Naphthalene Solubility in Binary Solvent Mixtures of 2,2,4-Trimethylpentane + Alcohols at 298.15 K

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The solubility of naphthalene in binary mixtures of 2,2,4-trimethylpentane + C_1-C_4 alcohols was determined at 298.15 K. The solubility increased with the addition of the alcohols to 2,2,4-trimethylpentane, reached the maximum values, and then decreased with further increase of alcohol concentrations. Results of these measurements were used to evaluate the prediction capability of a previously developed QSPR models employing the solubility data in monosolvents, and the overall mean deviation (OMD) of the models was varied between (6.0 and 19.1) %. Using ab initio prediction methods, the OMDs varied between (27.6 and 30.6) %.

Introduction

Solubility data are essential information for crystallization-based separations and chromatographic resolutions and also for designing new drug formulations. Mixing solvents is a common method to alter the solubility. However, there is a significant lack of solubility data for many solutes; therefore, efforts have been devoted to obtaining the required information with a minimum time and substance consumption. The development of the ab initio solubility prediction methods with an acceptable accuracy would be an ideal solution to address the problem. A number of mathematical models have been presented for this purpose, and a summary of the models was given in a recent paper.[1]

Experimental solubility data of naphthalene have been reported for aqueous mixtures of acetonitrile, methanol, and ethylene glycol,[2] in binary mixtures of benzene and carbon tetrachloride, cyclohexane, ethylbenzene, hexadecane, hexane, and toluene,[3] for binary mixtures of ethyl benzene and carbon tetrachloride, cyclohexane, hexadecane, hexane, and toluene.[4] The solubility data of naphthalene in binary mixtures of carbon tetrachloride and cyclohexane, hexadecane, and hexane,[5] for binary mixtures of toluene and carbon tetrachloride, cyclohexane, hexadecane, and hexane,[4] and also for cyclohexane + hexane, hexadecane + cyclohexane, and hexadecane + hexane[5] have been reported in the literature. However, there were no published data on the solubility of naphthalene in 2,2,4-trimethylpentane + alcohol mixtures. 2,2,4-Trimethylpentane is a highly branched saturated hydrocarbon which has been used in several partitioning studies to model the oil phase[6–8] and was also used as a reference solvent in solubility studies involving drug molecules.[9]

A numerical method was developed employing the Jouyban−Acree model, the Abraham solute parameters, and the Abraham solvent coefficients.[10] The basic Jouyban−Acree model is

$$\ln C_m^{\mathrm{Sat}} = x_1 \ln C_1^{\mathrm{Sat}} + x_2 \ln C_2^{\mathrm{Sat}} + x_1 x_2 \sum_{i=0}^{2} J_i (x_1 - x_2)^i \quad (1)$$

where C_m^{Sat} is the solute moles per liter solubility in the binary solvent mixtures; x_1 and x_2 are the mole fractions of solvents 1 and 2 in the absence of the solute; C_1^{Sat} and C_2^{Sat} denote the moles per liter solubility of the solute in the neat solvents 1 and 2, respectively, and J_i is the solvent−solvent and solute–solvent interaction terms. In a previous work,[10] QSPR models were proposed to calculate the numerical values of the J_i terms using Abraham's solvent coefficients of 22 solvents and Abraham's parameters of five solutes. The QSPRs enable us to predict the solubility of a solute in nonaqueous mixed solvent without employing any experimental data from mixed solvents.

The QSPR models proposed in an earlier work[10] using water-to-solvent coefficients were

$$J_0 = 0.028 + 2.123(c_1 - c_2)^2 - 0.160\,E(e_1 - e_2)^2 + 0.282S(s_1 - s_2)^2 + 1.713B(b_1 - b_2)^2 + 2.006V(v_1 - v_2)^2 \quad (2)$$

$$J_1 = 0.033 + 0.670(c_1 - c_2)^2 - 0.477E(e_1 - e_2)^2 + 0.051S(s_1 - s_2)^2 + 0.476B(b_1 - b_2)^2 - 0.234V(v_1 - v_2)^2 \quad (3)$$

$$J_2 = 0.022 + 2.024(c_1 - c_2)^2 - 0.204E(e_1 - e_2)^2 + 0.034S(s_1 - s_2)^2 + 0.243B(b_1 - b_2)^2 + 0.848V(v_1 - v_2)^2 \quad (4)$$

and the QSPR models using gas-to-solvent coefficients were

$$J_0 = 0.062 + 0.118(c_1 - c_2)^2 - 0.332E(e_1 - e_2)^2 + 0.410S(s_1 - s_2)^2 + 2.399B(b_1 - b_2)^2 + 15.715L(l_1 - l_2)^2 \quad (5)$$

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$$J_1 = 0.103 - 1.864(c_1 - c_2)^2 - 1.590E(e_1 - e_2)^2 + 0.119S(s_1 - s_2)^2 + 1.010B(b_1 - b_2)^2 - 9.493L(l_1 - l_2)^2 \quad (6)$$

$$J_2 = -0.008 + 1.075(c_1 - c_2)^2 + 0.053E(r_1 - r_2)^2 + 0.084S(s_1 - s_2)^2 + 0.414B(b_1 - b_2)^2 + 7.727L(l_1 - l_2)^2 \quad (7)$$

where c, e, s, b, v, and l are the model constants (i.e., the Abraham solvent coefficients); subscripts 1 and 2 denote solvents 1 and 2; E is the excess molar refraction of solute; S is the dipolarity/polarizability of the solute; B stands for the solute's hydrogen-bond basicity; V is the McGowan volume of the solute; and L is the logarithm of the solute gas−hexadecane partition coefficient at 298.15 K. The numerical values of c, e, s, b, v, and l employed in this work were listed in Table 1.

The aims of this work are to report the experimental solubility data of naphthalene in 2,2,4-trimethylpentane and C_1−C_4 alcohol binary mixtures at 298.15 K and also to check the prediction capability of a previously reported QSPR model for predicting the solubility of solutes in binary solvent mixtures.

Experimental method

Materials. Naphthalene (purity 99 %) was purchased from Fluka and used as received. Its purity was checked by IR spectroscopy, and also its melting point (356.95 K) was determined using a differential scanning calorimeter (Shimadzu, Japan). 2,2,4-Trimethylpentane (> 99 %), 1-butanol (99.5 %), 1-propanol (99.5 %), 2-propanol (99.5 %), absolute ethanol (99.9 %), and methanol (99.5 %) were purchased from Merck.

Apparatus and Procedure. The binary solvent mixtures were prepared by mixing the appropriate volumes of the solvents, and then the mole fractions of the solvents were computed considering the densities of the neat solvents. The solvent composition could be calculated to 0.002 mol fraction. The solubility of naphthalene was determined by equilibrating an excess amount of the solid with the binary solvent mixtures using a shaker (Behdad, Tehran, Iran) placed in an incubator equipped with a temperature controlling system at 298.15 ± 0.2 K. Attainment of the equilibrium was verified by measurements at different times and reached after 48 h. The solutions were filtered using hydrophobic Durapore filters (0.45 μm, Millipore, Ireland) and then diluted with methanol for spectrophotometric analysis at 274 nm quantified by a UV–vis spectrophotometer (Beckman DU-650, Fullerton, USA). The filter did not absorb the solute through filtration process. Concentrations of the dilute solutions were determined from a UV absorbance calibration graph with the molar concentration of naphthalene ranging from $\epsilon/(\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}) = 4968$ to $\epsilon/(\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}) = 550$ for the naphthalene compositions ranging from $(3.1\cdot10^{-4}$ to $4.0\cdot10^{-2})$ mol·L^{-1}. Each experimental data point is an average of at least three experiments with the measured mol·L^{-1} solubilities being reproducible to within ± 2.0 %. Calculated standard deviations ranged from $(\sigma_{n\text{-}1} = 0.003$ to $\sigma_{n\text{-}1} = 0.035)$ mol·L^{-1}.

Table 1. Abraham Solvent Coefficients Employed in This Work Taken from Reference 13

water to solvent	c	e	s	a	b	v
1-butanol	0.152	0.437	−1.175	0.098	−3.914	4.119
1-propanol	0.148	0.436	−1.098	0.389	−3.893	4.036
2-propanol	0.063	0.320	−1.024	0.445	−3.824	4.067
2,2,4-trimethylpentane	0.288	0.382	−1.668	−3.639	−5.000	4.461
ethanol	0.208	0.409	−0.959	0.186	−3.645	3.928
methanol	0.329	0.299	−0.671	0.080	−3.389	3.512

gas to solvent	c	e	s	a	b	l
1-butanol	−0.039	−0.276	0.539	3.781	0.995	0.934
1-propanol	−0.028	−0.185	0.648	4.022	1.043	0.869
2-propanol	−0.060	−0.335	0.702	4.017	1.040	0.893
2,2,4-trimethylpentane	0.275	−0.244	0.000	0.000	0.000	0.972
ethanol	0.012	−0.206	0.789	3.635	1.311	0.853
methanol	−0.004	−0.215	1.173	3.701	1.432	0.769

Computational Methods. The J_i terms of the Jouyban−Acree model were computed using eqs 2 to 4 and then were used to predict the naphthalene solubility data in binary solvent mixtures using eq 1 employing experimental values of C_1^{Sat} and C_2^{Sat}. This numerical method was called No. I. The same computations were carried out employing eqs 5 to 7, and it was called numerical method II. For solubility prediction methods I and II, the solubility data in monosolvent systems, i.e., two points for each binary solvent system, are required. To further reduce the experimental data requirement in the prediction process, it is possible to use the Abraham solvation models to predict the C_1^{Sat} and C_2^{Sat} values. The Abraham model for the water-to-solvent process is

$$\log\left(\frac{C_S}{C_W}\right) = c + e\cdot E + s\cdot S + a\cdot A + b\cdot B + v\cdot V \quad (8)$$

and for the gas-to-solvent process is

$$\log\left(\frac{C_S}{C_G}\right) = c + e\cdot E + s\cdot S + a\cdot A + b\cdot B + l\cdot L \quad (9)$$

where C_S (the same term as C_1^{Sat} and C_2^{Sat} from this work) and C_W are the solute solubility in the organic solvent and water (in mol·L^{-1}), respectively; a is the Abraham solvent coefficient; A denotes the solute's hydrogen-bond acidity; and C_G is the gas phase concentration of the solute. Equation 8 requires the aqueous solubility of the solute (C_W), and eq 9 requires the C_G value. The numerical values of the solute's Abraham experimental parameters for naphthalene are: $\log C_W = -3.61$, $E = 1.340$, $S = 0.920$, $A = 0.000$, $B = 0.200$, $V = 1.085$, and $L = 5.161$.[11] The $\log C_G = -5.340$ was taken from a reference.[12] The predicted C_1^{Sat} and C_2^{Sat} from eq 8 and J_i terms computed using eqs 2 to 4 were used to predict the C_m^{Sat}, and this numerical method was called III. A similar numerical analysis employing eqs 9 and 5 to 7 was called method IV.

All predicted solubilities ($(C_m^{\text{Sat}})_{\text{pred}}$) were compared with the corresponding experimental values, and the mean deviation (MD) was calculated as a criterion by

$$\text{MD} = \frac{\sum\left\{\frac{|(C_m^{\text{Sat}})_{\text{pred}} - (C_m^{\text{Sat}})|}{(C_m^{\text{Sat}})}\right\}}{N}$$

where N is the number of data points in each set.

Results and Discussion

Table 2 listed the experimental solubilities of naphthalene in binary solvent mixtures along with the predicted solubilities using methods I to IV. The maximum solubilities were observed at x_1 of 0.363, 0.450, 0.644, 0.520, and 0.564, respectively, for methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol. There are good agreements between the generated solubility of naphthalene in methanol, ethanol, and 1-propanol and the corresponding values from the literature.[14] The solubility of naphthalene in binary solvents was predicted using numerical methods I to IV. The predicted solubilities were compared with the corresponding experimental data, and the MD values were computed. The MD values of various numerical methods and

Table 2. Experimental Solubilities of Naphthalene C_m^{Sat} in Binary Mixtures of 2,2,4-Trimethylpentane (x_1) and Aliphatic Alcohols (2) at 298.15 K, Density (ρ) of the Saturated Solutions, and the Computed Solubilities Using Various Numerical Analyses[a]

x_1	C_m^{Sat}	ρ	$C_m^{\mathrm{Sat}}/\mathrm{mol\cdot L^{-1}}$			
mole fraction	$\mathrm{mol\cdot L^{-1}}$	$\mathrm{g\cdot cm^{-3}}$	method I	method II	method III	method IV
			Methanol			
1.000	0.692	0.710	0.692	0.692	0.313	0.421
0.687	0.823	0.733	1.306	1.734	0.706	1.206
0.494	0.871	0.744	1.338	2.095	0.808	1.583
0.363	0.922	0.752	1.235	2.096	0.804	1.675
0.268	0.882	0.758	1.106	1.888	0.760	1.571
0.196	0.850	0.762	0.978	1.596	0.701	1.370
0.140	0.746	0.777	0.862	1.303	0.638	1.145
0.095	0.705	0.790	0.761	1.047	0.578	0.938
0.058	0.668	0.798	0.675	0.836	0.524	0.761
0.026	0.623	0.802	0.602	0.670	0.475	0.618
0.000	0.540	0.808	0.540	0.540	0.433	0.504
			Ethanol			
1.000	0.692	0.710	0.692	0.692	0.313	0.421
0.760	0.796	0.735	0.882	1.007	0.497	0.706
0.584	0.871	0.744	0.902	1.093	0.596	0.849
0.450	0.901	0.750	0.871	1.091	0.650	0.917
0.345	0.847	0.758	0.826	1.046	0.679	0.936
0.260	0.820	0.760	0.778	0.976	0.691	0.918
0.190	0.746	0.779	0.729	0.892	0.690	0.874
0.131	0.700	0.787	0.682	0.803	0.682	0.815
0.081	0.652	0.795	0.638	0.715	0.667	0.748
0.038	0.596	0.800	0.596	0.633	0.649	0.678
0.000	0.558	0.810	0.558	0.558	0.628	0.611
			1-Propanol			
1.000	0.692	0.710	0.692	0.692	0.313	0.421
0.803	0.772	0.737	0.808	0.873	0.415	0.559
0.644	0.836	0.749	0.833	0.943	0.474	0.629
0.514	0.820	0.758	0.823	0.964	0.510	0.664
0.404	0.810	0.766	0.800	0.958	0.531	0.678
0.312	0.789	0.767	0.772	0.929	0.544	0.674
0.232	0.770	0.788	0.740	0.882	0.549	0.653
0.162	0.723	0.798	0.706	0.821	0.548	0.618
0.102	0.698	0.807	0.671	0.751	0.542	0.574
0.048	0.683	0.813	0.636	0.676	0.531	0.524
0.000	0.601	0.825	0.601	0.601	0.518	0.472
			2-Propanol			
1.000	0.692	0.710	0.692	0.692	0.313	0.421
0.807	0.804	0.731	0.816	0.826	0.399	0.519
0.650	0.835	0.740	0.838	0.866	0.437	0.559
0.520	0.865	0.746	0.823	0.868	0.453	0.573
0.410	0.816	0.754	0.793	0.852	0.456	0.572
0.317	0.778	0.758	0.759	0.823	0.454	0.561
0.236	0.751	0.773	0.723	0.783	0.447	0.542
0.166	0.730	0.779	0.686	0.736	0.436	0.515
0.104	0.693	0.787	0.647	0.683	0.422	0.483
0.049	0.649	0.792	0.609	0.627	0.406	0.448
0.000	0.571	0.800	0.571	0.571	0.388	0.411
			1-Butanol			
1.000	0.692	0.710	0.692	0.692	0.313	0.421
0.833	0.815	0.733	0.796	0.791	0.393	0.507
0.689	0.847	0.745	0.839	0.834	0.448	0.558
0.564	0.877	0.756	0.851	0.847	0.486	0.590
0.454	0.845	0.764	0.848	0.846	0.513	0.609
0.356	0.834	0.767	0.835	0.836	0.532	0.621
0.270	0.812	0.787	0.817	0.820	0.545	0.625
0.192	0.786	0.802	0.794	0.798	0.552	0.623
0.122	0.764	0.811	0.768	0.771	0.554	0.616
0.058	0.732	0.817	0.738	0.740	0.551	0.602
0.000	0.705	0.829	0.705	0.705	0.543	0.584

[a] I: Experimental C_1^{Sat} and C_2^{Sat} and computed J_i values using eqs 2 to 4. II: Experimental C_1^{Sat} and C_2^{Sat} and computed J_i values using eqs 5 to 7. III: Predicted C_1^{Sat} and C_2^{Sat} using eq 8 and computed j_i values using eqs 2 to 4. IV: Predicted C_1^{Sat} and C_2^{Sat} using eq 9 and computed J_i values using eqs 5 to 7.

their overall MD were listed in Table 3. The numerical methods employing the experimental solubilities in solvents 1 and 2 produced more accurate predictions, and the method I was the best prediction method. The numerical method IV was the best ab initio prediction method for naphthalene solubilities in the investigated solvent systems. These findings are in good agreement with the previous results obtained by employing 194 solubility data sets.[10]

Generally the same accuracy pattern on the overall MDs was observed in these computations when compared with the results

Table 3. Numerical Values of the Mean Deviation (MD) for the Solubilities of Naphthalene in 2,2,4-Trimethylpentane + Alcohols (2) Using Various Numerical Methods and Their Overall Values

	numerical method			
solvent 2	I	II	III	IV
	100·MD			
methanol	19.5	66.9	19.8	45.1
ethanol	2.9	15.1	20.1	13.5
1-propanol	2.4	10.6	32.6	21.2
2-propanol	3.1	2.4	43.5	31.8
1-butanol	0.9	1.2	37.4	26.8
overall MD %	5.8	19.2	30.7	27.7

of a previous work,[10] and this reveals that the developed QSPR models are robust and could be used for prediction purposes. Using experimental solubilities in monosolvents, more accurate predictions were obtained; however, the ab initio predictions were quite reasonable.

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