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Cooperativity between various types of polar solute–solvent interactions in aqueous media

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ABSTRACT

Partition coefficients of seven low molecular weight compounds were measured in multiple aqueous two-phase systems (ATPSs) formed by pairs of different polymers. The ionic composition of each ATPS was varied to include 0.01 M sodium phosphate buffer (NaPB), pH 7.4 and 0.1 M Na₂SO₄, 0.15 M NaCl, and 0.15 M NaClO₄ all in 0.01 M NaPB, pH 7.4. The differences between the solvent features of the coexisting phases in all the ATPSs were estimated from partitioning of a homologous series of dinitrophenylated-amino acids and by the solvatochromic method. The solute-specific coefficients for the compounds examined were determined by the multiple linear regression analysis using the modified linear solvation energy relationship equation. It is established that the solute specific coefficients characterizing different types of the solute–water interactions (dipole–dipole, dipole–ion, and H-bonding) for a given solute change in the presence of different salt additives in the solute specific manner. It is also found that these characteristics are linearly interrelated. It is suggested that there is a cooperativity between various types of solute–water interactions governed by the solute structure.

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1. Introduction

It is well known that interactions of any substance from small organic compounds to biological macromolecules with aqueous environment are fundamentally important for their functions in vivo [1–3]. Our current understanding of aqueous solvent–solute interactions is very limited, however. Recognizing the difficulties in describing water and its interactions with solutes on the molecular level led us to propose a new approach to quantify and understand these interactions based on solute partitioning in aqueous two-phase systems (ATPS) [4–6].

Mixtures of aqueous solutions containing two or more polymers (e.g., dextran (Dex) and polyethylene glycol (PEG)) above certain concentrations commonly separate to form two or more coexisting aqueous phases [7–9]. Phase separation occurs in aqueous mixtures of different polymers, including proteins and nucleic acids [10]. The coexisting phases have different solvent properties governing unequal distribution of solutes between the phases, and

aqueous two-phase systems have been suggested as a model for compartmentalization in cells [9–12].

The distribution of a solute in an ATPS is characterized in terms of the partitioning coefficient, K , defined as the ratio of the concentration of the solute in the top phase to that in the bottom phase. The solute preferential distribution between the aqueous phases is mainly driven by different solute–solvent interactions [13–17] and it can be described as [4–6,15–17]:

$$\log K = S_s \Delta\pi + B_s \Delta\alpha + A_s \Delta\beta + C_s c \quad (1)$$

where K is the solute partition coefficient; $\Delta\pi$, $\Delta\alpha$, $\Delta\beta$ and c are the differences between the solvent properties of the top and bottom phases (solvent dipolarity/polarizability, hydrogen-bond donor acidity, hydrogen-bond acceptor basicity, and electrostatic interactions, respectively); S_s , B_s , A_s , and C_s are constants (solute specific coefficients) that describe the complementary interactions of the solute with the solvent media in the coexisting phases; the subscript s designates the solute.

It has been shown recently that the solute specific coefficients may be determined for a given compound (including proteins) by analysis of partition coefficients of the compound in multiple ATPS with different polymers but the same ionic composition

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[4–6,15–17]. Once $\Delta\pi$, $\Delta\alpha$, $\Delta\beta$, and c parameters in multiple ATPS are determined, the solute specific coefficients can be calculated by multiple linear regression analysis. It was also shown [6] that the partition coefficients of compounds with pre-determined solute specific coefficients in new ATPS with established solvent properties of the phases could be predicted with 90–95% accuracy.

Recent studies [18–22] suggested that the solute properties in aqueous solutions of different ionic composition are linearly inter-related according to:

$$SP_{\text{salt-1}} = k_1 + k_2 \times SP_{\text{salt-2}} + k_3 \times SP_{\text{salt-3}} \quad (2)$$

where SP is the solute property (logarithm of partition coefficient in octanol–water system [21], in polymer–polymer or polymer–salt ATPSs [18,20], solubility [19], optical rotation [23]); k_1 , k_2 , and k_3 are constant coefficients dependent on the solute property and salt compositions. These results led us to suggest [18–22] that different solutes respond to different ionic composition by changes in the solute–solvent interactions in the solute structure specific manner.

The purpose of the present work was to explore if and to what extent the intensities of the different types of solute–solvent interactions change in the presence of different salts in aqueous solution. For this end partitioning of several different organic compounds was examined in multiple ATPS in the presence of different salt additives.

2. Material and methods

2.1. Material

2.1.1. Polymers

Dextran 75 (lot 124339), weight-average molecular weight (Mw) \cong 75,000 was purchased from USB (Cleveland, OH, USA). Polyethylene glycol 8000 (lot BCBJ3787V), Mw = 8000; and polyethylene glycol 4000 (lot BCBD2874), Mw = 4000; were purchased from Sigma–Aldrich (St. Louis, MO, USA). Ucon 50-HB-5100 (lot SJ1955S3D2), Mw = 3930 was purchased from Dow-Chemical (Midland, MI, USA). Ficoll 70 (lot 10085600), Mw \cong 70 000 was purchased from GE Healthcare Biosciences AB (Uppsala, Sweden). All polymers were used without further purification.

2.1.2. Solvatochromic dyes

The solvatochromic probes 4-nitrophenol (reagent grade, >98%), and 4-nitroanisole (GC, >97%) were supplied by Sigma–Aldrich (St. Louis, MO, USA). Reichardt's carboxylated betaine dye was kindly provided by Professor C. Reichardt (Philipps University, Marburg, Germany).

2.1.3. Dinitrophenylated amino acids

Dinitrophenylated (DNP) amino acids – DNP–glycine, DNP–alanine, DNP–norvaline, DNP–norleucine, DNP–DL– α -amino-n-octanoic acid (DNP–AO), were purchased from Sigma–Aldrich (St. Louis, MO, USA).

2.1.4. Other chemicals

Phenol, benzyl alcohol, 2-phenylethanol, vanillin, 4-nitrophenyl- α -D-glucopyranoside, coumarin (2H-chromen-2-one) and methyl anthranilate were purchased from Sigma–Aldrich (St. Louis, MO, USA). All salts and other chemicals used were of analytical-reagent grade.

2.2. Methods

2.2.1. Solvatochromic studies

The ATPSs of the compositions shown below (see in Table 1) were prepared as previously described [4–6]. The phases were separated and used for solvatochromic analysis. The solvatochromic

Table 1
Polymer compositions^a of aqueous two-phase systems used for partitioning.

ATPS	Polymer 1	[Polymer 1], %wt.	Polymer 2	[Polymer 2], %wt.
S1	Dextran-70	12.90	Ficoll-70	18.10
S2	Dextran-70	13.67	PEG-4000	6.15
S3	Dextran-70	20.00	PEG-1000	13.57
S4	Dextran-70	16.23	PEG-600	16.87
S5	Dextran-70	12.39	Ucon	10.08
S6	Ficoll-70	22.99	PEG-10000	9.90
S7	Ficoll-70	24.67	PEG-8000	10.42
S8	Ficoll-70	23.08	PEG-6000	9.87
S9	Ficoll-70	19.12	Ucon	15.47
S10	PEG-8000	15.00	Ucon	29.97

^a Polymer 1, predominant polymer in the bottom phase; polymer 2, predominant polymer in the top phase; all concentrations of polymers are in %wt.

probes 4-nitroanisole, 4-nitrophenol and Reichardt's carboxylated betaine (the carboxylated form of the dye of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate) were used to measure the dipolarity/polarizability π^* , H-bond acceptor (HBA) basicity β , and H-bond donor (HBD) acidity α in both phases of each particular ATPS using the technique previously described [6].

The results of the solvatochromic studies were used to calculate π^* , β and α as described by Marcus [24]. (a) *Determination of the solvent dipolarity/polarizability π^**

π^* was determined from the wave number ($\nu_{(1)}$) of the longest wavelength absorption band of the 4-nitroanisole dye using the relationship:

$$\pi^* = 0.427(34.12 - \nu_{(1)}) \quad (3)$$

(b) *Determination of the solvent hydrogen-bond acceptor basicity β*

β values were determined from the wave number ($\nu_{(2)}$) of the longest wavelength absorption band of the 4-nitrophenol dye using the relationship:

$$\beta = 0.346(35.045 - \nu_{(2)}) - 0.57\pi^* \quad (4)$$

(c) *Determination of the solvent hydrogen-bond donor acidity α*

α values were determined from the longest wavelength absorption band of Reichardt's betaine dye using the relationship:

$$\alpha = 0.0649E_T(30) - 2.03 - 0.72\pi^* \quad (5)$$

The $E_T(30)$ values are based on the solvatochromic pyridinium N-phenolate betaine dye as probe, and are obtained directly from the wavelength (λ , nm) of the absorption band of the carboxylated form, as

$$E_T(30) = 1/0.932(28591/\lambda - 3.335) \quad (6)$$

Note that although the $E_T(30)$ parameter is described and defined here, it is used only as an intermediary to calculate the value of parameter α , hence the corresponding data for $E_T(30)$ are not given.

2.2.2. Partitioning

Solutions of each compound were prepared in water at concentrations of 1–5 mg/mL. Varied amounts (e.g., 0, 10, 20, 30, 40 and 50 μ L) of a given compound solution and the complementary amounts (e.g., 100, 90, 80, 70, 60 and 50 μ L) of water were added to a set of the same polymer/buffer/salt mixtures using a Multipette Xstream pipette (Eppendorf, Hamburg, Germany). Systems were vortexed and centrifuged (HIMAC, CT15RE, VWR, Radnor, Pennsylvania, USA) for 30 min at 3500 \times g at 23 $^\circ$ C to accelerate phase settling. Aliquots of 20–70 μ L from the upper and lower phases were withdrawn with a Multipette Xstream pipette in duplicate for analysis. Two aliquots from both phases were diluted with water up to 250 μ L in microplate wells. Following moderate shaking at room temperature (23 $^\circ$ C), a Synergy-2 UV–vis plate reader (Bio-Tek Instruments, Winooski, VT, US) was used to measure optical

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