Influence of Temperature on Ultracentrifugal Stability of Emulsion of Benzene in Ethylene Glycol

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The ultracentrifugal stability of benzene in ethylene glycol nonaqueous emulsion stabilized with sodium dioctyl sulphosuccinate has been determined over the temperature range 10° to 35° in an ultracentrifuge at 25980 rpm. The emulsion is found to be less stable at higher temperatures.

Emulsions may be unstable with respect to temperature. The temperature dependence of stability of emulsions is of great practical importance, since commercial emulsions may have to be stored for varying periods of time in warehouses, where they may be exposed to high as well as low temperatures. In view of this, it is surprising that very little attention1,2 has been devoted to this aspect of emulsion stability.

In continuation of our earlier work3,4, the present communication reports the effect of temperature on the ultracentrifugal stability of oil-in-oil emulsion (nonaqueous system) prepared with benzene and ethylene glycol as two nonaqueous phases and sodium dioctyl sulphosuccinate as emulsifying agent.

The nonaqueous emulsion of benzene (BDH) in ethylene glycol (BDH) was prepared with 1:1 phase ratio by volume and 1-0% concentration of sodium dioctyl sulphosuccinate (BDH; w/v % of ethylene glycol). The heterogeneous mixture of benzene and ethylene glycol containing anionic surfactant was homogenized with a Braun emulsator, for final making of the emulsion.

A Beckman Spinco model E analytical ultracentrifuge was used in this work with a 12 mm light path and a 4-degree sector angle standard cell having a capacity of about 0.8 ml. After preparation of the 0/0 emulsion, 0.7 ml of the emulsion was injected into the ultracentrifuge cell with a hypodermic needle. The cell was then placed in an analytical rotor and subsequently centrifuged at 25980 rpm. The time required for acceleration to this constant speed was 2 min and 45 sec (± 15 sec). Zero time in the experiments was taken as the time at which constant speed was reached. Samples of the emulsion were ultracentrifuged at controlled temperatures between 10° and 35° (±0.2°) at the constant speed.

During centrifugation three layers develop in the cell: transparent layer of benzene, the remaining opaque, concentrated stable emulsion and the transparent layer of ethylene glycol. Photographic records were made of the cell at regular time intervals during the experiment at each temperature. The layers give sharp boundaries on a photographic plate which change position with time as more benzene is separated from the emulsion. Determination of the positions of the boundaries on a series of such plates taken at successive time intervals permits calculation of the rate of separation of benzene from the emulsion at all temperatures. Measurements were made with a travelling microscope determining the distance from the top of the cell to the benzene-emulsion and emulsion-ethylene glycol interfaces, and to the bottom of the cell.

The volume, \( V \), corresponding to a length, \( l \), in the cell is given by

\[
V = \frac{4\pi t[(d+l)^2-d^2]}{360}
\]

where \( d \) is the distance from the centre of rotation to the top of the cell, and \( l \) is the thickness of the cell. A graph was plotted of the volume as a function of the measured value of \( l \) from the top of the cell using an optical enlargement of 2:03. The plot was then used to determine the volume from the differences between the measured distances to the different interfaces.

The per cent of the initially emulsified benzene which separated at any given time was determined by dividing the volume of the benzene layer by the...
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sum of the volumes of the benzene layer and the creamed emulsion. At each temperature, the per cent of the initially emulsified benzene which separated was plotted against the time of ultracentrifugation. The rate of separation at known temperature and speed was determined from the slope of the linear portion of the curve. The slope of the line, i.e. the rate of separation of benzene in per cent per minute, is termed the ultracentrifugal stability.

The rate of separation of benzene in per cent per minute from the nonaqueous emulsion varied linearly with the time of ultracentrifugation at all temperatures (Fig. 1), subsequent to a brief period of initially more rapid separation of benzene. It is evident that the stability of the nonaqueous emulsion is less at higher temperatures and the separation of benzene in a given time interval increases with increasing temperature.

References

Electrical Conductance in Molten Salts:
Part VI—Potassium Nitrate–Strontium Nitrate Mixtures*

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Electrical conductance of binary mixtures of potassium nitrate with strontium nitrate, in molten state, up to 40 mole-per cent of the latter has been measured as a function of temperature. At a given composition, conductivity of the medium increases with the increase in temperature. Equivalent conductance–composition isotherms are linear over the composition range investigated. Partial equivalent conductivities of the constituents have also been reported. Considering conductance to be a rate process, enthalpy and entropy of activation for the conduction process have been evaluated.

EARLIER studies1–3 showed that addition of divalent ions, Ba2+ and Ca2+, to the melts of alkali metal nitrates causes a decrease in the conductivity and an increase in the enthalpy of activation for the conduction process. With a view to establishing some quantitative correlation between the observed variations and the basic parameters of the ions, studies have been extended to cover other stable mixtures of alkali-alkaline earth metal nitrates. Results of investigations on KNO3–Sr(NO3)2 mixtures over the accessible range of temperature and divalent-ion content are presented in this note.

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Analar (BDH) grade KNO3 was baked at 200° for several days before use. Strontium nitrate (BDH, LR) was recrystallized from aqueous solution, dried in vacuo for 24 hr and finally baked at 200–250° for several days. Details regarding the capillary type conductivity cell, the cell constant determination, the conductivity bridge and measuring techniques etc. have been reported earlier1,2,5. All the measurements were made at an ac frequency of 1kHz.

In the bridge employed, a parallel combination of resistance (Rr) and capacitance (Cr) was used in the measuring arm. Considering the electrical equivalent of the cell as a series combination of solution resistance (Rs) and double layer capacitance (Cp), one has from ac theory

\[ R_s = \frac{R_r}{1 + (R_r C_p 2\pi f)^2} \]  

where \( f \) is the frequency (in Hz) of the ac signal.

The specific conductance-temperature data for different mixtures are presented in Table 1. The specific conductance-temperature data could be described by a polynomial of the type: \( k = a + bf + cf^2 \). The constants \( a, b \) and \( c \) were in computing specific conductance at specified temperatures. Equivalent conductances (\( A \)) were computed using the equivalent volume data of McAuley et al.3. At a given temperature, equivalent conductance decreased linearly with increase in strontium nitrate content in the mixture (Fig. 1) and the linear plot can be expressed by Eq. 2

\[ \Lambda = A + BX' \]  

where X' is the equivalent fraction of the divalent ion and \( A \) and B are empirical constants characteristic of the temperature. A typical comparison (at 475°) of the decrease in equivalent conductance with the increase in \( \text{Sr(NO}_3\text{)}_2 \) content, with those

![Fig. 1 — Equivalent conductance (A) of KNO₃-M(NO₃)₂ mixtures at 475° as a function of divalent ion [(1) KNO₃-Ba(NO₃)₂; (2) KNO₃-Sr(NO₃)₂; (3) KNO₃-Ca(NO₃)₂ system.](image)