

# The solubility of dodecane in water-amide mixtures

C. MCDONALD

*Department of Pharmacy, The University, Manchester 13, U.K.*

The solubility of dodecane has been determined in formamide, and in mixtures of water with formamide, *N*-methylformamide (NMF), and dimethylformamide (DMF) by a radiotracer method at 15°, 25° and 35°. The solubility of dodecane increases as the concentrations of the amides increase. The standard free energies ( $\Delta G^\circ$ ), partial enthalpies ( $\Delta H^\circ$ ), and standard entropies ( $\Delta S^\circ$ ), of solution of dodecane have been calculated for the various systems. Positive values of  $\Delta G^\circ$  and negative values of  $\Delta H^\circ$  and  $\Delta S^\circ$  decrease numerically as the concentrations of amides increase.

THE solubilities of hydrocarbons in water and in mixed aqueous solvents are of intrinsic interest. Solutions of hydrocarbons in such solvents also provide useful, but approximate, model systems for studying, for example, interactions between non-polar side chains of amino-acid residues in proteins, and the effects of non-polar portions of surfactants in micellization processes.

The solubility of dodecane in water-amide mixtures has been determined and the results are reported here.

## EXPERIMENTAL

### *Materials*

Dodecane (Fluka Chemicals, Purum grade) was used without further purification. Dodecane-1-<sup>14</sup>C (Mallinkrodt Nuclear) was used without further purification. Formamide (B.D.H.) was stored over calcium oxide and was fractionated under reduced pressure before use and gave  $n_{25}^D = 1.4467$  ( $n_{25}^D = 1.4468$  Timmermans & Hennaut, 1935).

*N*-Methylformamide (NMF) (Fluka Chemicals, Purum grade) was treated as for formamide and gave  $n_{25}^D = 1.4315$  ( $n_{19}^D = 1.4313$ , Davies & Thomas, 1956). Dimethylformamide (DMF) (B.D.H.) was treated as for formamide and gave  $n_{25}^D = 1.4271$  ( $n_{25}^D = 1.4269$ , Ruhoff & Reid, 1937).

### *Solubility measurements*

The mixed solvents were prepared by weight. For H<sub>2</sub>O-formamide systems dodecane-1-<sup>14</sup>C was diluted with 2 ml dodecane, and 0.5 ml aliquots of the resulting solution were transferred to separate solubility flasks where they were diluted to 2 ml with dodecane. Samples from these solutions were taken, added to 4 ml of Bray's solution (Bray, 1960) and their radioactivities, expressed as disintegrations per minute, were determined using an I.D.L. liquid scintillation counter, Type 6012.

For H<sub>2</sub>O-NMF and H<sub>2</sub>O-DMF systems dodecane-1-<sup>14</sup>C was diluted to 5 ml with dodecane and 1 ml aliquots transferred to solubility flasks, leaving sufficient of the original solution to determine its radioactivity. Twenty ml quantities of the appropriate solvents were added to each flask. Samples were removed by syringe from

the solubility flask through an aperture closed with a vaccine bottle cap, which was previously washed in the appropriate solvent. As the aperture was below the level of the solvent-hydrocarbon interface, disturbance of this interface and possible contamination of the sample, by undissolved hydrocarbon, was avoided. The flasks were immersed in a thermostat bath at the required temperature, after allowing for vapour-saturation of the space above the liquids, and were shaken gently for 12 h. Preliminary experiments using decane and formamide had shown that saturation solubility was reached after approximately 8 h of shaking, but 12 h was thought to be a reasonable time to allow for any between solvent variations. After shaking was completed 100  $\mu\text{l}$  samples were withdrawn from the flasks at regular intervals until no further change in solubility indicated that separation was complete. Solubilities were calculated from the ratios of radioactivities of hydrocarbon-saturated solvents to radioactivities of known quantities of the original dodecane-1- $^{14}\text{C}$ -dodecane solutions. Densities were determined using a 25 ml pycnometer.

## RESULTS AND DISCUSSION

The solubility of dodecane in the various solvents is shown in Table 1. It can be seen that at any one temperature, solubility increases as do the concentrations of non-aqueous solvents, and the values are much greater than the solubility of dodecane in water,  $8.9 \times 10^{-10}$  mol fraction (25°) (Franks, 1966). The solubility behaviour is obviously complex and may, to some extent, depend on interactions between water and the amides. Water is a highly structured liquid (Nemethy & Scheraga, 1962a) and irrespective of the type of structuring present in liquid water, the introduction of large quantities of non-aqueous solvents would be expected to have some effect on water and hence on its dissolving power. However, on the

Table 1. *The solubility of dodecane in water-amide mixtures\* and in formamide*

Solvent	Temperature °C $\pm$ 0.1	Solubility (mol fraction)
Formamide .. ..	15°	$3.6 \times 10^{-5} \pm 5\%$
	25°	$2.6 \times 10^{-5} \pm 4\%$
	35°	$2.3 \times 10^{-5} \pm 5\%$
Formamide 75% w/w (0.545 mol fraction) .. ..	15°	$5.9 \times 10^{-6} \pm 6\%$
	25°	$3.8 \times 10^{-6} \pm 7\%$
	35°	$2.9 \times 10^{-6} \pm 8\%$
Formamide 55% w/w (0.328 mol fraction) .. ..	15°	$2.0 \times 10^{-6} \pm 6\%$
	25°	$1.1 \times 10^{-6} \pm 6\%$
	35°	$9.5 \times 10^{-7} \pm 7\%$
NMF 50% w/w .. ..	15°	$6.8 \times 10^{-6} \pm 3\%$
	25°	$6.0 \times 10^{-6} \pm 5\%$
	35°	$7.3 \times 10^{-6} \pm 3\%$
NMF 25% w/w .. ..	15°	$3.4 \times 10^{-6} \pm 5\%$
	25°	$3.0 \times 10^{-6} \pm 3\%$
	35°	$2.9 \times 10^{-6} \pm 1\%$
DMF 60% w/w .. ..	15°	$1.4 \times 10^{-5} \pm 3\%$
	25°	$1.2 \times 10^{-5} \pm 2\%$
	35°	$1.6 \times 10^{-5} \pm 2\%$
DMF 30% w/w .. ..	15°	$4.2 \times 10^{-6} \pm 3\%$
	25°	$3.6 \times 10^{-6} \pm 3\%$
	35°	$3.4 \times 10^{-6} \pm 3\%$

\* The solubilities were measured in these particular solvent mixtures to help elucidate the micellization process of some non-ionic surfactants with dodecyl hydrocarbon chains in the same solvents.

available evidence it is difficult to decide how the various amides affect, and are affected by, water. It has been suggested (Fratiello, 1963), from nuclear magnetic resonance measurements, that the breakup in the co-operative structure of water is greater in the presence of DMF than in the presence of either formamide or NMF. Further reference to Table 1 shows that, on a mol fraction basis, DMF is most effective, and formamide least effective in increasing the solubility of dodecane, which may be consistent with DMF's ability to disrupt the structure of water more than the other amides. Also, empirically, on the basis of "like dissolving like" it would be expected that DMF, with two methyl groups, would have a greater affinity for dodecane than would formamide, which has no methyl groups.

The effects of the various amides on the solubility of dodecane may be explained more rationally from a consideration of the solubility parameters of the solvents and of the solute. As solubility parameters were initially derived (Hildebrand & Scott, 1964a) to describe solubility characteristics of non-polar molecules they may not be strictly applicable to the solvents considered here. It has been shown, however (Burrell, 1955), that apparent solubility parameters of polar liquids are useful for the approximate characterizations of the solution power of such liquids. The apparent solubility parameters of H<sub>2</sub>O, formamide, NMF and DMF are 23.4, 19.4, 16.1 and 12.2 respectively (Walker, 1952; Bauder & Gunthard, 1958; Hildebrand & Scott, 1964b) and the solubility parameter of dodecane interpolated from the data of Hildebrand & Scott (1964c) is approximately 8.0. The solubility parameter of a mixed solvent will be intermediate between those of the individual components and will depend on their concentrations, which are most conveniently expressed as either volume fractions or mol fractions (Burrell, 1955). For H<sub>2</sub>O-amide mixtures containing the same mol fractions of formamide, NMF or DMF, the H<sub>2</sub>O-DMF solvent would have the lowest and the H<sub>2</sub>O-formamide solvent the highest solubility parameter, while the solubility of dodecane would be expected to be greatest in the former solvent and least in the latter, with the H<sub>2</sub>O-NMF solvent occupying an intermediate position in terms of solubility parameter and solubility of dodecane. This is confirmed in Table 1.

It is interesting to note that for the systems studied the dielectric constants of the amides at 25° are 109.5, 182.4 and 36.7 for formamide, NMF and DMF respectively (Leader, 1951; Leader & Gormley, 1951). Thus solvents containing formamide or NMF and water would have higher dielectric constants than water (78.5, 25°), and those containing DMF would have dielectric constants less than that of water. In all cases, irrespective of the resultant dielectric constants of the solvents, addition of amides increases the solubility of dodecane.

### *Thermodynamics of solution*

In calculating the thermodynamics of solution the standard states are taken as unit mol fractions in pure liquid hydrocarbon and in solution, at a pressure of 1 atmosphere (Nemethy & Scheraga, 1962b). By the choice of these standard states the calculated free energies and entropies can be explained on the basis of interactions between solute and solvent molecules and any changes in solvent structuring caused by these interactions (Kauzmann, 1959). The standard free energies of solution  $\Delta G^\circ$  are calculated from the solubility values ( $\Delta G^\circ = -RT \ln X$ ,  $X =$  mol fraction solubility) and partial enthalpies of solution,  $\Delta H^\circ$ , from temperature variations of

solubility. The standard entropy of solution,  $\Delta S^\circ$ , is calculated by combining  $\Delta G^\circ$  and  $\Delta H^\circ$ , (Equation 1):

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \dots \dots \dots (1)$$

The thermodynamic parameters at 25° are shown in Table 2.

Table 2. *Thermodynamics of solution of dodecane in various solvents at 25°*

Solvent	$\Delta G^\circ$ kJ mol <sup>-1</sup>	$\Delta H^\circ$ kJ mol <sup>-1</sup>	$\Delta S^\circ$ J mol <sup>-1</sup> deg <sup>-1</sup>
Formamide .. ..	26.1	-20.1	-155
Formamide 75% w/w .. ..	30.9	-25.9	-193
Formamide 55% w/w .. ..	33.9	-33.5	-226
NMF 50% w/w .. ..	29.8	0	-100
NMF 25% w/w .. ..	31.5	-6.3	-126
DMF 60% w/w .. ..	28.0	0	-92
DMF 30% w/w .. ..	31.0	-8.4	-134

In the formamide and H<sub>2</sub>O-formamide systems it may be seen that favourable enthalpy values are outweighed by large negative entropies thus giving positive free energies of solution and hence low solubilities. As the concentrations of formamide increase, the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  decrease numerically. For the solution of non-electrolytes in water, negative enthalpies and entropies are generally considered to be due to an increase in the structuring of water in the vicinity of the solute molecule (Frank & Evans, 1945). It would appear, therefore, that the addition of formamide to water results in a decrease in solvent structuring around the solute molecule. In the mixed H<sub>2</sub>O-formamide solvents, in the vicinity of the solute, this may be brought about by replacement of water molecules by formamide molecules alone, by the formation of H<sub>2</sub>O-formamide complexes, by a reduction in the size of the clusters of water which are thought to surround, partially, the solute molecules (Nemethy & Scheraga, 1962b), or by a combination of any or all of these factors. It is not possible to distinguish which factors are involved. In pure formamide the thermodynamic parameters still indicate the possibility of some solvent structuring around the solute molecule.

Similar thermodynamic parameters are obtained for the solution of dodecane in H<sub>2</sub>O-NMF and H<sub>2</sub>O-DMF solvents. For the solvents containing the lower quantities of NMF and DMF,  $\Delta H^\circ$  and  $\Delta S^\circ$  are negative but these values are much lower, i.e., nearer to zero, than in H<sub>2</sub>O-formamide systems, and in the solvents which are more concentrated with respect to NMF and DMF,  $\Delta H^\circ$  values are, within experimental error, zero. This would suggest that NMF and DMF have a greater disruptive effect on the structure of water, at least in regions close to solute molecules.

A study of the thermodynamic properties of a solution cannot give unambiguous evidence for, or against, a particular physical model for the solution, but they must be consistent, qualitatively, with the assumptions upon which the model is based. If Frank & Evans "iceberg" model for the solution of aliphatic hydrocarbons in water is taken as a starting point, the changes in the thermodynamics of solution of dodecane in the mixed solvents are consistent with a decrease in the size of the "iceberg" around the hydrocarbon. Other factors which might influence the thermodynamic parameters are the self-association of amide molecules, which will alter with

temperature (Fратиello, 1963), and possible changes in the configuration of the hydrocarbon chain in the various solvents.

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