Naphthalene Solubility in Cyclohexane, Carbon Tetrachloride, and Mixed Solvents Thereof between 10° and 70° C.

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The solubility of naphthalene has been determined in cyclohexane, carbon tetrachloride, and mixed solvents thereof from 10° to 70° C. Results are considered relative to regular solution equations. Spectral measurements in the ultraviolet region do not reveal change-transfer complexing between naphthalene and carbon tetrachloride at 25° C.

PREVIOUS SOLUBILITY MEASUREMENTS (*5*) at 25° C. have shown a significant difference in the excess free energy of mixing between the systems naphthalene–carbon tetrachloride and naphthalene–cyclohexane. In the present work this comparison is extended to include the range from 10° to 70° C. Solubility in the ternary system naphthalene–carbon tetrachloride–cyclohexane has also been measured to determine if the results agree with a pseudo-binary approach which treats a pair of the components as a mixed solvent. In addition, the possibility that the behavior in the naphthalene–carbon tetrachloride system might be explained by charge-transfer complexation has been investigated.

EXPERIMENTAL

Materials. Baker reagent grade naphthalene was used without further purification, as it had been found (*5*) that purification had no effect on the measured solubility. Cyclohexane and carbon tetrachloride were both purified by distilling Baker reagent grade solvent from phosphorus pentoxide at atmospheric pressure. An inert atmosphere of nitrogen purified by passage through sulfuric acid and sodium hydroxide was maintained during distillation. Product was recovered at a rate of 1 ml. per minute. Double distillation was used, and the middle half of the starting material of each distillation was recovered. For purified cyclohexane and carbon tetrachloride, respectively, the experimental refractive indices (sodium *D* line at 25.00° ±0.01° C.) were 1.42323 [lit., 1.42354 (*10*)] and 1.45709 [lit., 1.45704 (*2*), 1.45759 (*17*)].

Equipment. Solubilities were determined in the equipment shown in Figure 1 by the static method described by Satterfield and Haulard (*12*). The thermostat was a covered water bath constant to ±0.01° at 25° C., and to ±0.03° at 70° C. It was contained within an outer oil bath constant at ±0.1° at 25° C. and to ±0.3° at 70° C. Sealed ampoules containing the synthesized solid-solvent system were agitated by vertical displacement of one end of the horizontally mounted ampoule while the other end was fixed. Displacement was obtained by connection of one end to an off-center point on a disk rotated with a constant-speed 30-r.p.m. motor. Static temperatures were maintained for a minimum of 2 hours in testing for solvent saturation by the solid. The temperature of solution was obtained by bracketing, first crudely and then more precisely, so that one temperature was established, at which some solid remained undissolved, and another slightly above, at which no solid remained. The solution temperature was taken as the average of these two temperatures, with each temperature in turn being taken as the average within the temperature setting of the thermostat. The solution temperature of the contents of each ampoule was determined in duplicate, with duplicates agreeing within limits of 0.03° C. Presence of solid phase was determined visually (after momentary stoppage of the agitation) with a well defined light beam and a background suitable for clear vision. The light was used so briefly that no thermal effect on the bath could be detected. It was possible to note the disappearance of solid phase over a temperature range of 0.02° C.

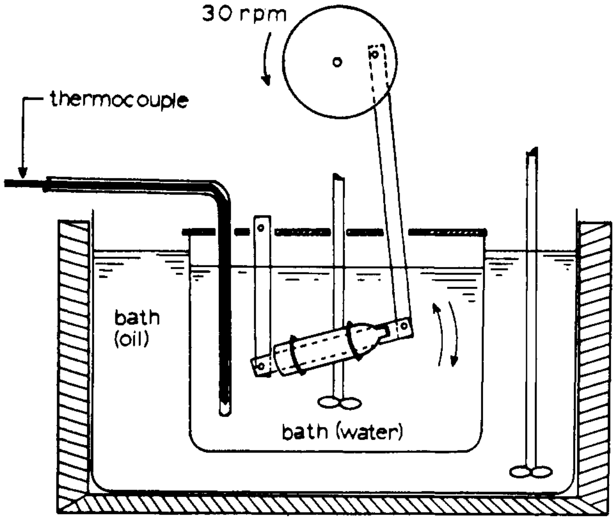

Figure 1. Equipment for static method of solubility measurement

Ampoules were maintained at dry ice temperatures during filling and sealing to prevent loss by evaporation. By this means it was possible to fill the ampoules sufficiently full that the correction in solution composition due to the vapor phase was negligible compared with the uncertainty in solution temperature.

Temperatures in the inner thermostat were measured with a seven-junction copper-constantan thermocouple calibrated against the freezing and boiling points of water and the freezing point of naphthalene, and against thermometers at several temperatures which had been calibrated against NBS certified standards. The voltage from the thermocouple was essentially balanced with a Leeds & Northrup 7556-B six-dial guarded potentiometer, and the small off-balance was fed through a Leeds & Northrup microvolt amplifier to the 5-mv. range of a

Sargent Model MR recorder. Temperature differences could thus be read from recorder chart paper to the nearest 0.005° C.

Spectral measurements were made with a Cary Model 15 spectrophotometer. The thermostated spectrophotometer cells had matched path lengths.

RESULTS

The solubility of naphthalene is given in columns 1 and 2 of Table I for the indicated solvent compositions. The relationship between the measured solubilities and the ideal solubility is shown in column 3 as $\overline{\Delta G_2}^E$, the relative partial molar excess Gibbs free energy of mixing of naphthalene (*7*),

$$\overline{\Delta G_2}^E = RT \ln \gamma_2 \qquad (1)$$

where γ_2 is the activity coefficient of naphthalene at saturation at each temperature. γ_2 is determined through the equation $\gamma_2 = (x_2^{\text{ideal}}/x_2)_{\text{sat}}$. The ideal solubility, x_2^{ideal}, is calculated through Raoult's law (*7*). Thermal data used in calculating ideal solubility are from Ward (*15*).

The pseudo-binary mixed solvent approach to multicomponent systems is associated with the regular solution model (*6*). By this model, for binary systems

$$\Delta G^E = (n_1 + n_2)\, \phi_1\phi_2 V_{12} w'_{12} \qquad (2)$$

This equation is commonly assumed to have greater validity than the *s*-regular model (*4*), because the latter assumes similarity in component molecular size and shape which frequently does not exist.

$$\Delta G^E = (n_1 + n_2) x_1 x_2 w_{12} \qquad (3)$$

In Equations 2 and 3, ϕ and x refer, respectively, to the volume and mole fractions of the indicated component. w'_{12} and w_{12} are free energy interaction parameters in the respective models.

Results of the present work were examined with both models; the regular model was found less suitable for present purposes than the *s*-regular model. Thus, in ternary systems the former led to curvature in plots of interaction *vs.* temperature described below, whereas the latter gave more useful linear corresponding plots. Results are described here, therefore, only with *s*-regular equations.

By partial differentiation of Equation 3,

$$\overline{\Delta G_2}^E = (1 - x_2)^2 w_{12} \qquad (4)$$

w_{12} (and similarly obtained w_{23}) values obtained with Equation 4 through experimentally evaluated $\overline{\Delta G_2}^E$ are listed in column 4 of Table 1 for the two binary systems.

Multicomponent systems may be treated with equations parallel to those given above for binary systems, by reducing the multicomponent mixture to a pseudo-binary by combining all components but one into a single "mixed-solvent component" (*6*). This convenience has been introduced into the *s*-regular equation in the present work. Thus, comparable to Equation 3,

$$\Delta G^E = (n_{MS} + n_2) x_{MS} x_2 w_{MS2} \qquad (5)$$

and to Equation 4,

$$\overline{\Delta G_2}^E = (1 - x_2)^2 w_{MS2} \qquad (6)$$

w_{MS2} values obtained with Equation 6 are listed in column 4 of Table I for the mixed solvent systems.

As solubilities in each of the six solvents were measured at a series of temperatures unequal to those in the other five solvents, the raw experimental results in the binary systems in column 4 cannot be used for comparing experimental and predicted results in the ternary systems. It is necessary to interpolate behavior in the binary systems at temperatures which correspond to those observed in the ternary systems. At the same time it is more desirable to compare all of the results statistically after they have been smoothed. Both goals may be achieved by treating w in each solvent as linearly dependent on temperature,

$$w = A + BT \qquad (7)$$

A and B are fitted constants obtained by least-squares regression analysis. It has been assumed that the uncertainty in T is negligible in comparison with that in w. For the present systems the ratio of the former to the latter ranges from about 1/50 to 1/100. w values were weighted in the regression analysis. The weighting factors were assumed to be the inverse of the square of the uncertainty in w, normalized to unit weight for the w of greatest uncertainty (*14*) for each solvent composition. The uncertainty in w was obtained by rearranging Equation 4 or 6 to the form $w = f\,(\overline{\Delta G_2}^E, x_2)$, and evaluating the variation in w by estimating that in $\overline{\Delta G_2}^E$ and x_2 due to the limit on the reproducibility of the solution temperature. The weighting factors become increasingly smaller at the higher temperatures. The latter measurements are of importance, nevertheless, in showing that the data continuously approach $\overline{\Delta G_2}^E = 0$ at the melting point of naphthalene. The smoothed w values are listed in column 5 of Table I for both binary and ternary systems. Included, also, are the values of A and B obtained for each system.

For regular solutions

$$(w'_{MS2})^{\frac{1}{2}} = \phi_1^\circ\ (w'_{12})^{\frac{1}{2}} + \phi_3^\circ\ (w'_{23})^{\frac{1}{2}} \qquad (8)$$

has been used as a means of predicting the pseudo-binary interaction parameter (*6*). ϕ_1° and ϕ_3° are the volume fractions of the indicated components in the binary 1 + 3 solvent mixture. In this work, where the *s*-regular model is adequate, an approach comparable to Equation 8 is

$$w^{\frac{1}{2}}{}_{MS2} = x_1^0 w_{12}{}^{\frac{1}{2}} + x_3^0 w_{23}{}^{\frac{1}{2}} \qquad (9)$$

Values of w_{MS2} predicted with Equation 9 are given in column 6 of Table I for the range of temperatures and compositions included in this work.

The spectra of carbon tetrachloride, napthalene, and carbon tetrachloride–naphthalene mixtures were compared to determine if charge-transfer complexation occurs in this system. Such an interaction, which would presumably be exothermic, could account for the difference in interaction between naphthalene and each of the two solvents in this study. Samples of mixtures for spectral analysis averaged about 5 × 10^{-3} *M* in naphthalene and about 0.1 *M* in carbon tetrachloride, using hexane as solvent at 25° C. The known concentrations of the mixture components were each varied over a range of one order of magnitude. The spectra were examined in the ultraviolet region, with repeated attention to that between 235 and 245 mμ. The concentration and spectral ranges noted here approximate those

Table I. Properties Related to Solubility of Naphthalene in Cyclohexane–Carbon Tetrachloride Solvent System

			Free Energy Interaction Parameter, *w*, Cal. per Mole		
Mole Fraction Naphthalene	Solution Temp., ° K.	$\overline{\Delta G}_2^E$, Cal./Mole, by Eq. 1	Exptl., by Eq. 4	Smoothed, by Eq. 7[a]	Calcd., by Eq. 9
		Mole Fraction CCl_4 in Solvent = 0			
0.1345	295.95	464	619	620	
0.1720	301.83	411	599	597	
0.2122	306.71	359	579	579	
0.3463	318.28	228	534	535	
0.4849	326.75	133	502	503	
0.6244	334.01	67.1	476	475	
0.7455	340.06	29.4	455	452	
0.8762	346.75	6.86	448	427	
		Mole Fraction CCl_4 in Solvent = 0.1780			
0.1318	292.22	414	549	545	543
0.2318	306.07	296	501	501	498
0.3093	313.35	227	476	478	474
0.3797	318.80	177	461	461	457
0.4899	325.86	114	438	438	434
0.6154	332.96	62.5	423	416	411
0.7386	339.41	27.1	397	395	390
0.8057	342.94	14.7	389	384	379
		Mole Fraction CCl_4 in Solvent = 0.3911			
0.1317	288.16	352	467	463	453
0.1587	292.88	318	450	450	441
0.2420	304.09	240	417	419	412
0.3658	315.68	156	388	387	381
0.4384	321.00	117	372	373	368
0.5719	329.55	64.3	351	349	345
0.6420	333.62	43.4	339	338	335
0.8137	343.16	10.8	312	312	310
		Mole Fraction CCl_4 in Solvent = 0.5805			
0.1493	287.86	275	380	379	372
0.2500	302.38	195	346	348	341
0.3182	309.63	155	333	332	326
0.4417	319.79	95.4	306	311	304
0.5505	327.41	59.8	296	294	288
0.7125	337.29	23.1	280	273	267
0.8122	342.95	9.35	265	261	255
		Mole Fraction CCl_4 in Solvent = 0.7788			
0.1530	285.24	221	307	302	299
0.2293	297.22	169	284	291	279
0.3296	308.67	119	265	263	260
0.4384	318.24	78.4	248	247	244
0.5635	327.44	45.1	236	232	229
0.6928	335.65	20.0	212	218	215
0.8022	342.20	7.96	203	207	205
		Mole Fraction CCl_4 in Solvent = 1			
0.1812	286.64	150	218	219	
0.2039	290.51	137	216	215	
0.2738	300.17	107	204	203	
0.4329	316.25	58.3	181	184	
0.5269	323.84	39.1	175	175	
0.5915	328.58	29.0	174	169	
0.6880	334.92	14.9	153	161	
0.8065	342.33	6.02	161	152	

[a] Assuming linear form of Equation 7: for six solvents in order given above A = 1744, 1471, 1252, 992, 778, 564 and $-B$ = 3.798, 3.168, 2.739, 2.132, 1.668, 1.204.

with which Prausnitz and coworkers (*1, 16*) have reported finding evidence of charge-transfer complexes of carbon tetrachloride with some other aromatic hydrocarbons. Our measurements do not establish the existence of a similar complex in the present system, however.

DISCUSSION

The $\Delta\overline{G}_2^E$ values in column 3 of Table I show both a well-defined continuous variation with temperature and clear approach to $\Delta\overline{G}_2^E = 0$ at the melting point of naphthalene. Solubilities in both binary naphthalene-solvent systems have been reported previously. Present results are in good agreement with those of Schroeder (*13*) for naphthalene–carbon tetrachloride, but in poor agreement with those of Linard (*8*) for naphthalene-cyclohexane. In the latter, present solubilities are systematically lower than those of Linard at lower temperatures, but gradually become systematically higher at the highest temperatures. The maximum difference is 0.07 mole fraction naphthalene at about 70° C. Both this work and that of Linard show that unit mole fraction naphthalene is approached as its melting point is approached.

The accuracy of the present arrangement for visual determination of solubility can be compared with that by an isothermal instrumental technique using previous results in the binary systems at 25° C. (*5*). By the latter for naphthalene-cyclohexane and naphthalene–carbon tetrachloride, respectively, 606 and 200 cal. per mole were reported for w, while interpolated values at this temperature from the present work are 602 and 205. The agreement is within the estimated uncertainties of the two methods. Thus, at 300° K., 5 cal. per mole in w corresponds to a change of about 0.3% in naphthalene solubility.

The uncertainty in experimental w in each of the six solvents in Table I increases from 2 cal. per mole at the lowest temperatures to a maximum at the highest temperature. This maximum for each solvent, in the order in which they are listed in Table I, is 22, 9, 10, 10, 10, and 11 cal. per mole. For 34 of the 45 points, the experimental and smoothed w values of Table I agree within the uncertainty in w, and the disagreement which does occur is randomly distributed for each solvent. The linearity of w *vs.* T by the *s*-regular model over the total range of solvent composition and temperature is well defined. The interval includes a span of solubilities from 0.13 to 0.88 mole fraction naphthalene and a span of temperatures from 285° to 347° K. Unfortunately, the fundamental significance of this linearity cannot be established with present measurements, because the determination of solubility at each temperature does not allow an unambiguous resolution of the temperature and composition dependence of the interactions—that is, the consistent behavior reported here may be only an internal agreement between empirical parameters which do not actually fit the proposed model. The practical significance of the linearity is an effective means of evaluating the suitability of the pseudo-binary mixed solvent approach in the present system.

Comparison of columns 5 and 6 of Table I shows that Equation 9 consistently yields w_{MS2} smaller than the experimental values. The maximum disagreement in each system is not, however, greater than from 5 to 7 cal. per mole. Thus, while Equation 9 cannot be considered quantitative, it provides a useful basis for a close estimate of the solubility in the present ternary systems over the total temperature range considered.

The reason for the failure in this work of the regular model to give a linear dependence of w' on temperature in the ternary systems is unknown. The molar volumes of naphthalene (as supercooled liquid), cyclohexane, and carbon tetrachloride are not greatly different, 124, 109, and 97 ml. per mole, respectively, at 25° C., and the thermal coefficients of expansion are similar. Moreover, in the binary systems the dependence of w' on temperature is linear.

A phase study has shown that a 1 to 1 compound of benzene and carbon tetrachloride is formed at low temperatures (*3*), and spectrophotometric evidence of the existence of a 1 to 1 charge-transfer complex of these components at 25° C. has been reported (*1*). If this system is compared with a typical regular solution involving benzene—benzene plus cyclohexane at 25° C., for example —significant differences are noted in several of the molar excess thermodynamic mixing properties (*11*). In the systems naphthalene–carbon tetrachloride and naphthalene-cyclohexane there is a similar difference in the excess free energy of mixing, and the difference is about twice as great as for benzene with these nonaromatic components. It is because of this similarity between the behavior of benzene and naphthalene that the present work included a search for spectral evidence of charge-transfer formation. The search was complicated by the significant absorptivity of both carbon tetrachloride and naphthalene in the spectral region presumed to be that where evidence of charge-transfer formation should be found. This complication should not have been sufficient, however, to mask a complex of absorptivity comparable to those reported by Prausnitz and coworkers for carbon tetrachloride–aromatic hydrocarbon complexes (*1, 16*).

McLaughlin and Ubbelohde (*9*) have proposed that fused-ring aromatic compounds assume a quasi-parallel configuration in the liquid state over limited regions. While this may have a bearing on the possibility of the complex formation considered here, the evidence to date is insufficient to assess this factor.

NOMENCLATURE

ΔG = molar Gibbs free energy of mixing, cal. per mole
$\Delta\overline{G}$ = relative partial molar Gibbs free energy of mixing, cal. per mole
n = moles
R = molar gas constant, cal. per deg. mole
T = absolute temperature
V = molar volume, ml. per mole
w = Gibbs free energy interaction parameter, cal. per mole
w' = Gibbs free energy interaction parameter, cal. per ml.
x = mole fraction
γ = activity coefficient
ϕ = volume fraction

Subscripts

1, 3 = solvent (cyclohexane and carbon tetrachloride)
2 = solute (naphthalene)
MS = mixed solvent (cyclohexane–carbon tetrachloride solutions)

Superscripts

o = solute-free solvent system
E = excess of property over Raoult's law behavior

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Gas-Liquid Equilibrium of the Oxygen–Carbon Dioxide System

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Gas-liquid equilibrium compositions for the O_2–CO_2 system were determined over the −50° to +10° C. temperature range and from 130 atm. down to the saturation pressure of CO_2. Activity coefficients are calculated, and a thermodynamic consistency test is applied to each isotherm.

THE GAS-LIQUID equilibrium of the oxygen–carbon dioxide system has been studied along a few isotherms (*10, 12, 16*), but until now no isobaric data have been reported. In this work, gas and liquid equilibrium phase compositions were determined for the O_2–CO_2 system at the −50°, −40°, −30°, −20°, −10°, 0°, and +10° C. isotherms at pressures from 130 atm. down to the saturation pressure of CO_2, in 10-atm. increments. Thus, both isothermal and isobaric phase diagrams may be constructed. Activity coefficients based on the unsymmetric normalization are calculated for each isotherm. The activity coefficients for CO_2 are referred to the pure component at the temperature of the system, whereas the activity coefficients for O_2 are referred to the infinitely dilute solution. The activity coefficients are furthermore referred to a constant pressure via the Poynting correction factor, making possible the application of the isothermal-isobaric form of the Gibbs-Duhem equation. This equation, in the form of an area test for thermodynamic consistency, is applied separately to each isotherm.

EXPERIMENTAL

The apparatus used here is of the vapor recirculation type; the gaseous phase is circulated through a stationary liquid phase enclosed in a chamber. The flow diagram of the system is shown in Figure 1, where the main vapor circulation path is indicated by a heavy line. The vapor phase, after leaving the pump (a Lapp model CPS-2 diaphragm compressor), enters the equilibrium cell via cooling coils, both cell and coil being immersed in a constant-temperature bath. The vapor phase bubbles through the liquid phase in the cell and finally goes back to the pump. The design of the cell, which is provided with windows to permit visual observation of the two phases, is given by Fredenslund (*7*).

Before obtaining the gas and liquid phase samples, the lines leading to bypass-valves BP1 and BP2 (Figure 1) and the liquid sample line leading from the bottom of the cell through valve LS2 are flushed. The gas circulation through the liquid is resumed, and the gas and liquid sampling spaces are evacuated. At the time of gas sampling, BP1 is opened. With VS1 and VS2 closed, the gas located in the space between VS1, VS2, VS3, and VS4 is sealed off, while gas circulation continues via BP1. To take the liquid sample, BP2 is opened, MS2 closed, and LS2 opened to transfer about 0.5 cc. of liquid sample into the space between valves LS2, LS3, and LS4, which are all located inside the cryostat. The gas and liquid samples may now be expanded into their respective sample chambers. The liquid sample is pumped through the path LS3-LS4-chamber to ensure that the gas composition in the chamber is the same as that in the lines immersed in the cryostat. From the sample chambers, the samples are sent to a gas chromatograph equipped with a 6-foot silica gel column for analysis.

Refrigeration of the constant-temperature bath is accomplished by forcing a regulated amount of liquid nitrogen through cooling coils located in the bath fluid. A Bayley temperature controller furnishes the final fine control by adding a small amount of heat via six resistance coils located in the bath. It proved possible to control the temperature to within ±0.005° C. for pro-

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