natural gas plus 0%, 5.5%, and 10.0% water in the sour natural gas. The uncertainty bands reflect three standard deviations as provided by the maximum likelihood computer program. They do not contain the unknown systematic errors. While the usual experimental diagnostics for adsorption were absent, the adsorption of one molecule out of 1000 causes about ±0.3 $\mathrm{cm}^3/\mathrm{mol}$ in B_{m} and ±75 $\mathrm{cm}^6/\mathrm{mol}^2$ in C_{m}. The usual effect of adsorption is to make the computed B_{m} too negative with C_{m} too positive for compensation.

Conclusions

PVT data plus second and third virial coefficients have been reported for six wet natural gas mixtures. The presence of small amounts of water is seen to have a major influence on the densities, B_{m} and, particularly, C_{m}.

It has been shown elsewhere (*7*) that B_{m} and C_{m} for the sweet natural gas mixtures to 5.0% water content are predicted within experimental uncertainties by the correlations of Tsonopoulos (*8*) and Orbey and Vera (*9*), respectively. The prediction is a priori in that the binary interaction constants k_{ij} contained in both correlations were not adjusted to fit the data but rather the values used were those of Prausnitz (*10*). The 10.0% water/sweet gas virial coefficients are not so well predicted possibly due to poor values of B_{ii} and C_{iii} for pure water. These correlations generally predict reasonable values of B_{ij} and C_{ijk} as long as no more than one polar molecule is involved in the interaction. Thus, a priori prediction of B_{m} and C_{m} for any of the sour gas systems is poor due to the presence of CO_2, H_2S, and, in the last two systems, water.

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Solubilities of Polynuclear Aromatic Hydrocarbons in Mixtures of Common Organic Solvents

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The solubilities of naphthalene, acenaphthene, fluorene, and phenanthrene have been determined experimentally in five binary mixtures and one quaternary mixture of four common organic solvents (benzene, cyclohexane, thiophene, and pyridine) from 25 °C to the melting points of the solutes. The results have been correlated by using the classical equation for solid–liquid solubility and the experimental activity coefficients obtained have been compared to the values predicted by regular solution theory, extended regular solution theory, Wilson's equation, and UNIQUAC, after obtaining binary parameters from the solubility of each solute in the pure solvents.

Introduction

With the present trend in the petroleum industry toward heavier feedstocks and coal-derived liquids, there is a strong need for expansion of the small database of thermodynamic data on heavier compounds that presently exists. As these heavier feedstocks, rich in polynuclear aromatic hydrocarbons (PAH's), become more common, there will be a corresponding increase in the need for thermodynamic data for design purposes. Activity coefficient data will be needed as will solubility limit data, which are important to ensure that precipitation of these heavy components, with consequent plugging of lines and vessels, does not occur.

The activity coefficient data, usually obtained from VLE results, will have to be obtained by other methods as VLE data will be difficult or impossible to obtain for binary mixtures of species with such widely disparate vapor pressures. The obvious source of the necessary data is solid–liquid solubility results. Because of the need for this type of data, there has been a renewed interest in investigations such as we report here, which have substantially extended the available database (*1*–*7*). A good discussion of this area through 1984 is available (*8*). In this work, we have extended the studies of McLaughlin and Zainal (*1*–*3*) and Choi and McLaughlin (*4*) to mixtures of solvents. This is a continuation of the work presented in Choi et al. (*5*).

The calculation of activity coefficients from solid–liquid solubility data is discussed in the next section. The third section presents the activity coefficient models used. The fourth and fifth sections present our experimental results and discuss our conclusions concerning the appropriate choice of activity coefficient models.

Experimental Procedures

The chemicals used in this study were purchased and purified by methods discussed in previous papers (*4*, *5*). These chemicals (the solutes) are recovered by rotary evaporation of the solvents in vacuo and reused. The purities of the recovered materials relative to the original are monitored by melting point determinations to ensure that no contamination or degradation

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Table I. Comparison of the Experimental and Predicted Activity Coefficients of Naphthalene in Five Binary Solvent Mixtures

			$l_{ij} = 0$		$l_{ij} \neq 0$		Wilson's eq		UNIQUAC	
temp/K	x_2(exptl)	γ_2(exptl)	γ_2(calcd)	Δ/%	γ_2(calcd)	Δ/%	γ_2(calcd)	Δ/%	γ_2(calcd)	Δ/%
70 mol % Benzene and 30 mol % Thiophene										
303.9	0.3433	1.085	1.074	−1.0	1.046	−3.6	1.074	−1.0	1.058	−2.5
314.8	0.4476	1.064	1.046	−1.7	1.029	−3.3	1.057	−0.7	1.049	−1.4
344.4	0.8424	1.021	1.003	−1.8	1.002	−1.9	1.006	−1.5	1.006	−1.5
336.2	0.7142	1.031	1.009	−2.1	1.006	−2.4	1.018	−1.2	1.018	−1.3
324.6	0.5520	1.055	1.027	−2.7	1.017	−3.6	1.041	−1.4	1.037	−1.7
70 mol % Benzene and 30 mol % Pyridine										
303.7	0.3421	1.084	1.046	−3.5	1.061	−2.1	1.055	−2.6	1.081	−0.2
315.0	0.4525	1.057	1.028	−2.7	1.037	−1.9	1.050	−0.6	1.066	+0.9
324.7	0.5619	1.043	1.016	−2.6	1.021	−2.1	1.040	−0.2	1.048	+0.5
335.4	0.7054	1.028	1.006	−2.1	1.008	−1.9	1.024	−0.4	1.025	−0.3
344.0	0.8382	1.019	1.002	−1.7	1.002	−1.7	1.009	−1.0	1.008	−1.1
70 mol % Cyclohexane and 30 mol % Thiophene										
308.2	0.2880	1.429	1.309	−8.4	1.326	−7.2	1.302	−8.9	1.305	−8.6
312.9	0.3593	1.271	1.232	−3.1	1.245	−2.0	1.236	−2.8	1.234	−2.9
319.7	0.4430	1.190	1.160	−2.5	1.168	−1.8	1.171	−1.6	1.166	−2.0
327.1	0.5486	1.122	1.096	−2.3	1.101	−1.9	1.108	−1.3	1.102	−1.8
337.9	0.7202	1.056	1.032	−2.3	1.034	−2.1	1.039	−1.6	1.036	−1.9
347.8	0.8998	1.017	1.004	−1.3	1.004	−1.3	1.005	−1.2	1.004	−1.3
70 mol % Cyclohexane and 30 mol % Pyridine										
314.8	0.4083	1.165	1.148	−1.5	1.166	+0.1	1.145	−1.7	1.136	−2.5
341.3	0.7832	1.036	1.015	−2.0	1.017	−1.8	1.016	−1.9	1.015	−2.1
347.2	0.8984	1.006	1.003	−0.3	1.003	−0.3	1.003	−0.3	1.003	−0.3
301.1	0.2763	1.264	1.256	−0.6	1.289	+2.0	1.238	−2.1	1.226	−3.0
322.2	0.5047	1.103	1.095	−0.7	1.107	+0.4	1.096	−0.6	1.089	−1.2
330.8	0.6189	1.072	1.052	−1.9	1.058	−1.3	1.053	−1.7	1.039	−2.1
70 mol % Thiophene and 30 mol % Pyridine										
303.8	0.3561	1.044	1.004	−3.8	1.022	−2.1	1.005	−3.7	1.003	−3.8
306.7	0.3822	1.040	1.004	−3.5	1.019	−2.0	1.009	−3.0	1.010	−2.8
317.8	0.4911	1.034	1.002	−3.1	1.012	−2.1	1.016	−1.7	1.024	−0.9
323.0	0.6737	1.028	1.001	−2.6	1.004	−2.3	1.014	−1.3	1.020	−0.7
346.0	0.8696	1.017	1.000	−1.7	1.001	−1.6	1.004	−1.6	1.005	−1.2

is occurring. All of the solvents are Aldrich Gold Label quality and are used on a "once through" basis as purchased.

The experimental procedures used are essentially the same as those described in previous publications (*1–5*). This consists of determining the temperature at which the last trace of a known quantity of the solid solute disappears while being slowly heated in a known quantity of solvent. The temperature obtained represents the liquidus line at that composition. The whole liquidus curve can be obtained by running samples at various compositions. This technique is fast and has proven to be very reliable.

The errors in composition are quite small with this method as both components are weighed out to 0.00001 g. If an accuracy of 0.002 g is assumed (quite conservatively) the largest expected error in solute mole fraction is ±0.0003 which is much less than 1% of the lowest values reported. The error in temperature measurement is less than 0.1 °C based on the accuracy of our thermometers. It should be noted, however, that the largest source of error in our measurement is human error in visually determining the end point. Though it is difficult to assign error bars to human error, we are confident that the end points can be determined to less than 0.3 °C all of the time and are usually much closer than that.

These errors have a minimal effect on the calculated activity coefficients, much less than the effect of possible errors in the literature values of the thermodynamic properties used. For these reasons, and because many of the samples have been repeated multiple times with a high degree of reproducibility, we have a high level of confidence in the data listed and in the experimental activity coefficients calculated.

Theory

The classical theory of solid–liquid equilibrium is well established and excellent discussions are available in many textbooks (*8*, *9*). By equating the fugacity of the pure solid to the fugacity of the solid in solution and making use of the applicable thermodynamic cycle, the following equation can be obtained for the solubility of a solute in a solvent or mixture of solvents

$$-\ln x_i = \frac{\Delta h_i^{\mathrm{f}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{m}}}\right) - \frac{\Delta C_{p_i} T_{\mathrm{m}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{m}}}\right) + \frac{\Delta C_{p_i}}{R}\ln\left(\frac{T_{\mathrm{m}}}{T}\right) + \ln\gamma_i + \frac{\Delta v_i}{RT}(P - P_i^{\mathrm{sat}}) + \lambda \quad (1)$$

where Δh_i^{f}, ΔC_{p_i}, and γ_i are the molar enthalpy of fusion of the solute at its triple point, the difference between its solid and liquid heat capacities at the triple point, and the liquid-phase activity coefficient, respectively. The triple point temperature has been replaced in eq 1 by the melting point, a simplification that introduces a negligible error. The last term in eq 1, λ, represents the effect on the solubility of a solid–solid lambda phase transition in the solute (*10*). It is zero if the temperature is above the transition temperature but for temperatures below the lambda transition it is given by

$$\lambda = \frac{\Delta h_i^{\mathrm{P}}}{RT} - \frac{\Delta s_i^{\mathrm{P}}}{R} \quad (2)$$

where Δs_i^{P} and Δh_i^{P} are the entropy and enthalpy changes of the lambda transition, respectively.

Table II. Comparison of the Experimental and Predicted Activity Coefficients of Acenaphthene in Five Binary Solvent Mixtures

			$l_{ij} = 0$		$l_{ij} \neq 0$		Wilson's eq		UNIQUAC	
temp/K	x_2(exptl)	γ_2(exptl)	γ_2(calcd)	Δ/%	γ_2(calcd)	Δ/%	γ_2(calcd)	Δ/%	γ_2(calcd)	Δ/%
			70 mol % Benzene and 3 mol % Thiophene							
301.5	0.2007	1.130	1.123	−0.6	1.103	−2.4	1.096	−3.0	1.078	−4.6
309.2	0.2514	1.106	1.098	−0.7	1.083	−2.1	1.080	−2.4	1.068	−3.3
317.9	0.3189	1.087	1.073	−1.3	1.062	−2.3	1.061	−2.4	1.057	−2.7
325.7	0.3959	1.057	1.052	−0.5	1.044	−1.3	1.045	−1.1	1.045	−1.1
335.2	0.5039	1.034	1.030	−0.4	1.026	−0.8	1.028	−0.6	1.030	−0.4
344.9	0.6414	1.005	1.014	+0.8	1.011	+0.6	1.013	+0.8	1.016	+1.0
355.6	0.8148	0.989	1.003	+1.4	1.003	+1.4	1.003	+1.4	1.004	+1.4
			70 mol % Benzene and 30 mol % Pyridine							
311.1	0.2524	1.158	1.058	−8.6	1.137	−1.8	1.131	−2.3	1.153	−0.4
349.6	0.7182	0.992	1.005	+1.2	1.011	+1.9	1.014	+2.2	1.014	+2.2
322.9	0.3545	1.105	1.037	−6.1	1.087	−1.6	1.090	−1.4	1.101	−0.3
331.8	0.4570	1.058	1.023	−3.3	1.054	−0.4	1.060	+0.1	1.065	+0.6
333.6	0.4786	1.051	1.021	−2.9	1.048	−0.3	1.054	+0.3	1.059	+0.7
340.3	0.5775	1.012	1.012	0.0	1.028	+1.6	1.034	+2.1	1.035	+2.3
			70 mol % Cyclohexane and 30 mol % Thiophene							
304.1	0.1511	1.610	1.532	−4.8	1.702	+5.7	1.559	−3.2	1.490	−7.4
310.2	0.1885	1.514	1.451	−4.2	1.591	+5.0	1.470	−2.9	1.422	−6.1
316.0	0.2332	1.418	1.372	−3.3	1.483	+4.6	1.384	−2.4	1.351	−4.7
321.5	0.2820	1.343	1.302	−4.0	1.389	+3.5	1.309	−2.5	1.287	−4.2
327.8	0.3519	1.250	1.223	−2.2	1.285	+2.8	1.226	−2.0	1.213	−3.0
333.5	0.4311	1.163	1.155	−0.7	1.197	+2.9	1.156	−0.6	1.149	−1.2
340.6	0.5381	1.092	1.091	−0.1	1.115	+2.1	1.090	−0.2	1.087	−0.5
348.0	0.6654	1.035	1.042	+0.7	1.053	+1.8	1.042	+0.6	1.040	+0.5
356.3	0.8193	0.997	1.011	+1.4	1.014	+1.6	1.011	+1.4	1.010	+1.3
			70 mol % Cyclohexane and 30 mol % Pyridine							
304.5	0.1702	1.444	1.373	−5.0	1.602	+10.9	1.419	−1.7	1.341	−7.2
310.3	0.2079	1.377	1.318	−4.3	1.508	+9.5	1.350	−1.9	1.292	−6.2
319.2	0.2810	1.274	1.234	−3.1	1.367	+7.3	1.249	−1.9	1.215	−4.6
326.8	0.3602	1.193	1.167	−2.2	1.258	+5.5	1.173	−1.7	1.153	−3.4
			70 mol % Thiophene and 30 mol % Pyridine							
311.5	0.2825	1.046	1.005	−3.9	1.061	+1.4	1.041	−0.5	1.041	−0.5
322.2	0.3619	1.064	1.003	−5.7	1.042	−2.1	1.036	−2.7	1.036	−2.7
331.2	0.4572	1.041	1.002	−3.8	1.027	−1.4	1.028	−1.3	1.038	−1.3
335.9	0.5195	1.019	1.002	−1.8	1.019	0.0	1.023	+0.4	1.023	+0.4
341.6	0.5956	1.006	1.001	−0.5	1.012	+0.6	1.017	+1.0	1.017	+1.0
350.4	0.7258	0.999	1.000	+0.1	1.005	+0.6	1.008	+0.9	1.008	+0.9

If the activity coefficient in eq 1 is unity (an ideal solution), the equation for the ideal solubility of a solute in a solvent remains. It is the deviations of actual solubilities from the ideal values due to liquid-phase nonidealities that are of interest.

While it may appear that eq 1, when combined with a suitable expression for the activity coefficient, makes solid–liquid solubility a closed subject, the reality is less simple. Equation 1 is only applicable in theory when the solute and solvents are completely immiscible in the solid phase. This is usually the case though there can be exceptions (*11*). It is only applicable in practice when the necessary calorimetric data are available. The number of compounds for which the necessary data exist is very limited. We have chosen to study four PAH's for which the required data exist. They are naphthalene, acenaphthene, fluorene, and phenanthrene. These compounds, while not as varied as we would have liked, are all commonly found in heavy feedstocks and coal liquids.

The next section presents the models we used to predict the activity coefficients for comparison with the experimental values found from eq 1.

Solution Models Considered

The following equations have been chosen to correlate the experimental activity coefficients: regular solution theory (*12*), Wilson's equation (*13*), and the UNIQUAC equation (*14*). Each of these equations is discussed briefly below.

Regular Solution Theory. Regular solution theory, as formulated by Scatchard and Hildebrand (*12*), gives the following equation for the liquid-phase activity coefficient of the solute (2) in a multicomponent mixture

$$RT \ln \gamma_2 = v_2^{l}(\delta_2 - \bar{\delta})^2 \qquad (3)$$

where

$$\bar{\delta} = \sum_i \Omega_i \delta_i \qquad (4)$$

$$\Omega_i = \frac{x_i v_i^{l}}{\sum_i x_i v_i^{l}} \qquad (5)$$

v_i^{l} and δ_i are the molar volume and solubility parameter of component i, respectively. The solubility parameter is defined by

$$\delta_i = \left(\frac{\Delta u_i^{v}}{v_i^{l}}\right)^{1/2} \qquad (6)$$

where Δu_i^{v} is the internal energy change for component i upon going from the liquid to the ideal gas state.

The theory assumes that the excess entropy of mixing is zero. It can predict only positive deviations from Raoult's law due to the use of the geometric mean approximation for unlike interaction energies in its derivation.

Table III. Comparison of the Experimental and Predicted Activity Coefficients of Phenanthrene in Five Binary Solvent Mixtures

			$l_{ij} = 0$		$l_{ij} \neq 0$		Wilson's eq		UNIQUAC	
temp/K	x_2(exptl)	γ_2(exptl)	γ_2(calcd)	Δ/%	γ_2(calcd)	Δ/%	γ_2(calcd)	Δ/%	γ_2(calcd)	Δ/%
70 mol % Benzene and 30 mol % Thiophene										
306.5	0.2479	1.236	1.285	+4.0	1.204	−2.6	1.205	−2.5	1.207	−2.3
311.6	0.2888	1.181	1.233	+4.4	1.168	−1.2	1.178	−0.3	1.180	−0.1
316.1	0.3223	1.161	1.197	+3.0	1.142	−1.7	1.157	−0.4	1.159	−0.3
324.8	0.4024	1.108	1.131	+2.0	1.096	−1.2	1.116	+0.6	1.116	+0.6
331.5	0.4710	1.081	1.092	+1.0	1.067	−1.3	1.087	+0.6	1.086	+0.5
338.7	0.5455	1.071	1.062	−1.0	1.044	−2.5	1.061	−0.9	1.060	−1.0
347.8	0.6550	1.044	1.030	−1.4	1.022	−2.1	1.033	−1.0	1.032	−1.1
356.5	0.7673	1.022	1.012	−1.0	1.009	−1.3	1.014	−0.8	1.013	−0.8
70 mol % Benzene and 30 mol % Pyridine										
313.4	0.2983	1.189	1.158	−2.6	1.159	−2.5	1.139	−4.2	1.195	+0.5
325.2	0.3993	1.127	1.096	−2.8	1.096	−2.7	1.106	−1.9	1.124	−0.3
334.3	0.5014	1.073	1.056	−1.6	1.056	−1.6	1.074	+0.1	1.075	+0.2
342.6	0.5968	1.055	1.032	−2.2	1.032	−2.2	1.049	−0.6	1.044	−1.0
351.8	0.7033	1.037	1.015	−2.1	1.015	−2.1	1.026	−1.0	1.021	−1.5
359.2	0.8075	1.014	1.006	−0.8	1.006	−0.8	1.011	−0.3	1.008	−0.5
70 mol % Cyclohexane and 30 mol % Thiophene										
301.9	0.1168	2.375	2.557	+7.7	2.617	+10.2	2.184	−8.1	2.202	−7.3
309.2	0.1558	2.082	2.239	+7.6	2.285	+9.7	1.985	−4.7	1.967	−5.5
316.5	0.2096	1.801	1.927	+7.0	1.958	+8.7	1.772	−1.6	1.727	−4.1
323.3	0.2759	1.570	1.660	+5.7	1.681	+7.0	1.575	+0.3	1.519	−3.3
330.7	0.3731	1.343	1.405	+4.6	1.417	+5.5	1.373	+2.3	1.149	−1.8
340.3	0.5165	1.165	1.190	+2.1	1.195	+2.5	1.187	+1.8	1.044	−0.7
351.6	0.7007	1.037	1.057	+2.0	1.059	+2.1	1.061	+2.3	1.051	+1.4
70 mol % Cyclohexane and 30 mol % Pyridine										
325.6	0.3442	1.318	1.383	+4.9	1.418	+7.5	1.313	−0.3	1.257	−4.6
338.2	0.5036	1.150	1.169	+1.6	1.183	+2.9	1.148	−0.2	1.115	−3.0
328.5	0.3830	1.255	1.317	+4.9	1.344	+7.1	1.263	+0.7	1.213	−3.3
345.7	0.6059	1.100	1.093	−0.7	1.100	0.0	1.084	−1.4	1.063	−3.4
355.4	0.7267	1.061	1.038	−2.1	1.041	−1.8	1.037	−2.3	1.026	−3.3
70 mol % Thiophene and 30 mol % Pyridine										
308.3	0.3038	1.049	1.046	−0.3	1.065	+1.5	1.029	−1.9	1.028	−2.0
309.7	0.3136	1.046	1.044	−0.2	1.062	+1.5	1.030	−1.5	1.033	−1.2
327.7	0.4599	1.028	1.021	−0.7	1.029	+0.1	1.034	+0.6	1.058	+2.9
344.4	0.6296	1.035	1.008	−2.6	1.011	−2.3	1.021	−1.3	1.036	+0.7
351.0	0.7157	1.007	1.004	−0.3	1.006	−0.1	1.014	+0.7	1.022	+1.5
351.1	0.7157	1.007	1.004	−0.3	1.006	−0.1	1.014	+0.7	1.022	+1.5

The solubility parameters (eq 6) are usually evaluated at 25 °C. Choi and McLaughlin (*4*) have shown that a more convenient (and equally correct) temperature is the melting point of the solid. They call this choice of temperature for the solubility parameters the floating datum point method. Their results indicated that the average error for the solubility at temperatures from 25 °C to the solute melting point was lower when the parameters were evaluated at the melting point. They concluded that this happened because of the inherent difficulty of trying to evaluate δ_i for the subcooled liquid solute at 25 °C.

Regular solution theory can be extended in a number of ways to be more widely applicable. The most common extension (*12*) is the addition of an adjustable parameter to eq 3, which becomes

$$RT \ln \gamma_2 = v_2^l \sum_i \sum_j \Omega_i \Omega_j [D_{i2} - \tfrac{1}{2} D_{ij}] \qquad (7)$$

where

$$D_{ij} = (\delta_i - \delta_j)^2 + 2 l_{ij} \delta_i \delta_j \qquad (8)$$

$$l_{ii} = D_{ii} = 0 \qquad (9)$$

l_{12} is a parameter that is obtained by fitting data at a single solubility point and represents the deviation of the unlike pair interaction from the geometric mean approximation. Another obvious extension is obtained by using eq 3 and allowing the solubility parameters to be functions of temperature. The values of δ_i for the solvent are calculated at various temperatures and fitted to a polynomial. The value of δ_i for the solute is calculated at its melting point but its value at 25 °C is determined by fitting the solubility results at 25 °C. These values are also fitted to a polynomial. Equation 3 is then used with these temperature-dependent parameters.

It should be noted that addition of l_{12} allows prediction of either positive or negative deviations from Raoult's law while the extension to temperature-dependent solubility parameters still only predicts positive deviations. This is not a serious limitation for the types of systems we are investigating as it has been demonstrated that they generally exhibit positive deviations from Raoult's law. Based on our analysis, there are approximately equal fits to the data using either extension so only the more common l_{12} extension has been used in the data analysis.

Wilson's Equation. Wilson's equation (*13*) is an entropic equation that utilizes the concept of local compositions in the liquid phase to predict the nonideality. The activity coefficient of the solute is given by

$$\ln \gamma_2 = 1 - \ln \left(\sum_j x_j G_{2j}\right) - \sum_k \left(\frac{x_k G_{k2}}{\sum_j x_j G_{kj}}\right) \qquad (10)$$

where

$$G_{ij} = \frac{v_j^l}{v_i^l} \exp\left(-\frac{\lambda_{ij}}{RT}\right) \qquad (11)$$

Table IV. Comparison of the Experimental and Predicted Activity Coefficients of Fluorene in Five Binary Solvent Mixtures

			$l_{ij} = 0$		$l_{ij} \neq 0$		Wilson's eq		UNIQUAC	
temp/K	x_2(exptl)	γ_2(exptl)	γ_2(calcd)	$\Delta/\%$	γ_2(calcd)	$\Delta/\%$	γ_2(calcd)	$\Delta/\%$	γ_2(calcd)	$\Delta/\%$
			70 mol % Benzene and 30 mol % Thiophene							
303.0	0.1578	1.168	1.218	+4.3	1.154	-1.2	1.142	-2.3	1.123	-3.8
310.7	0.1940	1.150	1.184	+2.9	1.130	-1.8	1.132	-1.5	1.114	-3.1
317.4	0.2316	1.130	1.154	+2.2	1.110	-1.8	1.122	-0.7	1.105	-2.2
325.4	0.2839	1.105	1.121	+1.4	1.086	-1.7	1.108	+0.3	1.092	-1.2
331.9	0.3332	1.084	1.096	+1.1	1.069	-1.4	1.095	+1.0	1.080	-0.4
339.3	0.3959	1.065	1.071	+0.6	1.051	-1.3	1.079	+1.3	1.065	0.0
347.5	0.4793	1.035	1.047	+1.1	1.034	-0.2	1.060	+2.4	1.048	+1.3
354.0	0.5530	1.016	1.031	+1.5	1.022	+0.7	1.044	+2.8	1.035	+1.9
			70 mol % Benzene and 30 mol % Pyridine							
308.7	0.1845	1.156	1.122	-2.9	1.187	+2.7	1.141	-1.3	1.207	+4.4
326.0	0.2736	1.163	1.081	-7.1	1.123	-3.5	1.110	-4.6	1.149	-1.2
333.1	0.3394	1.094	1.060	-3.1	1.091	-0.3	1.092	-0.2	1.117	+2.1
351.6	0.5031	1.067	1.027	-3.8	1.040	-2.6	1.051	-1.5	1.057	-0.9
359.8	0.6042	1.035	1.015	-1.9	1.022	-1.2	1.032	-0.3	1.034	-0.1
			70 mol % Cyclohexane and 30 mol % Thiophene							
300.5	0.0828	2.087	1.973	-5.5	2.424	+16.1	1.772	-15.1	1.745	-16.4
308.6	0.1108	1.914	1.835	-4.1	2.205	+15.2	1.698	-11.3	1.673	-12.6
316.0	0.1429	1.772	1.709	-3.6	2.009	+13.4	1.620	-8.6	1.594	-10.1
322.7	0.1792	1.648	1.594	-3.3	1.836	+11.4	1.541	-6.5	1.513	-8.2
331.1	0.2378	1.494	1.453	-2.7	1.626	+8.9	1.434	-4.0	1.403	-6.1
338.7	0.3073	1.355	1.330	-1.9	1.449	+7.0	1.331	-1.8	1.300	-4.0
345.2	0.3824	1.241	1.233	-0.6	1.313	+5.9	1.243	+0.2	1.215	-2.1
354.0	0.5005	1.122	1.130	+0.7	1.172	+4.4	1.143	+1.9	1.122	0.0
			70 mol % Cyclohexane and 30 mol % Pyridine							
325.8	0.2261	1.401	1.373	-2.0	1.608	+14.8	1.382	-1.4	1.314	-6.2
333.4	0.2836	1.318	1.288	-2.2	1.462	+10.9	1.292	-2.0	1.243	-5.7
335.8	0.3088	1.270	1.258	-1.0	1.410	+11.0	1.260	-0.8	1.217	-4.2
343.0	0.3898	1.167	1.178	+1.0	1.279	+9.6	1.178	+1.0	1.149	-1.6
347.1	0.4314	1.142	1.146	+0.4	1.227	+7.5	1.145	+0.3	1.121	-1.8
			70% mol % Thiophene and 30 mol % Pyridine							
308.0	0.1913	1.094	1.019	-6.9	1.047	-4.3	0.941	-14.0	0.927	-15.3
322.5	0.2731	1.078	1.013	-6.0	1.032	-4.3	0.980	-9.1	0.985	-8.7
330.3	0.3285	1.064	1.010	-5.1	1.025	-3.7	0.998	-6.2	1.008	-5.3
335.2	0.3644	1.063	1.008	-5.2	1.021	-4.0	1.006	-5.4	1.018	-4.2
340.3	0.4123	1.044	1.007	-3.5	1.016	-2.7	1.014	-2.9	1.026	-1.7
343.0	0.4378	1.039	1.006	-3.2	1.014	-2.4	1.017	-2.2	1.029	-1.0

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

		solids		pyridine		thiophene		benzene		cyclohexane	
	T_m/K	$\delta_2/10^4 \times$ $(J/m^3)^{1/2}$	$v_2^1/10^{-6} \times$ (m^3/mol)	$\delta_1/10^4 \times$ $(J/m^3)^{1/2}$	$v_1^1/10^{-6} \times$ (m^3/mol)	$\delta_1/10^4 \times$ $(J/m^3)^{1/2}$	$v_1^1/10^{-6} \times$ (m^3/mol)	$\delta_1/10^4 \times$ $(J/m^3)^{1/2}$	$v_1^1/10^{-6} \times$ (m^3/mol)	$\delta_1^1/10^4 \times$ $(J/m^3)^{1/2}$	$v_1^1/10^{-6} \times$ (m^3/mol)
biphenyl	342.6	1.9304[a]	155.16[b]	2.0259[a]	84.87[b]	1.8759[c]	83.78[d]	1.7274[j]	94.57[k]	1.5473[j]	114.82[k]
naphthalene	352.8	1.9662[a]	130.86[e]	1.9938[a]	85.86[b]	1.8426[c]	84.87[d]	1.6957[j]	95.96[k]	1.5203[j]	116.89[k]
phenanthrene	372.8	1.9772[a]	168.05[f]	1.9377[a]	87.31[b]	1.7759[c]	87.14[d]	1.6283[j]	98.63[k]	1.4501[j]	120.23[k]
fluorene	387.6	1.8508[g]	163.70[h]	1.8841[a]	89.36[b]	1.7259[c]	88.96[d]	1.5817[j]	100.40[k]	1.4411[j]	122.33[k]
acenaphthene	366.5	1.8930[g]	149.80[i]	1.9519[a]	87.19[b]	1.7974[c]	86.38[d]	1.6607[j]	97.64[k]	1.4845[j]	118.54[k]

[a] Enthalpy of vaporization was evaluated by using the Clausius–Clapeyron equation with the Antoine equation constants given by Reid et al. (*17*). [b] Timmermans (*18*). [c] Enthalpy of vaporization data from Advances in Chemistry Series, Vol. 15/22 (*19*). [d] International Critical Tables, Vol. 3 (*20*). [e] Weast et al. (*21*), Reid et al. (*17*), and Dean (*22*). [f] International Critical Tables (*20*). Extrapolated by using eq 12–3.2 of Reid et al. (*17*). [g] Antoine equation constants given by Dean (22). [h] McLaughlin and Ubbelohde (*23*). [i] Lange and Forker (*24*). [j] Heat of vaporization data from Figures 7B1·11 and 7B1·18 in API Data Book (*25*). [k] Figures 16–12, NGPSA Engineering Data Book (*26*).

Unlike regular solution theory, Wilson's equation can predict positive or negative deviations from Raoult's law. It also gives an explicit form of the temperature dependence of the activity coefficient, which is very important in solubility studies. The problem with Wilson's equation is that it requires fitting of solubility results in the pure solvent at a minimum of two different temperatures to obtain values for the binary interaction parameters (λ_{ij}).

UNIQUAC (Universal Quasi-Chemical Equation). The UNIQUAC equation (*14*) is very similar to Wilson's equation in form and underlying theory. It differs in two ways. The first is that it uses two pure component parameters, r_i and q_i, that are calculated from the van der Waals' areas and volumes (*14*, *15*) instead of molar volumes which are used in Wilson's equation. This is intended to allow more differentiation based on molecular shape. The other difference is that UNIQUAC has also been

Table VI. Values of the Binary Parameter,[a] l_{12}, and the Cross Parameter, l_{13}, Needed for the Extended Regular Solution Theory

A. Binary Parameter, l_{12}

	solvent (1)			
solute (2)	benzene	cyclohexane	pyridine	thiophene
naphthalene	-1.9183×10^{-3}	2.4006×10^{-3}	4.0199×10^{-3}	2.60127×10^{-4}
phenanthrene	-4.390×10^{-3}	3.3468×10^{-3}	3.8341×10^{-3}	-1.9394×10^{-4}
fluorene	-1.9541×10^{-3}	1.320×10^{-2}	6.7489×10^{-3}	-1.48616×10^{-3}
acenaphthalene	-4.991×10^{-4}	8.8279×10^{-3}	1.030×10^{-2}	5.5429×10^{-4}

B. Cross Parameter, l_{13}

	solvent system				
solute (2)	benzene (1)/ thiophene (3)	benzene (1)/ pyridine (3)	cyclohexane (1)/ thiophene (3)	cyclohexane (1)/ pyridine (3)	thiophene (1)/ pyridine (3)
naphthalene	0.003 268	−0.008 325	0.010 370	0.011 53	−0.000 601
phenanthrene	0.003 298	−0.010 127	0.009 978	0.008 70	−0.001 034
fluorene	0.003 546	−0.010 109	0.011 490	0.010 95	−0.000 866
acenaphthene	0.003 785	−0.009 138	0.011 570	0.012 33	−0.000 716

[a] These values were obtained by fitting the lowest mole fraction solubility data point in the pure solvent to the equation.

Table VII. Values of Wilson's Parameters, λ_{12} and λ_{21} (J/(g mol)), and UNIQUAC Parameters, A_{12} and A_{21} (J/(g mol)), Calculated by Fitting the Solubility Data for Each Solid/Single Solvent System

		solvent (1)			
solute (2)		benzene	cyclohexane	thiophene	pyridine
naphthalene	λ_{12}	2399.67	1071.91	2673.43	2788.92
	λ_{21}	−1601.94	2077.97	2204.14	2078.35
	A_{12}	−1083.38	1094.35	−1100.12	−1218.80
	A_{21}	1646.35	−321.74	1564.39	1736.60
phenanthrene	λ_{12}	1642.88	2074.96	2103.55	1272.75
	λ_{21}	−375.44	3733.33	−1675.53	−871.06
	A_{12}	−643.30	1501.35	−793.21	128.30
	A_{21}	1297.45	−411.44	1341.32	16.83
fluorene	λ_{12}	1196.53	1271.66	2861.72	1576.45
	λ_{21}	−308.22	3467.43	−2503.65	−955.66
	A_{12}	−513.50	1993.37	−1038.67	−741.22
	A_{21}	948.72	−880.65	1557.86	1073.33
acenaphthene	λ_{12}	474.90	930.13	1082.25	1350.07
	λ_{21}	380.51	2656.81	−924.23	311.44
	A_{12}	−96.82	1659.12	−741.72	−393.32
	A_{21}	355.06	−795.42	1070.99	704.42

formulated as a group contribution method called UNIFAC. Using UNIFAC, no fitting of data for the parameters is necessary, as long as the necessary group parameters exist. UNIQUAC is given, for a multicomponent system, by

$$\ln \gamma_2 = \ln \left(\frac{\Phi_2}{x_2}\right) + \left(\frac{z}{2}\right) q_2 \ln \left(\frac{\Theta_2}{\Phi_2}\right) + l_2 - \frac{\Phi_2}{x_2} \sum_j x_j l_j - q_2 \ln \left(\sum_j \Theta_j \tau_{j2}\right) + q_2 - q_2 \sum_j \left(\frac{\Theta_j \tau_{2j}}{\sum_k \Theta_k \tau_{kj}}\right) \qquad (12)$$

where

$$l_i = \left(\frac{z}{2}\right)(r_i - q_i) - (r_i - 1) \qquad (13)$$

$$\tau_{ij} = \exp\left\{-\frac{A_{ij}}{RT}\right\} \qquad (14)$$

$$\Theta_i = \frac{q_i x_i}{\sum_i q_i x_i} \qquad (15)$$

$$\Phi_i = \frac{r_i x_i}{\sum_i r_i x_i} \qquad (16)$$

Table VIII. Values of the Solvent–Solvent Cross Parameters Obtained from Literature VLE Data (*15*)

	system	
solvent pair	UNIQUAC/J/ (g mol)	Wilson's eq/J/(g mol)
benzene (1)–pyridine (3)	$A_{13} = -696.3793$	$\lambda_{13} = -2463.6339$
	$A_{31} = 721.3042$	$\lambda_{31} = 4403.5136$
benzene (1)–thiophene (3)	$A_{13} = -807.1058$	$\lambda_{13} = 1325.7378$
	$A_{31} = 1116.9375$	$\lambda_{31} = -697.8559$
cyclohexane (1)–pyridine (3)	$A_{13} = 2601.3891$	$\lambda_{13} = 990.3960$
	$A_{31} = -674.9525$	$\lambda_{31} = 3654.2786$
cyclohexane (1)–thiophene (3)	$A_{13} = 990.5763$	$\lambda_{13} = 681.7246$
	$A_{31} = -221.9814$	$\lambda_{31} = 1234.9231$
thiophene (1)–pyridine (3)	$A_{13} = 3430.9850$	$\lambda_{13} = 2133.3131$
	$A_{31} = -2059.2314$	$\lambda_{31} = 4215.6577$

The significance of the parameters is explained in the original reference (*13*).

Binary Solvent Mixtures

Experimental solubilities have been determined from ambient conditions to the melting points of the solutes for the following systems: Solutes naphthalene, acenaphthene, fluorene, and phenanthrene in solvents 70% benzene/30% pyridine, 70% benzene/30% thiophene, 70% cyclohexane/30% pyridine, 70% cyclohexane/30% thiophene, and 70% thiophene/30% pyridine.

The choice of solvents to study was based on the desire to produce data of use in the design of coal liquefaction plants. The criterion for useful solvents is a high solvation ability which translates to systems that are quite close to ideal. This choice can therefore make discrimination of the most appropriate activity coefficient model very difficult and possibly favors the simpler forms (like regular solution). The alternative is to choose solvents that are very poor solvents because they form very nonideal solutions with the solvents. These results would offer a more discriminating test of the equations. The data itself, however, would be of less value for design purposes so we have not taken this approach.

The solubility results are presented in Tables I–IV, along with the activity coefficients calculated from eq 1. The activity coefficients predicted by the models discussed in the last section are also presented, along with the percent deviation of those values from the experimentally determined values. The percent deviations are defined as

$$\Delta = [(\gamma_{\mathrm{calcd}} - \gamma_{\mathrm{exptl}})/\gamma_{\mathrm{exptl}}] \times 100.0$$

Table IX. Comparison of the Experimental and Calculated Activity Coefficients for the Four Parent Hydrocarbons in a Mixture of 25% Benzene, 25% Cyclohexane, 25% Thiophene, and 25% Pyridine

			$l_{ij} = 0$		$l_{ij} \neq 0$		Wilson's eq		UNIQUAC	
temp/K	x_2(exptl)	γ_2(exptl)	γ_2(calcd)	Δ/%	γ_2(calcd)	Δ/%	γ_2(calcd)	Δ/%	γ_2(calcd)	Δ/%
					Acenaphthene					
305.8	0.2214	1.149	1.109	−3.5	1.172	+2.0	1.136	−1.2	1.126	−2.0
312.0	0.2662	1.123	1.090	−2.9	1.141	+1.6	1.116	−0.6	1.112	−1.0
320.9	0.3415	1.093	1.065	−2.5	1.101	+0.8	1.087	−0.5	1.089	−0.3
328.9	0.4238	1.065	1.045	−1.9	1.069	+0.4	1.063	−0.2	1.067	+0.2
337.4	0.5270	1.039	1.027	−1.2	1.041	+0.2	1.039	0.0	1.044	+0.5
346.9	0.6649	1.012	1.012	0.0	1.018	+0.6	1.018	+0.6	1.022	+1.0
355.6	0.8101	0.994	1.003	+0.9	1.005	+1.1	1.005	+1.1	1.007	+1.2
					Phenanthrene					
303.5	0.2392	1.201	1.293	+7.7	1.276	+6.3	1.199	−0.1	1.210	+0.8
312.8	0.3053	1.146	1.212	+5.8	1.200	+4.7	1.166	+1.8	1.169	+2.0
321.9	0.3840	1.097	1.144	+4.3	1.136	+3.5	1.130	+3.0	1.127	+2.7
329.4	0.4575	1.068	1.098	+2.9	1.093	+2.4	1.100	+3.0	1.094	+2.4
338.1	0.5550	1.041	1.057	+1.6	1.054	+1.3	1.066	+2.4	1.060	+1.8
347.7	0.6777	1.008	1.025	+1.8	1.024	+1.6	1.033	+2.6	1.029	+2.1
353.4	0.7533	0.992	1.014	+2.2	1.013	+2.1	1.019	+2.7	1.016	+2.4
					Naphthalene					
307.7	0.3860	1.053	1.078	+2.4	1.073	+2.0	1.062	+0.9	1.074	+2.1
315.4	0.4655	1.036	1.054	+1.7	1.051	+1.5	1.052	+1.5	1.061	+2.4
326.6	0.5956	1.023	1.027	+0.5	1.026	+0.3	1.034	+1.2	1.039	+1.6
329.4	0.6262	1.029	1.023	−0.6	1.021	−0.7	1.030	+0.1	1.034	+0.5
338.1	0.7574	1.008	1.009	+0.1	1.008	0.0	1.015	+0.7	1.016	+0.8
					Fluorene					
303.8	0.1559	1.206	1.207	+0.1	1.290	+6.9	1.122	−7.0	1.129	−6.4
311.9	0.1958	1.173	1.172	−0.1	1.240	+5.7	1.117	−4.8	1.125	−4.1
322.4	0.2551	1.150	1.131	−1.6	1.182	+2.8	1.107	−3.8	1.114	−3.1
329.2	0.3039	1.122	1.105	−1.5	1.145	+2.1	1.097	−2.2	1.103	−1.7
338.3	0.3779	1.093	1.075	−1.7	1.103	+0.9	1.080	−1.1	1.084	−0.8
346.8	0.4613	1.061	1.050	−1.1	1.068	+0.6	1.062	+0.1	1.064	+0.3
354.1	0.5410	1.040	1.032	−0.8	1.044	+0.4	1.046	+0.5	1.046	+0.6

The values of the necessary constants are presented in Tables V–VIII. The constants that required data fitting (l_{12}, A_{12}, A_{21}, λ_{12}, λ_{21}) were obtained by fitting the solubility results for the solutes in the pure solvents from previously published data (*1–5*). The parameters for the solvent–solvent pairs (A_{13}, A_{31}, λ_{13}, λ_{13}, l_{13}) were obtained from the literature (*16*). For l_{13}, the VLE data was regressed to give the best fit. We have not presented the values for r_i and q_i needed in UNIQUAC as they are easily calculated, knowing only the structure of the compounds (*14*).

Examination of Tables I–IV reveals that none of the four activity coefficient equations give deviations greater than 16.4% for the systems studied and the average deviations are much smaller than this. The average deviation for each of the equations based on all the data presented are regular solution theory, 2.6%; extended regular solution theory, 3.4%; Wilson's equation, 2.1%; and UNIQUAC, 2.7%. These results show that Wilson's equation is slightly superior to regular solution theory for predicting the solubility in these solvent mixtures. This is to be expected since it contains two adjustable parameters while regular solution theory contains no adjustable parameters. The decision as to which equation to use should be based on the availability of pure solvent solubility data. If there are solubility data available (at least two temperatures are required), we recommend using Wilson's equation. If no pure solvent solubility data are available (or limited or unreliable data), then regular solution theory can be used with reasonable confidence.

Considering that it also has two adjustable parameters, we were somewhat surprised by the poor showing of UNIQUAC. This is possibly a consequence of the nearly ideal activity coefficients being predicted (it may have a high "noise" level) or it might imply that molar volumes are a better correlating parameter for these systems than the UNIQUAC r_i and q_i.

Quaternary Solvent Mixture

Based on the success of these activity coefficient expressions to predict the solubilities of these solutes in binary solvent mixtures, it is appropriate to test them on a more complex mixture, containing all four of the solvents (in equimolar amounts) that have been studied. The results, presented in Table IX, have again been correlated by using the same four equations. The average deviations for each are regular solution theory, 2.0%; extended regular solution, 2.0%; Wilson's equation, 1.7%; and UNIQUAC, 1.7%. Our conclusion is that the advantage gained by fitting parameters to the data, which is substantial for the solubilities in the pure solvents (*5*) becomes negligible as the number of components in the solvent mixture increases. While we still recommend using Wilson's equation if the pure solubility data exists, regular solution theory appears to be a very good alternative. Obviously, the results presented are not an exhaustive test of this conclusion but we feel they are a good indication of what can be expected when dealing with mixtures of good (nearly ideal) solvents.

Summary

The solubilities of four polynuclear aromatic hydrocarbons in mixtures of four organic solvents have been determined from ambient conditions to the solute melting point. These results have been used to determine the activity coefficient of the solute in the liquid solution. The results have been correlated by using four common activity coefficient expressions with the necessary binary parameters obtained by regression of the solubility data for the solutes in the pure solvents. The solvent–solvent parameters were obtained from literature VLE data.

The results show that all the models give reasonable predictions but that Wilson's equation is best overall.

Glossary

A_{ij}	UNIQUAC binary parameter, J/(g mol)
ΔC_{p_i}	heat capacity of liquid *i* or heat capacity of solid *i* measured at the melting point of *i*, J/(g mol K)
D_{ij}	defined by eq 8
G_{ij}	defined by eq 11
Δh_i^f	enthalpy of fusion of *i* measured at the melting point of *i*, J/(g mol)
Δh_i^p	enthalpy change of a solid–solid phase transition for component *i*, J/(g mol)
l_i	defined by eq 13
l_{ij}	extended regular solution model binary parameter
P	pressure, N/m^2
P_i^{sat}	vapor pressure of *i*, N/m^2
q_i	pure component parameter in UNIQUAC
r_i	pure component parameter in UNIQUAC
R	gas constant, J/(g mol K)
Δs_i^p	entropy change of a solid–solid phase transition of *i*, J/(g mol K)
T	temperature, K
T_m	melting-point temperature, K
Δu_i^v	internal energy of *i* in changing from a liquid to an ideal gas
Δv_i	molar volume of liquid *i* or molar volume of solid *i*, m^3/(g mol)
v_i^l	molar volume of liquid *i*, m^3/(g mol)
x_i	mole fraction of i

Greek Letters

Δ	$(\gamma_2(\text{exptl}) - \gamma_2(\text{calcd}))/\gamma_2(\text{exptl}) \times 100$
δ_i	solubility parameter of *i*
$\bar{\delta}$	defined by eq 4
γ_i	activity coefficient of *i*
λ	defined by eq 2
λ_{ij}	Wilson's eq binary parameter, J/(g mol)
Ω_i	volume fraction of component *i*
Φ_i	defined by eq 16
τ_{ij}	defined by eq 14
Θ_i	defined by eq 15

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