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Autooscillating Regime of Sorption of Low Molecular Weight Solvent by Ionomers

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Summary

The kinetics of differential and integral sorption of toluene by statistical copolymers of styrene and acrylic acid (3.8 and 8.0 mole %) has been investigated over the temperature range 20 - 40°C. The observed autooscillating regime of toluene sorption is due to the competition of different relaxation processes. The effect on sorption kinetics of toluene of the morphology of ionomer films was investigated by infrared spectroscopy.

Introduction

It is known that the introduction of salt side groups to the main chain of the polymer leads to a drastic change in its properties in the solid state. This change is due to crosslinking caused by multiple association of salt groups. The driving forces of this microphase separation are related to the low dielectric constant of the medium in which the salt groups aggregate by the mechanism of dipole-dipole interaction. These salt associates the size of which depends on various factors including the polymer structure and the temperature play part of nodes of a specific network; their lifetime being finite and comparable to that of usual routine experiments (EISENBERG 1977). We investigated the kinetics of sorption of toluene vapour by statistical copolymers of styrene and acrylic acid (3.8 and 8.0 mole %) with various degrees of neutralization (0 - 100%) in the temperature range 20 - 40°C.

Experimental

Ionomers based on styrene, acrylic acid and sodium acrylate (weight-average molecular weight $3 \cdot 10^5$) were obtained according to ref.(BOLOTNIKOVA 1974). Films under investigation were ∿ 100μm thick and were obtained by evaporation of the solvent from a 2% solution in tetrahydrofuran(THF) at room temperature with subsequent drying to constant weight. The films were annealed at 150°C for four hours under the pressure 10^{-3} tors with subsequent slow cooling to room temperature. The methods of low temperature nitrogen sorption and mercury porosimetry were used to establish the absence of pores in the films. Sorption experiments were carried out with the Mac Bain balance in a high vacuum setting. The diffusion cell and the whole sorption assembly were thermostated within ± 0.05°C and ± 0.3°C respectively. The sensivity of the quartz helix was 0.7 mg/mm. All measurements were carried out in isobaric-isothermal conditions.

Results and Discussion

The density of the fluctuating network with the nodes formed by associates of carboxylate groups varies with the degree of neutralization of the copolymers and the concentration of the solvent which affects the chain mobility. The kinetics of differential sorption of toluene by a styrene-(acrylic acid, 3.8 mole %) copolymer (St-3.8AA) (Fig. 1) (in this copolymer the network of salt associates is absent) are similar to those of benzene sorption by pure polystyrene (ODANI 1961). However, for polymers containing salt groups (degree of neutralization 20% and higher (LYUBIMOVA 1984) at certain toluene concentrations and relatively long times the kinetic sorption curves exhibit periodical maxima and minima which mean that the system attains equilibrium by alternating sorption and ejection of the solvent under isobaric-isothermal conditions (Fig. 2, a-c, neutralization degree 100%).

We assume the reason for sorption anomalies of this type is probably as follows. The degree of aggregation of salt groups in a medium with low dielectric constant is determined by the second virial coefficient of interactions between these groups and depends on temperature (JOANNY 1980). The film structure before sorption corresponds at least to the equilibrium structure at the glass transition temperature with low degree of aggregation. When the solvent is introduced into the film the mobility of polymer chains increases and as a result the salt groups acquire the possibility of attaining the equilibrium degree of association corresponding to the experimental temperature. The increase of cross-linking degree due to aggregation leads to a decrease in solubility for entropy reasons and as a result to a spontaneous ejection of the solvent.

Both the salt multiplets and clusters have a finite lifetime comparable to the diffusion time. On differential sorption, when the solvent is absorbed in small portions, the aggregates have enough time to be destroyed under the influence of swelling pressure. This disruption of aggregation leads to a decrease in cross-linking density and as result to an increase in solubility. Thus two relaxation processes are present, oppositely directed and with comparable rates.

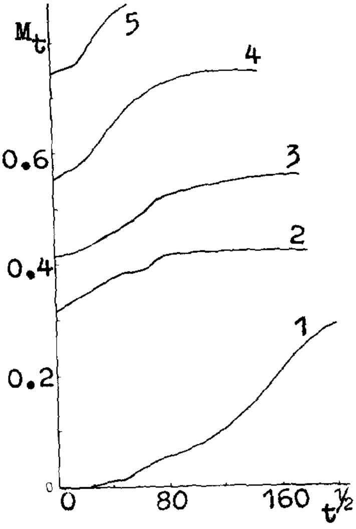

Fig. 1

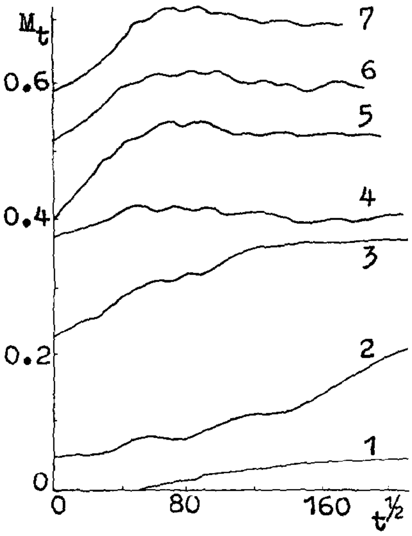

Fig. 2,a

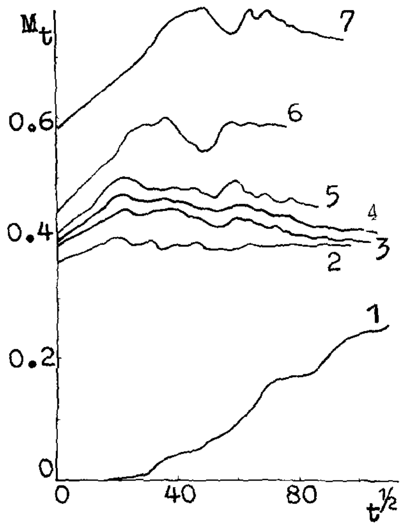

Fig. 2,b

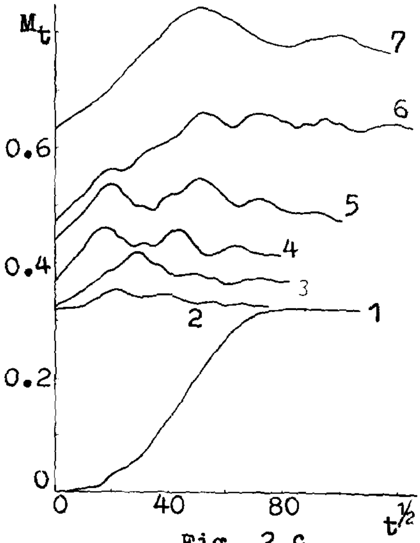

Fig. 2,c

Fig.1: M_t (weight of sorbed toluene in grams of toluene per grams of dry polymer) vs. $t^{1/2}$ (time in sec) for toluene sorption by St-3.8AA at 20°C. ΔP (toluene vapor relative pressure interval): 0-0.72(1), 0.72-0.75(2), 0.75-0.80(3), 0.80-0.83(4), 0.83-0.86(5). Fig.2: M_t vs. $t^{1/2}$ for toluene sorption by St-3.8NaA over range temperatures: 20(a), 25(b), 35°C(c); ΔP: 0-0.72(1), 0.72-0.75(2), 0.75-0.80(3), 0.80-0.83 (4), 0.83-0.86(5), 0.86-0.90(6), 0.90-0.93(7).

This interpretation is confirmed by high values of the exponent m in the phenomenological dependence of the amount of the absorbed solvent M_t on time t:

$$M_t = k \cdot t^m \qquad (1)$$

k being the kinetic constant, which correspond to oscillating parts of sorption kinetic curves (TABLE 1).

The occurrence of the oscillating regime during the swelling of the fluctuating network can be interpreted with the aid of the following theoretical considerations. The state of the network is determined by solvent concentration n and the number of crosslinks per unit volume S; when the deviation from equilibrium is small, the rate of concentration change is proportional to the deviation from the equilibrium concentration at a given crosslinking density

$$\frac{dn}{dt} = -\lambda[n - n_o'(S)]$$

where t is the time, λ is the kinetic constant characterizing the swelling process and $n_o'(S)$ is the solvent concentration corresponding to equilibrium swelling at a given crosslinking density S (not necessarily coinciding with the crosslinking density S_o at complete equilibration).

If the crosslinking density changes during sorption, the solvent concentration varies as follows:

$$n_o'(S) = n_o^o(S_o) - k_1(S - S_o) \qquad (2)$$

where $n_o^o(S_o)$ is the equilibrium concentration of the solvent at $S = S_o$, i.e. when complete equilibrium is attained and k_1 is a dimensionless proportionality coefficient.

When the deviation from equilibrium is small, then using a linear expansion of Eq. (2) and assuming that the rate of changes in crosslinking density is proportional to the deviation from the equilibrium degree of swelling we obtain

$$\left.\begin{aligned} \frac{dn}{dt} &= -\lambda\left[n - n_o^o(S_o)\right] - \lambda k_1(S - S_o) \\ \frac{dS}{dt} &= k_2[n - n_o^o(S_o)] \end{aligned}\right\} \qquad (3)$$

where k_2 is the relaxation parameter characterizing the crosslinking rate. Solving the system of Eqs.(3) one obtains an equation

$$\frac{d^2n}{dt^2} + \lambda\frac{dn}{dt} + \lambda k_1 k_2[n - n_o^o(S_o)] = 0 \qquad (4)$$

the solution of which describes the attenuating oscillating process with respect to n (at k_1 and $k_2 > 0$) (Fig. 3).

Table 1: The Effect of Temperature and Toluene Activity on the Exponent m in the Eq. $M_t = k\cdot t^m$ (for St-3.8NaA), $\Delta t^{1/2}$-time interval, $(sec)^{1/2}$.

ΔP	20°		25°		30°		35°	
	$\Delta t^{1/2}$	m	$\Delta t^{1/2}$	m	$\Delta t^{1/2}$	m	$\Delta t^{1/2}$	m
0.72-0.75	25-50	0.6	0-10	0.5	0-18	0.5	0-7	0.5
	80-110	1.2	10-18	0.8	18-29	1.8	7-18	0.9
	115-125	0	20-26	0.9	30-34	0.8	21-31	0.8
	130-170	0.7	26-31	0.8	34-37	0.9	31-41	0.7
			31-35	1.5	37-60	0.6	41-49	1.2
			59-66	1.3			49-55	1.5
0.75-0.80	0-18	0.5	0.14	0.5	0-19	0.5	0-18	0.6
	30-50	1.4	14-21	0.6	40-43	3.0	21-27	0.9
	62-70	1.2	23-27	0.7	44-48	3.2	29-44	1.5
	88-100	1.4	27-33	0.6	48-51	2.3	52-60	1.3
			47-53	1.3	58-67	6.2	60-71	0.8
			54-59	2.4	67-70	3.0	72-82	0.7
0.80-0.83	0-20	0.5	0-15	0.5	0-13	0.5	0-6	0.5
	20-48	0.9	11-20	0.8	13-27	0.6	6-13	0.7
	60-70	1.3	22-28	1.4	31-33	0.9	19-23	1.2
	150-160	1.2	30-35	0.6	40-52	1.5	34-41	1.1
	185-220	1.3	42-52	0.8	52-62	3.9	45-53	2.2
	235-255	1.5	52-62	1.3	70-78	6.4	54-60	4.9
			77-78	1.6	83-88	0.7	64-75	2.2
0.83-0.86	0-20	0.5	0-10	0.5	0-17	0.5	0-19	0.6
	20-30	1.1	10-17	0.7	17-27	0.7	20-28	1.3
	35-45	1.4	26-32	0.6	30-48	2.6	40-50	1.4
	50-63	1.3	47-53	0.8	48-51	12.0	52-65	1.4
	120-130	1.9	53-58	1.4	55-62	4.9	65-70	2.5
	148-162	1.5	60-63	0.9	69-77	1.6		
0.86-0.90	0-10	0.5	0-18	0.5	0-12	0.5	0-10	0.5
	10-35	1.0	18-24	1.2	12-20	1.7	10-17	0.8
	50-60	1.2	36-44	0.5	35-42	0.5	23-30	0.7
			45-49	0.7	50-54	2.5	40-50	0.7
			49-55	3.0	54-58	1.5	54-61	1.0
					63-71	1.4	61-67	1.2
0.90-0.93	o-16	0.5	0-24	0.6	0-13	0.6	0-12	0.5
	16-45	0.8	24-37	0.7	13-21	0.8	12-20	0.7
	55-65	1.2	50-57	0.7	22-27	0.9	55-80	0.8
	120-130	1.4	57-63	2.3	31-43	0.4	80-95	0.7
			64-66	4.4	51-56	0.5		
					58-69	1.8		

The aggregation process leads to a phase decomposition which is observed visually as a sharp increase in the film turbidity during sorption. Since during concentration fluctuations the cross-linking changes continuously the phase diagram of the gel also change continuously in ternary coordinates temperature - composition - cross-linking degree (DUSEK 1968, TANAKA 1979). This probably also contributes to the observed unusually sorption kinetics.

When the temperature is increased up to 30°C, the oscillating amplitude (as the exponent m in Eq.1) increases and attains a maximum value at this temperature. At the same temperature the solubility of toluene in the copolymers with salt groups investigated in this study also attains a maximum value (TABLE 2).

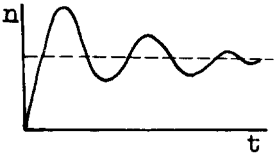

Fig.3:Solvent concentration vs.time curve calculated from Eq. (4)

It should be noted that the positions of maxima on all the curves of differential kinetics and those of the inflection points on the integral curves (Fig. 4) with respect to the time axis are of the same order for all copolymers containing 3.8 mole % of acid groups neutralized above 20% (LYUBIMOVA 1984) and independent of the increment of toluene concentration (Fig.5) and temperature. For styrene-(acrylic acid, 8.0 mole %, 50% neutralization degree) copolymer (St-8.0AA-50Na) the maxima are shifted towards long times (Fig.6) and are substantially less intensive due to a lower mobility of polymer chains as compared with St-3.8NaA.

Table 2: The Effect of Temperature, Sorption Kinetics and Ionomer Composition on the Toluene Equilibrium Concentration (in g/g) at the Relative Pressure 0.93.

Sorption kinetic	20°			25°	30°	35°	40°
	Neutralization degree of St-3.8AA						
	50%	75%	100%	100%	100%	100%	100%
differential	0.74	0.72	0.69	0.73	0.80	0.76	-
integral	0.62	0.60	0.57	0.65	0.75	0.62	0.55

The ionomers investigated exhibit also another feature. The equilibrium amount of absorbed toluene depends on the type of sorption, i.e. on integral sorption the salt copolymers absorb a substantially lower amount of toluene than on differential sorption (TABLE 2). The infrared spectra of the copolymers investigated were recorded before and after differential and integral sorption (to record the copolymer spectra after sorption the solvent was removed from the films by very rapid desorption). It is known (MACKNIGHT 1968) that the differences in ionomer morphology are due to different degrees of aggregation of their salt groups: these systems can form either salt multiplets (containing up to eight salt groups) or clusters (aggregates of salt multiplets). It has been established (ANDREEVA 1975) that different degrees of aggregation are distinctly revealed in the IR-spectra of the ionomers. Asymmetrical stretching vibrations of the COO^- anion are represented by two bands rather than by

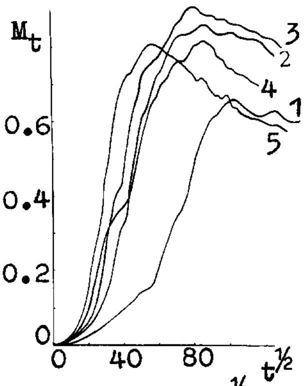

Fig.4: M_t vs. $t^{1/2}$ for toluene sorption by St-3.8NaA at constant Δ P (0-0.93) over range of temperatures: 20 (1), 25 (2), 30 (3), 35 (4) and 40°C (5)

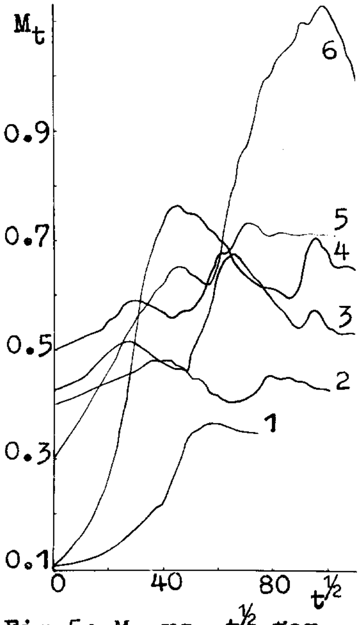

Fig.5: M_t vs. $t^{1/2}$ for toluene sorption by St-3.8NaA at 30°C. Δ P: 0.62-0.75(1), 0.80-0.83(2), 0.62-0.86(3), 0.62-0.88 (4), 0.86-0.90(5), 0.83-0.93(6).

a single one. One of these bands (ν_{as} = 1550 cm^{-1}) is due to the absorption of the COO^- groups of salt multiplets and the other one(ν_{as} =1565 cm^{-1}) is assigned to the absorption of the COO^- groups of salt clusters. Fig. 7 shows the IR-spectra of the initial film of the styrene-sodium acrylate copolymer and of the same sample after integral sorption at 20°C. It can be seen that during integral sorption the degree and type of aggregation change from multiplets (before sorption) to clusters (after integral sorption). During differential sorption the degree of aggregation does not increase (IR-spectra do not change after sorption). In the case of integral sorption the diffusion time is shorter than the lifetime of multiplets and in this case relatively large associates (clusters) can form, which are insoluble in toluene at low temperatures. The thermodynamic trend of the system

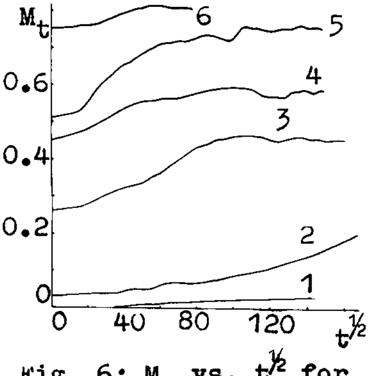

Fig. 6: M_t vs. $t^{1/2}$ for toluene sorption by St-8.0AA-50Na at 25°C. Δ P: 0-0.73(1), 0.73-0.80(2), 0.80-0.86(3), 0.86-0.91(4), 0.87-0.96(5), 0.96-0.98(6).

to formation of large clusters is realized on increase of the molecular energy (kT) up to such a value the activation energetic barrier is overdone. The formation of clusters during integral sorption leads to an increase in crosslinking density and/or to an increase in the functionality of nodes and hence to a decrease in the equilibrium degree of swelling. The structure formed on integral sorption can be destroyed by heating of the film above the glass transition temperature of the dry polymer or by the introduction of a solvent dissolving salt associates such as THF. This solvent is known to solvate sodium. In THF the network of salt associates is absent and the mentioned above anomalies are no more observed in this solvent (LYUBIMOVA 1984).

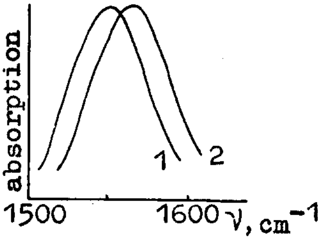

Fig.7: The absorption bands of assymmetrical stretching vibration of COO^- groups in St-3.8NaA; 1 - dry film (before sorption), 2 - the same film after toluene sorption at 20°C and Δ P: 0-0.93. The treatment of spectra same as in ref. ANDREEVA 1975.

Hence, we have probably for the first time observed an autooscillating sorption regime and proposed a more or less plausible molecular interpretation of this phenomenon.

Acknowledgements

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References

ANDREEVA, E.D. et al.: Vysokomol. Soed. B17, 773 (1975)
BOLOTNIKOVA, L.S. et al.: Kolloid. J. (Russian) 36, 203 (1974)
DUSEK, K. and PATTERSON,D.:J.Polym. Sci. A2, 6, 1209 (1968)
EISENBERG, A. and KING, M.: Ion-Containing Polymers, v. 2, Stein, R.S., Ed., Acad. Press, New York, 1977
JOANNY, J.F.: Polymer 21, 71 (1980)
LYUBIMOVA, V.A., FRENKEL, S.: Acta Polymerica 35, No. 2 (1984)(in press)
MACKHIGHT, W.L.: J. Phys. Chem. 72, 1122 (1968)
ODANI, H. et al.: Bull. Chem. Soc. Japan 34, 571 (1961)
TANAKA, T.: Polymer 20, 1404 (1979)

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