

Solubilities of Naphthalene and Acenaphthene in Chloro Derivative Solvents

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The solubilities of naphthalene and acenaphthene in six chloro derivative solvents, chloroform, tetrachloromethane, 1,1-dichloroethane, 1,2-dichloroethane, trichloroethylene, and tetrachloroethylene, have been experimentally determined in the temperature range between 288 K and 323 K. This range corresponds to that which was found by us as an optimal one for the growth of crystals of these solids. The experimental activity coefficients calculated by using the classical equation for solid in liquid solubility have been compared with those predicted from the Scatchard–Hildebrand regular solution theory. For all the investigated solutions these activity coefficients are predicted to within an average of 8% in the case of naphthalene and 9% in the case of acenaphthene. As it could be expected, when the binary parameter I_{12} determined from the lowest solubility datum point temperature has been added to the Scatchard–Hildebrand expression (extended model), the activity coefficients are predicted with substantially higher accuracy, which is 0.6% for both solids. Moreover, the root-mean-square deviations of solubility temperatures vary from 0.09 K to 10.63 K by the regular solution model and 0.07 K to 1.03 K by the extended regular solution model for all measured data.

Introduction

An increasing interest in solid–liquid equilibrium data of polycyclic aromatic hydrocarbon (PAH) nonelectrolyte systems is mainly associated with the present trend in the petroleum industry toward heavier feedstocks and coal-derived liquids.^{1,2} In addition these data are important in the studies of the growth and nucleation processes of organic molecular crystals. Widespread attention is paid to PAHs because they combine the properties resulting from easily accessible low-lying electronic states and considerable thermal stability, allowing purification by zone refining to the high standard. The outstanding features of solution growth are as follows: (i) growth at or near room temperature, (ii) relatively high perfection of bulky crystals by elimination of stress problems resulting from inhomogeneous contraction of the support or ampule material and the adhering crystal, and (iii) development of natural faces with the possibility of intended modification of crystal morphology by the choice of the solvent. Furthermore, the above solid–liquid equilibria are becoming increasingly important with respect to the carcinogenicity and/or mutagenicity of some aromatic hydrocarbons.³

With the exception of limited solubility data of a few aromatic hydrocarbons in some chloro derivative solvents, mainly in CCl_4 , generally such data are not readily available for the above group of compounds in this type of solvents.^{4,5}

As one can notice from the above Acree's monography, only the experimental solubility data of naphthalene in tetrachloromethane, 1,1-dichloroethane, 1,2-dichloroethane, and chloroform, which are composed of 21, 8, 6, and 6 data points, respectively, and acenaphthene in tetrachloromethane (4 data points) and chloroform (3 data points)

are available from the literature. It should be pointed out that no investigation concerning correlation of naphthalene and acenaphthene activity coefficients in these solvents has been made. For both above hydrocarbons such correlations are known, for example, for such solvents as thiophene and pyridine,⁶ benzene and cyclohexane,⁷ and decaline.⁸

This paper is a part of our extensive study of the solubility behavior of such PAHs in the series of chlorinated hydrocarbon solvents, which have been found as good media for the growth of bulky crystals of these PAHs.^{9,10}

Results of such studies for naphthalene and acenaphthene (denoted in this paper by the index 2) in tetrachloromethane (CCl_4), chloroform (CHCl_3), 1,1-dichloroethane ($1,1\text{-C}_2\text{H}_4\text{Cl}_2$), 1,2-dichloroethane ($1,2\text{-C}_2\text{H}_4\text{Cl}_2$), trichloroethylene (C_2HCl_3), and tetrachloroethylene (C_2Cl_4) (index 1) are presented. To predict the solubility data, the extended Scatchard–Hildebrand regular solution theory has been used.^{11–13}

To evaluate the influence of intermolecular interaction in solutions regarded by this theory as $I_{12} \neq 0$ on activity coefficients of solutes, these coefficients have been compared to those calculated for the binary parameter, I_{12} , equal to zero.

Materials and Measurements

Analytically pure naphthalene and acenaphthene purchased from Polish Chemical Reagents, Gliwice, Poland, and International Enzymes Limited, Windsor-Berkshire, England, respectively, were recrystallized twice from distilled benzene and then from anhydrous ethyl alcohol. Such prepurified materials were chromatographed on the column filled with Al_2O_3 , vacuum sublimed, and zone refined (100 zone melting passages with the rate of 10 mm/h in an inert atmosphere of spectrally pure nitrogen, under a pressure of about 53 kPa).

Gas chromatographic analyses (CGC/FID and CGC/MS) showed that the total impurity content in materials from

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central parts of the zone-refined ingots was less than 0.03 mass %. Such purity materials were also used for crystal growth experiments.^{9,10} The melting points of purified naphthalene and acenaphthene measured by differential scanning calorimetry (DSC, NETZSCH-Gerätebau GmbH Thermal Analysis) were 354.2 K and 366.8 K, respectively.

Chloroform, 1,2-dichloroethane, trichloroethylene, and tetrachloroethylene used without further purification were supplied by either Fluka or Sigma-Aldrich Co. and had a guaranteed purity of ≥ 99.5 mass %.

Tetrachloromethane and 1,1-dichloroethane produced by Polish Chemical Reagents, Gliwice, Poland, were dried over anhydrous sodium sulfate and then fractionally distilled in a packed column of 1 m height at large reflux ratio, just before each experiment. Solvent fractions boiling at the temperature range of 349.95 K to 350.15 K and 330.35 K to 330.85 K for tetrachloromethane and 1,1-dichloroethane, respectively, were collected and used for solubility measurements.

The solubilities were measured by using a synthetic–dynamic method that is based on the temperature determination at which the last trace of a known quantity of the solid solute disappears while being slowly heated in a known quantity of solvent.¹⁴ In our case, the Pyrex test tube containing known masses of solute and solvent with accuracy $\pm 1 \times 10^{-8}$ kg was sealed by a flexible rubber cap mounted on a calibrated mercury thermometer, which was subdivided by 0.1 K. Owing to such closure, the thermometer could be used both for the temperature measurement of the mixtures and for their agitation during the solids' dissolution. The solute–solvent mixture was heated by using an electrical glass furnace supplied by a temperature controller equipped with a platinum resistor, placed near the heater. The solid solute disappearance was observed against the background of a dark screen by means of a stereoscopic microscope with 8- to 12.5-fold magnification. To prepare a solid-phase structure convenient for this observation, with possibly the same crystal size and without overly large strains, the solute was carefully dissolved and the obtained solution was rapidly solidified in the salt–ice mixture. So prepared samples were then slowly heated at the rate of 3 K/h, near the expected equilibrium temperature. Reproducibility of measurements was ± 0.3 K, corresponding to a relative error in composition $< 1\%$.

Prediction of Activity Coefficients

The most general form of the equation on the solubility of solids (2) in liquids (1) when a phase transition does not take place in the solid phase can be expressed as follows:^{11–13}

$$\ln \gamma_2 = -\ln x_2 - \frac{\Delta_{\text{fus}}H_2}{RT_m} \left(\frac{T_m}{T} - 1 \right) + \frac{\Delta_{\text{fus}}C_{p2}}{R} \left(\frac{T_m}{T} - 1 \right) - \frac{\Delta_{\text{fus}}C_{p2}}{R} \ln \frac{T_m}{T} \quad (1)$$

where x_2 , $\Delta_{\text{fus}}H_2$, $\Delta_{\text{fus}}C_{p2}$, T_m , T , and γ_2 are the solute mole fraction, the fusion enthalpy of the solute at the triple point, the difference between its solid and liquid heat capacities at the triple point, the solute triple point, the equilibrium temperature, and the activity coefficient of the solute component in the solution, respectively.

Using eq 1, one can evaluate activity coefficients of the solute, γ_2 , if solubility data (x_2 vs T) are available, assuming that other physical constants of the equation are known.

Table 1. Physical Properties of Naphthalene and Acenaphthene at the Triple Point⁷

solid	T_m	$10^{-3}\Delta_{\text{fus}}H_2$	$\Delta_{\text{fus}}S_2$	$\Delta_{\text{fus}}C_{p2}$
naphthalene	K	$\text{J}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
acenaphthene	353.3	18.238	51.623	8.901
	366.6	21.476	58.573	14.855

For the two solids used in this study, the necessary physical properties, all taken from Choi et al.,⁷ are given in Table 1.

For correlation of the activity coefficients, the Scatchard–Hildebrand regular solution model (eq 2) was used.^{11–13} As found by Choi et al.,^{6,7} this model may be treated as the most useful for the PAH solutions in a single solvent.

According to this model, the activity coefficient of the solute, γ_2 , can be predicted from pure component properties only by using the following equation:

$$RT \ln \gamma_2 = V_2^L \Phi_1^2 (\delta_1 - \delta_2)^2 \quad (2)$$

where V_2^L , Φ_1 , and δ_1 and δ_2 are the molar liquid volume of the solute, the molar liquid volume fraction of the solvent, and the solubility parameters of the solvent and solute, respectively.

The solubility parameter δ_i is defined by^{15,16}

$$\delta_i = (\Delta U_i^N / V_i)^{1/2} \quad (3)$$

where ΔU_i^N is the internal energy change for component i upon going from liquid to the ideal gas state. At temperatures well below the critical temperature

$$\Delta U_i^N = \Delta H_i^N - RT \quad (4)$$

where ΔH_i^N is the molar enthalpy of vaporization of pure component i at the temperature T .

In subsequent calculations the molar volume was determined from

$$V_i = M/d_i \quad (5)$$

where d_i and M are the density of component i at the melting point of the solid and molecular weight, respectively.

We also tested the extended Scatchard–Hildebrand model (eq 6), in which the term with the binary parameter I_{12} was added to eq 2, giving

$$RT \ln \gamma_2 = V_2^L \Phi_1^2 [(\delta_1 - \delta_2)^2 + 2I_{12}\delta_1\delta_2] \quad (6)$$

This equation requires one experimental datum point for evaluation of the binary parameter I_{12} .

Solubility parameters and molar liquid volumes of the solutes and solvents which have served for calculation of activity coefficients were evaluated at the melting points of these solutes, according to the assumption of the floating datum point method introduced by Choi and McLaughlin⁶ (Table 2).

Results and Discussion

The measured solubility data, x_2 and T , of naphthalene and acenaphthene are listed in Table 3 and plotted as $\ln x_2$ versus $1/T$ in Figures 1 and 2.

The dashed lines in these figures correspond to an ideal solubility defined by eq 1 if γ_2 is equal to unity and ΔC_p is independent of temperature, while the solid lines were obtained by fitting by the least-squares method according

Table 2. Solubility Parameters and Molar Liquid Volumes of Solids and Liquids at the Melting Points of Solids

solute solvents	naphthalene at $T_m = 354.2$ K		acenaphthene at $T_m = 366.8$ K	
	$10^{-4}\delta$	$10^6 V^l$	$10^{-4}\delta$	$10^6 V^l$
	($\text{J}\cdot\text{mol}^{-3}$) ^{1/2}	$\text{m}^3\cdot\text{mol}^{-1}$	($\text{J}\cdot\text{mol}^{-3}$) ^{1/2}	$\text{m}^3\cdot\text{mol}^{-1}$
	1.9662 ^a	130.86 ^a	1.8930 ^a	149.80 ^a
CHCl ₃	1.7059 ^b	86.70 ^c	1.6616 ^b	88.27 ^c
CCl ₄	1.5977 ^b	104.65 ^d	1.5567 ^b	107.02 ^d
1,1-C ₂ H ₄ Cl ₂	1.6424 ^b	91.44 ^c	1.5984 ^b	93.28 ^c
1,2-C ₂ H ₄ Cl ₂	1.8678 ^b	83.77 ^c	1.8250 ^b	85.20 ^c
C ₂ HCl ₃	1.6945 ^b	95.89 ^c	1.6694 ^b	98.70 ^c
C ₂ Cl ₄	1.7481 ^b	110.86 ^c	1.7140 ^b	112.53 ^c

^a Choi et al.⁷ ^b Enthalpy of vaporization data given by Lide.¹⁸
^c Density data given by Riddick et al.¹⁹ ^d Density data given by Timmermans.²⁰

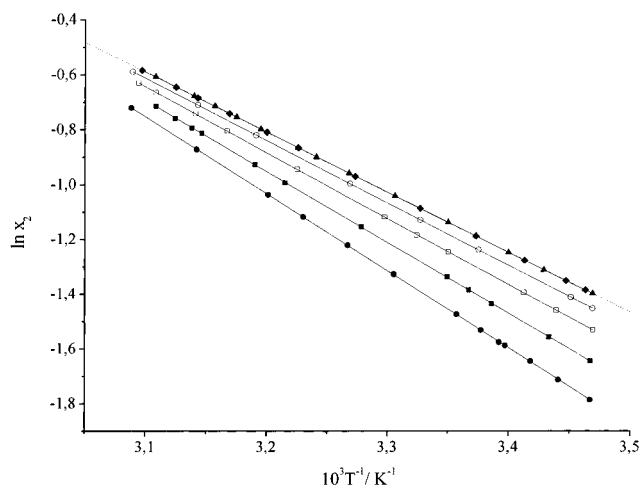


Figure 1. Measured solubilities of naphthalene: (▲) 1,2-dichloroethane; (◆) chloroform; (○) 1,1-dichloroethane; (□) trichloroethylene; (■) tetrachloromethane; (●) tetrachloroethylene. Ideal solubility curve calculated from eq 1 (---). The solid lines represent the least-squares fits according to eq 7. The constants are given in Table 4.

to the solubility equation in a general form (eq 7) to the experimental points

$$\ln x_2 = A - B/T \quad (7)$$

where A and B are constants and x_2 is the solute mole fraction.

The values of the above constants A and B for the ideal and experimental solubilities of both solids are listed in Table 4.

From a comparison of the measured and ideal solubility values one concludes that all the investigated solutions are nonideal and that the experimental solubilities of both hydrocarbons are lower than their ideal solubilities. The nonideality of these solutions increases in the order of the solvents used 1,2-C₂H₄Cl₂, CHCl₃, 1,1-C₂H₄Cl₂, C₂HCl₃, CCl₄, and C₂Cl₄ for naphthalene and CHCl₃, C₂HCl₃, 1,2-C₂H₄Cl₂, 1,1-C₂H₄Cl₂, CCl₄, and C₂Cl₄ for acenaphthene.

Moreover, a comparison of the measured solubilities of the solids, listed in Table 3, indicates that for each solvent the solubility of naphthalene is substantially higher than the solubility of acenaphthene. For example, at 298.15 K the solubility of naphthalene increases from 0.2293 for C₂Cl₄ to 0.3160 for 1,2-C₂H₄Cl₂, being in these solvents the lowest and the highest, respectively, whereas the solubility

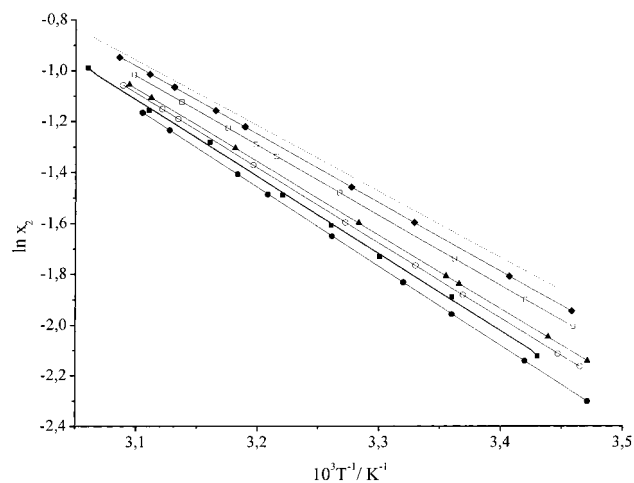


Figure 2. Measured solubilities of acenaphthene: (◆) chloroform; (□) trichloroethylene; (▲) 1,2-dichloroethane; (○) 1,1-dichloroethane; (■) tetrachloromethane; (●) tetrachloroethylene. Ideal solubility curve calculated from eq 1 (---). The solid lines represent the least-squares fits according to eq 7. The constants are given in Table 4.

of acenaphthene in these solvents changes only in the range from 0.1430 to 0.1878 for C₂Cl₄ and CHCl₃, respectively. The measured solubilities of these solids in CCl₄ are near to those reported by McLaughlin and Zainal.¹⁷ For example, the solubilities of both PAHs, measured by us at 303.15 K are 0.2983 for naphthalene and 0.1799 for acenaphthene, while those values given in the above work are 0.2986 and 0.1805, respectively. Moreover the average differences between the solubility temperatures of these PAHs for the same solute mole fractions are ± 0.24 K for naphthalene and ± 0.39 K for acenaphthene.

Experimental activity coefficients $\gamma_2(\text{exptl})$ for naphthalene and acenaphthene in the six solvents, evaluated for all data points using eq 1, are summarized in Table 3.

In the calculations, the observed melting points of the solutes were used so that the condition $\ln x_2 \rightarrow 0$ as $T_m/T \rightarrow 1$ was satisfied.

In Table 3, the experimental activity coefficients for naphthalene and acenaphthene in all the solutions are greater than one, and their values increase in the same order as the nonideality of particular solutions increases.

The activity coefficients $\gamma_2(\text{calcd})$ of naphthalene and acenaphthene in the solvents, given in Table 3, were calculated using Scatchard–Hildebrand regular solution theory (eqs 2 and 6). The binary parameters I_{12} in eq 6 were calculated at the lowest temperature at which the solubilities of naphthalene and acenaphthene in the solvents were measured.

The deviations Δ of the values from the experimental results, defined as

$$\Delta = \frac{\gamma_2(\text{exptl}) - \gamma_2(\text{calcd})}{\gamma_2(\text{exptl})} \times 100 \quad (8)$$

are given in Table 3. As can be seen from this table, the extended Scatchard–Hildebrand solution model, including the binary parameter I_{12} (eq 6), predicts activity coefficients of both these hydrocarbons with substantially higher accuracy than eq 2 for all the investigated solutions.

Equation 2 predicts the experimental activity coefficient within 8% for 71 data points of naphthalene and within 9% for 52 data points of acenaphthene, in all six solvents. If the activity coefficient was calculated from eq 6, the above deviation is 0.6% for both hydrocarbons in all

Table 3. Comparison of the Experimental and the Predicted Activity Coefficients of Naphthalene and Acenaphthene in Six Organic Chloro Derivative Solvents

<i>T</i> /K	x_2	$\gamma_2(\text{exptl})$	$I_{12} = 0$			$I_{12} \neq 0$			<i>T</i> /K	x_2	$\gamma_2(\text{exptl})$	$I_{12} = 0$			$I_{12} \neq 0$		
			$\gamma_2(\text{calcd})$	$ \Delta /\%$	$\gamma_2(\text{calcd})$	$ \Delta /\%$	$T_{\text{calcd}}/\text{K}$	$\gamma_2(\text{calcd})$				$ \Delta /\%$	$\gamma_2(\text{calcd})$	$ \Delta /\%$	$T_{\text{calcd}}/\text{K}$		
Naphthalene + 1,2-Dichloroethane ($I_{12} = 4.4 \times 10^{-5}$)																	
288.35	0.2466	1.0241	1.0233	0.08	1.0241	0.00	288.30	310.05	0.4201	1.0096	1.0108	0.12	1.0112	0.16	310.08		
291.65	0.2688	1.0213	1.0212	0.01	1.0219	0.06	291.63	313.05	0.4496	1.0082	1.0094	0.12	1.0097	0.16	313.08		
294.15	0.2866	1.0192	1.0198	0.05	1.0203	0.11	294.15	315.05	0.4701	1.0072	1.0085	0.13	1.0088	0.15	315.08		
296.55	0.3044	1.0176	1.0182	0.06	1.0188	0.12	296.56	316.85	0.4890	1.0066	1.0077	0.11	1.0080	0.13	316.87		
298.55	0.3199	1.0161	1.0170	0.09	1.0176	0.15	298.57	318.55	0.5074	1.0060	1.0070	0.10	1.0073	0.12	318.57		
302.55	0.3525	1.0137	1.0148	0.11	1.0153	0.15	302.58	320.05	0.5241	1.0054	1.0064	0.10	1.0066	0.12	320.07		
306.05	0.3830	1.0116	1.0129	0.12	1.0133	0.16	306.08	321.85	0.5445	1.0049	1.0058	0.07	1.0059	0.10	321.86		
308.55	0.4059	1.0103	1.0116	0.12	1.0120	0.16	308.58	MEAN	1.0121	1.0129	0.09	1.0134	0.12				
Naphthalene + Chloroform ($I_{12} = -8.6 \times 10^{-3}$)																	
288.85	0.2499	1.0236	1.1773	15.02	1.0236	0.00	288.80	312.55	0.4446	1.0084	1.0724	6.35	1.0100	0.16	312.60		
290.15	0.2585	1.0227	1.1707	14.47	1.0227	0.00	290.10	315.65	0.4763	1.0071	1.0618	5.42	1.0086	0.15	315.68		
293.05	0.2786	1.0203	1.1561	13.30	1.0209	0.06	293.02	318.25	0.5041	1.0062	1.0535	4.70	1.0075	0.13	318.27		
296.55	0.3044	1.0176	1.1391	11.94	1.0188	0.12	296.55	320.05	0.5241	1.0054	1.0481	4.24	1.0067	0.13	320.07		
300.65	0.3367	1.0149	1.1203	10.38	1.0163	0.1	300.67	322.95	0.5574	1.0044	1.0400	3.54	1.0056	0.12	322.97		
305.55	0.3785	1.0120	1.0992	8.62	1.0136	0.16	305.58	MEAN	1.0127	1.1017	8.76	1.0138	0.11				
310.05	0.4201	1.0096	1.0815	7.12	1.0112	0.16	310.08										
Naphthalene + 1,1-Dichloroethane ($I_{12} = -1.2 \times 10^{-2}$)																	
288.35	0.2337	1.0806	1.3193	22.08	1.0806	0.00	288.30	313.45	0.4399	1.0395	1.1236	8.10	1.0332	0.61	313.07		
289.85	0.2434	1.0779	1.3056	21.12	1.0775	0.04	289.78	318.25	0.4914	1.0322	1.0955	6.14	1.0259	0.61	317.86		
296.35	0.2895	1.0648	1.2485	17.26	1.0641	0.06	296.30	323.75	0.5543	1.0269	1.0681	4.02	1.0186	0.80	323.24		
300.65	0.3227	1.0589	1.2139	14.64	1.0558	0.30	300.45	MEAN	1.0537	1.1935	13.16	1.0502	0.33				
305.95	0.3687	1.0485	1.1734	11.91	1.0458	0.26	305.80										
Naphthalene + Trichloroethylene ($I_{12} = -2.9 \times 10^{-3}$)																	
288.35	0.2161	1.1687	1.2367	5.83	1.1686	0.00	288.30	315.85	0.4469	1.0780	1.0866	0.80	1.0628	1.41	315.03		
290.85	0.2321	1.1593	1.2214	5.36	1.1580	0.11	290.75	318.45	0.4756	1.0710	1.0755	0.42	1.0548	1.51	317.56		
298.55	0.2874	1.1310	1.1755	3.93	1.1259	0.45	298.28	321.75	0.5139	1.0626	1.0623	0.02	1.0453	1.62	320.78		
300.85	0.3056	1.1235	1.1625	3.47	1.1168	0.60	300.51	323.25	0.5321	1.0587	1.0567	0.19	1.0413	1.65	322.25		
303.35	0.3265	1.1150	1.1486	3.01	1.1070	0.72	302.94	MEAN	1.1102	1.1406	2.71	1.1010	0.85				
310.15	0.3885	1.0942	1.1133	1.75	1.0819	1.12	309.51										
Naphthalene + Tetrachloromethane ($I_{12} = -8.2 \times 10^{-3}$)																	
288.45	0.1930	1.3119	1.5505	18.19	1.3119	0.00	288.40	313.55	0.3952	1.1596	1.2290	5.99	1.1361	2.02	312.42		
291.35	0.2108	1.2926	1.5095	16.78	1.2903	0.18	291.20	317.95	0.4434	1.1366	1.1835	4.13	1.1099	2.35	316.61		
295.35	0.2377	1.2656	1.4538	14.87	1.2606	0.39	295.11	318.75	0.4520	1.1341	1.1762	3.71	1.1057	2.51	317.31		
297.05	0.2502	1.2531	1.4302	14.13	1.2479	0.41	296.80	320.15	0.4681	1.1280	1.1632	3.11	1.0981	2.66	318.61		
298.65	0.2625	1.2413	1.4082	13.45	1.2360	0.42	298.40	321.85	0.4893	1.1183	1.1472	2.58	1.0887	2.65	320.30		
305.15	0.3152	1.2041	1.3256	10.08	1.1906	1.13	304.54	MEAN	1.2015	1.3194	9.52	1.1856	1.37				
311.05	0.3699	1.1725	1.2564	7.16	1.1517	1.77	310.07										
Naphthalene + Tetrachloroethylene ($I_{12} = 9.9 \times 10^{-3}$)																	
288.45	0.1676	1.5107	1.1843	21.61	1.5107	0.00	288.40	302.65	0.2650	1.3516	1.1292	16.45	1.3450	0.49	302.36		
290.65	0.1804	1.4840	1.1759	20.76	1.4846	0.04	290.62	306.15	0.2946	1.3182	1.1158	15.36	1.3062	0.91	305.65		
292.65	0.1929	1.4609	1.1681	20.05	1.4606	0.02	292.64	309.65	0.3266	1.2871	1.1025	14.34	1.2688	1.42	308.87		
294.45	0.2043	1.4404	1.1612	19.38	1.4399	0.03	294.39	312.45	0.3542	1.2629	1.0921	13.52	1.2398	1.83	311.44		
294.85	0.2068	1.4370	1.1598	19.29	1.4355	0.10	294.75	318.35	0.4181	1.2157	1.0712	11.89	1.1825	2.73	316.80		
296.25	0.2160	1.4219	1.1545	18.80	1.4197	0.15	296.08	323.95	0.4861	1.1746	1.0529	10.36	1.1339	3.46	321.87		
297.95	0.2288	1.4004	1.1475	18.06	1.3988	0.11	297.85	MEAN	1.3666	1.1319	16.91	1.3585	0.86				
Acenaphthene + Chloroform ($I_{12} = -3.6 \times 10^{-3}$)																	
289.25	0.1425	1.1246	1.2250	8.93	1.1246	0.00	289.21	316.05	0.3139	1.0527	1.1016	4.65	1.0576	0.46	316.25		
293.55	0.1636	1.1089	1.2035	8.54	1.1131	0.38	293.68	319.45	0.3442	1.0442	1.0882	4.21	1.0501	0.56	319.70		
300.45	0.2021	1.0881	1.1701	7.54	1.0951	0.65	300.71	321.45	0.3621	1.0421	1.0810	3.73	1.0461	0.38	321.61		
305.25	0.2322	1.0777	1.1480	6.53	1.0831	0.51	305.45	324.05	0.3876	1.0364	1.0717	3.41	1.0408	0.43	324.24		
313.65	0.2943	1.0571	1.1112	5.12	1.0629	0.55	313.89	MEAN	1.0702	1.1334	5.85	1.0748	0.43				
Acenaphthene + Trichloroethylene ($I_{12} = -1.2 \times 10^{-3}$)																	
289.15	0.1342	1.1907	1.2266	3.01	1.1907	0.00	289.11	312.75	0.2746	1.1073	1.1232	1.43	1.1044	0.27	312.58		
292.35	0.1490	1.1765	1.2121	3.02	1.1787	0.18	292.39	315.05	0.2931	1.0995	1.1137	1.29	1.0964	0.28	314.87		
297.45	0.1752	1.1556	1.1891	2.90	1.1595	0.35	297.57	318.85	0.3248	1.0904	1.0990	0.79	1.0840	0.58	318.50		
306.15	0.2272	1.1280	1.1511	2.05	1.1278	0.02	306.10	322.85	0.3616	1.0794	1.0840	0.43	1.0714	0.74	322.41		
311.05	0.2620	1.1113	1.1301	1.70	1.1102	0.09	310.96	MEAN	1.1265	1.1477	1.85	1.1248	0.28				
Acenaphthene + 1,2-Dichloroethane ($I_{12} = 9.2 \times 10^{-3}$)																	
288.15	0.1172	1.3240	1.0189	23.04	1.3240	0.00	288.11	314.45	0.2707	1.1727	1.0096	13.91	1.1540	1.59	313.61		
290.85	0.1288	1.3035	1.0179	21.91	1.3053	0.14	290.87	321.35	0.3300	1.1407	1.0074	11.69	1.1162	2.15	320.17		
297.15	0.1587	1.2651	1.0157	19.71	1.2630	0.17	297.04	323.25	0.3478	1.1331	1.0068	11.14	1.1067	2.33	321.96		
298.15	0.1638	1.2602	1.0154	19.43	1.2564	0.30	297.98	MEAN	1.2274	1.0131	17.22	1.2174	0.90				
304.65	0.2019	1.2198	1.0130	16.95	1.2134	0.52	304.37										
Acenaphthene + 1,1-Dichloroethane ($I_{12} = -2.1 \times 10^{-3}$)																	
288.065	0.1147	1.3728	1.4496	5.59	1.3728	0.00	288.61	312.95	0.2531	1.2075	1.2332	2.12	1.1959	0.96	312.43		
290.15	0.1205	1.3653	1.4364	5.21	1.3622	0.23	290.02	319.15	0.3038	1.1744	1.1846	0.87	1.1556	1.60	318.28		
296.85	0.1521	1.3090	1.3738	4.95	1.3113	0.18	296.89	320.45	0.3159	1.1659	1.1746	0.75	1.1472	1.60	319.57		
300.35	0.1708	1.2840	1.3418	4.51	1.2853	0.10	300.35	323.75	0.3472	1.1487	1.1509	0.19	1.1274	1.85	322.07		
305.35	0.2022	1.2508	1.2949	3.53	1.2468	0.31	305.46	MEAN	1.2532	1.2933	3.08	1.2449	0.76				
Acenaphthene + Tetrachloromethane ($I_{12} = -5.7 \times 10^{-3}$)																	
291.15	0.1195	1.4172	1.6394	15.68	1.4172	0.00	291.11	316.95	0.2770	1.2199	1.3132	7.64	1.2119	0.66	316.57		
297.85	0.1509	1.3566	1.5508	14.32	1.3627	0.45	298.01	321.15	0.3140	1.1930	1.2659	6.10	1.1809	1.02	320.57		
302.65	0.1768	1.3203	1.4889	12.78	1.3241	0.29	302.74	327.15	0.3721	1.1618	1.2046	3.68	1.1403	1.85	326.10		
306.65	0.1999	1.2990	1.4403	10.87	1.2934	0.43	306.41	MEAN	1.2790	1.4122	10.17	1.2743	0.59				
310.15	0.2250	1.2644	1.3941	10.26	1.2640	0.03	310.10										
Acenaphthene + Tetrachloroethylene ($I_{12} = 9.4 \times 10^{-3}$)																	
288.15	0.1000	1.5517	1.1634	25.02	1.5517	0.00	288.11	311.75	0.2259	1.3122	1.1004	16.14	1.3199	0.59	311.99		
292.45	0.1172	1.5000	1.1525	23.17	1.5097	0.65	292.68	314.25	0.2444	1.2923	1.0935	15.39	1.2961	0.29	314.35		
297.65	0.1410	1.4438	1.1389	21.12	1.4586												

Table 4. Coefficients A and B and Standard Deviations σ (from Eq 7) and Root Mean Square Deviations of Temperature σ_T (from Eq 9)

solvent	A	B/K	$10^3\sigma$	σ_T /K
Naphthalene				
ideal	6.209	2193.57	0.55	
1,2-C ₂ H ₄ Cl ₂	6.209	2193.56	0.61	0.07
CHCl ₃	6.210	2194.00	0.55	0.07
1,1-C ₂ H ₄ Cl ₂	6.448	2278.08	0.82	0.28
C ₂ HCl ₃	6.813	2405.80	0.83	0.64
CCl ₄	7.312	2583.30	1.30	1.03
C ₂ Cl ₄	7.952	2808.54	1.15	0.85
Acenaphthene				
ideal	7.046	2583.02	0.61	
CHCl ₃	7.358	2691.17	1.19	0.27
C ₂ HCl ₃	7.478	2742.39	0.74	0.21
1,2-C ₂ H ₄ Cl ₂	7.869	2884.71	0.85	0.77
1,1-C ₂ H ₄ Cl ₂	8.049	2948.31	1.26	0.61
CCl ₄	8.205	3007.30	3.03	0.50
C ₂ Cl ₄	8.452	3098.30	0.65	0.39

solvents used. These small differences in deviation for particular equations are not surprising, as the solubilities of naphthalene and acenaphthene in the solvents investigated are of the same order. Moreover, eq 2 predicts the experimental activity coefficient for both solutes in particular solvents within 8% (23 data points), 7% (21 data points), 2% (20 data points), 8% (19 data points), 10% (20 data points), and 18% (22 data points) for 1,2-C₂H₄Cl₂, CHCl₃, C₂HCl₃, 1,1-C₂H₄Cl₂, CCl₄, and C₂Cl₄, respectively. Prediction accuracies of activity coefficients by eq 6 for the same number of data points are 0.5% for the above four former solvents and 0.9% and 0.7% for CCl₄ and C₂Cl₄, respectively.

This latter result not only indicates that owing to the binary parameter $I_{1,2}$ the Scatchard–Hildebrand regular solution model (eq 6) predicts γ_2 with higher accuracy but also signifies that solubility parameters can be evaluated at the melting temperature of the solute. It is also noteworthy that the γ_2 values calculated for both hydrocarbons at their melting points are nearly the same as those calculated at 298 K. Namely, activity coefficients calculated at the latter temperature are only 0.06% higher in the case of naphthalene and 0.3% lower in the case of acenaphthene. These differences increase to 8% and 27% for naphthalene and acenaphthene, respectively, when eq 2 was used. Thus the difficulties in obtaining solubility parameters of the solute components in their subcooled liquid state at 298 K can be eliminated by its replacement by the solute melting points.

Furthermore, the root-mean-square deviation of temperature, defined by eq 9, has been calculated by us and used as a measure of the fit goodness of the solubility curves

$$\sigma_T = \left[\frac{\sum_{i=1}^n (T_i^{\text{calcd}} - T_i)^2}{(n-1)} \right]^{1/2} \quad (9)$$

where T_i^{calcd} and T_i are the calculated and experimental temperatures of the i -th points, respectively, and n is the number of experimental points.

In Table 3 are given calculated temperatures T_{calcd} (eq 6) which have served for calculation of root-mean-square deviation of temperature σ_T ; these values are summarized in Table 4. The above results have shown that the differences between T_{exptl} and T_{calcd} are small; therefore, the σ_T values are low.

Equation 9 describes the solubility curves with σ_T ranging from 0.07 to 1.03 K and from 0.28 to 0.77 K in the case of naphthalene and acenaphthene, respectively. In the case of eq 2 the values of σ_T are from 0.09 to 9.63 K and from 1.06 to 10.63 K for the naphthalene and acenaphthene solubility curves, respectively.

The results obtained indicate that the extended Scatchard–Hildebrand model is a very good choice for prediction of solid solubility in solvents, if, as in our case, their dipole moment differences are slight.

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