; Clark and van Hart 1981). The Mars Exploration Rover has detected high concentrations (~30 wt%) of sulfate salts contained within shallow sediments in Meridiani Planum of Mars (Brueckner 2004; MER Rover web site 2004); those salts probably occur in a hydrated form of $MgSO_4 \cdot nH_2O$ (Clark 1978). However, the sulfate salts are poor depressors and none of them prevent the formation of ice below ~ -10°C (or 263 K) (Clark and van Hart 1981). The maximum surface temperature at the groundwater seepage and seepage-fed surface runoff of the eroded gullies of Newton Crater does not exceed the global mean annual temperature of Mars (217 K). Indeed, over half the Martian year the temperature in this region approaches nearly 125 K below the triple point of water (Malin and Edgett 2000a).

As for the candidate chloride salts, the strongest depressors are $CaCl_2$ and $FeCl_3$ (both forming brine eutectics at ~ -55°C or 218 K), followed by $MgCl_2$ at -35°C or 238 K, and NaCl at -21°C or 252 K (Brass 1980; Clark and van Hart 1981). According to Jakosky et al. (1995), several of the various ternary salt waters had freezing points below 225 K and Martian brines may have existed in the past and even now. Therefore, if seepage groundwater is in pure H_2O form, or contains only sulfate and chloride salts, the water would likely freeze while seeping to the surface of present-day Mars. Jean and Yang (2001) proposed that antifreeze compounds which serve to further resist freezing and suppress evaporation may be present in seepage fluids.

2.2 Liquid States of Potential Antifreeze Compounds and Aqueous Mixtures

Liquid water must persist on surface sites of groundwater seepage for several minutes to form gullies at latitudes 30 - 70°S under the present-day Martian atmospheric pressure of 6.1 mbar. This suggests that the temperature at which each candidate compound can remain in a liquid state must be in the range of 217 - 300 K. The melting points of ethylene glycol (compound 9), 1,3-propylene glycol (compound 10), diethylene glycol (compound 11), triethylene

glycol (compound 12), glycerol (compound 16), and salts (compound 17) are all above 217 K. Thus, if the Martian surface temperatures are above the melting point for each of these pure compounds, seepage water containing these compounds may emerge in liquid form. The liquid ranges for selected substances are illustrated in Fig. 1, where the lower and upper bounds of the solid bars represent the melting temperature and boiling temperature at 6.1 mbar, respectively. It should be noted that 6.1 mbar is lower than the triple-point pressures of 1,1,2-trichlorotrifluoroethane (compound 4) and carbon tetrachloride (compound 5). No liquid-phase exists for these two substances at pressures as low as 6.1 mbar. Compounds 1, 2, 3, 6, 7, and 13 mostly likely exist as vapor phases on the Martian surface. Compounds 9 (ethylene glycol), 10 (1,3-propylene glycol), 11 (diethylene glycol), and 12 (triethylene glycol) are mostly in the liquid range, as shown in Fig. 1. Thus, they may be the most likely candidate compounds in seepage groundwater on Mars. As for compound 16 (glycerol), its very high boiling point (404.7 K) can prevent evaporation. Although the global mean annual temperature (217 K) is lower than pure glycerol's freezing point of 291.2 K, aqueous glycerol mixtures may resist freezing due to freezing point depression.

Freezing point depression can be estimated from a solid-liquid equilibrium calculation. The criterion for solid-liquid equilibrium is given by Prausnitz et al. (1986):

$$\ln a_i = \ln (x_i \gamma_i)$$
$$= \frac{\Delta_{fus}H_i}{R}\left(\frac{1}{T_{t,i}} - \frac{1}{T}\right) - \frac{\Delta C_{p,i}}{RT}(T - T_{t,i}) + \frac{\Delta C_{p,i}}{R}\ln\frac{T}{T_{t,i}} \quad (1)$$

where a_i, γ_i, $T_{t,i}$, $\Delta_{fus}H_i$, and $\Delta C_{p,i}$ are activity, activity coefficient, triple-point temperature, the molar enthalpy of fusion, and the difference of heat capacities between subcooled liquid and solid for compound i, respectively. R is the gas constant and x_i is the saturated mole fraction of compound i in liquid phase at temperature T. The above equation can be simplified by replacing the triple-point temperature ($T_{t,i}$) with the normal melting temperature ($T_{m,i}$) and by neglecting the last two terms of the right hand side. Equation (1) thus becomes:

$$\ln a_i = \ln (x_i \gamma_i) = \frac{\Delta_{fus}H_i}{R}\left(\frac{1}{T_{m,i}} - \frac{1}{T}\right) \quad (2)$$

As noted by Prausnitz et al. (1986), this simplification usually introduces minor error. Activity coefficient models including the Non-Random Two-Liquid (NRTL) (Renon and Prausnitz 1968), the Wilson (Wilson 1964), and the van Laar (van Laar 1910), were used in this study to represent the non-ideality of water in various aqueous mixtures in the sol-

id-liquid equilibrium calculation. While the model parameters are given and the heat of fusion and the melting point of component i are known, the melting/freezing point (T) at a given liquid composition x_i can be solved from Eq. (2) by an iterative procedure of Newton's method.

Table 1 lists the model parameters for some selected binary aqueous systems. The parameters of the NRTL model were taken from the thermodynamic databank in the process simulation package, Aspen plus. The parameters of the NRTL model were not available in the databank for water + 1,3-propylene glycol and water + triethylene glycol systems. Fortunately, Suleiman and Eckert (1994) measured the vapor-liquid equilibrium data for water + 1,3-propylene glycol, and the authors report the parameters of the Wilson model for this aqueous system. Also, the parameters of the van Laar model for water + triethylene glycol were found in Herskowitz and Gottlieb (1984). Figure 2 shows how that the freezing (or melting) temperatures vary with the mole fraction of the anti-freezers (x_2) for various aqueous mixtures. The freezing temperatures decrease markedly with the increasing mole fraction of the anti-freezers.

Since the boiling point of pure water at 6.1 mbar of atmospheric pressure is about 273.15 K, pure water seeping to the Martian surface will boil if temperatures are higher than this value. Aqueous solutions, however, may exist due to the increase in boiling temperatures, provided that certain low volatile anti-freezers or salts have dissolved in them. The boiling temperatures and the vapor compositions can be
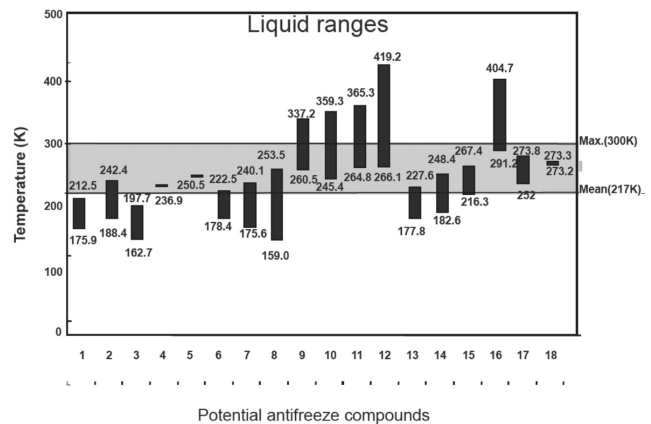

Fig. 1. Liquid ranges for 17 antifreeze candidate compounds and pure water in the present-day Martian seepage groundwater. The global mean annual temperature is 217 K and the maximal temperature is 300 K. The liquid ranges for selected substances are shown in the shadow zone, where the lower and upper bounds of the solid bars represent the melting and boiling temperatures, respectively (can be referred to in Table 2) (1. Methylene chloride; 2. Trichloroethylene; 3. Trichlorofluoromethane; 4. 1,1,2-trichlorotrifluoroethane; 5. Carbon tetrachloride; 6. Acetone; 7. Methanol; 8. Ethanol; 9. Ethylene glycol; 10. 1,3-propylene glycol; 11. Diethylene glycol; 12. Triethylene glycol; 13. Hexane; 14. Heptane; 15. Octane; 16. Glycerol; 17. Salts; 18. Pure water).

estimated via vapor-liquid equilibrium calculation, at given pressure and liquid composition, by solving simultaneously the equality of constituents' fugacities in the vapor and the liquid phases. In this study, the solution theory models with the binary parameters tabulated in Table 1 were also used in calculating the activity coefficient for the constituent components in the liquid phase, while the vapor phase was assumed as ideal gas mixtures due to very low pressure of 6.1 mbar. The results of the vapor-liquid equilibrium calculations are illustrated in Fig. 3, which indicates that the boil-

ing temperatures of the aqueous solutions increase with an increase of the mole fraction of anti-freezers (x_2). It should also be noted that adding acetone, methanol, or ethanol into water will, contrarily, lead to the depression of boiling points since these compounds are more volatile than water.

3. METHODS

The physical properties of the 17 antifreeze candidate compounds based on the five variables (normal melting

Table 1. Parameters of the activity coefficient models for some selected aqueous systems.

Second component (2)[a]	Model[b]	a_{12}	a_{21}	b_{12} (K)	b_{21} (K)	α
Acetone	NRTL	0.5440	6.3981	419.9716	-1808.9910	0.3
Methanol	NRTL	2.7322	-0.6930	-617.2687	172.9871	0.3
Ethanol	NRTL	3.4578	-0.8009	-586.0809	246.1800	0.3
Ethylene glycol	NRTL	0.3479	-0.0567	34.8234	-147.1373	0.3
1,3-Propylene glycol	Wilson	-	-	227.3200	-102.2300	-
Diethylene glycol	NRTL	0	0	241.9891	-226.3828	0.3
Triethylene glycol	van Laar	-0.4849	-1.8150	-	-	-
Glycerol	NRTL	-1.2515	-0.7318	272.6075	170.9167	0.3

[a] Water is the component 1.
[b] NRTL(Non-Random Two-Liquid) model:

$$ln\,\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1+x_2 G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2+x_1 G_{12})^2}\right]$$
$$with\ G_{ij} = exp(-\alpha\tau_{ij}),\ \tau_{ij}=a_{ij}+\frac{b_{ij}}{T},\ \tau_{ii}=0,\ G_{ii}=1$$

Wilson model:

$$ln\,\gamma_1 = -ln(x_1+\Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1+x_2}\right]$$
$$with\ \Lambda_{12}=\frac{\nu_2}{\nu_1}exp(-b_{12}/T),\ \Lambda_{21}=\frac{\nu_1}{\nu_2}exp(-b_{21}/T)$$

where ν_i is the molar volume of component i. The molar volumes of water and 1,3-propylene glycol are 18.0 and 72.27 cm^3 mol^{-1}, respectively.

van Laar model:

$$ln\gamma_1 = \frac{a_{12}}{\left(1+\frac{a_{12}x_1}{a_{21}x_2}\right)^2}$$
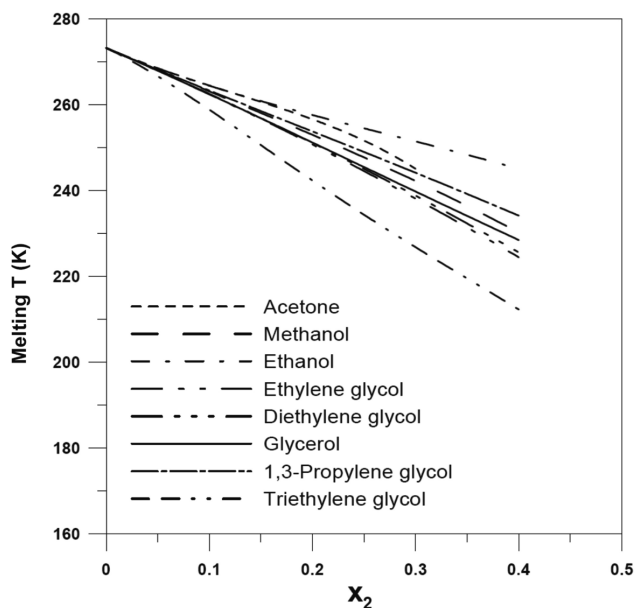
Fig. 2. The variations of the calculated freezing (or melting) point with liquid composition for various aqueous mixtures.
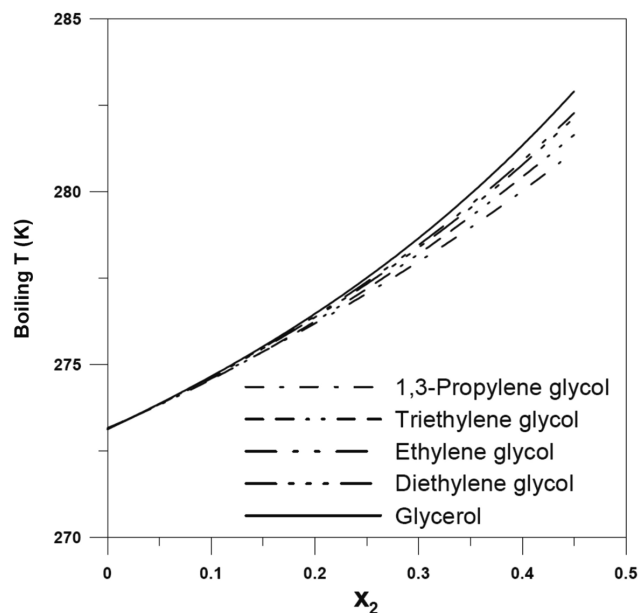

Fig. 3. The variations of the calculated boiling point with liquid composition at 6.1 mbar for some selected aqueous mixtures.

point, boiling point at 6.1 mbar, viscosity, solubility in water, and erosiveness) were analyzed for correlation coefficients, eigenvalues, factor loadings, and factor scores using the factor analysis of STATISTICA Version 6.0 (StatSoft web site 1998). The input value for erosiveness was rated from 1 to 5, in which the higher rating of a compound indicates more favorable conditions in compound erodability. Also, the input value for the solubility in water was assigned as 100 in case of infinite solubility.

In factor analysis, the principal component method was used to select a set of components, in which two common factors were extracted to explain the variances of original variables. The explained variance extracted from each common factor is termed as the eigenvalue. In order to maximize the variance of the loadings on the common factors, the factor varimax rotation was performed. The five variables were then reduced to two common factors (Factors 1 and 2) and weighted by factor loadings. The loadings are the weights at which the variables correspond to the factors. Those variables with factor loadings larger than 0.7, after factor varimax rotation, were used to explain the extracted factors. A name was assigned for each factor.

In this study, Factor 1 explains the higher percentages of total variance for the three variables (freezing point, boiling point, and viscosity) and was termed fluidity. Factor 2 explains the lower percentages of total variance for the two variables (solubility in water and erosiveness) and was termed erodability. The factor score for each case (or candidate compound) in each factor was then computed by summing the standardized Z scores multiplied by the factor score coefficients for all variables in each factor. The higher the factor score, the more likely the compound (and its aqueous mixture) can persist sufficiently long in a liquid state to allow transportation, erosion, deposition, and, ultimately, create fluid erosional landforms on the Martian surface.

4. RESULTS

4.1 Physical Properties for Antifreeze Candidate Compounds

The values of the physical properties of 17 antifreeze candidate compounds were tabulated in Table 2. The boiling points were solved from the Antoine equation at a given pressure of 6.1 mbar. The Antoine equation and the Antoine constants in the calculation were taken from the NIST (the National Institute of Standards and Technology, USA) Chemical WebBook (2003). While the boiling point is highly sensitive to pressure, the pressure effect on the melting point is relatively minor. For most substances, there is little difference between the normal melting temperature (at one atmosphere) and the melting temperature at 6.1 mbar. This means that the melting point at 6.1 mbar is very close to the tabulated normal melting point (Lide 2001) in Table 2. The glycols have moderate viscosities at 298.15 K. They are 16.1 cp for ethylene glycol, 40.4 cp for 1,3-propylene glycol, 30.2 cp for diethylene glycol, and 48.5 cp for triethylene glycol (Montgomery 1996). All of these glycols have infinite solubility in water (a few grams in 100 g of water) (Perry and Green 1984). Figure 1 shows that ethylene glycol, 1,3-propylene glycol, diethylene glycol, triethylene glycol, and glycerol are mostly in the liquid ranges when the temperature is between 217 - 300 K and pressure at

Table 2. Physical properties for potential antifreeze compounds in the present-day Martian seepage groundwater.

Case (Compound)\Variable	Normal melting point (K) (Lide 2001)	Boiling point (K) at 6.1 mbar (NIST Chemical WebBook 2003)	Viscosity (cp) at 298.15 K (Montgomery 1996)	Solubility in water (g/100 g of water) (Perry and Green 1984)	Erosiveness[a]
1. Methylene chloride	175.9	212.5	0.41	2 at 293.15 K	2
2. Trichloroethylene	188.4	242.4	0.54	0.1 at 298.15 K	2
3. Trichlorofluoromethane	162.7	197.7	0.42	Insoluble	1
4. 1,1,2-trichlorotrifluoroethane	236.9	213.4	0.67	Insoluble	1
5. Carbon tetrachloride	250.5	233.7	0.91	0.08 at 293.15 K	2
6. Acetone	178.4	222.5	0.31	Infinite	3
7. Methanol	175.6	240.1	0.54	Infinite	4
8. Ethanol	159.0	253.5	1.07	Infinite	4
9. Ethylene glycol	260.5	337.2	16.1	Infinite	4
10. 1,3-propylene glycol	245.4	359.3	40.4	Infinite	4
11. Diethylene glycol	264.8	365.3	30.2	Infinite	4
12. Triethylene glycol	266.1	419.2	48.5	Infinite	4
13. Hexane	177.8	227.6	0.30	0.014 at 288.15 K	3
14. Heptane	182.6	248.4	0.39	0.005 at 291.15 K	4
15. Octane	216.3	267.4	0.51	0.002 at 291.15 K	3
16. Glycerol	291.2	404.7	934	Infinite	3
17. Salts	252.0	273.8	0.97	35.7 at 273.15 K	5

[a] Rating for erosiveness: 5: very high; 4: high; 3: moderate; 2: low; 1: very low.

6.1 mbar. Our statistical analyses also show these compounds are most probably in liquid states.

4.2 Factor Analysis

Based on our factor analyses, two common factors with eigenvalues larger than 1 (or greater than the average of the variance for all variables) were extracted, which together accounted for about 81.3% of total variance. After the varimax rotation process (i.e., the rotation of the maximum variance) was performed, the first common factor (Factor 1) of "fluidity," whose eigenvalue was equal to 2.87, explained 57.4% of the total variance; the second common factor (Factor 2) of "erodability," whose eigenvalue was equal to 1.20, explained 23.9% of the total variance. The factor loadings for

the variables of melting point, boiling point, and viscosity in Factor 1 (that is, fluidity) are 0.86, 0.73, and 0.85, respectively. Thus, Factor 1 is highly correlated with these three variables and can explain 42.0% variance. As with Factor 2, the factor loadings for solubility in water and erosiveness (that is, erodability) are 0.82 and 0.93, respectively. Factor 2 is also correlated with these two variables and can explain 39.3% of variance. The correlation analysis in this study reveals that there are statistically significant correlations (p-level < 0.05, n = 17) among melting point and boiling point (correlation coefficient r = 0.8024, p = 0.0001060), boiling point and solubility in water (r = 0.6671, p = 0.003442), solubility in water and erosiveness (r = 0.6117, p = 0.009063), boiling point and erosiveness (r = 0.5323, p = 0.02785), boiling point and viscosity (r = 0.5181, p = 0.03315), and

melting point and viscosity (r = 0.5074, p = 0.03759).

To develop fluid erosional landforms (that is, gullies, channels, and valley networks) on Mars, the potential compounds must be able to resist freezing and evaporation and reduce the resistance of fluid flow, which may be represented by the melting point, boiling point, and viscosity of compounds in Factor 1. Also, the erodability of a potential candidate is closely related to its solubility in water and erosiveness in Factor 2.

4.3 Overall Potential for Antifreeze Candidate Compounds

The factor score coefficients for the five variables in Factor 1 are 0.44, 0.27, 0.49, -0.015, and -0.25, whereas those in Factor 2 are -0.072, 0.20, -0.23, 0.42, and 0.58. These factor scores were computed, as shown in Table 3, for the 17 potential antifreeze candidate compounds that are affected by the two common factors. The larger the fac-

tor score for each candidate compound, the more likely the compound could prevent Martian seepage groundwater from freezing or boiling. As seen on Table 3, triethylene glycol, diethylene glycol, ethylene glycol, and 1,3-propylene glycol have high and positive factor scores for both Factor 1 (fluidity) and Factor 2 (erodability), 0.83/1.19, 0.57/1.06, 0.39/1.00, and 0.37/1.07, respectively. Thus, these four compounds, categorized as Class A (very high potential), are suggested to be the most likely antifreeze candidates in Martian seepage groundwater. Glycerol, carbon tetrachloride, and 1,1,2-trichlorotrifluoroethane have positive scores in Factor 1 but negative in Factor 2 (3.20/-0.27, 0.33/-1.09, 0.33/-1.63, respectively), referred to as Class B (high potential), implying that their candidacy is also likely. Both the compounds of Class A and glycerol of Class B have infinite solubility in water, with a freezing point that can be lowered and a boiling point that can be elevated markedly. The category of Class C (fair potential) includes acetone, methanol, ethanol, heptane, and salts. They are negative for

Table 3. Factor scores.

Case (Compound)	Factor 1	Factor 2	Class[a]	Overall potential
1. Methylene chloride	-0.52	-1.01	D	Low
2. Trichloroethylene	-0.28	-0.96	D	Low
3. Tricholofluoromethane	-0.50	-1.55	D	Low
4. 1,1,2-trichlorotrifluoroethane	0.33	-1.63	B	High
5. Carbon tetrachloride	0.33	-1.09	B	High
6. Acetone	-0.70	0.34	C	Fair
7. Methanol	-0.88	0.89	C	Fair
8. Ethanol	-1.00	0.95	C	Fair
9. Ethylene glycol	0.39	1.00	A	Very high
10. 1,3-propylene glycol	0.37	1.07	A	Very high
11. Diethylene glycol	0.57	1.06	A	Very high
12. Triethylene glycol	0.83	1.19	A	Very high
13. Hexane	-0.66	-0.49	D	Low
14. Heptane	-0.75	0.06	C	Fair
15. Octane	-0.11	-0.44	D	Low
16. Glycerol	3.20	-0.27	B	High
17. Salts	-0.61	0.88	C	Fair

[a] Class A: Factor 1 > 0 and Factor 2 > 0; Class B: Factor 1 > 0 and Factor 2 < 0;
 Class C: Factor 1 < 0 and Factor 2 > 0; Class D: Factor 1 < 0 and Factor 2 < 0.

Factor 1 but positive Factor 2. They are moderate potential candidates for existing in Martian seepage groundwater.

Table 3 also shows that methylene chloride, trichloroethylene, trichlorofluoromethane, hexane, and octane are negative for both Factor 1 and Factor 2. The substances of this class, categorized as Class D (low potential), are the least likely candidates. Moreover the factor score (3.20) of glycerol in Factor 1 is the highest (Table 3), whereas the factor score (1.19) of triethylene glycol in Factor 2 is the highest. This could indicate that glycerol in water is the best candidate for allowing water to persist in a state of fluidity and triethylene glycol in water is the best candidate for erosion of gullies and channels. Our study suggests that one (or several) of the antifreeze candidate compounds of Classes A and B, listed in Table 3, mixed with salts (NaCl, MgSO$_4$) could greatly lower the freezing point (or melting point) and raise the boiling point of liquid water. The seepage fluids could have caused gully and channel erosions in the distant past and at the recently found groundwater seepage sites. Our models consider only one or more than one of these 17 antifreeze compounds were mixed in liquid water. These compounds are listed in the categories of brines as shown by Mark et al. (1985). Evaluation of the physical properties of "pure" compounds should be considered as the reasonable first step to test the exotic fluid model. Any comprehensive model must account for the concurrent presence of salts, antifreezes, and soluble gases such as CO$_2$. Such multi-component model, however, would become too complex and have too many possible variables (considering the total possible number of interactions and mixtures of differing proportion for a 10-component system) and deserves another research.

5. DISCUSSION

A plausible mechanism for gully formation by low freezing-point fluids is presented in this paper. Statistical evaluation of the physical properties of 17 various compounds was conducted to test this exotic fluid model. Our factor analyses indicate that triethylene glycol, diethylene glycol, ethylene glycol, and 1,3-propylene glycol are the most likely candidate compounds in the Martian seepage groundwater, as indicated by their physical properties and fluid states. Among 17 compounds considered in statistical analysis, only the boiling points of triethylene glycol, diethylene glycol, ethylene glycol, 1,3-propylene glycol of Class A and salts (Class C) are greater than that of pure water (Fig. 1). When these glycols or salts (NaCl, MgSO$_4$, etc.) are added to liquid water, the boiling point of the water is significantly elevated.

Various models have been proposed for the formation of Mars' fluid erosional landforms. We revisit alternative hypothesis and compare the relative merits of different scenarios. Any viable model for the formation of Mars' ero-

sional landforms must account for: (1) their young ages, (2) their latitudinal distribution and association with crater walls, and (3) the unique morphology of the gullies.

5.1 Shallow Liquid-Bearing Aquifer Model

Hartmann (2001) indicates that the hillside gullies found by Malin and Edgett (2000a) appear in many cases to be formed by water seepages produced by underground aquifers. Hartmann (2001) and Mellon and Phillips (2001) suggest that a shallow aquifer could be the source of liquid water that ultimately carved the gullies' features.

Malin and Edgett (2000a) exhibit outbursts of ~2500 m^3 of water containing ~30% of sulfate and NaCl salt antifreezers, fast enough to cause erosion before sublimation or freezing could end the event. However, sulfate and NaCl salts are poor depressors and can only reduce the freezing point of liquid water to 263 and 252 K, respectively (Clark and van Hart 1981), which exceed the average temperature of 222 K observed near the latitudes at which the gullies are observed (Mellon and Phillips 2001).

The results of our factor analysis reveal that the salts can be categorized as Class C and have fair potential to permit stable liquid water (Fig. 1). However, glycols (Class A) can be more efficient in reducing the freezing point of liquid water and are thus more likely agents of gully formation. The observations of Viking, Pathfinder, and the MER rovers (Vaniman et al. 2004) revealed that sulfate salts are common in soils globally distributed throughout Mars. Accordingly, we suggest that the expelled water or seepage groundwater contains not only salts, but also glycol or glycerol at certain locations, as indicated by factor analyses and geochemical evidence from Mars' meteorites (i.e., ALH 84001, EETA 79001, Nakhla, Murchison, and Murray meteorites). Figure 2 illustrates that the melting points of aqueous mixtures can be as low as 217 K if the binary aqueous solutions contain triethylene glycol, ethylene glycol, diethylene glycol, glycerol, and 1,3-propylene glycol at mole fraction about 0.36, 0.45, 0.47, 0.51, and 0.56, respectively. Concurrently, the boiling points of these binary aqueous mixtures are higher than 280 K, as shown in Fig. 3. Thus, the brine eutectics of the salts and glycols or glycerol are better able to lower the freezing point of seepage groundwater.

Martian fluid erosion landforms have smooth surfaces that lack new erosion or impact features, indicating their relatively young geologic age (e.g., Malin and Edgett 2000). The relatively young geologic age of these gullies is mysterious given the constrained occurrence and production of liquid water in Mars' freezing low-pressure environment (Heldmann and Mellon 2004). Photographs taken by the Mars Orbiter Camera on the Mars Global Surveyor show bright new deposits in two gullies, suggesting that they were deposited by recent flows of liquid water. These two gullies are inside craters in the Terra Sirenum (36.6° south

latitude and 161.8° west longitude) and the Centauri Montes regions (38.7° south latitude and 263.3° west longitude) of the southern hemisphere. These observations give the strongest evidence to date that water still flows occasionally on the surface of Mars.

The brine model (i.e., Knauth et al. 2000) offers a simple explanation for the forming of young water-cutting gullies and seepage features on the surface of the Mars. Martian discharge is likely saline or hypersaline, as supported by the accumulation of evaporitic minerals (Mg-K-Cl-sulfates) detected by various instruments carried by Mars Rovers. Our antifreeze fluids model has been motivated by the calculations presented in the paper, which shows that regular NaCl- and sulfate-rich brines may not be sufficient to resist freezing or suppress evaporation. The relative merits of brine vs. antifreeze scenarios are difficult to address, but we propose that a mixing of glycol or glycerol with evaporitic salts in the Martian seepage groundwater may have been more efficient in lowering water's freezing point and raising its boiling point. The exotic fluid model is very attractive. Without surface water or atmospheric input, the large-scale hydrologic cycle is likely absent on Mars. Any ancient groundwater should have had long subsurface residence times, which allow the water to acquire salinity and other anti-freezing materials through prolonged water-rock interaction.

Researchers have also suggested the presence of liquid CO_2 (Hoffman 2000; Musselwhite et al. 2001) and liquid alkanes (Yung and Pinto 1978). Since the triple point of carbon dioxide is at 5.11 bars and 216.8 K (Atkins 1986), liquid CO_2 cannot exist on present-day Mars. Furthermore, liquid CO_2 cannot condense in the Martian subsurface in sufficient quantity to form gullies and it is also an unlikely eroding agent in the carving of gullies (Hartmann 2001). Liquid alkanes have low viscosities at the current temperature on Mars, and could have contributed to the formation of channels (Yung and Pinto 1978). However, the solubility of alkanes in water is usually very limited (Table 2), causing its impact on boiling point elevation and melting point depression to be quite minor.

5.2 Cryovolcanism Model

Gaidos (2001) proposes a cryovolcanic model in which Martian gullies form when liquid water from deep aquifers (several kilometers deep) is forced to flow through dikes. The gullies thus should only be found poleward of 30° because the cryosphere is too thin closer to the equator and aquifers will not be confined and frozen (Heldmann and Mellon 2004). Once a significant volume of liquid water erupts to the surface, it has the potential to flow for significant distances before freezing (Gaidos 2001).

Cryovolcanism offers a simple explanation for the appearance of water-carved gullies and seepage features distributed over the surface of Mars. Freezing of the erupted water may concentrate dissolved solids within the remaining liquid and form brines whose freezing-point depression allows them to persist for a longer period (Gaidos 2001). Similar to shallow aquifers, we suggest that the erupted water or seepage groundwater from deep aquifers contains not only salts but also glycols. They form brine eutectics that allow the freezing point of liquid water to be greatly lowered, thus causing this liquid water to both persist longer and contribute to the formation of gullies.

5.3 Geothermal Model

Hartmann (2001, 2002) proposes that localized geothermal events could melt ice to form a water-bearing aquifer. This plausible model removes the requirement for low freezing-point fluids (brines, liquid CO_2, antifreeze-bearing groundwaters) as the agents for forming gully-like landforms. However, volcanism on Mars is very old and not common in the recent geologic past. Since the odds of finding an active volcano or geothermal outflows on Mars today are very small, it is unlikely that geologically-young erosion and drainage systems may be caused primarily by the melting of ground ice during volcanic eruptions or related geothermal activities.

It is uncertain what a geothermal heating source melts the ice and sustains it in a liquid phase long enough that it can produce the observed erosion and transport patterns. These subsurface heating events may not be sufficiently intense to create surface landform expressions. The question here is: why are the majority of the drainage and erosion features associated with the walls of craters and canyons where obvious geothermal or volcanic features are absent? Mars in the present day is tectonically stable, active hydrothermal systems, if any, may be restricted to small areas and can only create flow erosion gullies locally.

5.4 Surface Water Model

This model proposes that the erosion channels and drainage systems were probably formed a long time ago (3.5 to 4.5 billion years ago) when the surface temperature might also have been warmer and Mars might have had a denser atmosphere. Liquid water could have existed on the Martian surface billions of years ago as several minerals (hematite, calcite, etc.) found on the surface of Mars can only form by the action of water. This model of gully formation, however, neither explains their young ages nor their exclusive mid-latitudinal (higher than 30°) distribution (i.e., gullies should cluster around the equators where surface temperatures are higher). Moreover, many observed channels on Mars do not possess the typical dendritic (tree) drainage pattern as formed on Earth by running surface water on the top of flat-lying strata; the predominated isolated (i.e., with large un-dissected areas between branches) pat-

tern of Mars drainage systems could be better explained by groundwater seepage.

6. CONCLUSION

Since the boiling point of pure water at 6.1 mbar of atmospheric pressure is about 273.15 K, groundwater seeping to the Martian surface will boil if temperatures are higher than this value and will become a solid state if temperatures are lower than this value. Thus, pure water is not likely to be present as liquid on present-day Mars. Aqueous solutions, however, may exist, provided that some certain antifreezes or salts have dissolved in them. Our factor analyses of the liquid states of 17 antifreeze candidate compounds suggest that one or more of these compounds (especially triethylene glycol, diethylene glycol, ethylene glycol, and 1,3-propylene glycol, glycerol, and NaCl and sulfate salts) may be present in the Martian seepage groundwater. In order to shape Mars' fluid erosional landforms (that is, gullies, channels, and valley networks), these compounds must be able to substantially suppress evaporation and allow liquid to persist in a liquid state. The erodability of soil and rocks is linked to their erosiveness and solubility in water. In addition, the compounds must be able to resist freezing and reduce the resistance of fluid flow.

The fluidity of substances is closely correlated to their normal melting point, boiling point, and viscosity. The compounds that are beyond the liquid range and have low solubilities in water are less likely to resist freezing and suppress evaporation. The mixed proportions of the compounds with water can affect the physical properties of the mixtures. The statistical analysis of antifreeze and salt compounds allows us to better understand their physical properties and their influence on the extent to which liquid water can persist on the current Martian surface. It is suggested that the compounds and their proportions to water be included for detection in future Mars explorations.

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