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THERMODYNAMICS OF SOLUTION OF NAPHTHALENE IN VARIOUS TETRAMETHYLUREA–WATER MIXTURES

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ABSTRACT

The temperature dependence of the solubilities of naphthalene in water and in various water–tetramethylurea mixtures up to 0.07 mole fraction of tetramethylurea have been determined. A plot of the free energy of solution of naphthalene vs. mole fraction of tetramethylurea (TMU) present in the solvent is linear. The heat of solution of naphthalene in water is positive and becomes more positive as the TMU concentration is increased. This heat term is more than overcome by a concomitant large increase in the entropy of solution, the net effect being to solubilize the hydrocarbon by the addition of tetramethylurea. The addition of tetramethylurea to the aqueous phase is more effective in solubilizing naphthalene at higher temperatures. This phenomenon is discussed in terms of hydrophobic interactions of tetramethylurea upon the hydrocarbon solubility by loss of water structure. Dispersal of an iceberg or clathrate structure probably makes a significant contribution.

INTRODUCTION

The solubility of naphthalene in mixed organic solvents has been of interest recently [1] in the study of the ability of the enzyme(s) cytochrome P-450 to bind to naphthalene. Since the solubility of naphthalene was found to vary in an interesting manner with tetramethylurea–water mixtures at a single temperature and there are no data available on the effects of the addition of tetramethylurea (TMU) upon the aqueous solubility of naphthalene, it was decided to study the temperature dependence of the solution process in order to ascertain the effects of added TMU upon the thermodynamics of solution for naphthalene. Such a study might shed some light upon the process of solubilization of a single but fairly bulky aromatic hydrophobic compound by the addition of TMU to the aqueous medium.

The purpose of the present work is to determine the dependence of the thermodynamics of solutions of naphthalene in solvent mixtures ranging from pure water to a water–TMU mixture containing 0.07 mole fraction of TMU. In this range, it has been found that the free energy of solution varies linearly with the mole fraction of TMU.

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EXPERIMENTAL

Materials

The naphthalene was obtained from Fisher Scientific Co. and was zone-refined. The TMU was obtained from Sigma Chemical Co. and was purified as described elsewhere [2]. The water was double-glass-distilled water.

Solutions

Saturated solutions were prepared by stirring the naphthalene in 25.00-cm^3 volumetric flasks filled to the mark with the appropriate solvent mixture. The solvent mixtures were prepared by weight.

Apparatus and procedure

The solubility apparatus and procedure were similar to that described in a previous paper [3]. The concentration of naphthalene was determined spectrophotometrically using a spectrophotometer. The reference cuvette contained solvent of the same composition as that of the sample. Readings were made at 275 nm. The absorbance of naphthalene was found to follow Beer's law in the region of the mixtures studied. Each experimental point is based on at least five measurements. The content of naphthalene was found with the aid of the Beer's law calibration graph and the concentration of the saturated solutions was calculated taking into account the dilution. The spectrophotometer used was the Pye Unicam SP 552.

RESULTS

Naphthalene solubilities

The experimental solubilities of naphthalene in water and in various TMU–water mixtures are given in Table 1. The solubility values (converted to mole fraction) were fitted to an equation of the form

$$\ln \mathrm{sol} = \frac{-\Delta H_0^0}{RT} + \frac{\Delta C_p}{R} \ln T + I \qquad (1)$$

as suggested by Everett and Wynne-Jones [4]. The thermodynamic parameters at 25°C are tabulated in Table 2. The standard partial molar free energy change ΔG^0 is written as

$$\Delta G^0 = -RT \ln \mathrm{sol} \qquad (2)$$

$$\Delta H^0 = \Delta H_0^0 + \Delta C_p T \qquad (3)$$

TABLE 1

Experimental solubilities of naphthalene in water and various TMU–water solutions

Mole fraction of TMU	T(K)	Solubility × 10^6 (mole fraction)
0	287.95	2.960
	293.95	3.581
	298.35	4.321
	303.25	5.664
	308.35	6.472
	313.45	7.994
0.01564	287.95	6.452
	293.95	8.555
	298.35	11.832
	303.25	16.005
	308.35	21.232
	313.45	26.215
0.03407	287.95	15.921
	293.95	24.120
	298.35	40.124
	303.25	55.521
	308.35	74.930
	313.45	103.050
0.05882	287.95	47.723
	293.95	82.320
	298.35	158.032
	303.25	236.241
	308.35	352.340
	313.45	526.340
0.07453	287.95	117.305
	293.95	225.523
	298.35	526.234
	303.25	783.484
	308.35	1230.523
	313.45	1930.358

TABLE 2

Thermodynamic parameters for the solution of naphthalene in water and in various TMU–water solutions at 298.4 K (25°C)

Mole fraction of TMU	0	0.01564	0.03407	0.05882	0.07453
ΔG^0 (kcal mol^{-1})	7.31	6.729	6.002	5.187	4.476
ΔH^0 (kcal mol^{-1})	7.11	10.20	13.61	18.12	21.55
ΔS^0 (e.u.)	−0.6	11.63	25.49	43.33	57.23

TABLE 3

Constants for eqn. (1) in text

Mole fraction of TMU	$-\frac{\Delta H_0^0}{R}$	$\frac{\Delta C_p}{R}$	I
0	2567.7272	20.42028	−137.29381
0.1564	207.55703	19.28033	−122.17817
0.03407	−6754.1956	3.65446	−8.9877
0.05882	−28927.1020	−60.46228	431.84352
0.07453	−39117.5300	−88.5669	626.81081

where ΔH^0 is the standard partial molar change in heat content at a specific temperature under consideration. The corresponding entropy change ΔS^0 was calculated in the usual way. It is clear from Table 2 that solubilization takes place by means of an entropic effect, the heat of solution becoming more positive as the TMU concentration is increased. The constants for eqn. (1) are found in Table 3.

DISCUSSION

Comparison with literature data

A comparison of our data with previous work is in order. The solubility of naphthalene in water at 25°C as determined from our measurements is 2.40×10^{-4} M. The values obtained by Bennett and Canady [5] and Andrews and Keefer [6] are 2.43×10^{-4} and 2.45×10^{-4} M, respectively, which are in excellent agreement with our value. On the other hand, the corresponding value for the heat of solution at 25°C of naphthalene in water is 7.11 kcal mol^{-1} as compared to 7.13 kcal mol^{-1} from the data of Bohon and Claussen [7].

Solubilities and thermodynamic functions of solution

Figure 1 shows a plot of ΔG^0 of solution of naphthalene vs. mole fraction of TMU present in the TMU–water solutions at 298.4 K; good linearity is observed. Figure 2 shows the natural logarithm of the solubility plotted against mole fraction of TMU present at three temperatures: 287.9, 298.4 and 313.5 K. The same type of linearity is also observed for the other temperatures. The slope of the line increases as the temperature increases, indicating that solubilization of naphthalene by TMU is much more effective at higher temperatures. A similar relationship was observed for the system naphthalene in ethanol [5].

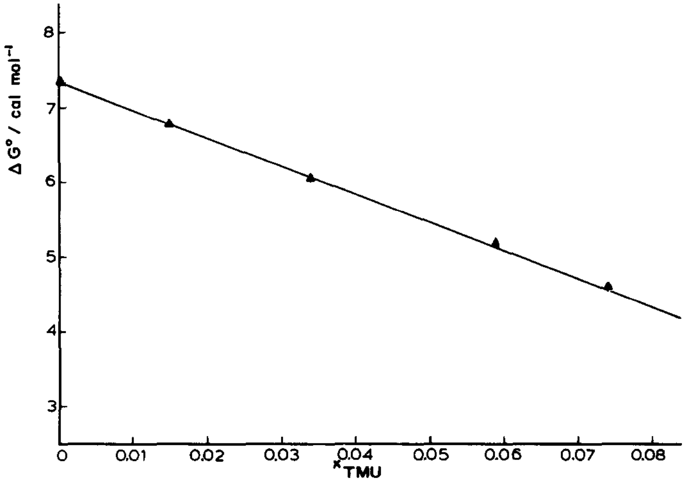

Fig. 1. Plot of the free energy of solution of naphthalene vs. mole fraction of TMU at 25°C.

Since it is generally observed that linear free energy relationships involve a compensation between the heat and entropy terms, Fig. 3 shows a plot of ΔH^0 vs. $T\Delta S^0$ for naphthalene at three temperatures, the good linearity

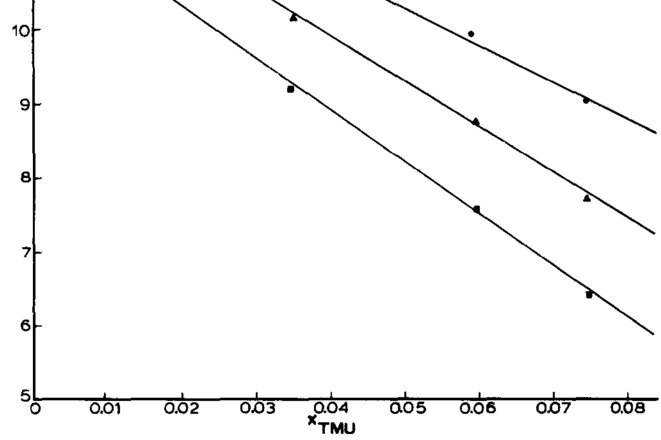

Fig. 2. Plot of the logarithm of the solubility of naphthalene vs. mole fraction of TMU at 15, 25 and 40°C. (●) 287 K, (▲) 298 K, (■) 313 K.

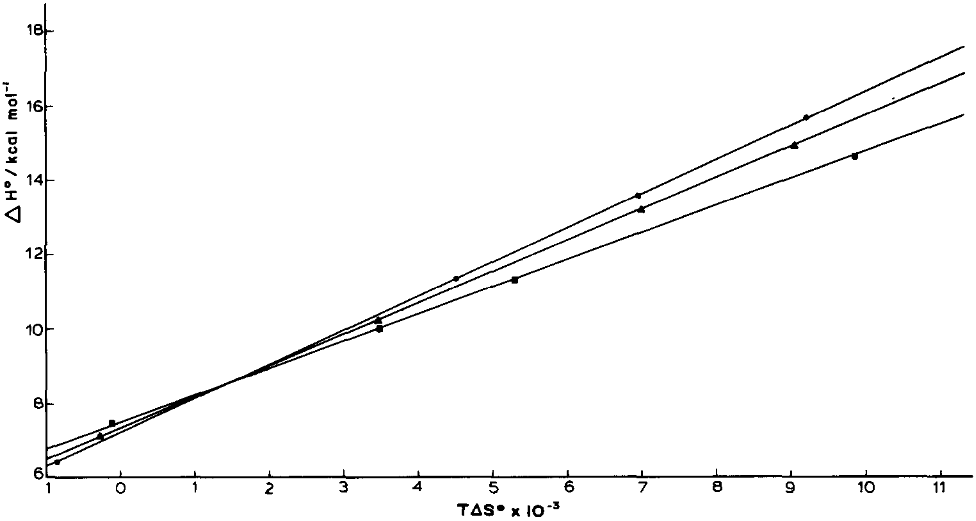

Fig. 3. ΔH^0 vs. $T\Delta S^0$ for the solution of naphthalene in water and various mole fractions of TMU at 15, 25 and 40°C. (●) 287 K, (▲) 298 K, (■) 313 K.

confirming this fact. Indeed, for naphthalene, ΔH^0 and ΔS^0 vs. mole fraction of TMU are themselves close to linear (Figs. 4 and 5). It seems as though heat–entropy compensation does take place in all cases studied thus far. Such heat–entropy compensations observed in various processes have been discussed in detail by Lumry and Rajender [8]. It is observed in Fig. 5, a plot of ΔS^0 vs. X_{TMU}, that all the lines pass through a common point at a

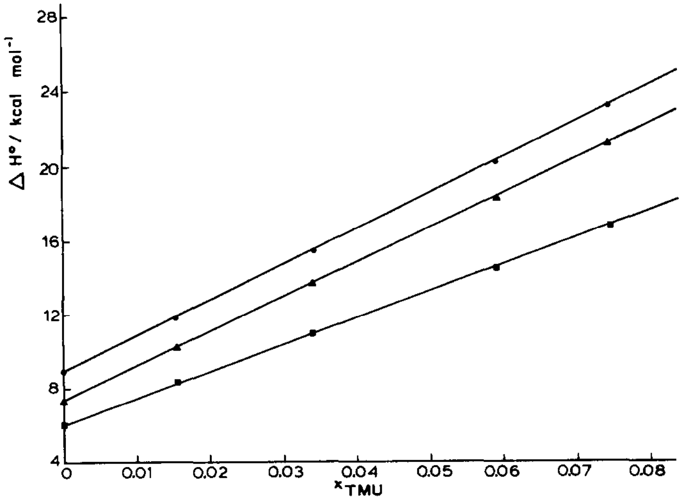

Fig. 4. ΔH^0 vs. mole fraction of TMU present for naphthalene. (●) 287 K, (▲) 298 K, (■) 313 K.

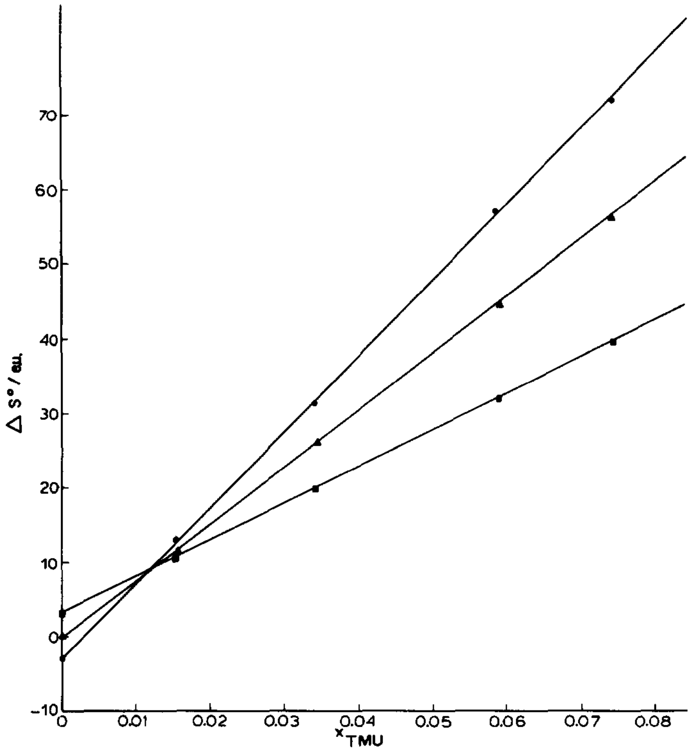

Fig. 5. ΔS^0 vs. mole fraction of TMU present for naphthalene. (●) 287 K, (▲) 298 K, (■) 313 K.

mole fraction of ~ 0.015. It seems as though at this point a structural phenomenon is operating.

It has been observed [2] that the addition of TMU increases the density of water with a maximum occurring at a mole fraction of ~ 0.2, which would infer an increase in water structure. Luttinghaus and Dirksen [9] have made the suggestion that TMU molecules fill voids in the water structure. Overall this would imply an increased structuring around the TMU molecules. With fewer voids available, more work must be done to form more voids in order to dissolve naphthalene molecules. This would explain an increase in ΔH^0 for the solution process with the addition of TMU.

The great over-balancing entropic effect may be due to the loss of water structure from the environs of both naphthalene and TMU molecules when hydrophobic interactions take place, the destruction of "iceberg" structure [10] possibly making a significant contribution.

For the present we feel that TMU exerts its influence upon hydrocarbon solubility by bringing about a decrease in water structure and the release of somewhat immobilized water molecules as the hydrophobic interaction between hydrocarbon and TMU takes place.

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