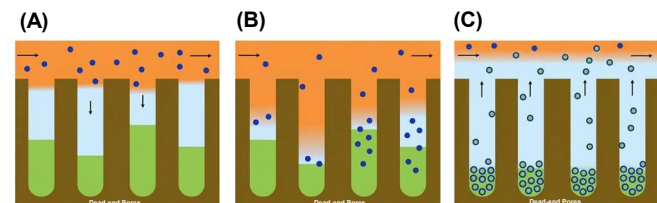


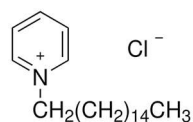
## Introduction

**Micelles** are spherical aggregates of surfactants with hydrophobic interior and a hydrophilic shell in water. They are crucial for solubilizing hydrophobic compounds with applications as extracting agents, solubilizers and drug carriers. Salt-induced micelle **diffusiophoresis** describes micelle migration induced by a salt concentration gradient.<sup>1,2</sup> This transport mechanism can be used to control directional motion of micelles. For example, it could be used to boost micelle insertion into dead-end pores of porous rock as shown in Fig. 1 for applications in enhanced oil recovery and soil remediation.<sup>3,4</sup> While diffusiophoresis has been investigated for rigid colloidal particles, it has not been investigated for ionic micelles yet.



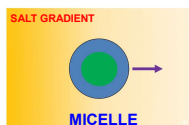
**FIG 1.** (A) Micelles (blue circles) approach pores of rock. (B) Micelles enter pores (C) Micelles extract hydrocarbons (green) from pores.

In this work, the cationic surfactant cetylpyridinium chloride (CPC, Fig. 2) in the presence of NaCl and KCl was characterized.



**FIG 2.** CPC chemical structure

## SALT-INDUCED MICELLE DIFFUSIOPHORESIS



$$v_p = -D_p (\nabla \ln C_p + d_p \frac{\nabla \mu_s}{k_b T})$$

$d_p$ : Diffusiophoresis coefficient  
 $v_p$ : Particle net migration rate  
 $\mu_s$ : Salt chemical potential  
 $D_p$ : Brownian mobility  
 $C_p$ : Micelle concentration  
 $k_b$ : Boltzmann constant  
 $T$ : Temperature

**FIG 3.** Micelle diffusiophoresis induced by gradient of salt concentration in water (color contrast).

## SALT-MICELLE PARTITIONING COEFFICIENT

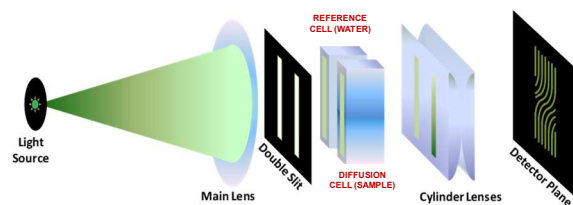


$$C = -\frac{\Delta C_s}{\Delta C_p}$$

**FIG 4.** Salt partitioning coefficient,  $C$ , describes change in salt concentration,  $C_s$ , due to a difference in concentration of micelles,  $C_p$ .

## Method

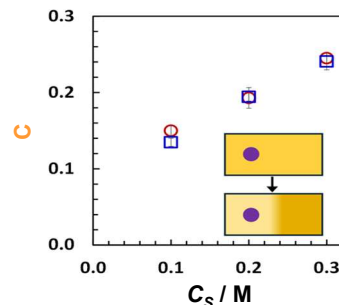
In this work, we use Rayleigh interferometry and the theoretical framework of multicomponent diffusion to characterize micelle diffusiophoresis and salt partitioning coefficient.<sup>2</sup>



**FIG 5.** Optical setup of Rayleigh interferometry. Two solutions with slightly different salt concentration are vertically positioned one on top of the other inside an optical cell (Diffusion Cell). Laser light goes through a double slit before entering the cell. The light is focused onto a detector, where a Rayleigh interference pattern is formed.

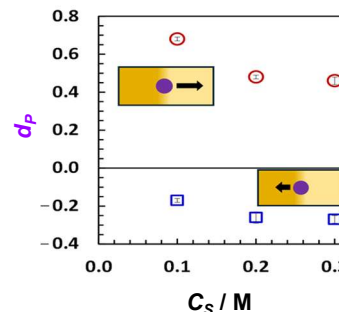
## Results

**Salt Partitioning coefficients** are found to be positive and independent of salt type (Fig. 6)



**FIG 6.** Salt partitioning coefficients,  $C$ , as a function of salt concentration,  $C_s$  in the NaCl ( $\circ$ ) and KCl ( $\square$ ) cases.

**Micelle diffusiophoresis coefficients** are found to be positive in the NaCl case and negative in the presence of KCl (Fig. 7)



**FIG 7.** Micelle diffusiophoresis coefficient,  $d_p$ , as a function of salt concentration,  $C_s$ , in the NaCl ( $\circ$ ) and KCl ( $\square$ ) cases.

## Electrophoresis and Electrical Double Layer Theory

The electrophoresis model of diffusiophoresis together with electrical double layer (EDL) theory were used to describe salt-induced diffusiophoresis of CPC micelle and related salt partitioning coefficients.<sup>1,2,5</sup>

**Poisson-Boltzmann Equation:**  $\nabla^2 \psi = \kappa^2 \sinh \psi$

$\psi$ : Electrostatic potential of micelle  
 $\kappa$ : Debye constant  
 $\zeta$ : zeta potential of micelle  
 $\beta$ : salt mobility ratio

**TABLE.** Calculated electrostatic and diffusiophoretic parameters as a function of concentration in NaCl and KCl cases

$C_s/M$	$\zeta/mV$	$C$	$\beta$ (NaCl)	$d_p$ (NaCl)	$\beta$ (KCl)	$d_p$ (KCl)
0.10	48.2	0.150	0.229	0.946	0.021	0.085
0.20	38.1	0.196	0.236	0.794	0.021	0.069
0.30	32.9	0.238	0.241	0.715	0.021	0.061

Experimental  $d_p$  are  $\sim 0.3$  lower than those calculated in table in all cases. This residual negative contribution is attributed to chemiphoresis (polarization of EDL due to salt gradient).

## Conclusion

- Diffusiophoresis of CPC micelles was found to be positive with NaCl and negative with KCl due to electrical double layer theory.
- Salt partitioning coefficient was found to be the same for both salts.
- The electrophoresis model of diffusiophoresis together with EDL theory was successfully used to describe salt partitioning coefficients and salt-induced diffusiophoresis of CPC micelle and related. A residual negative contribution to diffusiophoresis was attributed to chemiphoresis mechanism.

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