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Percolation View of Novolak Dissolution. 8. Effect of the Base Cation on Dissolution Rate

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ABSTRACT: The dissolution rate of novolak resins in aqueous bases is an important factor in their practical applications, and the cation of the base has a significant effect on that rate. To try and understand this effect, we have determined the activation energy and activation entropy of dissolution, and we find that both are affected by the size of the cation. The activation entropy becomes more negative for larger cations, and the activation energy decreases. The two effects oppose each other; their competition determines the dissolution behavior of the resin.

Introduction

It has been known for some time that the cation of the developer base has a significant effect on the dissolution rate of novolak films.[1] In the alkali hydroxides there is a progression from fast development in LiOH to slower dissolution in the other bases. Since dissolution is linked to the diffusion of base into the polymer matrix, it seemed reasonable to assume that this effect is caused by the difference in the size of the ions. For one particular resin we had earlier observed a linear correlation between dissolution rate and the inverse cross section $(\pi r^2)^{-1}$ of the ions.[2] The radii used in calculating the cross sections in ref 2 were the crystallographic radii derived from X-ray diffraction experiments (Pauling). More recently, with a commercial novolak (Hoechst-Celanese) we found somewhat different results, and these are shown in Figure 1. Willson and his group[3] observed a similar behavior on yet another novolak sample.

To probe the effect of base cations on dissolution rate we measured the activation energy of the dissolution process for the five alkali metal bases in 0.1 N solutions. The result was surprising: The activation energies decrease from Li^+ to Cs^+. With a lower activation barrier for ionic diffusion an increase in dissolution rate would be expected. Instead, the dissolution rate decreases in general from Li^+ to Cs^+. This very unusual behavior prompted us to investigate the diffusion of cations in phenolic resins more carefully and to attempt an interpretation of the observed phenomena in terms of the transition state theory of chemical kinetics.

Experimental Part

We prepared novolak films by spin coating a 25% solution in isoamyl acetate onto 2 in. silicon wafers. The novolak sample was a fairly narrow molecular weight fraction, $M_w = 2200$, of a commercial novolak provided to us by Hoechst Celanese Corp. In a similar way we prepared films of a sample of poly(vinylphenol) [poly(4-hydroxystyrene), $M_w = 29\,800$], supplied by Polysciences, Inc. The films were kept at 90° for 1 h.

The dissolution rates of the films in 0.1 N solution of the five alkali metal bases were measured by laser interferometry, as described in ref 4. Measurements were taken over a range of temperatures, 10−25 °C for novolak and 10−14 °C for the poly(vinylphenol) (PVP) samples. The temperature range was limited by T_g', the glass transition temperature of the penetration zone[5] of the dissolving films. Because of the narrow temperature range available, the experimental results for PVP are less accurate than those obtained with novolak.

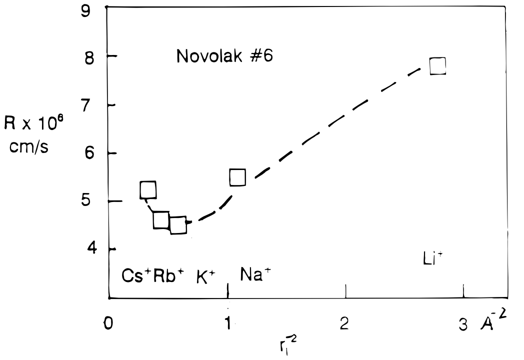

Figure 1. Dissolution rate of novolak sample no. 6 in 0.1 N solutions of the alkali metal bases plotted against the reciprocal of the square of the cation radii.

Transition State Theory of Diffusion

Eyring[6] has shown that in transition state theory, diffusion coefficients, D (diffusivities), can be described by the general equation

$$D = el^2\frac{kT}{h}\,e^{\Delta S^{\#}/R}e^{-E_a/RT} \tag{1}$$

where kT/h is the universal constant of transition state theory, l is the mean size of the diffusion transfer step (jump distance), R is the gas constant, E is the "experimental" activation energy, i.e. that value that is obtained from the slope of an Arrhenius plot of log diffusivity (dissolution rate) vs $1/T$, and $\Delta S^{\#}$ is the activation entropy of the process. Since dissolution is controlled by the diffusion of base into the matrix and the diffusivity of base is linked to the dissolution rate **R** by

$$D = \mathbf{R}\delta \tag{2}$$

an expression similar to eq 1 applies also to the dissolution rate **R**. The constant δ in eq 2 is the thickness of the penetration zone of the dissolving resin film.[5] It is of the order of 10^{-6} cm and, in fact, was assumed to be $\delta = 1 \times 10^{-6}$ cm exactly.

From the temperature dependence of the dissolution rate we determined the Arrhenius activation energy, E_a. From that and from the value of the dissolution rate (at 20 °C for novolak and at 10 °C for poly(vinylphenol)

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Table 1. Diffusivities of Cations and Activation Energies and Entropies of Diffusion for the Dissolution of Novolak in Alkali Metal Bases

	Novolak No. 6			poly(vinylphenol) 29800		
cation	$10^{12}D$ (cm^2/s)	E_a (kcal/mol)	$-\Delta S^\#$ (eu)	$10^{12}D$ (cm^2/s)	E_a (kcal/mol)	$\Delta S^\#$ (eu)
Li^+	7.80	7.87	17.9	1.70	3.3	36
Na^+	5.52	6.96	21.7	1.73	2.6	42
K^+	4.49	6.30	24.4	1.78	0.7	45
Rb^+	4.59	4.77	29.5	1.4	−1.5	54
Cs^+	5.27	2.98	35.4	0.63	−3.5	62

(PVP)) we derived the activation entropy of dissolution via eq 1. These results are collected in Table 1. It can be seen that the ionic diffusivities decrease from Li^+ to K^+ and increase slightly from Rb^+ to Cs^+. Evidently, the behavior of the dissolution rate in Figure 1 is caused by an overriding decrease in the activation entropy that more than compensates for the lowering of the energy barrier between sites.

Activation Entropy

Why should the activation entropy of diffusion be so much more negative for Cs^+ than for Li^+? Conventional transition state theory provides only part of the answer. In molecular terms the activation entropy of diffusion[6] is expressed as the ratio of the translational partition function ($F^\#$) of the mobile particle in the activated complex on top of the activation barrier to the partition function (F) in the ground state.

$$e^{\Delta S/R} = \frac{F^\#}{F}\frac{1}{{}^1/_3 v_f} = \frac{h}{(2\pi m^* kT)^{1/2}}\frac{1}{{}^1/_3 v_f} \qquad (3)$$

The constant v_f is here the mean free volume available to the moving particle in the elementary diffusional step. In eq 3 the individuality of the mobile particle (ion) is characterized only by its molecular mass; the size of the particle does not enter the argument, and yet the size of the traveling particle (the cation) appears to play an important role in controlling dissolution rate. The reason for this discrepancy is that eq 3 refers essentially to liquid systems where thermal motion constantly redistributes free volume and where, given sufficient time, adequate free volume becomes available at any location of the percolation field. In a solid environment, such as the penetration zone of the dissolving novolak film below its glass transition, the situation is different. The distribution of free volume is independent of time and is set at the moment of casting.

Thus, for a successful diffusional step to occur it is not enough that the two sites of the transition are within a critical transfer distance; there must also be available at the target site sufficient free volume to accommodate the arriving (transiting) particle. If that is not the case, the transition will not occur, no matter how long the particle may wait at the location.

We denote the probability (possibility) of transfer based on site separation alone as P_1 and the probability that an adequate free volume hole is available at the site as P_2. The probability of the simultaneous occurrence of both, and hence of a successful transition, is the product

$$P = P_1 P_2 \qquad (4)$$

The Boltzman relation between entropy and probability leads to

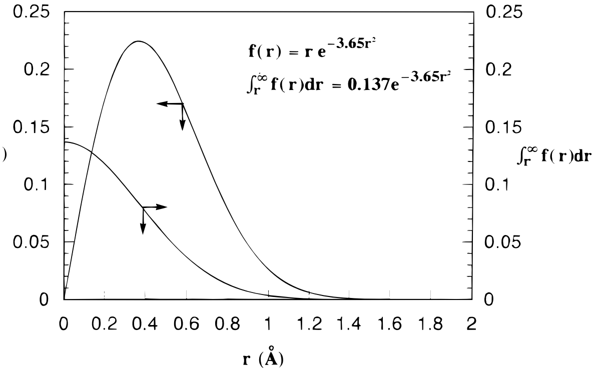

Figure 2. Distribution function of free volume hole sizes in novolak no. 6. The distribution function and the frequency of occurrence of free volume holes of radius r_i or larger are plotted against the hole radius in angstroms.

$$\Delta S^\# = \Delta S_1 + \Delta S_2 \qquad (5)$$

The first term, ΔS_1, is the activation entropy of barrier crossing represented by the translational partition functions (eq 3)

$$\Delta S_1/R = \ln[h^2/(2\pi kT)]^{1/2} - {}^1/_3 \ln v_f + {}^1/_2 \ln N_A - {}^1/_2 \ln M_i \qquad (6)$$

where N_A is Avogadro's number, R is the gas constant, and M_i is the molecular (atomic) weight of the ion. The only term in ΔS_1 that depends on the nature of the ion is the molecular weight term, ${}^1/_2 \ln M_i$.

The second entropy term, ΔS_2, measures the probability that an adequate free volume hole will be available at the site. That probability is the integral of the hole distribution function $f(r)$ in the interval from r_i to ∞.

$$P_2 = \int_{r_i}^{\infty} f(r)\, dr \qquad (7)$$

where r_i is the (effective) radius of the traveling ion. We have chosen the simple expression below as the distribution function of free volume holes in the system.

$$f(r) = r \exp(-ar^2) \qquad (8)$$

It has the appropriate shape (see Figure 2), and it is almost certainly the leading term in any more complex distribution function. The definite integral of this function in the interval from r_i to ∞ is the frequency of occurence of holes with radii equal to or larger than r_i, the ionic radius of the traveling ion. It is also the probability P_2.

$$P_2 = 1/(2a) \exp(-ar_i^{-2}) \qquad (9)$$

The activation entropy associated with this probability is

$$\Delta S_2 = -R \ln(2a) - Rar_i^2 \qquad (10)$$

The value of the adjustable parameter a can be obtained from the slope of a plot of $-\Delta S_2$ vs r_i^2, which is Ra. In Figure 3 this slope is $Ra = 7.30$, leading to a value of $a = 3.65$. That value was used in the distribution function of Figure 2.

The total activation entropy $\Delta S^\#$, as is derived from

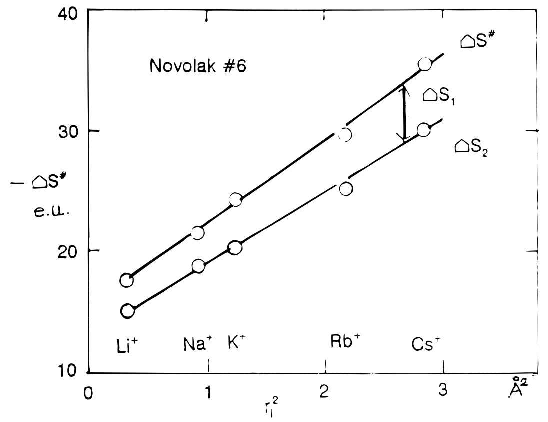

Figure 3. Plot of activation entropies vs the square of the ionic radii. $\Delta S^\#$ is the "experimental" activation entropy of dissolution, ΔS_1 is the entropy associated with the probability of transfer across a given site separation, and ΔS_2 is linked to the probability that a hole of radius r_i or larger will be available at the target site.

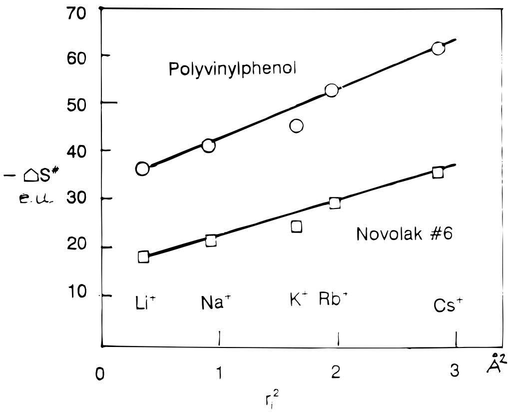

Figure 4. Activation entropies for the dissolution of novolak no. 6 and of polyvinylphenol, $M_w = 29\,800$, in 0.1 N solutions of the alkali metal bases, plotted against the square of the ionic radii.

Table 2. Entropies of Activation (eu) and Ionic Cross Sections (Å²)

ion	r_i^2	ΔS_1	ΔS_2	$\Delta S^\#$
Li⁺	0.36	−1.95	−15.0	−17.9
Na⁺	0.90	−3.13	−18.6	−21.7
K⁺	1.77	−3.66	−20.7	−24.4
Rb⁺	2.19	−4.44	−25.1	−29.5
Cs⁺	2.86	−4.88	−30.5	−35.4

the experimental data, is the sum of eqs 6 and 10.

$$\Delta S^\# = -R\ln(2a) - {}^1/_2 R\ln M_i - Rar_i^2 \qquad (11)$$

Activation entropies are listed in Table 2, together with the squares of the radii assigned to the five alkali metal ions. The data refer to the dissolution of novolak sample no. 6 in 0.1 N solutions of the bases.

In Figure 3 we have plotted the total activation entropy as a function of the square of the ionic radii. At the data points of $\Delta S^\#$ we have subtracted the values of ΔS_1 and in that way obtained values of ΔS_2. There is clearly a linear correlation between ΔS_2 and the effective cross section of the ions.

The behavior of polyvinylphenol is very similar to that of novolak. A plot of the activation entropies of dissolution for PVP runs almost parallel to the corresponding plot of novolak (Figure 4).

To sum up: the entropy of activation which controls the frequency factor of the rate equation for novolak dissolution is negative. It decreases quite steeply with the cross section (square of the radii) of the traveling base cation, in agreement with changes in the free volume requirement of the cations. This effect is larger than that of the lowering of the energy barrier between percolation sites. The activation energy of dissolution clearly decreases with increasing size of the cation. It remains to interpret this observation.

Activation Energy

The activation energy of dissolution is associated with the rate-determining step of the dissolution process. To identify that step, we remind ourselves that in the dissolution of a resist film a thin penetration zone is formed at the interface with the base solution. This zone is the result of the deprotonation of novolak by the base. The penetration zone consists of phenolate ions, water, and base ion-pairs. The progress of the zone in the direction of the virgin matrix is identical with the dissolution rate of the resin film.

The progress of the penetration zone is determined either by the diffusion of base through the zone or by the deprotonation of phenol that occurs at the interface of the zone with the virgin matrix. We found recently (see the preceding paper in this series[7]) that the base function propagates in the zone by a proton transfer mechanism similar to the Grotthus mechanism of ionic conduction in aqueous acids and bases.[8] In all probability, it is the deprotonation at the front of the penetration zone that is the rate-determining step in novolak dissolution. The cation of the base is involved in the deprotonation step

$$\mathrm{POH + OH^-,K^+ = PO^- + HOH + K^+ = PO^-,K^+ + H_2O}$$

------------------1------------------
--------------------------2-------------------

Deprotonation consists thus of two events: (1) the abstraction of a proton from phenol by the hydroxyl ion of the base and (2) the movement of the counter-cation (K⁺) from its starting position next to the last phenolate ion to the freshly created phenolate ion at the very front of the zone.

The movement of the cation is the slower event, and it ultimately determines the frequency of the completed deptronation step. *The activation energy of dissolution is associated with the movement of the counter-cation from a phenolate site at the front of the matrix to a newly created phenolate ahead.*

If this view is correct, the activation energy is the work required to free the cation from this starting position. The energy binding the cation to the phenolate is the electrostatic potential of the cation at its starting position next to the last phenolate ion. That potential is inversely proportional to the sum of the radii of the cation (r^+) and of the phenolate anion (r^-).

$$V_1 = \frac{\text{constant}}{r^+ + r^-}$$

However, the transiting cation is also in the attractive field of the target anion. The compound potential acting on the cation is therefore made up of two terms.

$$V = \frac{\text{constant}}{r^+ + r^-} - \frac{\text{constant}}{a - (r^+ + r^-)} = F(r) \qquad (12)$$

Here a is the (average) distance between phenolate sites (see Figure 5). We have used the ionic radii of Table 2, and for the phenolate ion, $r_i = 1.76$ Å. The distance

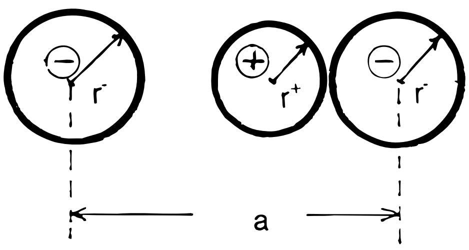

Figure 5. Sketch defining the ionic radii and the site separation at the moment of transfer of the cation between two anionic sites.

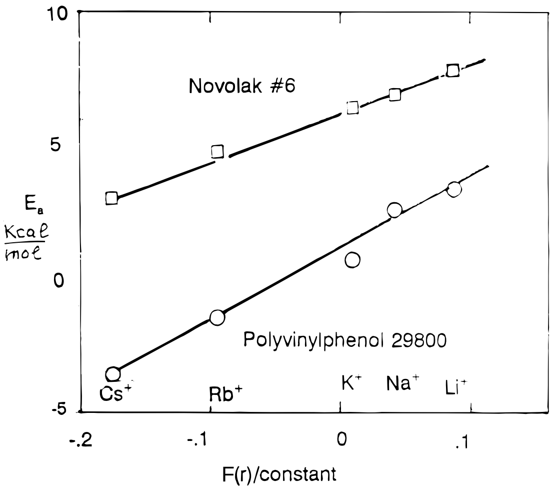

Figure 6. Activation energy of dissolution of novolak no. 6 and of polyvinylphenol, $M_w = 29\ 800$, in 0.1.N solutions of the alkali metal bases, plotted against the distance function $F(r)$/constant. See text.

Table 3. Distance Function $F(r)$/constant

ion	$a = 6.0$ Å	$a = 5.8$ Å	$a = 5.6$ Å
Li^+	0.124	0.106	0.088
Na^+	0.066	0.046	0.042
K^+	0.035	0.013	0.011
Rb^+	−0.036	−0.047	−0.094
Cs^+	−0.099	−0.132	−0.175

function $F(r)$/constant is listed in Table 3 for three relevant values of the intersite distance a.

The experimental activation energies of novolak no. 6 and of PVP 29 800 in 0.1 N solutions of the five alkali metal bases are plotted in Figure 6 against the distance function for $a = 5.6$ Å. The experimental points lie quite closely on straight lines, confirming a correlation between the activation energy and the size of the ions involved in the deprotonation step. (The function for $a = 5.6$ Å produced the best linear plot).

Negative Activation Energies of Dissolution

In several instances we found negative activation energies of dissolution, and that requires comment. Negative activation energies of novolak dissolution were reported earlier by Garza, Szmanda, and Fischer,[9] and these authors argued convincingly that negative values of E are possible if the activation step is coupled to an exothermic chemical reaction. In that case the observed activation energy is the sum of the energy barrier, E_b, and the enthalpy change of the chemical reaction.

$$E_a = \Delta H + E_b \tag{13}$$

If ΔH is strongly negative, E_a, the observed activation energy, may be negative, although the energy barrier, E_b, by its very nature, must be positive. We believe that this applies to our systems. The diffusional transfer step of the cation is coupled to the deprotonation reaction of the phenol at the front edge of the penetration zone.

$$POH + OH^- = PO^- + H_2O$$

This reaction is exothermic, being the sum of two processes.

$$POH = PO^- + H^+$$

$$H^+ + OH^- = H_2O$$

The second reaction has, in solution, a reaction enthalpy of $\Delta H = -10$ to -13 kcal/mol, and the first reaction is mildly endothermic.

Assuming for the deprotonation step in the solid matrix a reaction enthalpy of $\Delta H = -10$ kcal/mol, the energy barriers for the transfer of the cations between two phenolate sites become 18 kcal/mol for Li^+, 17 kcal/mol for Na^+, 16 kcal/mol for K^+, 15 kcal/mol for Rb^+, and 13 kcal/mol for Cs^+. These values are not unrealistic for a diffusional step in a solid environment. Barker and Thomas[10] found activation energies of the order of 20 kcal/mol for the migration of alkali ions in cellulose films.

In the context of a study of the mechanism of novolak dissolution the important aspect of these results is that the deprotonation reaction and the transfer of cations are clearly linked; otherwise the reaction could not contribute to the activation of the cation transfer. This is only possible if the cation transfer occurs at the very edge of the penetration zone. The deprotonation step at the front of the zone is, therefore, the rate-determining event of novolak dissolution. We shall return to this aspect in a future communication dealing with the effect of resin molecular weight on dissolution rate.

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