

THERMODYNAMIC FUNCTIONS FOR THE TRANSFER OF NAPHTHALENE FROM WATER TO MIXED AQUEOUS SOLVENTS AT 298.15 K

P. PEREZ-TEJEDA *, C. YANES and A. MAESTRE

Departamento de Química Física, Facultad de Farmacia, Universidad de Sevilla, 41012-Sevilla (Spain)

(Received 18 May 1989)

ABSTRACT

Values of free energies ΔG_t^\ominus , enthalpies ΔH_t^\ominus , and entropies ΔS_t^\ominus , of transfer of naphthalene from water to urea–water, acetonitrile–water, dimethylformamide–water and dimethylsulphoxide–water mixtures at 298.15 K in the water-rich region have been determined from solubility measurements at different temperatures. The cavity term from scaled particle theory has been used to explain qualitatively the experimental transfer free energies. We have also calculated molecular-pair interaction parameters in water for the four systems studied.

INTRODUCTION

In a previous paper [1] we studied thermodynamic transfer functions for non-ionized 1-naphthoic acid by measuring the temperature dependence of its relative solubilities in water and three aqueous mixed solvents (water + ethanol, water + *t*-butyl alcohol and water + dimethylsulphoxide). In the water-rich region, those transfer functions were interpreted by means of van der Waals interactions between the solute and the cosolvents. In order to eliminate the effects produced by the presence of the –COOH group on the amphiphilic 1-naphthoic acid molecule, we examined the transfer functions of naphthalene [2] from water to water + alcohols (MeOH, *n*-PrOH, *t*-BuOH and *n*-BuOH) with the aim of studying the influence of alkyl chain length of the alcohol on the wholly hydrophobic molecule.

In the present paper we continue the above work [2] with regard to determinations of thermodynamic transfer functions of naphthalene from water to various aqueous mixed solvents in the water-rich region. The cosolvents urea, acetonitrile (ACN), dimethylsulphoxide (DMSO) and

* Author to whom correspondence should be addressed c/o Profesor García González, Departamento de Química Física, Facultad de Farmacia, Universidad de Sevilla, s/n. 41012-Sevilla, Spain.

N,N-dimethylformamide (DMF) were chosen for their different extents of solvation in water. In this sense, urea and ACN are hydrophilic hydrated solutes while DMSO and DMF are weakly hydrophobic hydrated solutes [3,4]. From the transfer functions, solute–cosolvent molecular pair interaction parameters in water have been calculated.

EXPERIMENTAL

Reagents

Urea, ACN, DMF and DMSO (p.a., from Merck) were used without further purification. Naphthalene was Fluka (grade puriss., min. 99%) and was recrystallized from ethanol before use. Water was distilled twice using an all-glass apparatus. The solvents were prepared by mixing weighed quantities of water and each cosolvent.

Solubility measurements

The solubilities of naphthalene in water and the different water–cosolvent mixtures in equal steps of temperature ranging from 278.15 to 308.15 (± 0.05 K) were determined in the following manner. A weighed excess of naphthalene was added to 40 cm³ of water or mixed solvents in a Pyrex flask with a Teflon stopper and allowed to equilibrate at the working temperature for 50 min. The solutions were stirred at ca. 25 000 rpm for 8 min using a Virtis model 23 homogenizer. After equilibrium was reached, two or three aliquots of the same sample from each experiment were removed by filtering inside the thermostatted bath, and were diluted using an ethanol–water mixture (82.5%, v/v). The diluted samples were analysed spectrophotometrically in a Perkin–Elmer Lambda 5 spectrophotometer at 275.0 nm. At this wavelength the molar absorption coefficient of naphthalene is 5.56×10^3 dm³ mol⁻¹ cm⁻¹. Previously, we had checked that the water–cosolvent mixtures did not shift the above molar absorption coefficient of naphthalene. Using this method a solubility value of 2.63×10^{-4} mol dm⁻³ was obtained for naphthalene in water at 298.15 K, which agrees within experimental error with the findings of Bohon and Claussen [5] and Gordon and Thorne [6].

RESULTS AND DISCUSSION

The solubilities of naphthalene in water and in water + cosolvents (Table 1) were fitted by non-linear regression analysis to the expression

$$\lg S = A - B/T + C \ln T \quad (1)$$

TABLE 1

Solubilities (10^4 mol dm^{-3}) naphthalene in water and water-cosolvent mixtures at different temperatures.

$m_{\text{cosolvent}}$ (mol kg^{-1})	T (K)						
	278.15	283.15	288.15	293.15	298.15	303.15	308.15
Water	1.35	1.58	1.91	2.24	2.63	3.24	3.71
Water + urea							
0.8767	1.55	1.91	2.13	2.63	3.02	3.72	4.17
1.6257	1.79	2.09	2.57	3.02	3.39	4.27	5.13
3.0076	2.18	2.57	3.09	3.72	4.27	5.01	5.89
4.1028	2.63	3.09	3.63	4.47	4.90	6.17	7.41
5.3722	2.88	3.47	4.26	5.25	5.89	6.92	9.33
Water + ACN							
0.6465	1.26	1.62	2.19	2.82	2.95	3.98	5.12
1.4049	1.91	2.29	2.75	3.47	3.98	5.01	6.17
2.7077	2.82	3.80	5.12	5.62	6.92	8.32	9.33
4.3037	5.62	7.08	8.71	10.7	14.1	15.8	18.2
6.1142	12.9	15.1	16.6	22.4	30.9	32.4	36.3
Water + DMSO							
0.6556	1.62	2.14	2.63	3.24	3.55	4.68	5.62
1.3600	2.24	2.82	3.47	4.17	4.79	6.03	6.61
2.2120	3.02	3.80	4.90	5.75	6.76	8.51	10.5
2.9450	3.98	4.79	5.89	7.41	8.91	11.2	13.2
4.0890	5.25	6.61	8.32	10.0	12.3	14.8	17.8
Water + DMF							
0.8371	3.09	3.55	3.98	5.13	5.89	7.08	8.71
1.5621	5.01	6.03	7.24	8.91	10.5	12.9	15.8
2.4262	8.13	10.0	11.7	14.8	17.8	21.4	26.3
3.3996	13.8	16.2	19.5	24.0	28.8	34.7	42.7
4.5362	19.9	24.5	30.9	38.0	45.7	56.2	69.2

where S is the solubility in mol dm^{-3} , T is the temperature in K and A , B and C are adjustable parameters. The derived values of the standard transfer functions, ΔG_t^\ominus , ΔH_t^\ominus and ΔS_t^\ominus , were calculated from the equations

$$\Delta G_t^\ominus (\text{exp}) = -RT \ln \left(\frac{S_s}{S_w} \right) \left(\frac{\gamma_s}{\gamma_w} \right) \quad (2)$$

$$\Delta G_t^\ominus = (A'_s - A'_w)T + (B'_w - B'_s) + (C'_s - C'_w)T \ln T \quad (3)$$

$$\Delta H_t^\ominus = (B'_s - B'_w) + (C'_w - C'_s)T \quad (4)$$

$$\Delta S_t^\ominus = (A'_w - A'_s) + (C'_w - C'_s) + (C'_w - C'_s) \ln T \quad (5)$$

where the subscripts w and s represent water and water + cosolvent mixtures, respectively, $A' = -2.3RA$, $B' = 2.3RB$ and $C' = -2.3RC$. The values A , B and C in water and mixed solvents are given in Table 2, along with

TABLE 2

Coefficients and standard deviations of $\log S$ from eqn. (1) and thermodynamic functions for transfer of naphthalene from water to water-cosolvent mixtures at 298.15 K.

$m_{\text{cosolvent}}$ (mol kg ⁻¹)	A	B (K)	C	$s \times 10^3$	$-\Delta G_t^\ominus$ (kJ mol ⁻¹)	ΔH_t^\ominus (kJ mol ⁻¹)	ΔS_t^\ominus (JK ⁻¹ mol ⁻¹)
Water + urea							
0.8767	-23.766	167.87	3.6534	3.7	0.36 ± 0.05	-0.40 ± 0.08	-0.20 ± 0.05
1.6257	-88.833	-2634.4	13.435	3.8	0.71 ± 0.05	1.86 ± 0.08	8.3 ± 1.7
3.0076	1.7914	1281.0	-0.1510	1.5	1.19 ± 0.03	-0.82 ± 0.01	1.2 ± 0.3
4.1028	-110.19	-3598.4	16.644	3.9	1.63 ± 0.06	1.72 ± 0.09	10.9 ± 1.8
5.3722	14.128	1883.8	-1.9359	3.7	2.03 ± 0.06	0.57 ± 0.08	8.6 ± 1.6
Water + ACN							
0.6465	-23.443	562.48	3.8329	7.7	0.48 ± 0.10	8.35 ± 0.33	29.0 ± 7.0
1.4049	-116.28	-3698.6	17.637	2.3	1.07 ± 0.04	5.42 ± 0.03	21.6 ± 0.6
2.7077	234.37	11644	-34.833	6.3	2.42 ± 0.08	-0.34 ± 0.22	6.8 ± 4.6
4.3037	115.29	6441.0	-16.948	4.1	4.00 ± 0.06	1.95 ± 0.09	20.4 ± 1.9
6.1142	41.490	3120.9	-5.8958	12.7	5.74 ± 0.18	1.26 ± 0.89	24.7 ± 2.0
Water + DMSO							
0.6556	20.693	2326.4	-2.8620	6.4	0.91 ± 0.08	3.89 ± 0.22	15.5 ± 4.7
1.3600	97.639	5579.0	-14.433	3.6	1.54 ± 0.04	0.01 ± 0.07	5.0 ± 1.5
2.2120	-8.6077	1046.3	1.5734	4.1	2.41 ± 0.05	4.61 ± 0.09	23.3 ± 1.9
2.9450	-47.675	-660.09	7.4442	2.5	3.01 ± 0.03	5.37 ± 0.03	28.1 ± 0.7
4.0890	32.279	2827.7	-4.5116	1.1	3.80 ± 0.02	3.88 ± 0.01	25.8 ± 0.2
Water + DMF							
0.8371	-182.81	-6750.5	27.545	3.7	1.97 ± 0.06	3.48 ± 0.08	18.4 ± 1.6
1.5621	-97.123	-2914.7	14.809	2.2	3.44 ± 0.03	4.28 ± 0.03	25.8 ± 0.5
2.4262	-66.711	-1570.1	10.301	1.6	4.70 ± 0.03	3.75 ± 0.01	30.0 ± 0.3
3.3996	-87.885	-2544.4	13.481	1.7	5.90 ± 0.03	3.75 ± 0.01	32.4 ± 0.3
4.5362	-18.577	598.09	3.2029	0.4	7.08 ± 0.02	5.23 ± 0.01	41.4 ± 0.1
Water	-31.244	-143.56	4.7717	1.1	-	-	-

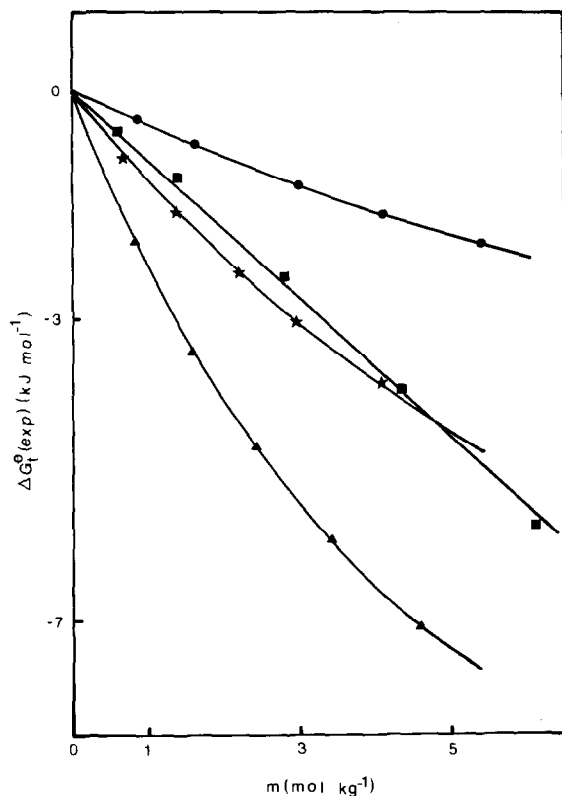


Fig. 1. Variation of $\Delta G_t^\ominus(\text{exp})$ in aqueous urea (●), ACN (■), DMSO (★) and DMF (▲) as a function of cosolvent molality m .

ΔG_t^\ominus , ΔH_t^\ominus and ΔS_t^\ominus at 298.15 K and their maximum uncertainties in terms of $\pm ts/N^{1/2}$ (95% confidence level), where t is from the Student t test, s is standard deviation and N is the number of experimental measurements. We have assumed that the ratio of the activity coefficients of naphthalene in the saturated solution is unity.

From Fig. 1 it can be observed that ΔG_t^\ominus decreases as the molalities of cosolvents increase. This fact indicates a preferential solvation of naphthalene by the cosolvents. The entropy term (Table 2) governs the sign of ΔG_t^\ominus for all water-cosolvent mixtures, excepting water + urea at 0.8767 mol kg⁻¹.

The transfer free energies may be considered as consisting of cavity and interaction terms

$$\Delta G_t^\ominus(\text{exp}) = \Delta G_t^\ominus(\text{cav}) + \Delta G_t^\ominus(\text{int}) \quad (6)$$

where $\Delta G_t^\ominus(\text{cav})$ is the difference in cavity formation energies in the reference solvent, water, and the aqueous solvent mixture. $\Delta G_t^\ominus(\text{int})$ is the difference of interaction energies of naphthalene with water and mixed solvent.

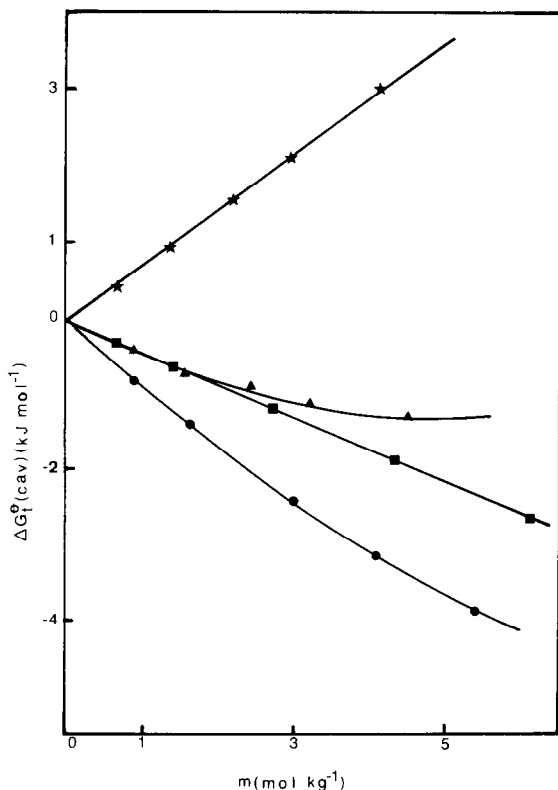


Fig. 2. Plots of $\Delta G_t^\ominus(\text{cav})$ as a function of cosolvent molality (m). ●, Urea; ■, ACN; ★, DMSO; and ▲, DMF.

We have computed $\Delta G_t^\ominus(\text{cav})$ values from the scaled particle theory (SPT) by following Lucas and Feillolay [7]. In order to calculate $\Delta G_t^\ominus(\text{cav})$ it was necessary to know the diameters of naphthalene, water and cosolvents, together with the density of water + cosolvent mixtures at each molality. The diameter of naphthalene was calculated from the molar volume [8], giving $\sigma = 7.35 \text{ \AA}$; the diameters of water, urea, ACN, DMF and DMSO were 2.75, 4.41, 4.12, 4.98 and 5.05 \AA , respectively [9–11]. The required densities for water + cosolvent mixtures were obtained from refs. 4 and 12–14. The $\Delta G_t^\ominus(\text{cav})$ values are shown in Fig. 2. The cavity term is favourable for the urea, ACN and DMF aqueous mixtures, and unfavourable for the water + DMSO mixture. It is known that the cavity term calculated from SPT may implicitly include some ‘structural’ aspects of the real solvents besides the solvent–solvent interaction involved [15,16]. In the water-rich region (as in our case) urea, ACN, DMSO and DMF modify the water structure in different ways. It has been suggested that urea [17,18] and ACN [19] reduce the three-dimensional water structure, DMF scarcely affects it [4] and DMSO enhances it [20,21]. In relation to water + DMSO mixtures, it has also been suggested that the properties of aqueous DMSO

are dominated by direct association interaction of water and DMSO at molar fractions of DMSO higher than 0.01 [22]. These considerations are in agreement with the calculated $\Delta G_t^\ominus(\text{cav})$ values.

On the other hand, $\Delta G_t^\ominus(\text{int})$ for a hydrophobic solute, like naphthalene, may be considered as the sum of two interaction terms: $\Delta G_t^\ominus(\text{int}) = \Delta G_t^\ominus(\text{van der Waals}) + \Delta G_t^\ominus(\text{hydrophobic})$. In the case of urea–water mixtures $\Delta G_t^\ominus(\text{int})$ will be unfavourable as expected from the high polarity of urea (the cavity term being the dominating factor for the sign of $\Delta G_t^\ominus(\text{exp})$). For the other mixtures, the van der Waals forces will contribute favourably, giving the sequence $\text{ACN} < \text{DMSO} \approx \text{DMF}$, since the diameters, polarizabilities [22], and dipole moments [19] follow the same order. The hydrophobic interaction term should increase favourably as the hydrophobic character of the cosolvent increases ($\text{ACN} < \text{DMSO} < \text{DMF}$) [4]. From Fig. 1, it can be seen that $\Delta G_t^\ominus(\text{exp})$ follows the sequence $\text{urea} < \text{ACN} < \text{DMSO} < \text{DMF}$, which could be explained by a balance between the cavity and the two interaction terms. For urea–water mixtures the cavity term is the dominating factor for the sign of $\Delta G_t^\ominus(\text{exp})$. In ACN + water mixtures, the van der Waals and cavity terms both contribute favourably. In the case of DMSO–water the two interaction terms outweigh the unfavourable cavity term, and for the DMF–water mixtures both interaction terms and cavity term are favourable.

In order to obtain a more direct representation of naphthalene behaviour in the mixtures studied, it is interesting to interpret the transfer functions in terms of solute–cosolvent interactions. By following the McMillan–Mayer approach [23], we have calculated molecular-pair interaction parameters of naphthalene–cosolvent ($f_{\text{N-C}}$, f representing any molecular-pair interaction parameter, i.e. the Cubbs free energy pair parameter g , the enthalpy pair parameter h or the entropic pair parameter Ts) in water, on the basis of the Gibbs free energies and enthalpies of transfer. The $Ts_{\text{N-C}}$ values were derived from $g_{\text{N-C}}$ and $h_{\text{N-C}}$. The $f_{\text{N-C}}$ values are given in Table 3.

The favourable decrease of $g_{\text{N-C}}$ from urea to DMF and the $h_{\text{N-C}}$ and $Ts_{\text{N-C}}$ values may be rationalized by taking the overlap co-sphere model of Desnoyers and co-workers [3]. From this model, the overlap between a

TABLE 3

Pair interaction parameters between naphthalene and cosolvents in water at 298.15 K.

Cosolvent	g_{NC} (J kg mol ⁻²)	h_{NC} (J kg mol ⁻²)	Ts_{NC} (J kg mol ⁻²)
Urea	-208	-298	-90
ACN	-367	-112	255
DMSO	-622	1763	2385
DMF	-1259	2423	3682

hydrophobic hydrated solute and hydrophilic or hydrophobic cosolvent will contribute positively to the entropic term. In the present case the hydrophilic character of cosolvents follows the order urea > ACN > DMSO > DMF; a scrutiny of Table 3 reveals that positive Ts_{N-C} values decrease and become negative as the hydrophilic character of the cosolvent increases. The sign of h_{N-C} is in accord with that of Ts_{N-C} ; while exothermic enthalpic terms are found for urea and ACN, these terms are endothermic for DMSO and DMF.

REFERENCES

- 1 M.C. Pérez-Camino, E. Sánchez, M. Balón and A. Maestre, *J. Chem. Soc., Faraday Trans. 1*, 81 (1985) 1555.
- 2 P. Pérez-Tejeda, C. Yanes and A. Maestre, *J. Chem. Thermodyn.*, submitted for publication.
- 3 C. Visser, G. Perron and J.E. Desnoyers, *J. Am. Chem. Soc.*, 99 (1977) 5894.
- 4 C. Visser, W.J.M. Heuvelsland, L.A. Dunn and G. Somsen, *J. Chem. Soc., Faraday Trans. 1*, 74 (1978) 1159.
- 5 R.L. Bohon and W.F. Claussen, *J. Am. Chem. Soc.*, 73 (1951) 571.
- 6 J.E. Gordon and R.L. Thorne, *J. Phys. Chem.*, 71 (1967) 4390.
- 7 M. Lucas and A. Feillolay, *Bull. Soc. Chim. Fr.*, 4 (1970) 1267.
- 8 W.E. May, S.P. Wasik and D.H. Freeman, *Anal. Chem.*, 50 (1970) 997.
- 9 R.A. Pierotti, *J. Phys. Chem.*, 69 (1965) 281.
- 10 N. Desrosiers and J.E. Desnoyers, *Can. J. Chem.*, 54 (1976) 3800.
- 11 C. Treiner, *Can. J. Chem.*, 55 (1977) 682.
- 12 International Critical Tables of Numerical Data Physics, Chemistry and Technology. McGraw-Hill, New York, 1928, p. 111.
- 13 A.V. Benedetti, M. Cilense and E.H. Friishio, *Ecl. Quim.*, 8 (1983) 33.
- 14 D.J. Pruet and L.K. Felken, *J. Chem. Eng. Data*, 30 (1985) 452.
- 15 M. Lucas, *J. Phys. Chem.*, 80 (1976) 3592.
- 16 P. Pérez-Tejeda, A. Maestre, M. Balón, J. Hidalgo, M. Muñoz and M. Sánchez, *J. Chem. Soc., Faraday Trans. 1*, 80 (1987) 1029.
- 17 J.H. Stern and J.D. Kulluk, *J. Phys. Chem.*, 73 (1969) 2795.
- 18 R.B. Cassel and R.H. Wood, *J. Phys. Chem.*, 78 (1974) 2460.
- 19 V. Zelano and P. Mirti, *Z. Phys. Chem., Neue Folge*, 138 (1983) 31.
- 20 F. Fusch and C.P. Hagan, *J. Phys. Chem.*, 77 (1973) 1797.
- 21 M.F. Fox and K.P. Whittingham, *J. Chem. Soc., Faraday Trans. 1*, 71 (1975) 1407.
- 22 J.B.F.N. Engberts, in: F. Franks (Ed.), *Water: A Comprehensive Treatise*, Vol. VI. Plenum, New York, 1978, Chap. 4.
- 23 W. McMillan and J. Mayer, *J. Chem. Phys.*, 13 (1945) 176.