

Solubility of 2-naphthol in organic nonelectrolyte solvents. Comparison of observed versus predicted values based upon mobile order and regular solution theories[†]

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Experimental solubilities are reported at 25.0°C for 2-naphthol in several different organic nonelectrolyte solvents; results of these measurements are compared with the solubility equations derived from mobile order and regular solution theories.

Keywords: 2-naphthol solubilities, solubility prediction, mobile order theory

The importance of solubility predictions to areas as diverse as drug delivery,¹ coating,² polymer blending³ petroleum industry, *etc.*, has motivated an extensive effort to predict solubilities and to understand solution properties. The prediction of the solubility of a solid solute in a given solvent requires, from a thermodynamic point of view, knowledge of its ideal solubility and activity coefficient. The ideal solubility of a solid solute is related to the energy needed to transform that solute from its solid to its hypothetical liquid state at the experimental temperature. Once the solute is dissolved, the activity coefficient indicates the degree of deviation of the solute–solvent system formed with respect to the ideal behavior. Various models dealing with the estimation of the activity coefficients can be found in the literature.^{4,5}

The mobile order theory is at the basis of a new thermodynamic treatment of the liquid state, the quantitative development of which led to equations describing the effect of solvents–solvent, solute–solute and solute–solvent interactions on the chemical potential of solute.^{6–20} In the present communication, we report 2-naphthol solubilities in several different organic solvents at 25.0±0.1 °C. Results of the measurements are used to further test the applications and limitations of predictive expressions derived from the mobile order model.

Experimental

Solute and solvents were Merck product and were used as received. Excess solute and solvent were placed in sealed glass bottles and allowed to equilibrate in a constant temperature water bath (multitemp III thermostat) at 25.0 ±0.1°C for three days. Aliquots of saturated 2-naphthol solutions were transferred into a tared volumetric flask to determine the amount of sample, and were diluted quantitatively with methanol for spectrophotometric analysis at 273nm, 284nm and 329nm on a Shimadzu UV-Visible spectrophotometer (UV-265FW). Concentration of the dilute solutions were determined from a Beer-Lambert law. The calculated average molar absorptivity from standard solution of 2-naphthol are $\epsilon(273)=4650$ l/mol.cm, $\epsilon(284)=3360$ l/mol.cm, $\epsilon(329)=2118$ l/mol.cm.

Experimental 2-naphthol solubilities (mole fraction X_B) in solvents are listed in Table 1. Numerical values represent the average between four independent experiments.

Results and discussion

Solvents listed in Table 1 include both noncomplexing and complexing non-associated solvents. A general predictive solubility model has been developed according to the mobile order theory,

containing several contributions accounting for the influence of solvent–solvent, solute–solute and solvent–solute interactions on the chemical potential of solute.^{6–9,17} Based on a correct description of the enthalpy and entropy changes accompanying the fusion and solution processes, the predictive equation for solubility in volume fraction, Φ_B , completely describes the free energy change when a solute B is dissolved in a solvent S. Depending upon the functional groups present on the solute and solvent molecules, the complete mobile order theory derived solubility expression may contain up to six different terms.^{6–9,17}

$$\ln \Phi_B = A + B + D + F + O + OH \quad (1)$$

The term A represents the fluidisation of the solute or its ideal solubility. At temperature T of interest, the A term is calculated from the solute molar enthalpy of fusion, ΔH_{fus} and the normal melting point temperature, T_m :

$$A = \frac{-\Delta H_{\text{fus}}}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) \quad (2)$$

The term B is a correction factor for the entropy of mixing derived from the difference in size of the molecules in solution.

$$B = 0.5 \Phi_S \left(\frac{V_B}{V_S} - 1 \right) + 0.5 \ln \left(\Phi_B + \Phi_S \frac{V_B}{V_S} \right) \quad (3)$$

The term D accounts for the effect on the solubility related to the changes in the solute–solute, solvent–solvent and solute–solvent non-specific interactions (induced dipole-induced dipole, induced dipole–dipole and dipole–dipole cohesion forces) accompanying the transfer of liquid solute from its pure phase to the solvent.

$$D = - \frac{1}{[1.0 + \max(K_{\text{O}_i}, K_{\text{OHi}}) \frac{\Phi_S}{V_S}]} \frac{\Phi_S^2 V_B}{RT} (\delta'_B - \delta'_S)^2 \quad (4)$$

where $\max(K_{\text{O}_i}, K_{\text{OHi}})$ stands for the association constant governing the strongest intermolecular H-bond displayed by the molecular groups in solution. The symbols δ'_B and δ'_S denote the modified solubility parameters of solute and solvent, respectively. The modified solubility parameters refers to dispersion and dipolar forces, excluding H-bonds.

The term F describes the hydrophobic effect, which accounts for the reduction in solubility that results from the formation of H-bonded chains between amphiphilic solvent molecules

$$F = -r_S \Phi_S \frac{V_B}{V_S} \quad (5)$$

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[†] This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Comparison between experimental 2-naphthol mole fraction solubilities $X_{B(\text{Exp.})}$ and predicted values based upon mobile order theory $X_{B(\text{M.O.})}$ and regular solution theory $X_{B(\text{R.S.})}$

Organic solvent	$X_{B(\text{Exp.})}$	$X_{B(\text{M.O.})}$	%Dev.	$X_{B(\text{R.S.})}$	%Dev.
<i>n</i> -Pentane	0.0015064	0.002250	50	0.001040	-31
<i>n</i> -Hexane	0.0016525	0.002597	57	0.001730	5
<i>n</i> -Octane	0.0026437	0.002875	9	0.002801	6
<i>iso</i> -Octane	0.0017908	0.002318	40	0.000933	-48
<i>o</i> -Xylene	0.0249104	0.01412	-43	0.033918	36
<i>p</i> -Xylene	0.0279859	0.013716	-51	0.025916	-33
Carbon tetrachloride	0.0048254	0.005763	19	0.018608	-61
Chloroform	0.0228816	0.029537	-54	0.041422	-36
Chlorobenzene	0.0228816	0.01594	-30	0.039511	73
Bromobenzene	0.0277605	0.012966	-53	0.082332	197
Diethyl ether	0.2860261	0.20616	-28	0.002572	-99
Dioxane	0.4325992	0.23792	-45	0.107068	-75
N,N-Dimethylformamide	0.5209428	0.25506	-45	0.173928	-67
Acetone	0.4631091	0.26189	-20	0.074318	-84
Average deviation			-14		-15

where r_s represents the 'structuration factor' of the solvent, which is equal to 0 for non-associated solvents, to 1 for alcohols and to 2 for water and diols.

The term O expresses the effect on solubility of H-bonds formed between proton acceptor sites of the solute and proton-donor solvents.

$$O = \sum v_{O_i} \ln \left[1 + K_{O_i} \left(\frac{\phi_S}{V_S} - v_{O_i} \frac{\phi_B}{V_B} \right) \right] \quad (6)$$

where K_{O_i} is the group interaction stability constant and v_{O_i} is the number of active and independent type i proton-acceptor sites on the solute molecule.

The term OH describes the effect on solubility of the amphiphilic groups on the solute.

$$OH = \sum v_{OH_i} \left[\ln \left(1 + K_{OH} \frac{\phi_S}{V_S} + K_{BB} \frac{\phi_B}{V_B} \right) - \ln \left(1 + \frac{K_{BB}}{V_B} \right) \right] \quad (7)$$

where v_{O_i} indicates the number of active and independent proton donor sites of type i on the solute molecule and K_{OH_i} is association or insertion constant. The constant K_{BB} is the stability constant which governs the solute self-association in solution.

To predict the solubility of 2-naphthol by applying Eqn (1) one needs to know the following physical properties of solute; its melting point, T_m , its enthalpy of fusion, ΔH_{fus} , its molar volume, V_B , in solution and its modified solubility parameter, δ'_B . The values of these properties, $T_m=396.1\text{K}$, $\Delta H_{\text{fus}}=17510\text{ J/mol}$, $V_B=129.8\text{ cm}^3/\text{mol}$ and $\delta'_B=18.03\text{ MPa}^{1/2}$ were taken from refs 21 and 12 respectively. The molar volumes, V_S , and the modified solubility parameters, δ'_S , of the solvents in which the solubilities of the solid 2-naphthol are predicted are listed in Table 2.

The results of the predictions, as well as the corresponding experimental values, are listed in Table 1. An estimation of the quality

Table 2 Molar volume (V_i), modified solubility parameter (δ'_i) and total solubility (δ_i) parameter

Component(i)	V_i (cm ³ /mol) ^a	δ'_i (MPa ^{1/2}) ^a	δ_i (MPa ^{1/2}) ^b
<i>n</i> -Pentane	116.1	14.18	14.4
<i>n</i> -Hexane	131.6	14.56	14.9
<i>n</i> -Octane	163.5	14.85	15.4
<i>iso</i> -Octane	166.1	14.3	14.3
<i>o</i> -Xylene	120.6	17.5	18.5
<i>p</i> -Xylene	123.9	17.3	18.1
Carbon tetrachloride	97.1	17.04	17.6
Chloroform	80.7	18.77	18.7
Chlorobenzene	102.1	19.48	18.7
Bromobenzene	105.3	21.22	20.1
Diethyl ether	104.8	18.78	15.3
Dioxane	85.8	20.89	20.7
N,N-Dimethylformamide	77	22.15	24.1
Acetone	74	21.91	19.7
2-Naphthol	129.8	18.03	24.3

^a Ref.9

^b Ref.23

of the prediction is furthermore given by the relative error defined by Eqn(8)

$$\text{deviation (\%)} = 100.0(X_B^{\text{pred}} - X_B^{\text{exp}}) / X_B^{\text{exp}} \quad (8)$$

To predict the solubility of 2-naphthol by applying Eqn(1), one must consider that our solvents are not complexing associated so $r_s=0$ and therefore the term F is equal to zero. On the other hand, since none of the solvents have proton-donor sites, so the O term will be omitted. Therefore, for mentioned solvents Eqn(1) reduces to Eqn(9):

$$\ln \Phi_B = A + B + D + OH \quad (9)$$

The predicted values of Φ_B in Table 1 were calculated by applying Eqn(9).

As the logarithm of the solubility, $\ln \Phi_B$, results from the sum of four terms, it is interesting to analysis the relative contributions of each of these terms to the solubility. For such a purpose, Figure 1 demonstrates the respective contributions of the terms B , D and OH vs. the solvents. On the basis of information which is represented in Fig. 1 it becomes evident that the behavior of complexing non-associated and non-complexing solvents are different. Therefore, the results will be discussed separately for each of the two sets of solvents.

Solubility in complexing non-associated solvents: For these set of solvents (acetone, DMF, dioxane and diethyl ether), the contribution of the D term can be neglected because their modified solubility parameter δ'_S is close to that of solute δ'_B . The contribution of B is important and positive, because the molar volumes of solvents, V_S , are smaller that that of solute, V_B . This positive entropic factor leads to an increase in the solubility. The contribution of the OH term is also important and positive, because of the interaction of proton acceptor site of solvent and the proton donor site of solute which leads to the increase of solubility.

The melting processes, A term, represents the most hindrance to the solubility (the absolute value of A is greater than the other terms but has a negative sign).

Solubility in non-complexing solvents: For the remaining solvents, the contribution of the A term is important and negative and represents the hindrance to the solubility. The contribution of the D term is also negative to the solubility but its importance is lower than that of the A term.

For non-complexing solvents, the solubility of 2-naphthol is mainly governed by the OH term and this term represents the most important hindrance to the solubility (the absolute value of OH is greater than the other terms but has a negative sign); because the solvents have no proton acceptor site and in the absence of this interaction the self association between 2-naphthol molecules becomes more important.

The contribution of the B term (entropy of mixing) is nearly important for halogenated solvents of this set (chloroform, carbon tetrachloride, chlorobenzene and bromobenzene), but this term can be neglected for the remaining non-complexing solvents (*n*-pentane, *n*-hexane, *n*-octane, *iso*-octane, *o*-xylene and *p*-xylene). It is apparent that the entropic factor is negligible for non-complexing solvents *i.e.*

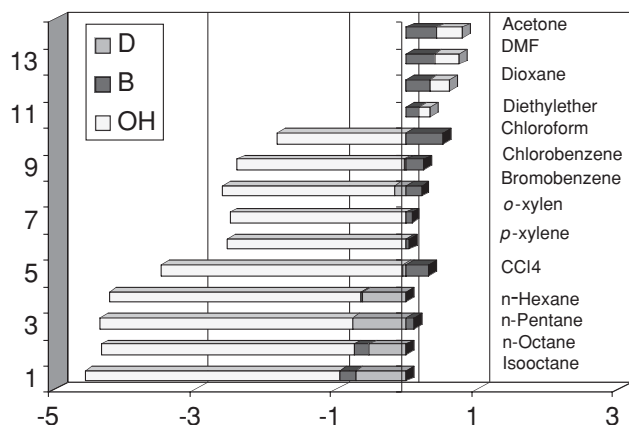


Fig. 1 Contribution of the B,D and OH terms to the solubility of 2-naphthol at 25.0 °C.

the influence of these solvents on the chemical potential of solute is only the energetics effects (or these solutions are regular).

For further amplification of this conclusion, we calculated the solubility of 2-naphthol in solvents of Table 1, based upon regular solution theory.²² The regular solution equation of Hildebrand and Scatchard for solids dissolved in liquid solvents is:

$$-\ln X_B = -\ln X_B^i + A(\delta_s - \delta_B)^2 \quad (10)$$

$$A = V_B \Phi_S^2 / RT \quad (11)$$

where V_B and Φ_S have their previous meaning, X_B^i is the ideal solubility, X_B is the mole fraction of solute and δ_s and δ_B are total solubility parameters of solvent and solute respectively. The values of δ_s and δ_B are listed in Table 2.

The predicted values of solubility based upon regular solution theory are listed in Table 1. The results of calculation by regular solution theory which are presented in Table 1 reveal that the solubility of 2-naphthol in alkanes and xylenes is regular, because the deviation of calculated solubilities in these solvents from the experimental values are low. So the regular behavior of these solutions are in agreement with the predictions of mobile order theory. For the remaining solvents, the deviation of calculated solubilities from the experimental data are high and therefore it is concluded that the behavior of these solutions are not regular; in other words, the factors which affect the solubility of 2-naphthol in these solvents are both energetic and entropic.

The entries in Table 1 show that the average deviation between predicted and observed values are *ca* -14% and -15% for mobile order and regular solution theories respectively. Although the average deviations of two theories are nearly the same the range of deviations for mobile order theory is from -54% to 57% while for regular solution theory it is from -99% to 197%. These results reveal that

mobile order theory does provide reasonable estimates of the solubility of 2-naphthol in a wide range of organic solvents. If ideal solution behavior is assumed then the average deviation increases significantly to *ca* -3120% between predicted and experimental values.

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References

- 1 P. Bustamante, B. Escalera, A. Martin and E. Selles, *J.Pharm.Sci.*, 1989, **78**, 576.
- 2 M.S. Chuu, C.J. Knauss, R.J. Ruch and R.R. Myers, *ACS Symp.Ser.*, 1983, **227**, 141.
- 3 F.M.Fowkes, *et al*, *J.Polym.Sci.Polym.Chem.Ed.* 1984, **106**, 6638.
- 4 R.L. Scott, *Acc.Chem.Res.*, 1987, **20**, 97.
- 5 W.E. Acree, Jr. and J.H.Rytting, *Int.J.Pharm.* 1983, **13**, 197.
- 6 P.L. Huyskens and G.G. Siegel, *Bull.Soc.Chim.Belg.* 1988, **97**, 821.
- 7 P.L. Huyskens, *J.Mol.Liq.* 1990, **46**, 285.
- 8 G.G. Siegel, P.L. Huyskens and L. Vanderheyden, *Ber.Bunsen-Ges.Phys.Chem.* 1990, **94**, 549.
- 9 P. Ruelle, *et al*, *Pharm.Res.* 1991, **8**, 840.
- 10 J.S. Chickos, G. Nicholas and P. Ruelle, *J.Chem.Inf.Comput.Sci.* 2002, **42**, 368.
- 11 W.E. Acree, Jr. and M.H. Abraham, *Can.J.Chem.* 2001, **79**, 1466.
- 12 P. Ruelle, *J.Chem.Inf.Comput.Sci.* 2000, **40**, 681.
- 13 H. Iloukhani and S. Azizian, *Orint.J.Chem.* 2000, **16**, 253.
- 14 K.M. De Fina, T.T. Van, K.A. Fletcher and W.E. Acree, Jr. *Can.J.Chem.* 2000, **78**, 449.
- 15 K.M. De Fina, T.T. Van and W.E. Acree, Jr. *Can.J.Chem.* 2000, **78**, 459.
- 16 K.M. De Fina, T.L. Sharp, M.A. Spurgin, I. Chuca, W.E. Acree, Jr., C.E. Green and M.H. Abraham, *Can.J.Chem.* 2000, **78**, 184.
- 17 P. Ruelle, *J.Phys.Org.Chem.* 1999, **12**, 769 and references therein.
- 18 M.E.R. Mc Hale, K.S. Coym, L.E. Roy, C.E. Hernandez and W.E. Acree, Jr. *Can.J.Chem.* 1997, **75**, 1403.
- 19 K.A. Fletcher, M.E.R. Mc Hale, K.S. Coym and W.E. Acree, Jr. *Can.J.Chem.* 1997, **75**, 258.
- 20 K.A. Fletcher, M.E.R. Mc Hale, J.R. Powell, K.S. Coym and W.E. Acree, Jr. *Phys.Chem.Liq.* 1997, **34**, 41.
- 21 W.E. Acree, Jr. *Thermochim.Acta*, 1991, **189**, 37.
- 22 A. Martin, P.L. Wu, A. Adjei, A. Beerbower and J.M. Prausnitz, *J.Pharm.Sci.* 1981, **70**, 1260.
- 23 F. Allan and M. Barton, *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Inc. Boca Raton, Florida 1998.