X mole fraction of the organic component in water

Registry No. CO, 630-08-0; methanol, 67-56-1; acetic acid, 64-19-7; ethanol, 64-17-5; propionic acid, 79-09-4.

Literature Cited

(1) Roth, J. F.; Craddock, J. H.; Hershman, A.; Paulik, F. E. *Chem. Technol.* **1971**, *10*, 600.

(2) Dake, S. B.; Kolhe, D. S.; Chaudhari, R. V. *J. Mol. Catal.* **1984**, *24*, 99.

(3) Wilhelm, F.; Battino, R. *Chem. Rev.* **1973**, *73*, 1.

(4) Seidell, A. "Solubilities of Inorganic and Organic Compounds"; Van Nostrand: Princeton, NJ, 1952; Vol. 191.

(5) Radhakrishnan, K.; Ramachandran, P. A.; Brahme, P. H.; Chaudhari, R. V. *J. Chem. Eng. Data* **1983**, *28*, 1.

(6) "Handbook of Chemistry and Physics"; 53rd ed.; Weast, R. C.; Ed.; The Chemical Rubber Co.: Cleveland, OH, 1972-1973.

Received for review April 24, 1984. Revised manuscript received March 1, 1985. Accepted April 30, 1985.

Solubility of Aromatic Hydrocarbon Solids in Mixtures of Benzene and Cyclohexane

Peter B. Choi, Christopher P. Williams, Kenneth G. Buehring, and Edward McLaughlin*

Department of Chemical Engineering, Louisiana State University, Baton Rouge, Louisiana 70803

The solubilities of five solutes, biphenyl, naphthalene, fluorene, phenanthrene, and acenaphthene, in pure benzene and cyclohexane and in mixtures of benzene and cyclohexane, have been determined. The activity coefficients of the five solutes in cyclohexane are correlated to within an average of 0.6% by Wilson's equation compared to 9.3% by the Scatchard–Hildebrand expression. Similarly for the solutes in benzene, the activity coefficients were correlated to within an average of 0.5% and 1.2%, respectively, by the same two methods. For the ternary mixtures Wilson's method correlates the activity coefficients for the 78 measured data points within 1.4% compared to 2.6% by the Scatchard–Hildebrand expression. As expected, when the solution exhibits a significant deviation from ideal behavior, regular solution theory becomes inadequate and Wilson's equation is proposed as a more appropriate correlation. The solubility data can also be correlated as functions of reduced temperature T_m/T where T_m is the melting point temperature.

Introduction

The correlation of equilibrium solubility behavior of aromatic hydrocarbon solutes in binary mixtures of benzene and cyclohexane by both Scatchard–Hildebrand regular solution theory and Wilson's equation requires four sets of experimental data: solubilities of the aromatic hydrocarbons in pure benzene and pure cyclohexane, VLE data for the benzene–cyclohexane system, necessary to determine the parameters of the chosen activity coefficient model, and solubilities of the aromatic hydrocarbons in the three binary solvent mixtures.

In the present study, the solubilities of the five aromatic hydrocarbons, biphenyl, naphthalene, fluorene, phenanthrene, and acenaphthene have been determined (from around room temperature to near the melting points of the solids) in both pure and mixed solvents for use with the extensive VLE data for the benzene–cyclohexane system that has been compiled by Gmehling et al. (*1*) Experimental activity coefficients of solutes in ternary systems are evaluated by using these data and compared with values predicted from theory.

Experimental Work

Biphenyl and naphthalene were purchased from Eastman Kodak, phenanthrene and fluorene from Eastern Chemical, and acenaphthene from British Drug Houses. All samples, except acenaphthene, were purified further by liquid chromatography on activated alumina by using toluene as eluant. The solids were then recrystallized and toluene removed by evaporation in a vacuum. After recrystallization, fluorene was batch distilled to remove low boiling impurities and acenaphthene was zone refined.

The purified samples were analyzed on a GC mass spectrometer and their melting points determined. The results were as follows: biphenyl 99.67 wt (342.6 K), naphthalene 99.21 wt % (352.8 K), fluorene 97.85 wt % (387.6 K), phenanthrene 98.67 wt % (372.8 K), and acenaphthene 99.2 wt % (366.5 K). The liquid samples of benzene and cyclohexane were "gold label" Aldrich products and were used without further purification.

Mixtures of predetermined composition of single solids with the pure and mixed solvents were made in glass ampules, and sealed while they were frozen in a Dewar bottle containing dry ice. The ampules were then placed in a constant temperature bath, and the temperature at which the last trace of solid disappeared was visually determined, while the bath temperature was increased at a rate of 0.1 K every 1200 s near the expected melting temperature, with the ampules rotated at a speed of 0.25 rps. Measurements were made at least twice for each ampule. The experimental system and techniques were similar to that of McLaughlin and Zainal (*2*, *3*). The solubility data taken in this study are listed in columns 1 and 2 of Tables I–III.

Correlation and Discussion

Equations for the Solubility of Solids. The solubility of a solid in a liquid can be used to evaluate the activity coefficient of the solute component in the solution by eq 1. This equation is valid

$$-\ln X_2 = \frac{\Delta S_2{}^{f}}{R}\left\{\frac{T_m}{T} - 1\right\} - \frac{\Delta C_{p2}{}^{f}}{R}\left\{\frac{T_m}{T} - 1\right\} + \frac{\Delta C_{p2}{}^{f}}{R}\ln\frac{T_m}{T} + \ln\gamma_2 \tag{1}$$

if no phase transition takes place in the solid phase between the system temperature T and the solute melting temperature T_m, and if the Poynting correction is neglected. When a phase transition does take place between T and T_m eq 1 must be modified to include the effect of the transition on solubility at solution temperatures below the transition point. For a first-

0021-9568/85/1730-0403$01.50/0 © 1985 American Chemical Society

Table I. Comparison of the Experimental and Predicted Activity Coefficients of Aromatic Hydrocarbon Solids in Three Mixed Solvents

			$l_{ij} = 0$		$l_{ij} \neq 0$		Wilson's eq	
temp/K	$(X_2)_{exptl}$	$(\gamma_2)_{exptl}$	$(\gamma_2)_{calcd}$	Δ/%	$(\gamma_2)_{calcd}$	Δ/%	$(\gamma_2)_{calcd}$	Δ/%
Biphenyl/70 mol % Benzene and 30 mol % Cyclohexane								
290.25	0.2843	1.171	1.189	1.5	1.204	2.8	1.200	2.4
300.85	0.3846	1.105	1.119	1.3	1.128	2.1	1.139	3.1
306.75	0.4484	1.080	1.088	0.7	1.094	1.3	1.108	2.6
314.55	0.5491	1.043	1.051	0.8	1.055	1.2	1.069	1.6
323.55	0.6784	1.017	1.023	0.6	1.024	0.7	1.033	1.6
Biphenyl/50 mol % Benzene and 50 mol % Cyclohexane								
290.45	0.2524	1.326	1.297	2.2	1.354	2.1	1.338	0.9
298.65	0.3304	1.224	1.209	1.2	1.248	1.9	1.252	2.3
307.85	0.4376	1.134	1.126	0.6	1.149	1.3	1.163	2.6
314.05	0.5274	1.074	1.080	0.5	1.094	1.8	1.108	3.1
323.55	0.6672	1.034	1.034	0.0	1.040	0.6	1.049	1.5
324.95	0.6953	1.020	1.028	0.7	1.032	1.2	1.040	1.9
Biphenyl/30 mol % Benzene and 70 mol % Cyclohexane								
297.05	0.2704	1.442	1.355	6.1	1.470	2.0	1.461	1.3
302.95	0.3361	1.325	1.294	4.6	1.347	1.6	1.350	1.9
309.05	0.4182	1.217	1.181	3.0	1.235	1.4	1.245	2.3
313.35	0.4857	1.149	1.130	1.7	1.168	1.6	1.180	2.6
319.45	0.5826	1.089	1.077	1.1	1.098	0.9	1.109	1.8
325.95	0.6990	1.036	1.035	0.1	1.045	0.9	1.052	1.6
Naphthalene/70 mol % Benzene and 30 mol % Cyclohexane								
299.65	0.2844	1.187	1.287	8.5	1.264	6.6	1.175	0.9
312.65	0.4045	1.123	1.171	4.3	1.158	3.1	1.127	0.4
321.55	0.5071	1.084	1.105	2.0	1.097	1.2	1.090	0.6
334.35	0.6854	1.037	1.037	0.0	1.034	0.3	1.039	0.2
337.95	0.7417	1.027	1.024	0.4	1.022	0.5	1.027	0.0
Naphthalene/50 mol % Benzene and 50 mol % Cyclohexane								
302.95	0.2850	1.280	1.370	7.1	1.366	6.7	1.261	1.5
313.25	0.3891	1.183	1.237	4.6	1.234	4.4	1.188	0.4
318.65	0.4520	1.144	1.178	3.0	1.176	2.8	1.150	0.5
326.65	0.5598	1.090	1.104	1.2	1.103	1.1	1.096	0.5
329.75	0.6047	1.074	1.080	0.6	1.080	0.6	1.077	0.3
340.75	0.7848	1.024	1.021	0.3	1.021	0.3	1.023	0.1
Naphthalene/30 mol % Benzene and 70 mol % Cyclohexane								
297.15	0.2041	1.557	1.648	5.8	1.703	9.4	1.504	3.4
311.85	0.3400	1.313	1.366	4.1	1.395	6.3	1.314	0.1
323.55	0.4931	1.162	1.183	1.9	1.197	3.0	1.170	0.7
326.05	0.5308	1.136	1.152	1.4	1.163	2.4	1.143	0.7
339.25	0.7535	1.037	1.035	0.1	1.038	0.1	1.037	0.0
Fluorene/70 mol % Benzene and 30 mol % Cyclohexane								
311.65	0.1596	1.433	1.502	4.8	1.496	4.4	1.410	1.6
330.35	0.2777	1.260	1.288	2.2	1.285	2.0	1.250	0.8
339.85	0.3603	1.184	1.196	1.0	1.194	0.9	1.175	0.8
346.85	0.4353	1.127	1.137	0.9	1.135	0.8	1.125	0.2
356.55	0.5477	1.077	1.075	0.1	1.075	0.1	1.071	0.5
Fluorene/50 mol % Benzene and 50 mol % Cyclohexane								
317.05	0.1558	1.668	1.657	0.7	1.748	4.8	1.596	4.3
331.95	0.2548	1.421	1.412	0.6	1.465	3.1	1.380	2.9
343.15	0.3643	1.252	1.249	0.2	1.278	2.1	1.232	1.5
351.45	0.4636	1.156	1.153	0.2	1.171	1.3	1.145	1.0
359.35	0.5730	1.083	1.085	0.2	1.094	1.0	1.081	0.2
Fluorene/30 mol % Benzene and 70 mol % Cyclohexane								
319.65	0.1346	2.050	1.907	7.0	2.190	6.8	1.955	4.6
327.45	0.1809	1.816	1.724	5.1	1.937	6.6	1.750	3.6
342.15	0.3111	1.437	1.397	2.8	1.501	4.4	1.398	2.7
350.65	0.4192	1.259	1.239	1.6	1.297	3.1	1.236	1.8
359.25	0.5471	1.132	1.124	0.8	1.152	1.7	1.121	1.0
Phenanthrene/70 mol % Benzene and 30 mol % Cyclohexane								
307.95	0.2041	1.564	1.742	11.4	1.605	2.6	1.546	1.2
314.65	0.2567	1.434	1.566	9.2	1.466	2.2	1.437	0.2
324.55	0.3521	1.274	1.350	5.9	1.291	1.3	1.291	1.3
351.55	0.6910	1.052	1.047	0.4	1.040	1.1	1.047	0.5
362.65	0.8556	1.008	1.009	0.1	1.007	0.1	1.009	0.1
Phenanthrene/50 mol % Benzene and 50 mol % Cyclohexane								
305.35	0.1503	2.000	2.264	13.2	2.110	5.5	1.939	3.1
318.65	0.2503	1.597	1.739	8.9	1.658	3.8	1.592	0.3
327.25	0.3415	1.386	1.465	5.7	1.418	2.3	1.392	0.5
343.55	0.5629	1.132	1.142	0.9	1.729	0.3	1.132	0.0
360.85	0.8177	1.026	1.018	0.8	1.017	0.9	1.018	0.8

Table I (Continued)

			$l_{ij} = 0$		$l_{ij} \neq 0$		Wilson's eq	
temp/K	$(X_2)_{\text{exptl}}$	$(\gamma_2)_{\text{exptl}}$	$(\gamma_2)_{\text{calcd}}$	Δ/%	$(\gamma_2)_{\text{calcd}}$	Δ/%	$(\gamma_2)_{\text{calcd}}$	Δ/%
		Phenanthrene/30 mol % Benzene and 70 mol % Cyclohexane						
312.25	0.1469	2.386	2.588	8.5	2.539	6.4	2.310	3.2
320.25	0.2123	1.943	2.109	8.5	2.078	6.9	1.935	0.5
326.85	0.2800	1.677	1.780	6.1	1.759	4.9	1.672	0.3
353.75	0.7018	1.074	1.068	0.6	1.067	0.7	1.067	0.7
360.65	0.8147	1.027	1.023	0.4	1.023	0.4	1.024	0.3
		Acenaphthene/70 mol % Benzene and 30 mol % Cyclohexane						
312.75	0.2467	1.237	1.256	1.5	1.247	0.8	1.226	0.9
319.65	0.3050	1.188	1.198	0.9	1.192	0.3	1.173	1.3
333.25	0.4545	1.099	1.100	0.2	1.097	0.1	1.084	1.3
338.55	0.5240	1.073	1.070	0.2	1.068	0.4	1.058	1.4
344.55	0.6148	1.042	1.042	0.0	1.041	0.1	1.034	0.8
		Acenaphthene/50 mol % Benzene and 50 mol % Cyclohexane						
314.45	0.2400	1.327	1.350	1.7	1.375	3.6	1.327	0.0
325.85	0.3459	1.216	1.220	0.4	1.235	1.6	1.198	1.5
333.15	0.4347	1.146	1.147	0.1	1.157	0.9	1.128	1.5
343.15	0.5815	1.069	1.069	0.0	1.073	0.4	1.058	1.0
350.25	0.7010	1.031	1.031	0.0	1.033	0.2	1.026	0.5
		Acenaphthene/30 mol % Benzene and 70 mol % Cyclohexane						
303.95	0.1333	1.820	1.710	6.0	1.862	2.3	1.790	1.6
314.55	0.2015	1.585	1.524	3.8	1.630	2.8	1.551	2.1
325.25	0.3032	1.368	1.338	2.1	1.402	2.5	1.335	2.4
333.45	0.4059	1.236	1.215	1.7	1.253	1.4	1.203	2.6
339.95	0.5084	1.140	1.131	0.8	1.153	1.1	1.120	1.8

order phase transition, as given for example by Weimer and Prausnitz (*4*),

$$-\ln X_2 = \frac{\Delta S_2^{\text{f}}}{R}\left\{\frac{T_{\text{m}}}{T} - 1\right\} - \frac{\Delta C_{p2}^{\text{f}}}{R}\left\{\frac{T_{\text{m}}}{T} - 1\right\} + \frac{\Delta C_{p2}^{\text{f}}}{R}\ln\frac{T_{\text{m}}}{T} + \frac{\Delta S_2^{\text{p}}}{R}\left\{\frac{T^{\text{p}}}{T} - 1\right\} + \ln\gamma_2 \quad (2)$$

and for a λ point transition eq 1 is modified to eq 3, as discussed by Choi and McLaughlin (*5*).

$$-\ln X_2 = \frac{\Delta S_2^{\text{f}}}{R}\left\{\frac{T_{\text{m}}}{T} - 1\right\} - \frac{\Delta C_{p2}^{\text{f}}}{R}\left\{\frac{T_{\text{m}}}{T} - 1\right\} + \frac{\Delta C_{p2}^{\text{f}}}{R}\ln\frac{T_{\text{m}}}{T} + \ln\gamma_2 + \lambda \quad (3)$$

where λ, the additional effect of the λ point transition, is given by

$$\lambda = \frac{1}{RT}\int_{T_{\text{a}}}^{T_{\text{b}}}(C_{p_l} - C_{p_l}^{\text{B}})\,\mathrm{d}T - \frac{1}{R}\int_{T_{\text{a}}}^{T_{\text{b}}}\left(\frac{C_{pl} - C_{pl}^{\text{B}}}{T}\right)\mathrm{d}T \quad (4)$$

In eq 4, C_{pl} represents the specific heat of the solid during a λ point transition from temperature T_{a} to T_{b} and C_{pl}^{B} the base line specific heat as if no phase transition occurred. Experimental X_2 vs. T data therefore permit evaluation of the activity coefficients of the solute γ_2 by using one of the above equations provided the necessary physical properties of the solid are available. For the five solids used in this study, the necessary physical properties are available and are given in Table IV. It should be noted that the solubility equations to be used do not contain properties of the solvent and can therefore be used directly to obtain the solute activity coefficient in mixed as well as single solvents.

Solubility in Multicomponent Systems. Scatchard–Hildebrand Regular Solution Theory. Of the various theories that can be used to correlate the solute activity coefficients of the systems investigated, the Scatchard–Hildebrand regular solution theory has so far been the only one we have investigated extensively for our work in single solvents (*6*).

For this model, the activity coefficient of the *r*th component in a multicomponent mixture of *C* components is given by Malesinski (*7*) as

$$RT\ln\gamma_r = V_r^{\text{l}}\,\tfrac{1}{2}\sum_{i=1}^{C}\sum_{j=1}^{C}\{A_{ri} + A_{rj} - A_{ij}\}\,\phi_i\phi_j \quad (5)$$

with $A_{ii} = A_{jj} = 0$, $A_{ij} = A_{ji}$, and $r = 1, 2, \ldots C$. The A_{ij}'s are themselves related to the solubility parameters δ_i by the equations

$$A_{ij} = (\delta_i - \delta_j)^2 + 2l_{ij}\delta_i\delta_j \quad (6)$$

where

$$\delta_i = \{\Delta E_i^{\text{vap}}/V_i^{\text{l}}\}^{1/2} \quad (7)$$

$$\phi_i = \frac{X_iV_i^{\text{l}}}{\sum_i X_iV_i^{\text{l}}} \quad (8)$$

It has already been shown by Choi and McLaughlin (*6*) that for the present solutes in thiophene and pyridine $l_{ij} \neq 0$ and so the accuracy of prediction can be greatly enhanced if l_{ij}'s are indeed used, which are currently only available by fitting the equations to experimental data.

When eq 5 is expanded for a ternary mixture of a single solute 2 in solvents 1 and 3, we get

$$RT\ln\gamma_2 = V_2^{\text{l}}\{A_{12}\phi_1^2 + A_{23}\phi_3^2 + (A_{12} + A_{23} - A_{13})\phi_1\phi_3\} \quad (9)$$

For a solute 2 in a single solvent 1 eq 9 further reduces to

$$RT\ln\gamma_2 = V_2^{\text{l}}A_{12}\phi_1^2 \quad (10)$$

and in the absence of experimental data, l_{ij} may be assumed zero, then using eq *6* for A_{12}

$$RT\ln\gamma_2 = V_2^{\text{l}}\phi_1^2(\delta_1 - \delta_2)^2 \quad (11)$$

For the solvent mixtures, values of l_{13} representing the solvent–solvent interaction were evaluated from three sets of isothermal data giving 18 experimental activity coefficients,

Table II. Comparison of the Experimental and Predicted Activity Coefficients of Aromatic Hydrocarbon Solids in Benzene

			$l_{12} = 0$		$l_{12} \neq 0$		Wilson's eq	
temp/K	$(X_2)_{\text{exptl}}$	$(\gamma_2)_{\text{exptl}}$	$(\gamma_2)_{\text{calcd}}$	$\Delta/\%$	$(\gamma_2)_{\text{calcd}}$	$\Delta/\%$	$(\gamma_2)_{\text{calcd}}$	$\Delta/\%$
				Biphenyl				
307.95	0.4833	1.043	1.040	0.3	1.043		1.055	1.2
313.85	0.5561	1.028	1.027	0.2	1.029	0.1	1.040	1.1
316.85	0.5932	1.027	1.021	0.5	1.023	0.4	1.033	0.6
323.65	0.6897	1.016	1.011	0.4	1.012	0.4	1.019	0.3
328.95	0.7711	1.010	1.006	0.5	1.006	0.4	1.010	0.0
333.15	0.8422	1.004	1.002	0.2	1.003	0.2	1.005	0.1
				Naphthalene				
310.35	0.3964	1.083	1.088	0.5	1.083		1.085	0.3
315.55	0.4494	1.070	1.069	0.2	1.065	0.5	1.075	0.4
323.45	0.5391	1.054	1.044	1.0	1.041	1.2	1.056	0.2
334.35	0.6885	1.027	1.018	0.9	1.017	1.0	1.029	0.2
344.15	0.8422	1.011	1.004	0.7	1.004	0.7	1.008	0.2
				Fluorene				
307.75	0.1665	1.249	1.302	4.3	1.249		1.252	0.2
313.45	0.1950	1.224	1.263	3.2	1.218	0.5	1.225	0.1
318.15	0.2215	1.203	1.233	2.4	1.193	0.9	1.203	0.0
323.05	0.2528	1.179	1.201	1.9	1.167	1.0	1.180	0.1
330.45	0.3055	1.148	1.158	0.9	1.131	1.4	1.146	0.1
336.25	0.3525	1.124	1.126	0.2	1.105	1.7	1.121	0.3
340.65	0.3957	1.096	1.103	0.6	1.086	0.9	1.101	0.5
348.35	0.4744	1.064	1.069	0.5	1.058	0.6	1.071	0.6
354.85	0.5477	1.043	1.046	0.3	1.039	0.4	1.049	0.6
				Phenanthrene				
312.75	0.2815	1.258	1.327	5.5	1.258		1.271	1.0
316.75	0.3128	1.230	1.279	4.0	1.221	0.7	1.239	0.7
325.25	0.3958	1.149	1.184	3.1	1.147	0.2	1.170	1.8
334.75	0.4949	1.098	1.109	1.0	1.087	1.0	1.108	0.9
341.85	0.5771	1.074	1.067	0.6	1.054	1.8	1.071	0.3
342.15	0.5792	1.075	1.060	0.8	1.054	2.0	1.070	0.5
				Acenaphthene				
306.55	0.2253	1.154	1.164	0.9	1.154		1.165	1.0
312.95	0.2724	1.126	1.134	0.7	1.125	0.1	1.134	0.7
319.85	0.3309	1.100	1.103	0.3	1.097	0.3	1.103	0.2
328.05	0.4158	1.065	1.070	0.5	1.066	0.1	1.069	0.3
335.95	0.5101	1.040	1.044	0.3	1.041	0.1	1.043	0.2
345.75	0.6498	1.011	1.019	0.8	1.018	0.7	1.018	0.7

which were fitted to eq 10 by using the solubility parameters and liquid molar volumes listed in Table V for each particular system for which l_{13} is required.

Wilson's Equation. The use of Wilson's equation to predict the activity coefficient of a solute in both a pure and a mixed solvent system ought to show a marked improvement over regular solution theory for systems exhibiting a significant deviation from ideal behavior.

Wilson's equation for g^E, of a C component mixture, is given by (*8*)

$$\frac{g^E}{RT} = (-)\sum_{i=1}^{C} X_i \ln \{\sum_{j=1}^{C} \Lambda_{ij} X_j\} \tag{12}$$

where

$$\Lambda_{ij} = \frac{V_j^L}{V_i^L} \exp\left\{\frac{-(\lambda_{ij} - \lambda_{ii})}{RT}\right\} \tag{13}$$

$$\Delta\lambda_{ij} = \lambda_{ij} - \lambda_{ii}$$

$$\Lambda_{ij} \neq \Lambda_{ji} \quad \Lambda_{ii} = \Lambda_{jj} = 1$$

The resulting expression for the activity coefficient of the ith component in a mixture of C components is given by (*8*)

$$\ln \gamma_i = 1 - \ln \{\sum_{j=1}^{C} X_j \Lambda_{ij}\} - \sum_{k=1}^{C} \left\{\frac{X_k \Lambda_{ki}}{\sum_{j=1}^{C} X_j \Lambda_{kj}}\right\} \tag{14}$$

When eq 14 is expanded for the activity coefficient of solute 2 in mixed solvents of 1 and 3, we get

$$\ln \gamma_2 = 1 - \ln \{X_1\Lambda_{21} + X_2 + X_3\Lambda_{23}\} - \left\{\frac{X_1\Lambda_{12}}{(X_1 + X_2\Lambda_{12} + X_3\Lambda_{13})} + \frac{X_2}{(X_1\Lambda_{21} + X_2 + X_3\Lambda_{23})} + \frac{X_3\Lambda_{32}}{(X_1\Lambda_{31} + X_2\Lambda_{32} + X_3)}\right\} \tag{15}$$

Eq 15 contains six adjustable parameters, two from each of the three binary mixtures. Recommended values of the solvent-solvent binary interaction parameters Λ_{13} and Λ_{31} are given by Gmehling et al. (*1*), in the form of $\Delta\lambda_{13}$ and $\Delta\lambda_{31}$, from VLE data for the benzene–cyclohexane system.

Equation 14 may be rewritten for a binary solute-2, solvent-1 mixture as

$$\ln \gamma_2 = -\ln (X_2 + \Lambda_{21}X_1) - X_1\left\{\frac{\Lambda_{12}}{X_1 + X_2\Lambda_{12}} - \frac{\Lambda_{21}}{X_1\Lambda_{21} + X_2}\right\} \tag{16}$$

Taking note of the fact that the differences in the characteristics energies $(\lambda_{ij} - \lambda_{ii})$, $\Delta\lambda_{ij}$, in eq 13, are approximately independent of temperature over modest temperature ranges, then eq 16 can be solved iteratively for both $\Delta\lambda_{ij}$ and $\Delta\lambda_{ji}$ by comparing the results of eq 16 determined for two different experimental data points and corresponding activity coefficients.

Table III. Comparison of the Experimental and the Predicted Coefficients of Aromatic Hydrocarbon Solids in Cyclohexane

			$l_{12} = 0$		$l_{12} \neq 0$		Wilson's eq	
temp/K	$(X_2)_{\text{exptl}}$	$(\gamma_2)_{\text{exptl}}$	$(\gamma_2)_{\text{calcd}}$	Δ/%	$(\gamma_2)_{\text{calcd}}$	Δ/%	$(\gamma_2)_{\text{calcd}}$	Δ/%
			Biphenyl					
302.35	0.2348	1.898	1.573	17.1	1.898		1.898	0.0
310.45	0.3540	1.503	1.338	11.0	1.510	0.5	1.507	0.3
314.65	0.4319	1.347	1.236	8.2	1.350	0.2	1.349	0.2
320.85	0.5616	1.178	1.121	4.8	1.176	0.2	1.178	0.0
326.95	0.6929	1.080	1.052	2.6	1.075	0.5	1.078	0.2
333.05	0.8252	1.023	1.015	0.8	1.022	0.1	1.023	0.0
			Naphthalene					
300.15	0.1597	2.126	1.872	11.9	2.126		2.130	0.2
308.25	0.2254	1.816	1.667	8.2	1.849	1.8	1.831	0.8
315.15	0.3025	1.576	1.489	5.6	1.614	2.4	1.589	0.8
325.45	0.4612	1.284	1.248	2.8	1.306	1.7	1.287	0.3
333.15	0.6073	1.137	1.118	1.7	1.143	0.5	1.134	0.3
343.05	0.8082	1.032	1.025	0.7	1.030	0.2	1.028	0.3
			Fluorene					
310.95	0.0537	4.186	2.871	31.4	4.186		4.195	0.2
316.25	0.0684	3.729	2.705	27.4	3.862	3.6	3.767	1.0
321.75	0.0871	3.323	2.529	23.9	3.524	6.1	3.348	0.8
327.35	0.1122	2.922	2.336	20.1	3.164	8.3	2.930	0.3
331.85	0.1384	2.610	2.171	16.8	2.864	9.7	2.605	0.2
336.45	0.1733	2.296	1.990	13.3	2.545	10.8	2.282	0.6
341.45	0.2200	2.003	1.797	10.3	2.216	10.6	1.973	1.5
346.25	0.2787	1.739	1.610	7.4	1.909	9.8	1.706	1.9
			Phenanthrene					
307.65	0.0606	5.232	4.646	11.2	5.232		5.235	0.1
313.85	0.0819	4.423	4.115	7.0	4.591	3.8	4.449	0.6
319.65	0.1093	3.730	3.597	3.6	3.971	6.5	3.744	0.4
321.85	0.1228	3.469	3.389	2.3	3.724	7.4	3.479	0.3
325.85	0.1530	3.038	3.000	1.3	3.266	7.5	3.008	1.0
333.25	0.2430	2.178	2.232	2.5	2.375	9.0	2.174	0.2
339.55	0.3568	1.664	1.690	1.5	1.760	5.7	1.648	1.0
			Acenaphthene					
303.35	0.0853	2.798	2.210	21.0	2.798		2.831	1.2
307.35	0.1031	2.574	2.108	18.0	2.632	2.2	2.612	1.5
312.05	0.1274	2.353	1.987	15.5	2.437	3.6	2.372	0.8
316.45	0.1565	2.140	1.865	12.8	2.245	4.9	2.147	0.3
320.95	0.1931	1.937	1.737	10.3	2.047	5.7	1.930	0.4
325.65	0.2421	1.729	1.598	7.6	1.837	6.2	1.714	0.9
329.95	0.2984	1.551	1.470	5.2	1.649	6.3	1.535	1.0
334.65	0.3697	1.394	1.345	3.5	1.469	5.4	1.374	1.4
339.85	0.4645	1.246	1.223	1.8	1.299	4.3	1.231	1.2
346.45	0.5992	1.113	1.110	0.3	1.144	2.8	1.108	0.4
354.45	0.7742	1.018	1.030	1.2	1.039	2.1	1.029	1.1

Table IV. Physical Properties of Five Aromatic Hydrocarbon Solids

	T_m/K	Δh_2^f/ J·mol^{-1}	ΔS_2^f/ J·mol^{-1}·K^{-1}	ΔC_{p2}^f/ J·mol^{-1}·K^{-1}	Δh_2^P/ J·mol^{-1}	ΔS_2^P/ J·mol^{-1}·K^{-1}
biphenyl	341.3[a]	18.659×10^3[a]	54.671	36.274[a]		
naphthalene	353.3[b]	18.238×10^3[b]	51.623	8.901[b]		
fluorene	387.9[c]	19.591×10^3[c]	50.493	1.444[c]		
phenanthrene	372.4[c]	16.474×10^3[c]	44.254	12.586[c]	1.307×10^3[c]	3.853[c]
acenaphthene	366.6[c]	21.476×10^3[c]	58.573	14.855[c]		

[a] According to Spaght et al. (*10*). [b] According to Timmermans (*11*). [c] According to Finke et al. (*12*). T_m, Δh_2^f, ΔS_2^f, and ΔC_p^f are values at the triple point.

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

		solids		benzene		cyclohexane	
	T_m/K	$10^{-4}\delta_2$/ (J·m^{-3})$^{1/2}$	$10^6 V_2^l$/ m^3·mol^{-1}	$10^{-4}\delta_1$/ (J·m^{-3})$^{1/2}$	$10^6 V_1^l$/ m^3·mol^{-1}	$10^{-4}\delta_3$/ (J·m^{-3})$^{1/2}$	$10^6 V_1^l$/ m^3·mol^{-1}
biphenyl	342.6	1.9304[a]	155.16[b]	1.7274[h]	94.57[i]	1.5473[h]	114.82[i]
naphthalene	352.8	1.9662[a]	130.86[c]	1.6959[h]	95.96[i]	1.5203[h]	116.89[i]
phenanthrene	372.8	1.9772[a]	168.05[d]	1.6283[h]	98.63[i]	1.4501[i]	120.23[i]
fluorene	387.6	1.8508[e]	163.70[f]	1.5817[h]	100.40[i]	1.4117[h]	122.33[i]
acenaphthene	366.5	1.8930[e]	149.80[g]	1.6607[h]	99.64[h]	1.4845[h]	118.54[i]

[a] Enthalpy of vaporization was evaluated by using the Clausius–Clapeyron equation with Antonie equation constants given by Reid et al. (*13*). [b] According to Timmermans (*11*). [c] According to Weast et al. (*14*), Reid et al. (*13*), and Dean (*15*). [d] International Critical Tables (*16*). Extrapolated by using eq 12–3.2 of Reid et al. (*13*). [e] Antoine equation constants given by Dean (*15*). [f] According to McLaughlin and Ubbelohde (*17*). [g] According to Lange and Forker (*18*). [h] From ref *19*. [i] From ref *20*.

Table VI. Binary Parameters Used in Eq 6

	l_{12}[a]	l_{23}[b]	l_{13}[c]
biphenyl	0.0004	0.0102	0.0150
naphthalene	−0.0005	0.0060	0.0154
fluorene	−0.0020	0.0132	0.0170
phenanthrene	−0.0036	0.0037	0.0160
acenaphthene	−0.0005	0.0088	0.0157

[a] Benzene (1), solute (2). [b] Cyclohexane (3), solute (2). [c] Benzene (1), cyclohexane (3).

Table VII. Characteristic Energy Differences Used in Eq 13

	benzene (1)		cyclohexane (3)	
solute (2)	$\Delta\lambda_{12}$/ J/mol	$\Delta\lambda_{21}$/ J/mol	$\Delta\lambda_{23}$/ J/mol	$\Delta\lambda_{32}$/ J/mol
biphenyl	1786.4	−1270.7	2139.0	1449.7
naphthalene	2436.8	−1607.6	1990.4	1158.6
fluorene	1287.1	−412.1	3605.9	1190.4
acenaphthene	494.8	397.5	2942.5	780.1
phenanthrene	1680.2	−348.5	3785.3	2041.9

Benzene (1) Cyclohexane (3)

$\Delta\lambda_{13}$/ J/mol	$\Delta\lambda_{31}$/ J/mol
771.4	417.5

Values of $\Delta\lambda_{ij}$ and $\Delta\lambda_{ji}$ were determined by using the lowest experimental solubility data point and each of the other experimental binary data points in sequence, on approaching the melting temperature. Arithmetic averages were then taken to obtain overall values of the characteristic energy difference. The lowest solubility data point, and hence the largest deviation from ideality, was always used in these determinations as it was felt that the corresponding value of γ, the activity coefficient, would likely be more accurate for the calculations due to its magnitude. If side-by-side data points were used, this produced instabilities in the iterative calculations. This procedure was repeated for all 10 solute–solvent binary mixtures.

Discussion

Experimental activity coefficients of biphenyl, naphthalene, fluorene, and acenaphthene in the mixed solvents were calculated by using eq 1 and for phenanthrene by using eq 3 for temperatures below the end of the λ point transition and eq 1 above the end of the transition. 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. For biphenyl, values of ΔS_2^f and ΔC_{p2}^f were taken as listed in a previous study on the solubility in thiophene and pyridine (*6*).

These values of experimental activity coefficients are compared to those correlated by the methods discussed earlier with the differences defined by Δ, given by

$$\Delta = \frac{(\gamma_2)_{\text{exptl}} - (\gamma_2)_{\text{pred}}}{(\gamma_2)_{\text{exptl}}} 100 \qquad (17)$$

Binary Mixtures. As can be seen from Tables II and III for solutes with either pure benzene or cyclohexane and with $l_{12} = 0$, and the floating datum point method applied to the Scatchard–Hildebrand regular solution theory, eq 11 predicts the experimental activity coefficient for the five solutes in benzene within 1.2% for the 32 data points given in Table II and within 9.3% for the 38 data points of Table III for the solutes in cyclohexane. This difference in accuracy is not surprising as solutions in cyclohexane are considerably more nonideal than in benzene and the model therefore is expected to be less successful.

If eq 10 is used with l_{12} of eq 6 evaluated at the lowest temperature at which solubility measurements were taken, then as seen from Tables II and III, the results for benzene are within 0.6% and for cyclohexane within 4.0%. The l_{ij}'s used are given in Table VI.

The additional parameter of the Wilson equation should allow a further improvement in the correlation of the activity coefficient. If we use eq 16 and evaluate the binary parameters as discussed earlier, the results for benzene are within 0.5% and for cyclohexane within 0.6%. The values of the characteristic energy differences, $\Delta\lambda_{ij}$, of the binary Wilson parameters are given in Table VII.

In order to test these methods with solubilities at other than saturation conditions a comparison can be made of the calculated and experimental activity coefficients of benzene (1) at infinite dilution with phenanthrene (2), $\gamma_1^{\infty 2} = 1.444$ at 393 K compared with the experimental value of 1.41 at 393 K and 3.31×10^5 N·m^{-2} determined by Turek et al. (*9*) using gas–liquid chromatography.

Ternary Mixtures. Table I gives a comparison of experimental activity coefficients and values produced by both Scatchard–Hildebrand regular solution theory and Wilson's equation for the five solutes in three solvent mixtures. The activity coefficients, calculated with the floating datum point method of Choi and McLaughlin (*6*) with the l_{ij}'s = 0, show an average reproducibility of 2.6% for 78 data points. On the other hand, when the activity coefficients are calculated with the l_{ij}'s $\neq$ 0, the average reproducibility improved to 2.2%. However, the extent of improvement depended upon the solute being considered and the composition of the solvent mixture. Indeed for some solutes, particularly biphenyl, the reproducibility decreased. In general however, improvement was more noticeable for solvent mixtures with a higher proportion of cyclohexane.

The activity coefficients correlated by the Wilson equation had an average reproducibility of 1.4% and the improvement above the Scatchard–Hildebrand regular solution theory is readily seen in Table I. Again this improvement is more noticeable for solvent mixtures with a higher proportion of cyclohexane which exhibit a greater deviation form ideal behavior.

Generalization of the Solubility of Solids. It was shown by McLaughlin and Zainal (*2*, *3*) and Choi and McLaughlin (*6*) that the solubility of solids in binary systems can be generalized when $-\log X_2$ was plotted as a function of (T_m/T). Similar plots have been made for the five solids in each of the three mixed solutions, 70, 50, and 30 mol % benzene, each showing a straight line trend with correlation coefficients of 0.993, 0.994, and 0.993, respectively.

The equation of the straight line, which was obtained by a least-squares fit of the solubility data for each solvent, can be represented by eq 18. The value of ΔS_2^l in eq 18 can be used

$$-\log X_2 = \frac{\Delta S_2^l}{2.303R}\left\{\frac{T_m}{T} - 1\right\} \qquad (18)$$

to compare the average nonideality of the solutes in each solution. ΔS_2^l, for example, becomes 60.833, 65.719, and 74.492 J·mol^{-1}·K^{-1} for the solutions with the three mixed solvents 70, 50, and 30 mol % benzene, respectively. McLaughlin and Zainal (*2*, *3*) obtained 57.778 and 101.739 J·mol^{-1}·K^{-1} for ΔS_2^l in solutions with benzene and cyclohexane, respectively. Nonideality of solutes in the three solutions thus lies between that in benzene and in cyclohexane solutions, with increasing departure from ideality for increasing concentrations of cyclohexane.

This result can be expected, however, if one examines eq 19, another form of eq 9 with $l_{ij} = 0$; we have

$$RT \ln \gamma_2 = V_2^l \phi_0^2 (\delta_2 - \delta_0)^2 \qquad (19)$$

where

$$\delta_0 = \frac{\phi_1\delta_1 + \phi_3\delta_3}{\phi_1 + \phi_3} \tag{20}$$

$$\phi_0 = \phi_1 + \phi_3 \tag{21}$$

For a given value of ϕ_0, δ_0 approaches δ_3 as the volume fraction of cyclohexane ϕ_3 increases in eq 20. Accordingly, γ_2 of the ternary solution approaches γ_2 of the cyclohexane solution while the concentration of cyclohexane in the solvent mixture increases.

Generalization is possible due to the fact that $\Delta S_2{}^f$ and δ_2 of the five solids are similar in magnitude. Accordingly, the solubility of a different solute in a ternary solution of the three mixtures of solvents can be predicted approximately if $\Delta S_2{}^f$ and δ_2 of the new solute are similar to those of the five solutes used in this study.

Glossary

$\Delta C_{p2}{}^f$	difference of molar specific heat between those of liquid and solid at fusion temperature, J/mol·K
ΔE^V	molar energy of vaporization, J/mol
g^E	excess molar Gibbs free energy, J/mol
$\Delta h_2{}^p$	molar enthalpy change of phase transition, J/mol
Δh^V	molar enthalpy of vaporization, J/mol
l_{ij}	binary parameter
R	gas constant
ΔS^E	excess molar entropy of mixing, J/mol·K
$\Delta S_2{}^f$	molar entropy change of fusion, J/mol·K
$\Delta S_2{}^l$	least-squares-fitted value, J/mol·K
$\Delta S_2{}^p$	molar entropy change of phase transition, J/mol·K
T	system temperature, K
T_m	melting temperature, K
T^p	temperature of first-order phase transition, K
V^l	molar liquid volume, m^3/mol
X	mole fraction

Greek Letters

Λ_{ij}	binary interaction parameter, Wilson equation
γ	activity coefficient
δ	solubility parameter
ϕ	volume fraction
λ	characteristic energy, J/mol

Subscripts

1, 3	solvent
2	solute (solid)

Registry No. Benzene, 71-43-2; cyclohexene, 110-82-7; biphenyl, 92-52-4; naphthalene, 91-20-3; fluorene, 86-73-7; phenanthrene, 85-01-8; acenaphthene, 83-32-9.

Literature Cited

(1) Gmehling, J.; Onken, U.; Arlt, W. "Chemistry Data Series"; Dachema: Frankfurt, 1980; Part 6a.
(2) McLaughlin, E.; Zainal, H. A. *J. Chem. Soc.* **1959**, 863.
(3) McLaughlin, E.; Zainal, H. A. *J. Chem. Soc.* **1960**, 2485.
(4) Weimer, R. F.; Prausnitz, J. M. *J. Chem. Phys.* **1965**, *42*, 3643.
(5) Choi, P. B.; McLaughlin, E. *AIChE J.* **1983**, *29(1)*, 150.
(6) Choi, P. B.; McLaughlin, E. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 46.
(7) Malesinski, W. "Azeotropy and other Theoretical Problems of Vapor-Liquid Equilibrium"; Interscience: London, 1965.
(8) Prausnitz, J. M.; Eckert, C. A.; Orye, R. V.; O'Connell, J. P. "Computer Calculations for Multicomponent Vapor-Liquid Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1967.
(9) Turek, E. A.; Arnold, D. W.; Greenkorn, R. A.; Chao, K. C. *Ind. Eng. Chem. Fundam.* **1976**, *18*, 426.
(10) Spaght, M. E; Thomas, S. Bb.; Parks, G. S. *J. Phys. Chem.* **1932**, *36*, 882.
(11) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: New York, 1950/1965; Vol. I, II.
(12) Finke, H. L.; Messerly, J. F.; Lee, S. H.; Osborn, A. G.; Douslin, D. R. *J. Chem. Thermodyn.* **1977**, *9*, 937.
(13) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. "The Properties of Liquids and Gases", 3rd ed.; McGraw-Hill: New York, 1977.
(14) Weast, R. C. "CRC Handbook of Chemistry and Physics"; CRC Press: Boca Raton, FL, 1979.
(15) Dean, A. "Lange's Handbook of Chemistry", 12th ed.; McGraw-Hill: New York, 1979.
(16) National Research Council. "International Critical Tables": McGraw-Hill: New York, 1926.
(17) McLaughlin, E.; Ubbelohde, A. R. *Trans. Faraday Soc.* **1957**, *53*, 628.
(18) Lange, N. A.; Forker, G. M. "Handbook of Chemistry", 10th ed.; McGraw-Hill: New York, 1961.
(19) "API Technical Data Book"; API: New York, 1968.
(20) "NGPSA Data Book"; NGPSA: Oklahoma, 1972.

Received for review May 29, 1984. Revised manuscript received April 5, 1985. Accepted May 13, 1985.