

The Solubility of Hydrocarbons in Water

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The dissolution of a hydrocarbon, R, in water is tentatively considered as a two-step process: (1) The transfer to water, and (2) the solvation. The solvation is regarded as a relaxation to the equilibrium $R + n H_2O \rightleftharpoons R(H_2O)_n$ and as such it enhances the solubility. The low solubility of hydrocarbons in water is ascribed to the strong attractive forces between water molecules in the liquid state. The increase of the solubility with decreasing temperature, characteristic of hydrocarbons in water, is explained by displacements of the solvation equilibrium with changes in the temperature ($\Delta H_{\text{solv}}^{\ominus} < 0$). Estimated values of thermodynamic parameters which, according to the considered model, determine the solubility are given for methane and ethane.

Hydrocarbons are sparingly soluble in water and, below some given temperature, the solubility of a hydrocarbon decreases with increasing temperature as illustrated in Fig. 1 for methane and ethane. The negative enthalpy change of solution (calculated from the temperature dependence of the solubility), compared with the positive change in standard Gibbs energy (the low solubility) indicates that entropy-low water structures are introduced by the nonpolar solute species. This striking feature of water as a solvent was first pointed out by Frank and Evans,¹ and it has led to the currently accepted view that the solubility of hydrocarbons in water is low *because* the solute particles introduce entropy-low structures in the water.^{2–5}

An alternative approach to the thermodynamics of aqueous solutions of hydrocarbons⁶ has, however, led to the conclusion that the solubility of nonpolar molecules in water is low due to the positive 'normal' enthalpy of mixing components of different nature, and that the formation of entropy-low (and energy-low, 'icelike'¹) structures in the

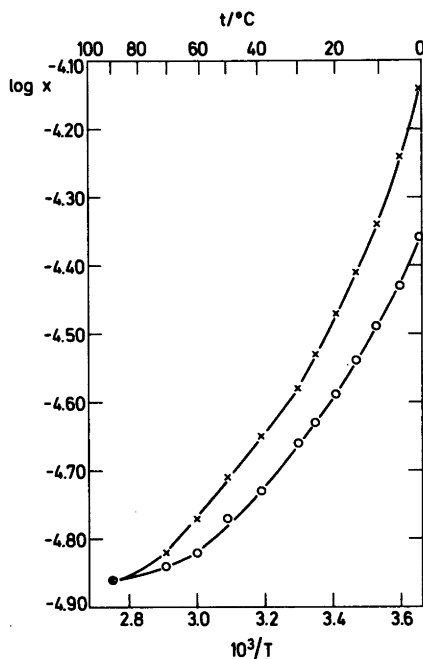


Fig. 1. The temperature dependence of the solubility of methane (○), or ethane (×) in water. x is the mol fraction of the hydrocarbon in an aqueous solution in equilibrium with the hydrocarbon gas at atmospheric pressure. The data is from Ref. 14.

solvent *promotes* the solubility.^{6–8} This latter point of view is shared by the present author and is elaborated on in this paper.

In the following an aqueous solution of a hydrocarbon, R, in water is regarded as a binary mixture, and the interaction of the components in the mixture is considered as a "chemical" equilibrium



for which $\Delta H^\ominus < 0$, $\Delta S^\ominus < 0$, and $\Delta V^\ominus > 0$. $R(H_2O)_n$ denotes an R molecule surrounded by a solvation sphere of n water molecules with a structure more 'icelike' than the (average) structure of bulk water.

An outstanding discussion of the role of solvent structure in solution theory in terms of radial and angular dependence of the molecular correlation function is presented in Ref. 9. However, this discussion is beyond the scope of the primitive, thermodynamic model of aqueous hydrocarbon solutions considered here. The aim of the present paper is to illustrate that the temperature dependence of the solubility of hydrocarbons in water is in accordance with the existence of solute-solvent interactions of the type described in eqn. (1). Such equilibria enhance the solubility of hydrocarbons in water, while the low solubility is ascribed to strong attractive forces between water molecules in the liquid state.^{4,10}

THE MODEL

The dissolution of a hydrocarbon, R, in water is regarded as a two-step process: (1) The mixing of the components (R and H_2O), and (2) the structural relaxation to the equilibrium state (1), *i.e.* the hydrophobic solvation. Thus the change in Gibbs energy of the dissolution is expressed as a sum of two terms; eqn. (2)

$$\Delta G = \Delta G_{\text{mix}} + \Delta G_{\text{solv}} \quad (2)$$

The first step in the dissolution process — before solvation occurs — is considered as the formation of a simple ('regular'), binary mixture;¹¹ ΔG_{solv} (< 0) is the change in Gibbs energy of the relaxation of this mixture to the equilibrium state (1). The main difference between the model here discussed and the two-step model proposed by Ben-Naim,¹³ and discussed in Ref. 9, is the consideration of the change in Gibbs energy of the solvation process.

'Regular' solutions. The molar Gibbs energy of a binary mixture in which molecules of the same size are (nearly) randomly distributed — a so-called 'regular' solution¹¹ — may be expressed as eqn. (3).

$$G = x_1(\mu_1^* + RT \ln x_1) + x_0(\mu_0^* + RT \ln x_0) + (\Delta \varepsilon L)x_1x_0 \quad (3)$$

In eqn. (3) x denotes mol fraction, and the subscripts 1 and 0 refer to the components. The superscript * indicates the pure, liquid state. ε is the intermolecular energy, $\Delta \varepsilon = \varepsilon_{01} - 1/2(\varepsilon_{11} + \varepsilon_{00})$, and L is the Avogadro constant.

The chemical potential of the components of the mixture, obtained from eqn. (3), is as eqn. (4).

$$\mu_i = \mu_i^* + RT \ln x_i + (\Delta \varepsilon L)(1 - x_i)^2, \quad i = 0, 1 \quad (4)$$

The expression (4) has been generalized to include mixtures of molecules of different sizes.¹³ The molar Gibbs energy of a solution of a polymer (an r -mer) in a monomer solvent (the component 0) is expressed as eqn. (5)

$$G = x_r(\mu_r^* + RT \ln \phi_r) + x_0(\mu_0^* + RT \ln \phi_0) + (\Delta \varepsilon L)x_0\phi_r \quad (5)$$

In eqn. (5) ϕ denotes volume fraction, $\phi_r = rx_r/(rx_r + x_0)$. It is assumed that the polymer molecules behave as random chains, and $\Delta \varepsilon$ is defined for solvent molecules and polymer segments. For $r = 1$, eqn. (5) is identical with eqn. (3).

In (polymer) solutions in which the component 0 is present in large excess the chemical potential of a monomer is given by eqn. (6).

$$\mu_1 \cong \mu_1^\ominus + RT \ln \phi_1; \quad \mu_1^\ominus = \mu_1^* + (\Delta \varepsilon L) \quad (6)$$

In the following, the $R(H_2O)_n$ complex in eqn. (1) is considered as a polymer. The volume of the complex is assumed to be equal to the sum of the volumes of the $(n + 1)$ constituent monomers.

The hydrophobic solvation. Let us now assume that subscript 1 in eqn. (3) refers to a hydrocarbon, and 0 to water, so that eqn. (3) is the molar Gibbs energy of a 'regular' mixture of the nonsolvated hydrocarbon and water. If the components interact according to eqn. (1), a relaxation of the mixture to the equilibrium state (the solvation) takes place.

If p is the extent of the solvation

$$p = \frac{[R(H_2O)_n]}{[R] + [R(H_2O)_n]}, \quad (7)$$

the mol fraction, x , and the volume fraction, ϕ , of the species R, H_2O and $R(H_2O)_n$ at equilibrium are

$$x_R = x'_1 = \frac{(1-p)x_1}{1-px_1}; \quad \phi_R = \phi'_1 = (1-p)x_1$$

$$x_{H_2O} = x'_o = 1 - \frac{x_1}{1-px_1}$$

$$\phi_{H_2O} = \phi'_o = 1 - (1+pn)x_1 \quad (8)$$

$$x_{R(H_2O)_n} = \frac{px_1}{1-px_1}; \quad \phi_{R(H_2O)_n} = p(n+1)x_1$$

In eqn. (8) x_1 is the stoichiometric mol fraction of the hydrocarbon.

The change in Gibbs energy of the relaxation, ΔG_{solv} , obtained from eqn. (6) is

$$\Delta G_{\text{solv}} = RT[x_1 \ln(\phi'_1/x_1) + x_o \ln(\phi'_o/x_o)]. \quad (9)$$

The Gibbs energy of an aqueous solution of a hydrocarbon. The molar Gibbs energy of a solution of a hydrocarbon in water, obtained from eqns. (3) and (9), is

$$G = x_1[\mu_1^* + RT \ln \phi'_1] + x_o[\mu_o^* + RT \ln \phi'_o] + x_1 x_o \Delta H_{\text{trf}}^\ominus \quad (10)$$

ϕ'_1 and ϕ'_o are given in eqn. (8), and $\Delta H_{\text{trf}}^\ominus = \Delta \varepsilon L$ is the enthalpy change of the transfer of one mol of the hydrocarbon from the pure liquid state to the unsolvated state at infinite dilution in water. Due to the exceptionally strong attraction between the water molecules in liquid water ($\varepsilon_{oo} < \varepsilon_{o1}, \varepsilon_{11}$ (< 0)), $\Delta \varepsilon = \varepsilon_{o1} - 1/2(\varepsilon_{oo} + \varepsilon_{11}) > 0$, so $\Delta H_{\text{trf}}^\ominus$ is positive.

The molar excess Gibbs energy of the solution, G^E , is

$$G^E = RT[x_1 \ln(\phi'_1/x_1) + x_o \ln(\phi'_o/x_o)] + x_1 x_o \Delta H_{\text{trf}}^\ominus$$

$$\begin{array}{ccc} < 0 & < 0 & > 0 \end{array} \quad (11)$$

The sign of the terms in eqn. (11) is indicated below the equation in order to illustrate — in accordance with Refs. 6 and 7 — that the immiscibility of hydrocarbons and water (the positive value of G^E) is due to energy effects. The contribution to the Gibbs energy of the solutions from the hydrophobic solvation is negative.

If $px_1 \ll x_o$ — a condition presumably met in aqueous solutions of hydrocarbons — the chemical potential of the hydrocarbon is

$$\mu_1 \cong \mu_1^* + RT \ln \phi'_1 + \Delta H_{\text{trf}}^\ominus$$

$$= \mu_1^* + RT \ln(1-p)x_1 + \Delta_{\text{trf}}^\ominus \quad (12)$$

p varies with the concentration and the temperature. If K is the equilibrium constant of the equilibrium (1) in terms of mol fractions

$$K = \frac{p}{1-p x_{H_2O}^n}; \quad p = \frac{K x_{H_2O}^n}{1 + K x_{H_2O}^n}, \quad (13)$$

we have

$$\left(\frac{\partial p}{\partial \ln x_{H_2O}} \right)_T = np(1-p) \quad (> 0) \quad (14)$$

and

$$\left(\frac{\partial p}{\partial T^{-1}} \right)_{x_{H_2O}} = \left(\frac{\partial p}{\partial \ln K} \right)_{x_{H_2O}} \frac{d \ln K}{dT^{-1}} =$$

$$-p(1-p) \frac{\Delta H_{\text{sol}}^\ominus}{R} \quad (> 0).$$

$\Delta H_{\text{sol}}^\ominus$ is ΔH^\ominus of the solvation equilibrium (1).

The enthalpy of an aqueous solution of a hydrocarbon. In accordance with eqn. (2) the molar enthalpy of an aqueous solution of a hydrocarbon is expressed as

$$H = x_1 H_1^* + x_o H_o^* + \Delta H_{\text{mix}} + \Delta H_{\text{sol}} \quad (16)$$

where

$$\Delta H_{\text{mix}} = x_1(1-x_1)\Delta H_{\text{trf}}^\ominus$$

and

$$\Delta H_{\text{sol}} = px_1 \Delta H_{\text{sol}}^\ominus$$

For $x_1 \ll 1$, the apparent molar enthalpy of the hydrocarbon is

$$H_1 \cong H_1^* + \Delta H_{\text{trf}}^\ominus + p \Delta H_{\text{sol}}^\ominus \quad (17)$$

COMPARISON BETWEEN THE MODEL AND EXPERIMENTAL DATA

The decrease with increasing temperature of the solubility of hydrocarbons in water,^{1,4,5,14} as well as

direct calorimetric measurements of the heat of solution of liquid hydrocarbons in water,¹⁵ show that below room temperature the enthalpy of solution of hydrocarbons in water is negative. For the model described in the preceding paragraphs it means that in eqn. (17) $\Delta H_{\text{trf}}^{\ominus} + \Delta H_{\text{solv}}^{\ominus} < 0$. Hydrogen bonds between water molecules are broken in the transfer process in the creation of a cavity in water holding a hydrocarbon molecule ($\Delta H_{\text{trf}}^{\ominus} > 0$), but more bonds, or stronger bonds, seem to be formed in a solvation sphere.

The heat capacity of the aqueous hydrocarbon solutions studied is, however, so large^{4,5,14} that a minimum in the solubility is to be expected at higher temperatures. The existence of such a minimum is demonstrated in calculations of the solubility of hypothetical liquid hydrocarbons.⁶ The calculations in Ref. 6 are based on available data on the solubility

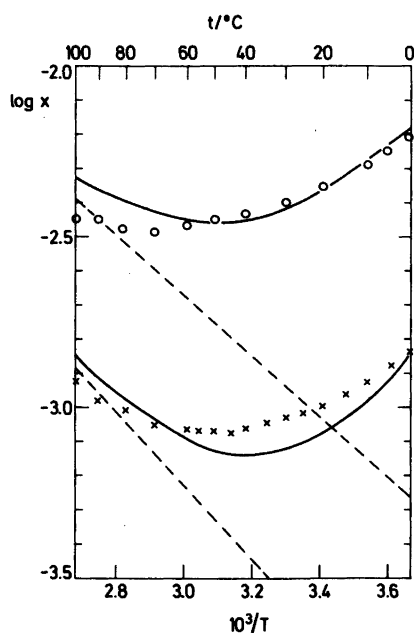


Fig. 2. The temperature dependence of the solubility in water of hypothetical liquid hydrocarbons, methane (○) or ethane (×). x is the mol fraction of the hydrocarbon in an aqueous solution in equilibrium with the pure liquid hydrocarbon. The points are replotted from Fig. 1 in Ref. 6.

The curves are calculated according to eqn. (18) for the values of the thermodynamic parameters given in Table 1. The dashed lines represent the estimated solubility of the nonsolvated hydrocarbons.

of the hydrocarbons at atmospheric pressure, and results obtained for methane and ethane are shown in Fig. 2.

In Ref. 6 and in Fig. 2 the solubility of a hydrocarbon in water is defined as the mol fraction, $x_{1,\text{sat}}$, of the hydrocarbon in an aqueous solution in equilibrium with the pure liquid hydrocarbon. From eqn. (12) one obtains

$$\log x_{1,\text{sat}} = -\log(1 - p_{\text{sat}}) - \Delta H_{\text{trf}}^{\ominus}/RT \ln 10 \quad (18)$$

In order to estimate approximate values of thermodynamic parameters of the two-step model considered here eqn. (18) has tentatively been fitted to the data from Ref. 6. Considering the low solubility of hydrocarbons in water, the concentration dependence of p [eqn. (14)] is ignored so that in the calculations p_{sat} is calculated for $x_{\text{H}_2\text{O}} = 1$, i.e. $(1 - p_{\text{sat}}) = (1 + K)^{-1}$, where $K = \exp(-\Delta H_{\text{solv}}^{\ominus}/RT + \Delta S_{\text{solv}}^{\ominus}/R)$. The values obtained of the model parameters are reported in Table 1, and the accordance between the model and the available data is illustrated in Fig. 2. In this figure the full curves are calculated according to eqn. (18) for the values of the parameters given in Table 1. The dashed lines represent the solubility of the nonsolvated hydrocarbons,

$$\log x = -\Delta H_{\text{trf}}^{\ominus}/RT \ln 10.$$

Fig. 2 illustrates the extent to which the simple model described here is able to account for the observed temperature dependence of the solubility of hydrocarbons in water. The large values reported in Table 1 of enthalpy and entropy changes following the dissolution of hydrocarbons in water are in accordance with the notion that enthalpy-entropy compensation phenomena are a ubiquitous property of water.¹⁶ $\Delta G_{\text{solv}}^{\ominus}$, i.e. the change in Gibbs energy when n mol of water are transferred from pure water to the solvation spheres of 1 mol of a hydrocarbon in water, calculated from the values in Table 1, is, at room temperature

Table 1. Values of thermodynamic parameters used in calculations from eqn. (18) of the curves in Fig. 2.

| | Methane | Ethane |
|--|---------|--------|
| $\Delta H_{\text{trf}}^{\ominus}/\text{kJ mol}^{-1}$ | 17 | 20.5 |
| $\Delta H_{\text{solv}}^{\ominus}/\text{kJ mol}^{-1}$ | -35 | -42 |
| $(\Delta H_{\text{solv}}^{\ominus}/\Delta S_{\text{solv}}^{\ominus})/\text{K}$ | 323 | 313 |

$$\Delta G_{\text{sol}}^{\ominus, 298\text{K}} = \begin{cases} -2.7 \text{ kJ mol}^{-1} & (\text{CH}_4) \\ -2.0 \text{ kJ mol}^{-1} & (\text{C}_2\text{H}_6) \end{cases}$$

The corresponding values of the extent of the solvation at infinite dilution is

$$p(x_{\text{H}_2\text{O}} = 1; 298 \text{ K}) = \begin{cases} 0.75 & (\text{CH}_4) \\ 0.69 & (\text{C}_2\text{H}_6) \end{cases}$$

The p values (< 1) indicate that the nonpolar molecules fluctuate between solvated and non-solvated states. This interpretation of the experimental data is in accordance with the conception³ that solvation spheres around nonpolar molecules appear as 'flickering clusters'. Consideration of the concentration dependence of the volume and the heat capacity of aqueous solutions has led to a similar conception of the solvation of nonpolar groups of amphiphilic molecules dissolved in water.^{17,18} The probability of finding a nonpolar group in the solvated state decreases with increasing solute concentration and with increasing temperature; the solvation can be observed experimentally only in very dilute aqueous solutions.

The most important point of the present discussion of the solubility of hydrocarbons in water is the support of the conclusion⁶⁻⁸ that the formation of 'icelike' water structures around nonpolar solute particles, just as any other type of solvation of solute molecules, enhances the solubility.

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