oscillation. When these reagents were added after irradiation for a period of time approximating the time required for the first peak in the wave-like variation of concentration of peroxyde to occur, further irradiation caused only a decrease in the concentration of peroxyde (Fig. 5).

The complete mechanistic elucidation of this phenomenon of oscillation of peroxyde concentration when reagents are irradiated in suspensions of zinc oxide in hydrocarbon media, must await a more detailed study. However, some deductions can be made from the present observations. The alcohol and dissolved oxygen and to a lesser extent solvent molecules are adsorbed on the ZnO surface. It has been suggested that on irradiation of ZnO, the electrons in the conduction band escape to the surface and their capture by adsorbed O₂ results in the formation of O₂(ads.) and what may be pictured as a ZnO⁺(hole). This is synchronized by the drift of electrons from adsorbed alcohol to ZnO⁺(hole). The C—H bond of the alcohol (RH) is ruptured by O₂(ads.) leading eventually to the formation of R⁻, HO₂⁻ and then RO₂⁻ radicals. Hydrogen peroxyde can be formed by the self-reaction of HO₂⁻ or reaction of RO₂⁻ with adsorbed alcohol (RH). Thus there would be a steady rise in the concentration of peroxyde with irradiation. H⁺ formed as a result of the homolytic cleavage of alcohol or hydrocarbon by ZnO can remain adsorbed.

Adsorbed H⁺ can react with hydrogen peroxyde giving OH⁻ radicals in a chain process causing decomposition of hydrogen peroxyde. The decomposition may outweigh the formation when a certain critical concentration of hydrogen peroxyde is reached. This concentration is controlled by the proportion of vacant sites. When the concentration of OH⁻ reaches a critical value its combination with H⁺ to yield H₂O will be a dominant process.

This occurs when the concentration of peroxyde reaches the minimum. When OH⁻ and H⁺ are destroyed the concentration of peroxyde can again increase. If the concentration of alcohol is increased or if alcohol is the solvent itself, all the sites can be occupied by alcohol and fewer sites may be available for the released hydrogen atom. In such a case H⁺ is removed more as HO₂⁻. The maxima and minima would not occur. In fact it is interesting to note the absence of maxima and minima when alcohol concentration is high. Amides form a surface complex with irradiated ZnO (IR studies). This would cause depletion of vacant sites.

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References


Lithium Isotope Effects in Ion-exchange Equilibria in Mixed Solvents

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Lithium isotope effects in cation-exchange equilibria on Dowex 50W×8 resin have been investigated in 76% (w/w) methanol-water, 44-2% (w/w) acitone-water, 53-8% (w/w) DMSO-water and 20-7% (w/w) isopropanol-water mixtures by the breakthrough technique using lithium acetate or lithium chloride feed solutions. The single stage separation factor (α) increases appreciably in MeOH—H₂O mixture, remains unchanged in acetone-water and DMSO—H₂O mixtures and decreases in isopropanol-water as compared to the value in aqueous medium. α values for the mixed solvent systems have been interpreted in terms of the differences in the state of solvation of Li⁺ ions in the solution and in the resin phase taking into consideration the solvent fractionation effects exhibited by the resin in mixed solvent systems.

The single stage separation factors for lithium isotopes (α) in ion-exchange equilibria on polystyrene sulphoneic acid type ion-exchange resins (Eq. 1),

\[ ^{6}\text{Li}^{+} + ^{7}\text{LiR} \rightleftharpoons ^{7}\text{Li}^{+} + ^{6}\text{LiR} \]

... (1)

are small in aqueous systems. The effect of mixed solvents in these systems has also been investigated by a few workers but their observations differ. The isotope effects, in aqueous medium, have been explained by Lee and Begum in terms of...
differences between the states of hydration of Li⁺ ion in solution and the resin phases, and differences in the corresponding zero-point energies of the hydrated lithium species in the two phases. In mixed solvents, besides different swelling behaviour compared to that in aqueous medium, the resins exhibit solvent fractionation effects contributing to differences in the solvation of Li⁺ ion in the resin and the solution phase. Some information can be obtained about the solvation of Li⁺ ion in a mixed solvent medium from ΔG° values, i.e. free energy of transfer of Li⁺ from water to the mixed solvent. Ascertainment of the change in solvation of Li⁺ ion in the exchanger phase in going from aqueous medium to the mixed solvent medium is, of course, more difficult due to the changes in resin swelling and the solvent fractionation effects. In order to have a better understanding of the role of mixed solvent in such systems, lithium isotope effects in cation-exchange equilibria (Eq. 1) in a few aqueous-nonaqueous solvent systems have been investigated.

In the present study, 76% (w/w) MeOH-H₂O, 52-5% (w/w) DMSO-H₂O, 44-2% (w/w) acetone-H₂O and 20-7% (w/w) i-PrOH-H₂O solvent systems were used. AR grade organic solvents and chemicals were employed. Breakthrough experiments were performed using 0.22±0.033 M LiCl or LiAc feed solutions at flow rates of 0.35±0.1 ml/min on a Dowex 50W×8 (H⁺) column (Bed ht = 120 cm; i.d. = 12 mm; capacity = 340 meq). Lithium in the effluent samples was estimated gravimetrically and isotopic analysis was carried out mass spectrometrically. The accuracy in the estimation of ⁶Li/²⁷Li atom ratio of samples was ±0.0007 (natural 0.0025 ±0.0007).

The mass spectrometric analysis of all frontal samples showed a depletion of ⁶Li thereby indicating that ⁶Li enriches in solution and ⁶Li in the resin phase as in the aqueous systems.

The single stage separation factor, α⁺, given by Eq. (2),

\[
α⁺ = \frac{[^7\text{Li}]_{\text{resin}}}{[^7\text{Li}]_{\text{solution}}} = \frac{[^7\text{Li}]_{\text{resin}}}{[^7\text{Li}]_{\text{solution}}}
\] ...

has been computed for the various aquo-organic systems by the relation* given in Eq. (3).

\[
α⁺ = 1 + \frac{\sum_{i=1}^{N} V_{i} C_{i} (S_{i} - 1)}{Q}
\] ...

Here, \( V_{i}, C_{i} \) and \( S_{i} \) represent respectively the volume, concentration and overall separation factor in the effluent sample \( i \) and \( Q \) is the total exchanger capacity of the resin bed. \( N \) represents the sample when \( S_{i} = 1 \). The numerator in the second term on the RHS was obtained by computing the area under the curve in the plot of enrichment factor versus the quantity of the lithium in the effluent sample. The \( α⁺ \) values for the various systems are summarized in Table 1. An estimated upper limit in the measurement of \( α⁺ \) values is ±0.0004 for these systems though actual deviations are expected to be much lower.

**MeOH-H₂O system** — The breakthrough experiments were carried out with LiCl and LiAc as feed solutions. The requirement for a sharp lithium front, with LiCl as the feed, was high selectivity of the resin for Li⁺ ions. It has been shown earlier that Dowex 50W×8 has highest selectivity for Li⁺ ions in 76% (w/w) methanol-water mixture. Hence the same composition was selected for the present isotope effect experiments.

The data in Table 1 show clearly that \( α⁺ \) increases appreciably in these systems in comparison with its value in aqueous medium. \( ΔG° \) (Li⁺) values are negative for transfer from water to water-methanol mixtures. Also these \( ΔG° \) (Li⁺) values become more negative with increasing methanol content in the mixtures. Further, it has been shown in an earlier study that the solvent composition is nearly 60% (w/w) methanol-water inside the Li⁺ form of Dowex 50W×8 in equilibrium with 76% (w/w) methanol-water. Both these factors increase the Li⁺ ion solvation in the solution phase as compared to that in the resin phase. Therefore, besides the factors responsible for differences in the solvation of Li⁺ ions in the two phases in aqueous medium, an additional contribution comes from solvent fractionation effects resulting in greater \( α⁺ \) value in 76% (w/w) MeOH-H₂O systems.

\( α⁺ \) value in 76% methanol is higher with LiCl as the feed solution than that with LiAc as the feed solution. Similar trends are seen in aqueous medium also where \( α⁺ \) value on Dowex 50W×16 is higher with LiCl feed (1-0037) compared to that with LiAc feed (1-0027). The DMSO-H₂O system — As sharp lithium fronts could not be obtained with LiCl in various DMSO-H₂O mixtures, LiAc was employed as feed and the choice of 1:1 by volume (52.5% (w/w)) DMSO-H₂O mixture was based on considerations of viscosity. The value of \( α⁺ \) in this DMSO-H₂O mixture is the same (within experimental accuracy) as for the aqueous medium. \( ΔG° \) (Li⁺) shows a negative value for this medium showing greater solvation of Li⁺ in the mixture compared to that in water. However, Li⁺ form of Dowex 50W×8 does not show any solvent fractionation in DMSO-H₂O mixtures. Also, there is only about 10% change in the total swelling of this resin in 52.5% DMSO-H₂O medium compared to the swelling in water. Thus, in 52.5% DMSO, the difference in Li⁺ solvation in the two phases remains more or less the same as in aqueous medium. Hence, the observation that \( α⁺ \) remains unchanged in 52.5% DMSO-H₂O is understandable.
Acetone-H₂O and i-PrOH-H₂O systems — For concentrations greater than 1:1 by volume [44±2% (w/w)] of acetone, dry patches used to appear in the resin bed while in the isopropanol-H₂O mixtures, the i-PrOH content had to be limited on viscosity considerations to 1:3 by volume [20-7% (w/w)] of isopropanol. Sharp fronts of lithium could not be obtained in these mixed solvent systems using LiCl feed solutions. Consequently LiAc was employed as the feed in both these cases.

While in acetone-H₂O mixture, the ζ value was close to that in aqueous medium, i-PrOH-H₂O mixture showed a lowering of ζ (Table 1). Due to lack of information on ΔG° (Li⁺) values in acetone-water and i-PrOH-H₂O mixtures, and the solvent fractionation behaviour of Li⁺ form resonate in the latter solvent systems, the isoeto effects in these media cannot be discussed any further.

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References


Kinetics of Reaction of Aniline Blue with Alkali

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The reaction leading to the decolourization of aniline blue in alkaline medium has been studied kinetically. The specific reaction rate data and various activation parameters have been calculated. The reaction shows first order dependence on [dye] and zero order dependence on [alkali]. An SN1 mechanism for the reaction has been suggested.

Kinetics of decolourization of several triphenylmethyl dyes in the presence of alkali or acid have been reported earlier. Recently Katyar et al. have reported the kinetics and mechanism of decolourization of Rousseline and para rosseline in alkaline medium. However, no work has been reported on the reaction of aniline blue, a diphenyl derivative of rosseline, with alkali. Therefore, the kinetics of the reaction of aniline blue with sodium hydroxide were studied spectrophotometrically and the results are reported in this note.

The chemicals used were aniline blue (E. Merck), sodium hydroxide (AR, BDH) and potassium chloride (AR, S.M) and acetone (AR, BDH) which was purified before use. Conductivity water was used in all the experiments.

Since the fading of aniline blue colour in alkaline medium is reversible, the kinetic studies were carried out under pseudo-first order conditions by keeping a large excess of alkali over the [dye].

The reaction was followed by noting the decrease in optical density of the reaction mixture spectrophotometrically. Aniline blue having λmax 520 nm in aqueous solution obeyed Beer’s law up to [dye] = 1-6 × 10⁻⁴ M. The reaction was, therefore, studied at [dye] < 1-6 × 10⁻⁴ M. The rate constants were found to be reproducible within ± 0-2 × 10⁻⁵ sec⁻¹.

The colour fading of aniline blue in alkaline medium followed first order kinetics in [dye] as evidenced by a linear plot of log absorbance versus time. This was further confirmed by the constant values of k over a wide range of [dye] (Table 1).

To examine the dependence of rate on [alkali], studies were carried out at constant [dye] (8 × 10⁻⁵ M) while varying the [alkali] in the range 1 × 10⁻² to 5 × 10⁻³ M. The plots of log absorbance versus time were linear with identical slope values thereby indicating that the rate of reaction is independent of [alkali] (Table 1).

Effect of varying ionic strength on the reaction rate was studied by adding different amounts of KCl at constant dye and alkali concentrations. It was observed that increase in ionic strength had negligible effect on the rate of reaction.

The reaction was studied at different temperatures in the range 301-217 K in order to evaluate various activation parameters. The values of various activation parameters obtained from Arrhenius plots were E_r^* = 18-0 kcal mole⁻¹; ΔH_r^* = 17-3 kcal mole⁻¹; log P^* = 10-8 and ΔS_r^* = -11-5 e.u.

Based on the above observations a mechanism as shown in Scheme I has been proposed to explain the fading of aniline blue colour in alkaline medium.

Table 1 — Dependence of Rate on [Aniline Blue] and [NaOH] at 28°C

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