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Abstract
A method of estimating the solubility of water in hydrocarbons as a function of temperature is given here. Hydrocarbons, lacking strong permanent dipoles or traditional hydrogen bonding, do not strongly attract water molecules. The extreme case of a medium bereft of attractive forces is a vacuum, into which water, nonetheless, evaporates. The solubility of water in hydrocarbons at various temperatures can be correlated to the vapor pressure of water at those temperatures. A simple thermodynamic explanation of the dependence on vapor pressure is offered.

Keywords: Hydrocarbons; vapor pressure; solubility; water.

1. Introduction

The solubility of water in hydrocarbons, even at ambient temperatures, can have great practical importance [1]. For instance, should moist gasoline or aviation fuel cool, the water dissolved in it can freeze and block the fuel line or pipe. Thus, prediction of the change solubility of water in hydrocarbons with temperature can be of value.

Formulations, of varying complexity with explicit or implicit dependence on temperature for water solubilities in hydrocarbons based on theoretical or empirical considerations have been published [1-7]. None, however, results in a simple correlation of temperature dependence of solubility of water in hydrocarbons with the vapor pressure of water at the corresponding temperature. We present here simple correlations using on published data [8]. It turns out that these correlations, based on both empirical relationships and simple thermodynamic arguments, are excellent.

Hydrocarbons, with rare exceptions, are non-polar, and van der Waals forces (London forces or dispersion forces) are the only intermolecular attractive forces in pure, saturated hydrocarbons. Water, on the other hand, is polar and pure water exhibits van der Waals forces, dipole-dipole attraction as well as hydrogen bonding, in order of increasing strength. The old principle of "*similia similibus solvuntur*", "like dissolves like", applies here: hydrocarbons, lacking the stronger attractive forces present in water, do not attract a water molecule as strongly as do the other water molecules in liquid water. The extreme case of such an environment, which exhibits no force of attraction to the water molecules, would be a vacuum. Nonetheless, water evaporates into a vacuum until it achieves equilibrium vapor pressure which, like its solubility in hydrocarbons, is temperature dependent. Thus, the vapor pressure of water at a given temperature may be suspected to relate the solubility of water in a particular hydrocarbon at that temperature. We felt this would be a fruitful hypothesis to investigate.

2. Methods

Énglin *et al.* [8] have tabulated water solubilities, in weight percent, for a number of hydrocarbons at ten degree intervals between 0 °C and 50 °C. For this study, we have chosen to treat the six pure hydrocarbons for which solubilities over the full range of temperatures were given. Multiplying their values by the molar mass of the hydrocarbon and dividing by the molar mass of water yields, essentially, the mole percent at these low water concentrations (Table 1). Plots of vapor pressure of water [9] (in kPa) versus solubility (Figure 1) appear linear except for two aromatic compounds, cumene and 1-methylnaphthalene, which showed distinct curvature.

Figure 1: Vapor Pressure of water *vs*. solubility of water in hydrocarbons
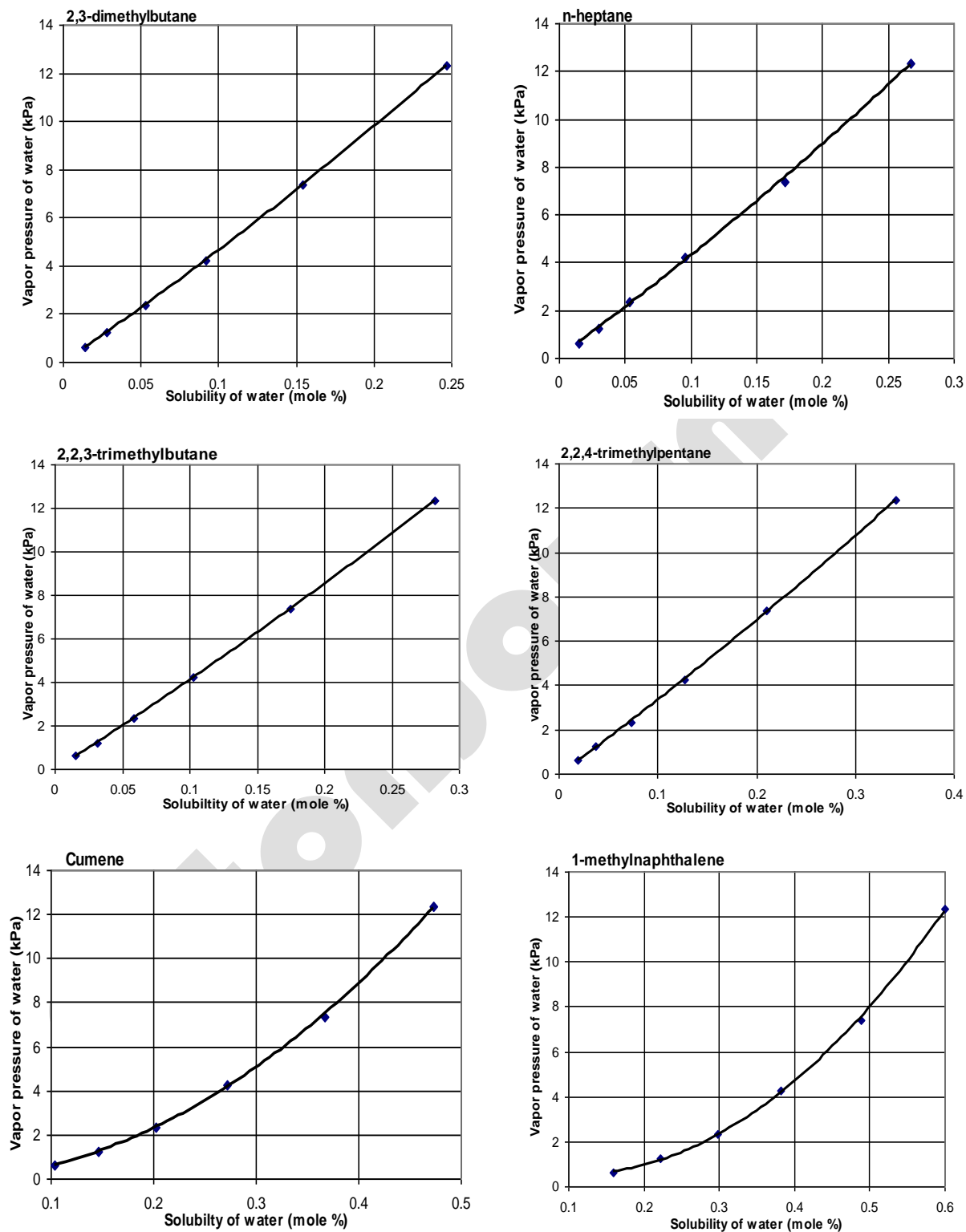**Equation of line is vp = a(sol)^2 + b(sol) + c: a, b and c listed in Table 2**

Table 1:   Solubility of water (mole %) in hydrocarbons at various temperatures [8].

Temperature, °C	0	10	20	30	40	50
Hydrocarbon						
2,3-Dimethylbutane	0.01387	.02774	0.05262	0.091845	0.1545	0.2468
n-Heptane	0.01501	0.03003	0.05338	0.09564	0.1712	0.2669
2,2,3-Trimethylbutane	0.01501	0.0317	0.05894	0.1023	0.1752	0.2819
2,2,4-Trimethylpentane	0.01965	0.03739	0.07288	0.1274	0.2104	0.3410
Cumene	0.1041	0.1461	0.2021	0.2715	0.3669	0.4736
α-Methylnaphthalene	0.1594	0.2225	0.2975	0.3827	0.4885	0.6000

Table 2:   Raw and adjusted constants for the solubility of water as a function of vapor pressure of water.

Compound	Raw			Adjusted, c = 0		
	a	b	c	a	b	R^2
2,3-dimethylbutane	24.3559	44.0360	-0.01683	26.30584	43.5423	1
n-heptane	21.58536	40.03782	0.06023	15.97836	41.61862	0.9992
2,2,3-trimethylbutane	14.25068	39.80561	-0.02161	16.19122	39.24507	0.9999
2,2,4-trimethylpentane	10.71523	32.71578	-0.04952	13.74218	31.66047	0.9998
cumene	51.87286	1.644429	-0.11184	54.07494	0.504046	0.9997
α-methylnaphthalene	48.7151	-10.68233	1.142757	37.88802	-2.91373	0.9970

We note that aromatic hydrocarbons show higher equilibrium concentrations of water than the saturated hydrocarbons at the same temperatures. In the liquid phase, structural features appear between aromatic molecules arising from non-covalent molecular interactions [10-17] which may include parallel (or displaced parallel) or perpendicular stacking. Their polarizability leads to quadrupole interactions (the attraction between the "negative potential of the π face and the positive potential of the periphery" [18] arising from electronegativity differences) and, in the presence of water, can result in stabilization resulting from dipole-induced dipole forces, in particular, non-traditional hydrogen bonding [2, 3, 19-25], a concept supported by spectroscopic data [26-28]. "[Non-traditional hydrogen bonds]… are subtle, multifaceted, more than the sum of their parts and undoubtedly important. Theoretical models not taking them into account can fail dramatically in describing structure, physical properties, and even reactivity."[29]. Thus, it is not surprising that the variation of solubility with temperature is more complex for aromatic hydrocarbons than for saturated hydrocarbons which lack these forces. While including molecules with stronger interactions with water exceeded the original model, it lead to a refinement which gives a better fit to saturated hydrocarbons as well. For all six hydrocarbons, a simple relationship applies relating the tabulated vapor pressure to the experimental solubility of water (Equation 1). For saturated hydrocarbons, the *b* term is greater than the *a* term and for the aromatics, the *a* term is larger than the *b* term. The *c* term is relatively small in all cases.

$$vp = a(sol)^2 + b(sol) + c \qquad\qquad 1$$

where *vp* is the vapor pressure of pure water and *sol* is the solubility of water in the particular hydrocarbon at the same temperature. The best fit parameters are listed in Table 2 and plotted as solid lines in Figure 1. Equation 1 could be solved for the solubility of water as a function of vapor pressure by subtracting the vapor pressure from both sides and applying the quadratic formula. The result leads to a problem with the value of *c*. At a temperature so low that the solubility of water is close enough to zero, for negative values of c (as is the case for 2,3-dimethylbutane, below a mole percent of water equal to approximately 0.00038), the vapor pressure at that temperature would be negative, which is physically meaningless. The same is true of Equation 1 when the solubility is equal to zero. These discrepancies could indicate greater complexity or that c is an artifact of random error in the solubility values.   Thus, the value of c was set equal to zero for all cases and minor adjustment made to the values of *a* and *b* to achieve slope = 1 and intercept = 0. Solving Equation 1 with the intercept set at zero

does not yield a better result than the method just described. When this adjustment is done, a corresponding equation (Equation 2) with similar values of a and b results. Adjusting the values of a and b, does not affect R^2 significantly.

$$sol = \sqrt{\frac{b^2}{4a^2} + \frac{vp}{a}} - \frac{b}{2a} = f(vp) \qquad\qquad 2$$

3. Results and Discussion

Application of equation 2 gives excellent *linear* correlations between the function of vapor pressure of pure water, f(vp), and the solubility of water in all six hydrocarbons. The derived parameters are given in Table 2. The results, using Equation 2 to produce the function of vapor pressure to compute the solubility of water in 2,3-dimethylbutane and in heptane, are shown in Figure 2.

Figure 2: Solubility vs f(vp) of 2,3-dimethylbutane and heptanes.

Solubility of water in 2,3-dimethylbutane vs. the function of vapor pressure of water

Solubility of water in heptane vs. function of the vapor pressure of water
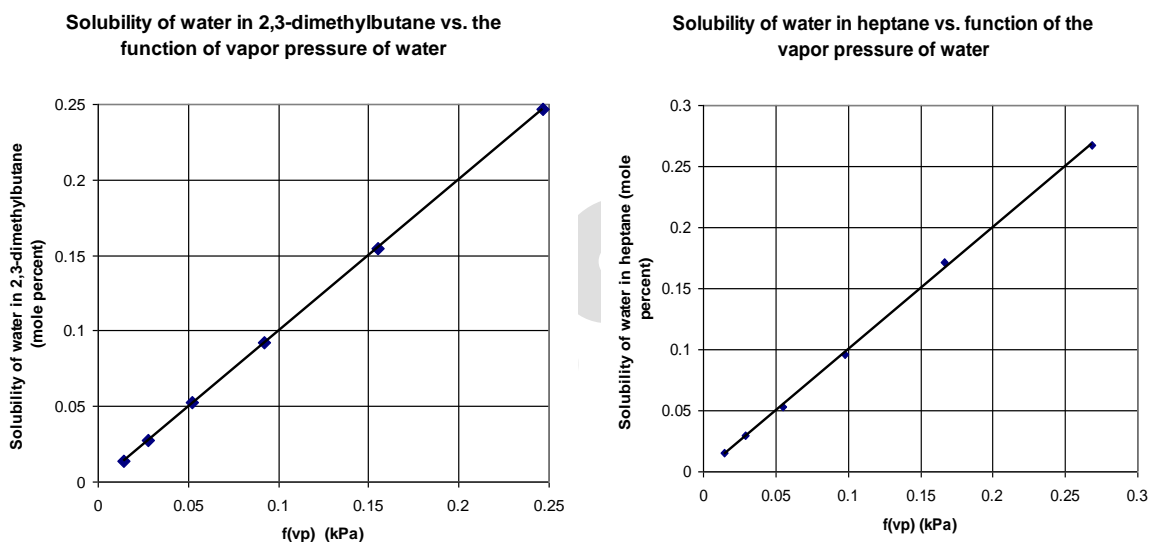
Attempts to correlate the constants in Equation 2 with physical properties of the corresponding hydrocarbons yielded limited success. Modest correlations were to index of refraction (*r*) [8] with the adjusted *a* values (for saturated hydrocarbons) and the adjusted *b* values. These were too approximate to be useful, but are shown in Figure 3 and 4, respectively, for illustrative purposes. These correlations may be only coincidental. A better correlation was achieved between the adjusted *b* and the van der Waals *a* (in $barL^2/mole^2$) [30, 31], but this was a cubic equation, which is more apt to fit the points for five values of *a* (the value for 1-methylnaphthalene does not seem to be available): $b_{adjusted} = -0.08468\,a^3 + 7.07716\,a^2 - 196.05061\,a + 1840.533$, $R^2 = 1.0000$, where *a* is the van der Waals constant for each of the hydrocarbons. Despite the shortcomings of this formulation described above, the coefficients correspond (with $R^2 = 0.9998$) to those given in the more esthetically pleasing equation 3, in which p = -98.4777 $barL^2/mole^2$, which makes all of the terms in the brackets additive without conflicting units.

$b_{adjusted} = 2.1392 \times 10\text{-}4\ [\ 4/3\ \pi a^3 p + \pi a^2 p^2 + a p^3\ ] + 1840.533$ \qquad\qquad 3

Figure 3:

$a_{adjusted}$ for saturated hydrocarbons vs index of refraction

$a = -747.75\, r + 1051.6 \qquad R^2 = 0.9882$

Figure 4:

$b_{adjusted}$ vs index of refraction
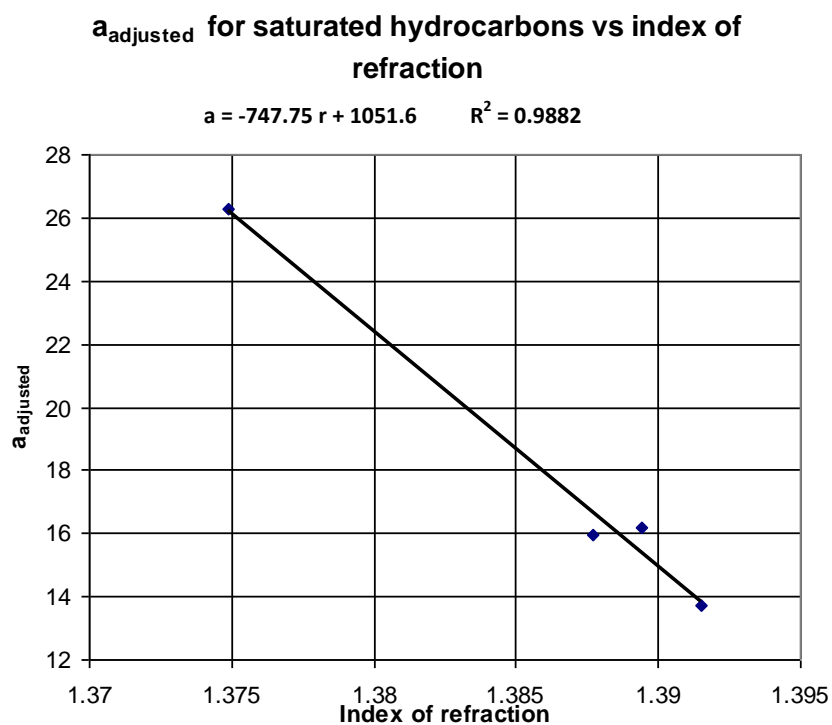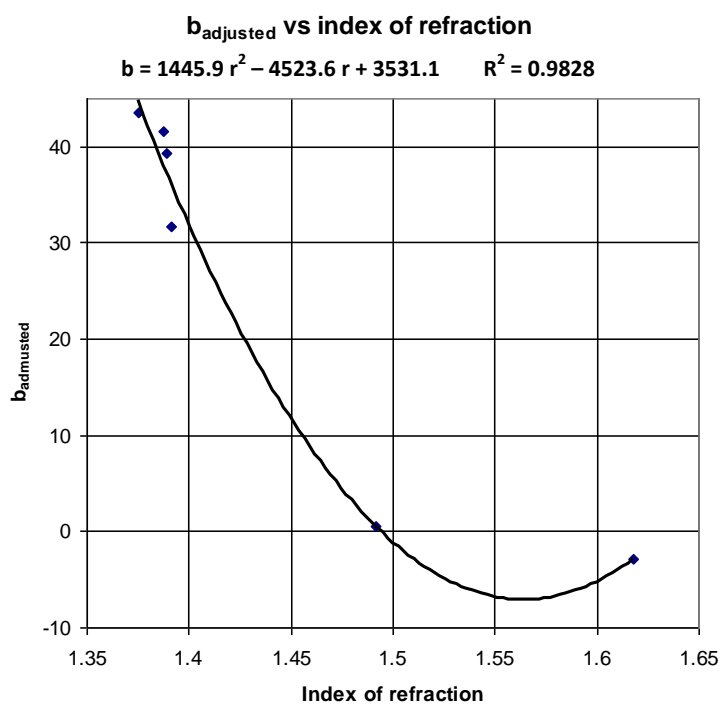
$b = 1445.9\, r^2 - 4523.6\, r + 3531.1 \qquad R^2 = 0.9828$

The fact that all six data sets fit to a rather simple empirical relationship is evidence of common, underlying features. We found a relation between temperature-dependent solubility and vapor pressure of water, which accounted for the curvature, without the need for sophisticated theory.

A theoretical explanation for the non-linearity of the correlation can be derived, which gives a similar equation to that of Thompson *et al.* [32] for the solubility of *solutes in water* based on their experimental vapor pressure. Although that paper's derivation is different, it points out the *caveat* that the relationship is only strictly valid when all activity and fugacity coefficients are unity. According to Hess' Law, the free energy change for water going from pure liquid into solution in a hydrocarbon, $\Delta G^0_{l \to s}$, will be equal to the free energy change of water in going from pure liquid to vapor, $\Delta G^0_{l \to v}$, minus the free energy change of water going from solution in a hydrocarbon to water vapor, $\Delta G^0_{s \to v}$: equation 4.

$$\Delta G^0_{l \to s} = \Delta G^0_{l \to v} - \Delta G^0_{s \to v} \tag{4}$$

$\Delta G^0_{l \to v}$ relates to the equilibrium $K_{l \to v} = a_v/a_l$ where a_v is the activity of the water vapor and a_l is the activity of pure water. The activity of pure water is 1. Thus, $K_{l \to v}$ equals the activity of water vapor at a given temperature divided by 1 for pure water. The pressure for activity = 1 is one atmosphere, or the vapor pressure in kPa divided by 101.325, equation 5.

$$\Delta G^0_{l \to v} = -RT \ln\left(\frac{vp}{101.325}\right) \tag{5}$$

The free energy change for water going from solution in hydrocarbon to vapor is a function of the enthalpy and entropy of the transitions (equation 6) and the values for some hydrocarbons were determined by Henn and Kauzmann [7].

$$\Delta G^0_{s \to v} = \Delta H^0_{s \to v} - T\Delta S^0_{s \to v} \tag{6}$$

The equilibrium constant for the solution of water in hydrocarbon can be derived from $\Delta G^0_{l \to s}$.

$$\Delta G^0_{l \to s} = -RT \ln\left(K_{l \to s}\right) \tag{7}$$

Substituting equations 5, 6, and 7 into equation 4 and dividing both sides of the equation by –RT,

$$\ln K_{l \to s} = \ln\left(\frac{vp}{101.325}\right) + \frac{\Delta H^0_{s \to v}}{RT} - \frac{\Delta S^0_{s \to v}}{R} \tag{8}$$

The mole fraction of water in the hydrocarbon can be approximated from the equilibrium constant, given that the concentration of pure water, [water], is taken to be 1.

$$K_{l \to s} = \frac{[water_{solution}]}{[water][hydrocarbon]} = \frac{[water_{solution}]}{[hydrocarbon]} \propto \chi_{water} \tag{9}$$

Substituting the expression for the mole fraction of water and using and taking the anti-log of each side gives equation 10.

$$\chi_{water} \propto \frac{vp}{101.325} \exp\left(\frac{\Delta H^0_{s\to v}}{RT} - \frac{\Delta S^0_{s\to v}}{R} \right) \qquad\qquad 10$$

This expression can be simplified, in that $\dfrac{\Delta S^0_{s\to v}}{R}$ is relatively invariant with temperature.

$$\chi_{water} \propto vp \times \exp\left(\frac{\Delta H^0_{s\to v}}{RT} \right) \qquad\qquad 11$$

This is illustrated for *n*-heptane in Figure 5. Thus, we see that the relationship between the vapor pressure of water and its solubility in hydrocarbons (Figure 1) is, indeed, nonlinear because of the exponential term as seen in Figure 6.
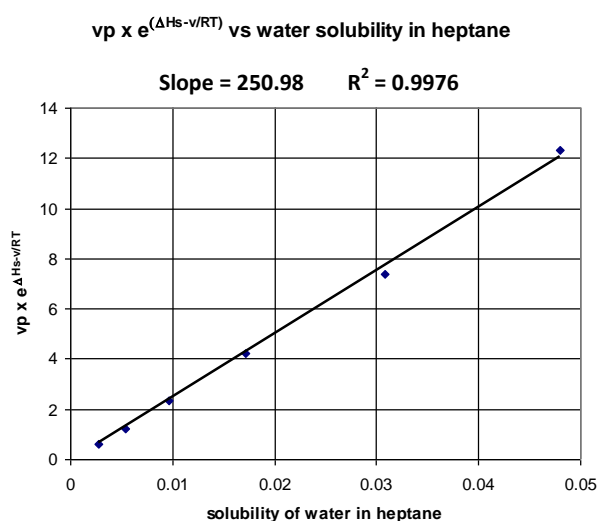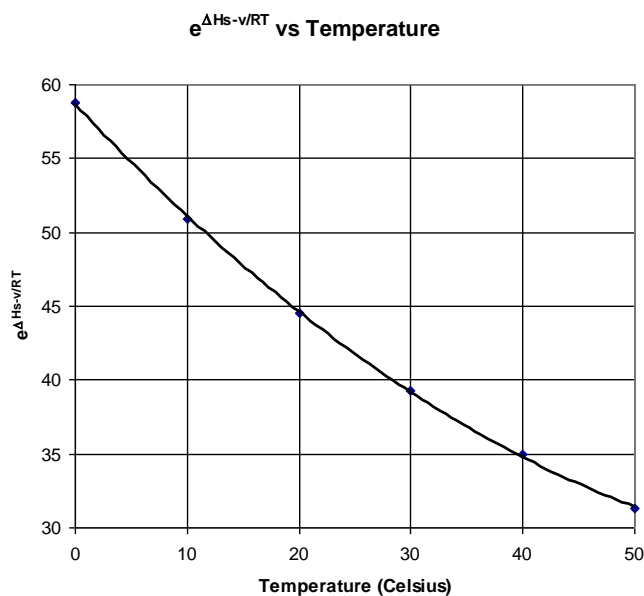
Figure 5:

vp x e$^{(\Delta Hs\text{-}v/RT)}$ vs water solubility in heptane

Slope = 250.98   R^2 = 0.9976

Figure 6:

e$^{\Delta Hs\text{-}v/RT}$ vs Temperature

4. Conclusion

We have shown that, for all six hydrocarbons for which the full complement of data points are available, a simple relationship exists between the vapor pressure of pure water and the solubility of water in those hydrocarbons. Thus, given the solubility of water in a particular hydrocarbon at three or more different temperatures and the corresponding vapor pressures of pure water, it should be possible to predict the solubility of water at other temperatures by the method shown here. We are confident that this treatment can be extended to other hydrocarbons as well.

Competing Interests

The authors declare no competing interests.

Authors' Contributions

Both authors made significant contributions to this collaboration.

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