742 *J. Chem. Eng. Data* **2003,** *48,* 742−745

Thermodynamic Functions for Transfer of Anthracene from Water to (Water + Alcohol) Mixtures at 298.15 K

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The solubilities of anthracene in $(1 - x)$water + x ethanol and $(1 - x)$water + (x)*tert*-butyl alcohol mixtures (mole fractions of alcohol, x, from 0 to 0.8) have been determined at four different temperatures, 298.15 K, 303.15 K, 308.15 K, and 313.15 K, respectively. From the solubility data, the values of thermodynamic functions for the transfer of anthracene from water to $(1 - x)$water + x ethanol or to $(1 - x)$water + (x)*tert*-butyl alcohol mixtures were derived. The results are discussed on the basis of the sign of transfer functions and in terms of solute−solvent interactions.

Introduction

The solubility data of hydrophobic substances in water by cosolvents is of both fundamental and practical importance to such disciplines as chemical engineering, pharmacology, toxicology, and environmental science. These data are also important for people to understand the characteristics and intermolecular/intramolecular interactions of solute−solvent in various different organic solvents/aqueous media. The solubility data and the thermodynamic properties including thermodynamic properties of transfer for a number of monoaromatics and their derivatives in organic/aqueous cosolvent mixtures, such as benzene, toluene, trimethylbenzene,[1,2] benzoic acid,[3−9] substituted benzoic acids,[7,10,11] phenylacetic acid,[8] and *p*-nitroaniline,[9,12] are widely reported in the literature and our previous works. The solubility data and the thermodynamic properties of transfer for hydrophobic polycyclic aromatic hydrocarbon compounds (PAHs) and their derivatives in organic/aqueous cosolvent mixtures have received little attention; especially, no such studies were conducted with respect to anthracene, although the solubilities of anthracene in some pure organic and binary and ternary organic solvents were reported,[13−16] and several solubility data in organic solvent/aqueous mixtures and thermodynamic properties of transfer in the water-rich region for naphthalene have been given in the literature.[17−21] In this paper, the solubility data of anthracene in $(1 - x)$water + (x)ethanol and $(1 - x)$water + (x)*tert*-butyl alcohol are studied at four different temperatures, 298.15 K, 303.15 K, 308.15 K, and 313.15 K, respectively. Standard thermodynamic functions of transfer of anthracene from water to $(1 - x)$water + (x)ethanol mixtures or to $(1 - x)$water + (x)*tert*-butyl alcohol mixtures at $T = 298.15$ K have been derived from solubility data. The results are discussed on the basis of the signs of the transfer functions and in terms of solute−solvent interactions.

Experimental Section

Materials. Alcohols used in this work were G. R. grade from Shanghai Chemical Reagent Corporation**,** China Medicine (Group), and were purified by standard methods of fractional distillation. The experimental values of the refractive index at 20 °C (n_D^{20}) were 1.3614 for ethanol and 1.3846 for *tert*-butyl alcohol, respectively, in good agreement with literature data.[22] Their purities, determined by GC (GC-Mass, HP Turbomass), were better than 99.7 mass % for ethanol and better than 99.6 mass % for *tert*-butyl alcohol. Anthracene (Merch Schuchardt, grade puriss. ≥ 99.5%) was recrystallized three times from absolute ethyl alcohol before use. It was dried at room temperature in a vacuum desiccator over blue gel. The purity of anthracene was determined with LC (LC-Mass, HP1100MSD). Twice-distilled water, treated with ion-exchange resin before being distilled, was used, and its conductivity was 1.18×10^{-4} S·m^{-1}.

Procedure. Saturated solutions of anthracene were obtained by following these procedures: 15 mL of mixed solvents of different composition and a slight excess amount of anthracene were added to glass tubes with ground mouths. Then, the tubes were sealed with a tight-fitting ground stopper and Parafilm, followed by equilibration in a DZK-2 thermostated water bath (specially made by Shanghai Jinghong Experimental Instrument Co. LTD) at (298.15, 303.15, 308.15, and 313.15) K, respectively. The fluctuation of temperature was ±0.05 K. The equilibrium time was about 12 days, depending on the temperature. The equilibrium time was selected on the basis of the condition test by the following procedures: When the time to achieve constant temperature was up to 3 to 4 days, the supernatant solution was analyzed by spectrophotometry, and the operation was repeated at intervals of 3 to 4 days until there was no change of absorbance beyond the experimental error. After the condition test, the sealed glass tubes were not opened before determination of solubilities in order to avoid a tiny effect of volume change of solvent on experimental results. The concentrations for the saturated solutions of anthracene in different mixed solvents were determined on a PCS UV spectrophotometer

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10.1021/je034016r CCC: $25.00

Table 1. Solubilities, S, of Anthracene in Water and (1−x)Water + (x)Alcohol Mixtures

	tert-butyl alcohol				ethanol			
	$S/10^{-6}$ mol·dm^{-3} at the following temperatures							
x	298.15 K	303.15 K	308.15 K	313.15 K	298.15 K	303.15 K	308.15 K	313.15 K
0	0.2834	0.3868	0.4860	0.5915	0.2834	0.3868	0.4860	0.5915
0.01	0.4377	0.5985	0.7764	0.9694	0.4350	0.5863	0.7737	0.9517
0.02	0.6455	0.8899	1.211	1.518	0.5404	0.7530	0.9550	1.227
0.03	0.8642	1.262	1.970	3.002	0.6255	0.8800	1.126	1.487
0.04	2.040	2.986	4.542	6.505	0.8247	1.142	1.475	1.898
0.045	3.501	5.127	7.561	9.791	0.9369	1.296	1.725	2.255
0.05	6.147	10.62	15.46	21.71	1.037	1.445	1.951	2.599
0.06	16.52	25.86	39.12	50.27	1.248	1.767	2.640	3.413
0.08	74.61	103.2	137.0	171.9	1.815	3.220	4.546	5.795
0.10	165.7	219.3	305.9	372.2	4.221	6.771	10.57	13.31
0.15	443.1	578.4	775.9	1028	25.35	39.19	50.12	57.54
0.20	751.4	979.4	1259	1764	73.40	125.7	172.7	195.9
0.30	1347	1777	2250	3070	375.8	660.7	851.1	966.1
0.40	1901	2536	3224	4174	951.7	1423	1702	2026
0.60	2891	3866	4943	6064	2729	3512	4126	5137
0.80	3577	4889	6354	7784	4984	5919	7073	8363

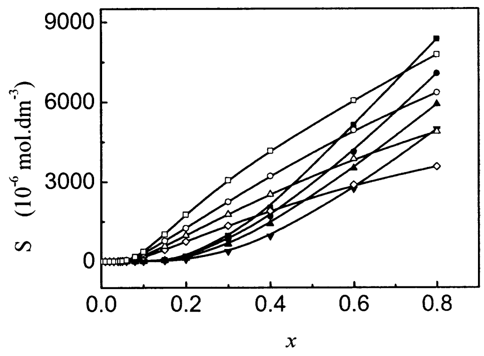

Figure 1. Solubilities of anthracene in (1 − x)water + (x)alcohol. Ethanol: ▼, 298.15 K; ▲, 303.15 K; ●, 308.15 K; ■, 313.15 K. *tert*-Butyl alcohol: ◇, 298.15 K; △, 303.15 K; ○, 308.15 K; □, 313.15 K.

(made by Shanghai Unico Co. LTD) after proper dilution with their respective solvents at 252 nm. The solubility measurements in all cases were repeated thrice independently for each solvent composition, and the precision was within ±0.3%. The solvents were prepared by mixing weighed quantities of water and ethanol or *tert*-butyl alcohol. Mass was weighed by using an FA1604A (made by General Shanghai Balance Instrument Factory, measurement range (0 to 160 g), precision ±0.0001 g) analytical balance. The mole fractions, x, of ethanol and *tert*-butyl alcohol in mixed solvents, respectively, were in the range 0 to 0.8. The uncertainties of $\Delta_{tr}G°$ and $\Delta_{tr}S°$ were estimated as better than 0.3% and 1.1%, respectively. At 298.15 K, the mole fraction solubility of anthracene in water was 0.51×10^{-8}. The value is somewhat lower than that of the literature,[23] 0.62×10^{-8}.

Results and Discussion

The solubilities of anthracene (S/mol·dm^{-3}) in water and various mixtures of (1 − x)water + (x)alcohol at (298.15, 303.15, 308.15, and 313.15) K were presented in Table 1 and Figure 1, respectively. As shown in Figure 1, the solubilities of anthracene in (1 − x)water + (x)alcohol mixtures increased with increasing x very slowly at low x and sharply at $x \geq 0.08$ and 0.055 for (water + ethanol) and (water + *tert*-butyl alcohol) mixtures, respectively. A similar result has been observed in (water + *tert*-butyl alcohol) mixtures for benzene, toluene, and trimethylbenzene in our previous papers.[1,2] The free energies of solutions ($\Delta_s G°$) of anthracene at different temperatures were calculated using eq 1

$$\Delta_s G° = -RT \ln S \tag{1}$$

The standard Gibbs free energies of transfer ($\Delta_{tr}G°$) for anthracene from medium 1 to medium 2 can be calculated by using eq 2

$$\Delta_{tr}G° = -RT \ln(S_2/S_1) \tag{2}$$

S_1 and S_2 in eq 2 are the saturated solubilities of solute in medium 1 and medium 2. The functional relationship of $\Delta_{tr}G°$ with the temperature T can be fitted to a nonlinear equation. The selected function is as follows:

$$\Delta_{tr}G° = a + bT + cT \ln T \tag{3}$$

where a, b, and c are constants independent of temperature, and their values vary with the composition and species and so forth of mixed solvents.

Equation 2 + eq 3 gave eq 4

$$-RT \ln S = a + bT + cT \ln T \tag{4}$$

then

$$\ln S = -a/(RT) - b/R - (c/R) \ln T \tag{5}$$

Equation 5 can be regressed by a method of least squares based on the experimental points of ln S versus T. Designing a program for eq 5 by using Origin 6.0, a, b, and c and the nonlinear correlation coefficient γ can be obtained.

The standard free energy of transfer of solute from water to (1 − x)water + (x)alcohol mixtures is then calculated using eq 6

$$\Delta_{tr}G° = \Delta_s G° - \Delta_w G° = (a_s - a_w) + (b_s - b_w)T + (c_s - c_w)T \ln T \tag{6}$$

The subscripts s and w refer to the solvent mixtures and water, respectively. According to the functional relationship of Gibbs−Helmholtz, the standard entropy of transfer ($\Delta S_{tr}°$) can be derived with eq 7

$$\Delta_{tr}S° = -\left(\frac{\partial \Delta_{tr}G°}{\partial T}\right)_P \tag{7}$$

Table 2. Thermodynamic Functions of Transfer for Anthracene from Water to (1−*x*)Water + *x* Alcohol Mixtures at 298.15 K, Coefficient *a*, *b*, and *c* and Correlation Coefficients γ of Regression Eq 5

alcohol	x	$\Delta_{tr}G°$ / kJ·mol^{-1}	$\Delta_{tr}S°$ / J·K^{-1}·mol^{-1}	a / J·mol^{-1}	b / J·mol^{-1}·K^{-1}	c / J·mol^{-1}·K^{-1}	γ
	0	0	0	50 6762.1	−10318.90	1534.790	0.9996
ethanol	0.01	−1.06	3.89	391 423.6	−7729.74	1147.628	0.9996
	0.02	−1.60	5.74	347 104.9	−6735.85	998.949	0.9985
	0.03	−1.96	7.18	258 085.5	−4736.08	700.154	0.9980
	0.04	−2.65	9.02	307 820.7	−5858.09	867.403	0.9994
	0.045	−2.96	11.79	226 207.0	−4015.95	591.945	0.9999
	0.05	−3.10	14.68	166 167.9	−2656.42	388.526	1.0000
	0.06	−3.68	51.31	372 285.2	−7087.59	1044.660	0.9966
	0.08	−4.60	167.82	1 513 345.4	−32078.09	4758.530	0.9991
	0.1	−6.70	143.15	1 084 182.6	−22624.17	3350.670	0.9975
	0.15	−11.14	121.41	1 373 191.0	−29341.13	4356.819	0.9993
	0.2	−13.78	201.46	1 902 558.8	−40835.48	6061.050	0.9999
	0.3	−17.82	216.74	2 033 634.0	−43784.55	6499.094	0.9973
	0.4	−20.13	112.20	1 050 406.2	−22344.65	3313.560	0.9929
	0.6	−22.74	26.72	131 047.0	−2237.82	324.228	0.9949
	0.8	−24.24	3.76	−6 647.1	691.41	−109.700	0.9999
tert-butyl alcohol	0.01	−1.08	4.86	390 925.7	−7713.26	1145.016	0.9999
	0.02	−2.04	20.93	406 613.1	−7995.46	1184.750	0.9993
	0.03	−2.76	34.99	−268 787.6	7240.50	−1092.189	0.9995
	0.04	−4.89	52.75	39 093.0	377.70	−70.175	0.9993
	0.045	−6.23	75.15	526 319.9	−10469.63	1546.067	0.9983
	0.05	−7.63	147.0	921 749.7	−18975.21	2805.284	0.9990
	0.06	−10.08	130.40	874 055.9	−18052.79	2670.040	0.9987
	0.08	−13.82	57.10	419 395.3	−8341.21	1230.973	0.9999
	0.1	−15.80	56.72	350 042.0	−6829.42	1005.308	0.9952
	0.15	−18.23	30.24	−113 826.1	3384.38	−515.723	0.9998
	0.2	−19.54	12.70	−380 336.3	9241.89	−1387.683	0.9987
	0.3	−20.99	27.28	−196 894.0	5171.24	−782.073	0.9982
	0.4	−21.85	48.83	102 619.5	−1452.89	203.732	0.9994
	0.6	−22.88	67.40	371 470.5	−7409.68	1090.351	1.0000
	0.8	−23.41	84.28	478 400.5	−9727.43	1433.888	0.9999

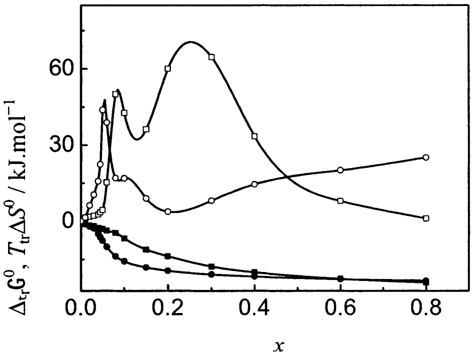

Figure 2. Variation of $\Delta_{tr}G°$ and $T_{tr}\Delta S°$ from water to (1 − *x*)water + (*x*)alcohol at 298.15 K. Ethanol: ■, $\Delta_{tr}G°$; □, $T_{tr}\Delta S°$. *tert*-Butyl alcohol: ●, $\Delta_{tr}G°$; ○, $T_{tr}\Delta S°$.

Combination of eq 6 with eq 7 gives eq 8

$$\Delta_{tr}S° = (b_w - b_s) + (c_w - c_s)(1 + \ln T) \tag{8}$$

The Standard enthalpy of transfer ($\Delta_{tr}H°$) can then be caculated by using eq 9 based on the thermodynamic relationship $\Delta H° = \Delta G° + T\Delta S°$

$$\Delta_{tr}H° = \Delta_{tr}G° + T\Delta_{tr}S° \tag{9}$$

The coefficients *a*, *b*, and *c* and the nonlinear correlation coefficient γ in eq 5 were given in Table 2. The data of nonlinear correlation coefficients γ showed that the nonlinear regressions of ln *S* versus *T* in various (water + alcohol) solvents were reliable, as reflected by the values of $\gamma > 0.99$.

Table 2 and Figure 2 show the variations of $\Delta_{tr}G°$ and $\Delta_{tr}S°$ of anthracene with *x* from water to (1 − *x*)water + (*x*)alcohol mixtures. The curves of $\Delta_{tr}G°$ of anthracene, on the whole, decreased along with the increase of *x*. This decrease indicates preferential solvation of anthracene by alcohols. $\Delta_{tr}S°$ can be used as a probe for elucidating the structure of mixed solvents.[3,5,6,9,12] It can be observed from Figure 2 that the curves of $T\Delta_{tr}S°$ showed a typical double peak curve in (1 − *x*)water + (*x*)ethanol mixtures and a complex change in (1 − *x*)water + (*x*)*tert*-butyl alcohol mixtures (somewhat of a double peak curve in the water-rich region at $x < 0.251$). All of these phenomena have not yet been observed in the literature. The first peak of $T\Delta_{tr}S°$ (at $x = 0.851$ and 0.055 in (water + ethanol) and (water + *tert*-butyl alcohol) mixtures, respectively) related to the formation and collapse of clathrate (or solvent cage)[1−3,5,12] in the water-rich region of (water + alcohol) systems. The second peak at $x = 0.251$ and 0.113 (shoulder peak) in (water + ethanol) and (water + *tert*-butyl alcohol) systems, respectively, most is probably because of the maximum rupture of H_2O−alcohol H-bonds after a low valley of $T\Delta_{tr}S°$ corresponding to the maximum formation of H-bonds between ethanol and water. In addition, it also can be observed from Figures 1 and 2 that the difference is much more obvious in the solubilities, $\Delta_{tr}G°$ and $\Delta_{tr}S°$ between (1 − *x*)water + *x* ethanol and (1 − *x*)water + (*x*)-*tert*-butyl alcohol systems. This can be attributed to the difference of intermolecular interactions in water alcohol systems.

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Received for review January 20, 2003. Accepted February 27, 2003. This project was supported by the China Postdoctoral Science Foundation ([2002]N0.11)

JE034016R