

DETERMINATION OF CIRAZOLINE HCl-SODIUM DODECYL SULPHATE SOLUBILITY PRODUCTS BY AUTOMATED CONDUCTIOMETRIC TITRATION

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Automated conductiometric titrations have been used to study interactions between large oppositely charged organic ions; resultant complexes were termed coacervates and their solubility products (K_s) determined from inflexions in conductivity curves concomitant with phase separation, (Mukhayer et al, 1975; Tomlinson et al, 1979). In this study temperature (T) and flow rate effects on the interaction between cirazoline HCl and sodium dodecyl sulphate (SDDS) were investigated by auto-titrating SDDS (0.01M) into 50.0 mls of stirred cirazoline HCl solution, (1×10^{-3} M), using a syringe pump (Sage Instruments). Conductivity was measured using a dip cell (Mullard E7591B) and conductivity bridge (Wayne-Kerr B642) coupled to a chart recorder (Servogor). At 30°C and flow rate of $170 \mu\text{l min}^{-1}$ the conductivity-concentration profile resembles literature examples (fig 1A) and the insoluble phase is a liquid coacervate. At slower flow rates, e.g. $20 \mu\text{l min}^{-1}$ (fig 1B), abnormal decrease in conductivity occurs associated with precipitation of crystalline complex. Static equilibrium studies have shown that the true equilibrium solubility product is given by extrapolation of the second linear curve to the first, (solid K_s , fig 1B) and that the liquid coacervate form is metastable, crystallising with time.

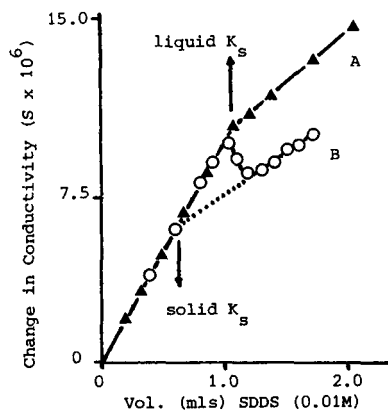


Fig 1. Conductivity-SDDS volume plots taken from titration curves at flow rates of A) $170 \mu\text{l min}^{-1}$ and B) $20 \mu\text{l min}^{-1}$

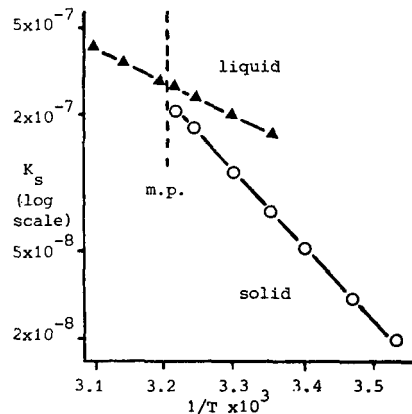


Fig 2. Van't Hoff Plot for K_s against $1/T$ for cirazoline HCl-SDDS systems.

	solid	liquid
ΔH° (kJ/mol)	-63	-28
ΔS° (J/mol/K)	-74	+34
ΔG_{30}° (kJ/mol)	-40	-39

Table 1. Thermodynamic parameters for complex formation.

K_s -temperature data obeyed the Van't Hoff equation for both types of complex system (fig 2). Above 37.5°C only liquid phase separation occurred whereas below this value either species could be formed depending on flow rate; it is proposed that this temperature is the melting point of the hydrated complex. The thermodynamic parameters in table 1 are consistent with this hypothesis.

These results show that although automated conductiometric titration is a rapid method for determining ion-pair solubility products, it should be validated against equilibrated systems to differentiate between possible metastable and equilibrium solubility products.

Mukhayer, G. I. et al (1975) J. Pharm. Sci. 64: 147-151.

Tomlinson, E. et al (1979) in Solution Chemistry of Surfactants, Vol. 1, Ed. Mittal, Plenum Press N.Y.: 3-43.