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THERMODYNAMIC PROPERTIES OF AQUEOUS SOLUTIONS OF MACROMOLECULAR COMPOUNDS

II. EFFECT OF DEGREE OF ACETYLATION OF POLY(VINYL ALCOHOL) ON THE PROPERTIES OF ITS AQUEOUS SOLUTIONS

A. A. MASIMOV*

Azerbaydzhan State University, Baku (U.S.S.R.)

B. Yu. ZASLAVSKY

Institute of Elementoorganic Compounds, Academy of Sciences of the U.S.S.R., Moscow 117813 (U.S.S.R.)

A. A. GASANOV

Azerbaydzhan State University, Baku (U.S.S.R.)

and

Yu. A. DAVIDOVICH and S. V. ROGOZHIN

Institute of Elementoorganic Compounds, Academy of Sciences of the U.S.S.R., Moscow 117813 (U.S.S.R.)

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SUMMARY

 Partitioning of a homologous series of DNP-amino acids with aliphatic side-chains in *n*-octanol–aqueous polymer solution and in *n*-octanol–water as a reference system was studied. The effect of poly(vinyl alcohol)s of various molecular weights and of various degrees of acetylation on partitioning of the above solutes was examined. The results obtained were used to calculate the relative hydrophobicity of the aqueous polymer solution and the relative hydration power of water in the solution.

INTRODUCTION

 It has been shown previously[1,2] that examination of the partitioning of a homologous series of solutes with different aliphatic chain lengths in water–organic solvent and in aqueous polymer solution–organic solvent two-phase systems makes it possible to calculate the relative hydrophobicity of the aqueous polymer solution and the relative hydration power of water in the solution. It has been shown particularly[1–3] that the above characteristics of the aqueous polymer solution depend on the chemical nature of the polymer.
 In this study, we have attempted to elucidate the relationship between the ability of poly(vinyl alcohol) (PVA) to modify the relative hydrophobic character and the relative hydration power of water in the aqueous polymer solution at pH 7.4 and the degree of acetylation of the polymer.

EXPERIMENTAL

Materials

Poly(vinyl acetate) was obtained from Minchimprom (U.S.S.R.). The polymer was converted into the alcohol according to Beresniewicz[4]. The percentages of acetate groups in the PVA samples obtained were determined as described in ref. 5, and were 1% (PVA-I), 6% (PVA-II), 12% (PVA-III) and 18% (PVA-IV). The PVA samples were fractionated by precipitation from water (solvent) with methanol (non-solvent). The molecular weights of the fractions of PVA with different degrees of acetylation were determined using equilibrium centrifugation in a thin-layer technique as described elsewhere[6].

Sodium salts of dinitrophenylated glycine, alanine, norvaline, norleucine and 2-amino-*n*-octanoic acid were prepared as described previously[7]. 1-Octanol and other chemicals and salts were of analytical-reagent grade and were used without further purification.

Methods

Two-phase systems were prepared by mixing 1–2 ml of octanol with an equal volume of a polymer solution containing buffer, sodium chloride, PVA and 2,4-dinitrophenyl (DNP)-amino acid at the concentrations desired. The concentrations of sodium phosphate buffer (pH 7.4) and sodium chloride in the aqueous phase were adjusted to 0.01 and 0.15 M, respectively. The mixture was mixed with a Vortex mixer, incubated at 25°C for 30–45 min, and centrifuged for 20–30 min at 1200 g to speed up phase settling. Aliquots of both phases were then taken with a pipette and analysed for DNP-amino acid concentration by measuring the absorbance at 360 nm (aqueous phase) and 350 nm (octanol phase) after appropriate dilution with water (or octanol) against a correspondingly diluted blank.

The absence of the polymer from the octanol phase was checked in separate experiments by refractive index measurements of the octanol phase.

Partition coefficients, P, defined as the ratio of the solute concentration in the octanol phase to that in the aqueous phase, were measured for each DNP-amino acid over approximately 10-fold concentration ranges and were found to be independent of the solute concentration in the phase systems. The partition coefficient for each solute was determined as the mean of 3–5 measurements on three dilutions from each partition experiment carried out 3–4 times in a given two-phase system.

The intrinsic viscosity, $[\eta]_0$, in water at 25 ± 0.1°C was determined for each fraction of PVA-I, -II, -III and -IV with an Ubbelohde dilution viscosimeter.

A Beckman analytical ultracentrifuge, Model E, was used for centrifugation experiments.

RESULTS

The relationships observed between the intrinsic viscosity of the aqueous solutions of the different PVA fractions and their molecular weights, M_w, are shown in Fig. 1. The relationships established fit the Mark–Houwink equations as follows:

$$[\eta]_0 = 1.64 \cdot 10^{-3} M_w^{0.56} \quad \text{(PVA-I, 1\% of acetate groups)} \qquad (1)$$
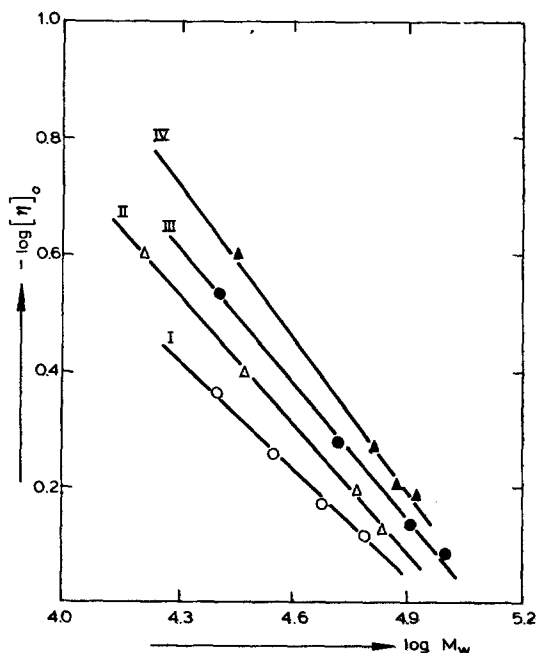
Fig. 1. Intrinsic viscosity of PVA with different degrees of acetylation in water at 25°C as a function of molecular weight. Degree of acetylation: I, 1%; II, 6%; III, 12%; IV, 18%.

$$[\eta]_0 = 3.51 \cdot 10^{-4} M_w^{0.69} \quad \text{(PVA-II, 6\% of acetate groups)} \qquad (2)$$

$$[\eta]_0 = 5.94 \cdot 10^{-5} M_w^{0.83} \quad \text{(PVA-III, 12\% of acetate groups)} \qquad (3)$$

$$[\eta]_0 = 9.88 \cdot 10^{-6} M_w^{0.98} \quad \text{(PVA-IV, 18\% of acetate groups)} \qquad (4)$$

All the relationships are valid for molecular weights from $17 \cdot 10^3$ to $100 \cdot 10^3$, which may be the reason for the apparent disagreement between the results obtained here and those reported by Beresniewicz[4].

To determine the thermodynamic characteristics of PVA aqueous solutions, the approach used previously[1–3] was applied. This approach is based on the existance of a linear relationship between the logarithm of the partition coefficient and the number of CH_2 and CH_3 groups in the aliphatic chain of the solute being partitioned:

$$\ln P = C + En \qquad (5)$$

where n is the equivalent number of CH_2 and CH_3 groups in the aliphatic chain of the solute (the amino acid side-chain in this instance)[8], C is the increment of $\ln P$ per ionopolar fragment of the molecule of the solute (that of DNP-glycine in this instance) and E represents the average $\ln P$ increment per CH_2 group. It is clear that E is related to the free energy of transfer of a CH_2 group from one to the other phase of a given two-phase system (ΔG^{CH_2}) according to the equation $\Delta G^{CH_2} = -RTE$, where R is the gas constant and T is the absolute temperature. The ΔG^{CH_2} value

specific for *n*-octanol–0.15 *M* sodium chloride in 0.01 *M* sodium phosphate buffer (pH 7.4) is known[1-3] to be 618 cal/mole of CH_2. Hence, it is possible to calculate the free energy of transfer of a CH_2 group between the phases of the hypothetical two-phase buffer–polymer solution system, Δg^{CH_2}. The Δg^{CH_2} values determined are plotted as a function of the PVA concentration in Fig. 2. It should be noted that Δg^{CH_2} appears to be independent of the molecular weight of a given PVA sample in the M_w range examined.

The *C* values are plotted in Fig. 3 as a function of PVA concentration.

DISCUSSION

It should be noted that the coefficients K_r and α_r in the Mark–Houwink viscosity equation $[\eta]_0 = K_r M^{\alpha_r}$ as given in eqns. 1–4 appear to depend on the percentage of acetate groups in PVA. The relationships observed appear to be described by

$$K_r = 2.176 \cdot 10^{-3}(0.74075)^N \ (r^2 = 0.999) \tag{6}$$

and

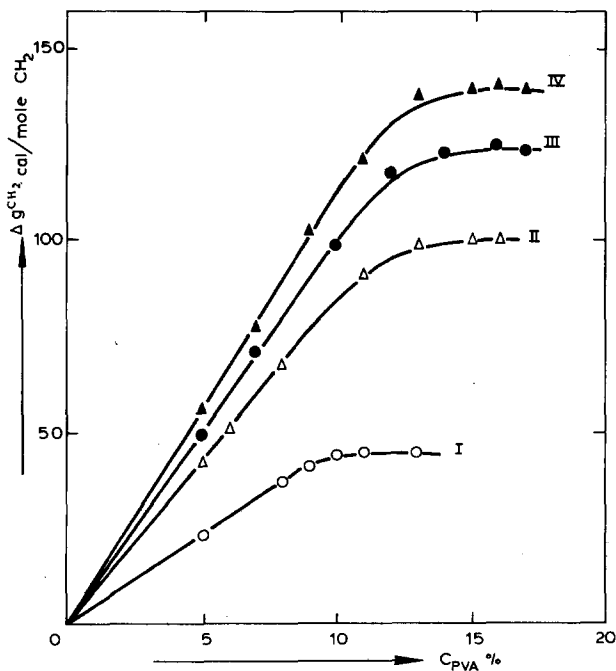$$\alpha_r = 0.5379 + 0.0245 \ N \ (r^2 = 0.999) \tag{7}$$

Fig. 2. Free energy of hypothetical transfer of a CH_2 group from 0.15 *M* sodium chloride in 0.01 *M* sodium phosphate buffer (pH 7.4) to the same salt solution containing PVA (Δg^{CH_2}) as a function of the polymer concentration (c_{PVA}). Numbers as in Fig. 1.
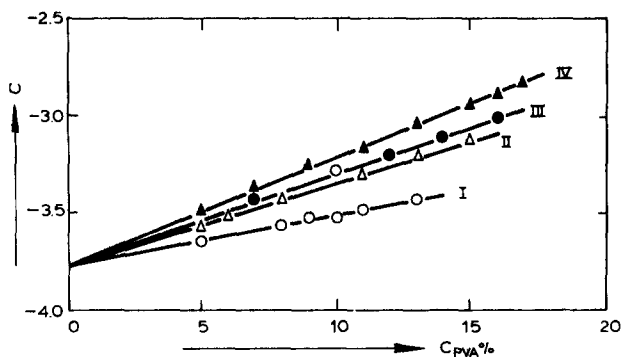
Fig. 3. Parameter C as a function of the concentration of PVA in the aqueous salt solution as in Fig. 2. Numbers as in Fig. 1.

where K_r and α_r are the coefficients indicated above, N is the percentage of acetate groups in PVA (varied from 1% to 18%) and r^2 is the correlation coefficient.

The observed dependence of both K_r and α_r seems to indicate that the percentage of acetate groups in PVA may affect the relative intensity of the polymer–water interactions. This conclusion appears to be supported by the results considered below.

It should be noted that the data in Figs 2 and 3 indicate that the molecular weight of PVA, in contrast to the degree of acetylation, does not influence the effect of PVA concentration on the relative hydrophobicity of the aqueous solution of the polymer (expressed in terms of Δg^{CH_2}) and on the relative hydration power of water in the solution (measured in terms of C)[9].

It can be seen from Fig. 2 that the relative hydrophobicity of the polymer solution attains the limit, $\delta(\Delta g^{CH_2})$, specific for the given degree of acetylation of the polymer. The $\delta(\Delta g^{CH_2})$ value appears to depend on the degree of acetylation of PVA but not on the molecular weight of the polymer in the M_w range examined.

The relationship between $\delta(\Delta g^{CH_2})$ and the degree of acetylation of PVA is plotted in Fig. 4 in linear and logarithmic coordinates. It follows that the relationship observed is described by

$$\delta(\Delta g^{CH_2}) = 46.074 N^{0.398} \quad (r^2 = 0.996) \tag{8}$$

where N is the degree of acetylation of PVA (varied from 1% to 18%).

The effect of a PVA with a given degree of acetylation on C in the PVA concentration range used is described by

$$C = -3.776 + \alpha c_{PVA} \tag{9}$$

where c is the concentration of the polymer (in weight-%); α specifies the concentration effect of PVA on the relative hydration power of water in relation to the α-carboxyl group of DNP-amino acid[9,10] in the presence of 0.15 M sodium chloride in 0.01 M sodium phosphate buffer (pH 7.4).

It seems reasonable that the degree of acetylation of PVA influences the effect
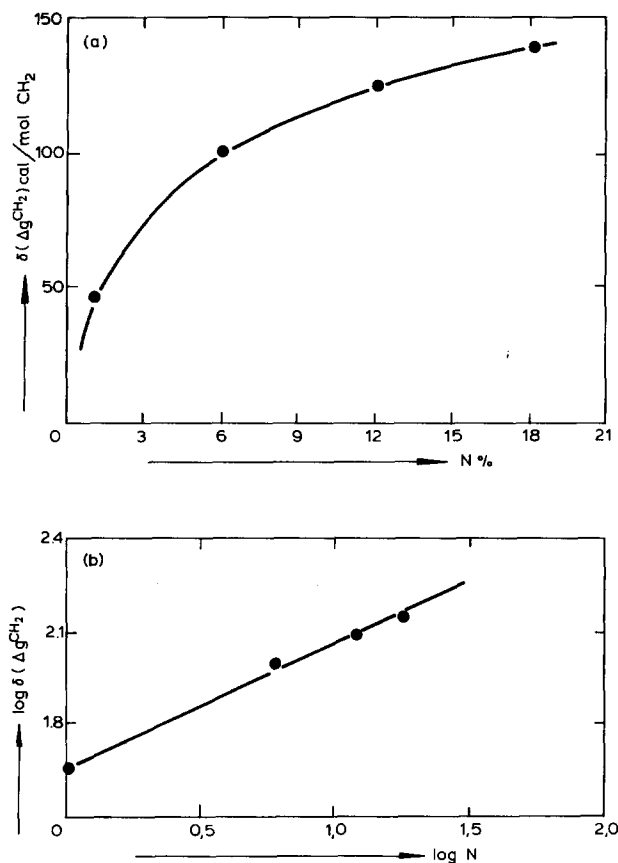
Fig. 4. Parameter $\delta(\Delta g^{CH_2})$ as a function of the degree of acetylation (N) of PVA in (a) linear and (b) logarithmic coordinates.

of the polymer on the thermodynamic properties of the aqueous polymer solution under examination. It was unexpected, however, to find the lack of an influence of the molecular weight of the polymer on the $\delta(\Delta g^{CH_2})$ and C values. As a working hypothesis, it seems possible to suggest that the effects under consideration result from the direct interactions of the groups in the polymer with the aqueous environment. The lack of an influence of the molecular weight of the polymer on these interactions may be due to the fixed number of groups capable of participating in the water–macromolecule interactions and not engaged in the intramolecular interactions. If that is the case, and if the ratio of hydroxyl and acetate moieties of the above type in the PVA macromolecule is constant in the M_w range examined, this ratio can be considered as the factor governing the effects of PVA on the thermodynamic properties of the aqueous polymer solution. It is possible that an influence of the molecular weight of PVA on the polymer's effects under consideration might be observed if the M_w range is extended.

REFERENCES

1 B. Yu. Zaslavsky, A. A. Masimov, L. M. Miheeva, S. V. Rogozhin and D. P. Hassaev, *Dokl. Akad. Nauk SSSR*, 261 (1981) 669.
2 N. K. Shcherbukhina, B. Yu. Zaslavsky, V. D. Shcherbukhin, D. P. Hasaev and A. A. Masimov, *Prikl. Biokhim. Mikrobiol.*, 18 (1982) 548.
3 A. A. Masimov, B. Yu. Zaslavsky, A. A. Gasanov and S. V. Rogozhin, *J. Chromatogr.*, 284 (1984) 337.
4 A. Beresniewicz, *J. Polym. Sci.*, 39 (1959) 63.
5 V. D. Besuglyi (Editor), *Analis Polymernyh Plastmass*, Khimiya, Moscow, 1965, p. 450.
6 C. H. Emes, in D. Rickwood (Editor), *Centrifugation: a Practical Approach*, Information Retrieval Ltd., London, 1980, p. 173.
7 B. Yu. Zaslavsky, N. M. Mestechkina, L. M. Miheeva and S. V. Rogozhin, *J. Chromatogr.*, 240 (1982) 21.
8 B. Yu. Zaslavsky, L. M. Miheeva, N. M. Mestechkina and S. V. Rogozhin, *J. Chromatogr.*, 253 (1982) 139.
9 B. Yu. Zaslavsky, L. M. Miheeva, N. M. Mestechkina and S. V. Rogozhin, *J. Chromatogr.*, 253 (1982) 149.
10 B. Yu. Zaslavsky, N. M. Mestechkina, L. M. Miheeva and S. V. Rogozhin, *J. Chromatogr.*, 256 (1983) 49.