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NOTE

WATER VAPOR SORPTION BY THE POLYELECTROLYTE COMPLEX OF POLY (ACRYLIC ACID) AND POLY (4-VINYLN-ETHYLPYRIDINIUM BROMIDE)

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INTRODUCTION

A great number of studies of polyelectrolyte complexes have been carried out by various investigators; most of them concentrated on the reaction between oppositely charged polyelectrolytes [1-3]. The structure and properties of the resultant complexes have been investigated to a lesser extent, and the understanding of this new class of polymer materials is still insufficient. Thus, we have been investigating the sorption of water vapor by the complexes and the morphological changes caused by this sorption [4, 5].

The present paper deals with the equilibrium sorption of water vapor in stoichiometric and nonstoichiometric complexes of poly(acrylic acid) and poly(4-vinyl-*N*-ethylpyridinium bromide). These complexes consist of loosely crosslinked networks but have a different ionic character [5].

EXPERIMENTAL

Poly(acrylic acid) (PAA) was commercially obtained. Poly(4-vinyl-*N*-ethylpyridinium bromide) (PVPyEtBr) was prepared by the reaction of poly(4-vinylpyridine) with ethyl bromide in nitromethane at 50°C.

Films of the stoichiometric and nonstoichiometric complexes were prepared by solvent casting from solution in 1:1 water:formic acid. The 1/1 complex is stoichiometric, while the 1/2 complex contains 1 mol poly(acrylic acid) to 2 mol poly(4-vinyl-*N*-ethylpyridinium bromide).

The details of sorption apparatus and sorption experiments have been described elsewhere [4, 5].

RESULTS AND DISCUSSION

Figure 1 gives the water sorption isotherms for the PAA/PVPyEtBr complex at 30°C and, for comparison, for the complex of poly(acrylic acid)/poly(4-vinylpyridine) (PAA/PVPy)[6]. The difference between the PAA/PVPy curve and the 1/1 curve corresponds just to the change of polymer components from 0.5 mol VPy to 0.5 mol VPyEtBr. The difference between the 1/1 curve and the 1/2 curve corresponds to the conversion of $0.5 \times 1/3$ mol

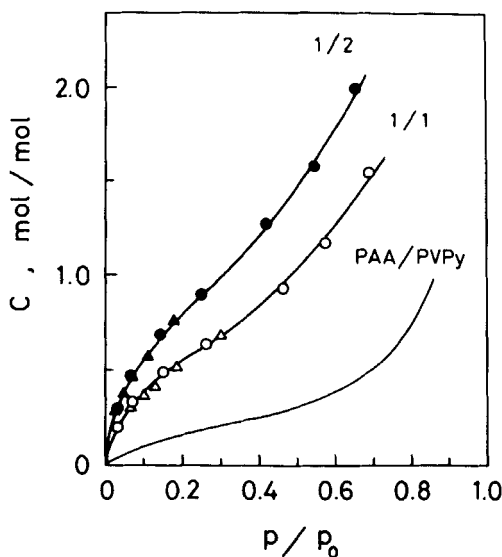


FIG. 1. Sorption isotherms of water in the 1/1 complex, the 1/2 complex, and the PAA/PVPy complex at 30°C. (○, ●): Data from integral sorption experiments. (△, ▲): Data from successive differential sorptions. C is mol H_2O sorbed per mol structural unit; p/p_0 is relative vapor pressure.

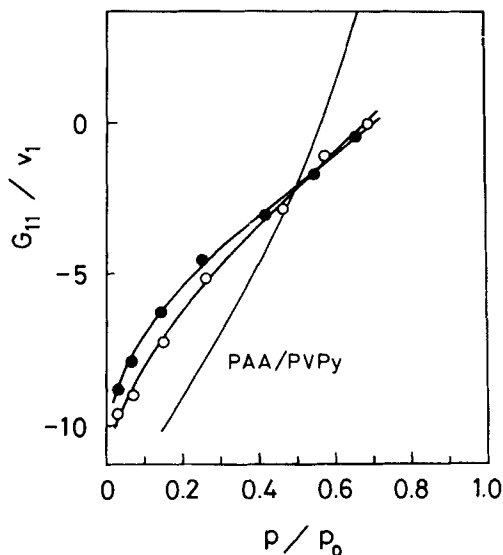


FIG. 2. Cluster function G_{11}/ν_1 as a function of relative vapor pressure. (○): 1/1 Complex. (●): 1/2 Complex.

AA to $0.5 \times 1/3$ mol VPyEtBr. The PAA and PVPy polymers are not much ionized because they are weak polyelectrolytes. In contrast, PVPyEtBr is a strong polyelectrolyte, and hence its ionic character is high.

The sorption of ionic networks can be described in terms of the charges on the polymers and the elastic reaction of the networks [7]. The charges increase the amount of water incorporated, while the elastic reaction tends to suppress the penetration of water. As mentioned above, the PAA/PVPyEtBr complexes consist of a loosely crosslinked network, as do the PAA/PVPy complexes [4]. Consequently, the elastic reaction does not play an important part in the water sorption of these complexes.

Sorption is also affected by the morphology of polymer materials. All these complexes are glassy in the dry state and undergo very similar structural changes during moisture sorption [4, 5]. The differences in sorption, therefore, must be ascribed to the ionic character of the complexes.

Figure 2 shows the cluster function G_{11}/ν_1 calculated from the sorption isotherms [8]. Values higher than -1 indicate a tendency toward clustering of sorbate molecules, while those below -1 show sorbate molecules isolated from each other by the polymer medium. As can be seen from Fig. 2, G_{11}/ν_1

TABLE 1. Differential Heat of Sorption as a Function of the Water Content

H ₂ O sorbed, mol/mol	$-\Delta\bar{H}$, kcal/mol ^a				
	0.4	0.6	0.8	1.0	1.2
1/1 Complex	2.0	1.4	1.1	0.7	—
1/2 Complex	2.1	1.7	1.3	1.1	0.9

^aCalculated from isotherms for 15 and 30°C.

takes on large negative values for all of these complexes, suggesting specific polymer sites-water interactions in the low vapor-pressure region. The G_{11}/ν_1 values for the PAA/PVPy complex increase to highly positive values, indicating clustering in the high vapor-pressure region; e.g., $G_{11}/\nu_1 = 10$ at $p/p_0 = 0.8$. On the other hand, the values for the 1/1 and 1/2 complexes are near zero at $p/p_0 = 0.7$; i.e., there is no tendency for water in the complexes to cluster.

Opacity is observed when the films of the PAA/PVPyEtBr complexes are immersed in water; the opacity is related to the clustering [9]. Thus, the water sorbed in the 1/1 and 1/2 complexes can be dispersed homogeneously in the networks if there is less than about 1.2 mol/mol. The lack of a clustering tendency for the PAA/PVPyEtBr complexes is attributed to their ionic character.

Table 1 shows that the sorption process is accompanied by the evolution of heat but that the magnitude of this effect diminishes as the concentration of water increases. The effect for the 1/2 complex, which is highly ionic, appears to continue to higher concentrations. The $\Delta\bar{H}$ values are rather small compared to those for viscose rayon and high-tenacity rayon, which have three hydroxyl groups in a structural unit [10].

The ionic character of the complexes was not reflected in successive differential sorptions, while it affected integral sorptions [4, 5]. The ionic character appears to affect equilibrium sorptions significantly but not the sorption rate processes.

REFERENCES

- [1] A. B. Zezin and V. B. Rogacheva, in *Advances in Polymer Science* (Z. A. Rogovin, ed.), Wiley, New York, 1974, p. 1.
- [2] E. A. Bekturov and L. A. Bimendina, *Adv. Polym. Sci.*, **41**, 99 (1981).
- [3] E. Tsuchida and K. Abe, *Ibid.*, **45**, 1 (1982).

- [4] Y. Hirai and T. Nakajima, *J. Appl. Polym. Sci.*, **35**, 1325 (1988).
- [5] Y. Hirai and T. Nakajima, *J. Macromol. Sci.—Phys.*, **B27**, 359 (1988).
- [6] Y. Hirai and T. Nakajima, *The 1987 International Congress on Membranes and Membrane Processes, Tokyo, June 1987, Abstracts*, p. 566.
- [7] P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1975, p. 584.
- [8] B. H. Zimm and J. L. Lundberg, *J. Phys. Chem.*, **60**, 425 (1956).
- [9] J. A. Barrie, in *Diffusion in Polymers* (J. Crank and G. S. Park, eds.), Academic, London, 1968, p. 271.
- [10] R. Jeffries, *J. Text. Inst.*, **51**, T339 (1969).

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