Surface Tension of Micelle-Forming Solutions

Hans M. Cassel

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Surface Tension of Micelle-Forming Solutions

HANS M. CASSEL
Chicago, Illinois
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*T*HE capillary curves of some soaps[1] and other long chain molecules in aqueous solution exhibit a peculiar minimum of the surface tension (s.t.) at relatively low concentrations (less than 0.01 molar), the s.t. becoming smaller than half that of water. McBain in numerous publications,[2] as well as Nutting, Long, and Harkins,[3] believes that the observations correspond to true equilibria and that, according to Gibbs' equation, the adsorbed quantities vanish at the concentrations of the minima. In other words, it is assumed that there the composition of the surface layers equals that of the solutions. On the other hand, it can be proved by surface viscosity measurements and direct tests[4] that rather dense surface films do exist at the same concentrations. To reconcile the contradictory conclusions, McBain has recurred to postulating a void of solute in the deeper layers of the solutions. On this basis, the existence of very thin, double-faced structures, like soap bubbles, is hard to understand.

In writing Gibbs' equation: $d\sigma/dm = -\Gamma \cdot d\mu/dm$ (σ designates the s.t.; m, the concentration of solute; Γ, its superficial density; μ, its thermodynamic potential) one notices immediately that $d\sigma/dm$ will vanish when either one of the factors of the second member of the equation tends towards zero. Since a decrease of Γ is out of the question the alternative has to be considered that a gradual fading of the change in potential goes on as the concentration increases.

Unfortunately, there is not much information available about the activities of these solutions in the low concentration range and at the temperature of the s.t. measurements. Values derived by Randall, McBain, and White[5] from vapor pressure measurements show that Na palmitate and stearate start to approach constant activities above a molality of 0.3 at 90°C. Hence, it may be concluded that these and similar substances behave identically at room temperature in a much lower concentration range.

Such a behavior is not surprising in view of the fact that all solutions with which the s.t. minimum is encountered display definite signs, and are indeed typical examples, of micelle formation.[6] Some of these solutions are notoriously very close to being saturated. The conditions obtaining are analogous to certain features of monomolecular films spread on water. Langmuir[7] has put forward the theory that the almost horizontal portion following a kink in the *A-F* curves is due to the condensation of single molecules into two-dimensional micelles.

Also J. E. Mayer's ideas[8] on the condensation process in general seem to support the expectation that in certain cluster-forming systems at sufficiently low temperature the Gibbs potential tends to a limiting value as saturation is approached (Case "a" of Born and Fuchs[9]). This effect may be enhanced if the interfacial tension of the particles is very small.[10]

The above considerations, of course, do not account for the ascending branch of the capillary curve. It is probable that the surface films at higher concentrations assume a crystalline or liquid-crystalline structure. Unless such films are formed in a reversible way they are likely to be in a state of stress which, to be released, takes much longer periods of time than usually spent for the observations. A superposition of s.t. and surface stress may be reponsible for time effects also before the minimum concentration is reached.

[1] H. M. Cassel, J. Am. Chem. Soc. **57**, 2009 (1935).
[2] J. W. McBain and G. F. Mills, *Report on Progress in Physics* (1939) Vol. 5, p. 30.
[3] G. C. Nutting, F. A. Long, and W. D. Harkins, J. Am. Chem. Soc. **62**, 1496 (1940).
[4] J. W. McBain and L. A. Word, Proc. Roy. Soc. **A174**, 286 (1940).
[5] M. Randall, J. W. McBain, and A. M. White, J. Am. Chem. Soc. **48**, 2517 (1926).
[6] H. V. Tartar, V. Sivertz, and R. E. Reitmeier, J. Am. Chem. Soc. **62**, 2375 (1940).
[7] I. Langmuir, J. Chem. Phys. **1**, 756 (1933).
[8] J. E. Mayer and S. F. Harrison, J. Chem. Phys. **6**, 91 (1938).
[9] M. Born and K. Fuchs, Proc. Roy. Soc. **A166**, 391 (1938).
[10] M. Volmer in cooperation with the author, Zeits. f. physik. Chemie **125**, 156 (1927). See also J. Frenkel, J. Chem. Phys. **7**, 538 (1939).

Polarization of Luminescence in Crystals

B. V. THOSAR
College of Science, Nagpur, India
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*T*HE state of polarization[1] of the sharp red luminescent doublet of ruby at λ6936, and also of the anti-Stokes bands shifted from the doublet by 756 cm⁻¹, 523 cm⁻¹, and 368 cm⁻¹, respectively, has been quantitatively investigated. The technique usually employed for studying the polarization of Raman lines was used, the observations being made visually. The crystal was kept with its optic axis vertical, along OZ, and the intensity of luminescence polarized parallel to this direction was compared with that polarized perpendicular to it (along OX). Table I gives the

TABLE I.

Lines and bands	Intensity	$\rho = I_{OZ}/I_{OX}$
λ6936 (doublet)	sharp, intense	0.16
$\Delta\nu$ 756 cm⁻¹	intense, broad	0.70
523 cm⁻¹	v. intense, broad	0.37
368 cm⁻¹	weak	>1.00

ratio I_{OZ}/I_{OX} of the intensities polarized parallel and perpendicular to the optic axis of the crystal.

When the crystal is mounted with the optic axis along the direction of observation OY the ratio ρ is unity for all the lines and bands listed above.

(1) The bands have been explained as due to the superposition of internal vibration frequencies in the crystal on the sharp line radiation. Since the latter is strongly linearly polarized perpendicular to the crystal axis, this is a case analogous to the excitation of Raman lines by initially polarized light. The degree of polarization of the bands would be of help in assigning them to the different possible modes of vibrations within the crystal.

(2) Regarding the polarization of the sharp doublet, it is to be noted that there is a striking resemblance between the above observations and the phenomena of polarization of resonance radiation of mercury, observed by Hanle.[2] The red luminescence lines of ruby behave as though the crystal is a natural resonance lamp with an inherent magnetic field along the optic axis. The examination of the x-ray structure of corundum shows that the fluorescent Cr^{+++} ion, which replaces the Al atom, is situated in crystalline fields of axial symmetry and in accordance with the theory[3] of paramagnetic crystals, the orbital moment of the ion should be quenched in all directions but one—the symmetry axis, i.e., the optic axis. The orbital moment being conserved only along the direction of the optic axis, the electric vector in the emitted radiation is confined to the orbital plane, i.e., the plane normal to the optic axis.

(3) The present evidence seems to show that the Cr^{+++} ions in ruby are subjected to external crystalline fields strong enough to break the L-S coupling but not strong enough to break the coupling of individual l's to give the resultant L and of individual spins to give S. The energy levels of Cr^{+++} ion available from Bowen's work[4] then explain the principal emission and absorption lines according to the following plan:

Transition	Bowen's value	Observed lines
$^4P \rightarrow ^4F$	14200 cm^{-1}	λ6936 doublet (emission)
$^2G \rightarrow ^4F$	15200 cm^{-1}	λ6580 doublet (absorption)
$^2H \rightarrow ^4F$	21200 cm^{-1}	$\{\lambda$4752, λ4762 (absorption)
$^2D_a \rightarrow ^4F$	20600 cm^{-1}	

This scheme is supported by the fact that $^4P \rightarrow ^4F$ transition being between two quartet levels is much more probable and accounts for the large intensity of the red emission lines. The other lines caused by transitions between doublet and quartet levels are shown only in absorption.

(4) The occurrence of one or more lines for the $^4P \rightarrow ^4F$ transition in Cr^{+++} ion, when it is bedded in different crystals[5] seems to be related either to the degree of symmetry of the crystalline field in which it is situated or to the number of non-equivalent positions in which it can replace the metal atom of the ground-lattice. In spinel-type crystals, which are regular, there is one line and in Al_2O_3 and Ga_2O_3, there are two. This point cannot further be discussed here.

I regard the above explanation of the polarization of luminescence of ruby as only a particular case of a more general interpretation of crystal luminescence, based on the following concepts:

(a) The polarization of luminescence is caused by the quenching of orbital moment of the "center" in all but one direction (or a few discreet ones) determined by the nature and symmetry of the crystalline fields.

(b) The absence or existence of luminescence is conditioned by the complete quenching of the orbital moment of a possible center or its conservation along one or more directions within the crystal.

Such an interpretation is being attempted.

[1] B. V. Thosar, Phys. Rev. 60, 616 (1941); Phil. Mag. 26, 878 (1938).
[2] Mitchell and Zemansky, Resonance Radiation and Excited Atoms (Cambridge, 1934), p. 262.
[3] J. H. Van Vleck, Theory of Electric and Magnetic Susceptibilities (Oxford, 1932), p. 288.
[4] J. H. Van Vleck, J. Chem. Phys. 8, 793 (1940).
[5] Deutschbein, Physik. Zeits. 33, 874 (1932).

The Migration of Colloids Through the Interface Between Immiscible Liquids under the Influence of an Electric Field, and the Formation of Ultra-Colloids

G. E. GIBSON AND L. BALDWIN
University of California, Berkeley, California
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IT has been shown by Lash Miller and R. H. McPherson that colloidal arsenic sulfide will distribute itself between the two phases of a mixture of water, acetone, and ether provided the mixture is very close to the critical mixing composition (plait point). A very slight excess of ether causes the colloid to go completely into the water-rich phase, when the volumetric ratios are: water : acetone : ether $= 1.2 : 1.9 : 1.0$.

Placing the two-phase system in a U-tube with electrodes in the upper ether-rich phases we have found that an e.m.f. of 200 volts will cause the arsenic sulfide to go back through the interface into the ether-rich phase, provided the ether is only slightly in excess; otherwise greater voltages are necessary. In similar fashion gold, bentonite clay, and carbon colloids have been made to traverse such an interface.

The phenomenon has been viewed through the ultra-microscope, using gold and bentonite clay. Surprisingly violent motions of the colloid, not visible to the naked eye, became apparent soon after the application of the electric field. Surges back and forth parallel to the interface were observed, always in opposite directions in the two phases, accompanied by vertical wave motions near the interface. After some time a dark band appeared in the ether-rich upper phase immediately above the interface. From time to time particles of greater than average size approaching the interface in an oblique direction would shoot with great velocity through this dark band into the ether-rich phase. This dark band must be a region of high potential gradient, which becomes visible owing to the formation of an extremely fine colloid, not resolvable by the ultra-microscope. The formation of this ultra-colloid has been observed in gold and bentonite and presumably is due to attrition of the larger particles as they shoot through the interface. It probably will occur with other colloids also.