A Solution Thermodynamic Study of Soybean Oil/Solvent Systems by Inverse Gas Chromatography[1]

Jerry W. King* and **Gary R. List**

Northern Regional Research Center, Agricultural Research Service/USDA, 1815 North University Street, Peoria, IL 61604

Inverse gas chromatography (IGC) has seen wide application in the characterization of molten polymers, fibrous materials, and natural products, such as proteins and carbohydrates, over the past fifteen years. This study describes a relatively simple IGC technique for evaluating solute-solvent interactions using a refined soybean oil as a solvent. Utilizing soybean columns that are 5–20% by weight of the inert support has allowed the determination of a number of thermodynamic solution parameters for 22 solute-solvent pairs in the temperature range of 55–125°C. Weight and mole fraction activity coefficients, along with Henry's Law constants at infinite dilution, are presented for six solute classes. In general, activity coefficients increase with carbon number for n-alkanes, alkyl-substituted benzenes, and n-alkanoic acids at all temperatures investigated, while the reverse is found for the n-alkanols. The activity coefficient data indicate that aromatic solutes, chlorinated hydrocarbons, ketones, and cyclohexane can readily dissolve soybean oil. Calculated heats of mixing for n-alkanols were found to be positive (to 2.84 kcal/mole) while recorded enthalpic interactions were weak for aromatic solutes, lower alkanes, and chlorinated hydrocarbons. The relevance of the above data to such problems as oil dissolution and solvent devolatilization are discussed.

Solvent extraction is a traditional method for removing triglyceride-based oils from seeds in the oleochemical industry. Several studies (1,2) have been conducted to determine the most appropriate solvent for vegetable oil extraction, although the selection process has been empirical by nature and without thermodynamic rationale. There is a paucity of solution thermodynamic data in the literature upon which to design extraction or desolventization conditions. This problem is particularly acute in the dilute solution range where the organic solvent is present in trace concentrations in the vegetable oil matrix. Removal of such solvent residuals from the extracted oil is a crucial step in the oil refining process and critical to the production of a safe product for consumer use.

With the exception of the partial pressure measurements of n-hexane above heated soybean oil, conducted by Smith in 1951 (3–5), there appears to be no data in the literature for solute concentrations approaching infinite dilution. Solution thermodynamic parameters, such as activity coefficients and Henry's Law constants in this concentration range, are important for optimizing the solvent removal process, and in addition yielding insight into the basic molecular interactions between solute and solvent. The relative magnitudes of these parameters allow

extraction solvent selection to be based on solution thermodynamic criterion of deviation from an ideal solution.

A convenient experimental method for measuring the above parameters at conditions approaching infinite dilution is the technique of inverse gas chromatography (IGC). In IGC, the non-volatile binary solution component is distributed on a chromatographic packing material which is held under specified conditions in the chromatographic column. Injection of a small quantity of solute vapor into the column will approximate a dilute solution of the solute in the vegetable oil. Solution thermodynamic parameters are derived from precise retention volume measurements of the solute as it migrates through the chromatographic column. Thus, in the IGC technique, the solvent is the vegetable oil, and the solutes are common organic solvents.

The IGC method has been applied for characterizing a variety of materials, including molten polymers (6,7), sorbents (8), proteins (9,10) and fibers (11). Despite the fact that many oleophilic derivatives were used as stationary phases during the early development of gas chromatography, we found no citations in the literature of an IGC study involving vegetable oils. In this study, we have applied the IGC technique to characterize solute-solvent interactions in soybean oil over the temperature range of 60 to 125°C.

EXPERIMENTAL PROCEDURES

A modified Varian 1400 gas chromatograph equipped with a flame ionization detector was employed for measuring solute retention volumes. Column inlet pressures were determined using a mercury-filled U-tube manometer, whie oven temperatures were ascertained with a sheathed iron-constantan thermocouple. A Hewlett-Packard 3465B digital multimeter was used for recording the thermocouple voltages which were taken randomly throughout each experimental run. Chromatographic peak profiles were recorded on a Houston Instruments Omniscribe recorder whose chart speed was checked against stop-watch readings. High purity-grade helium was used as the carrier gas, and its flow rate was measured by a soap-bubble flow meter. Mobile phase flow-rate readings were taken under ambient conditions several times a day by diverting the carrier gas flow upstream from the column proper. The measured flow rate was corrected according to the procedure of Laub and Pecsok (12) to yield the outlet column flow rate. Both injector and detector block temperatures were set high enough to assure volatilization of the highest boiling solutes used in this study.

Chromatographic columns were prepared from solvent-rinsed, 1/4 inch O.D. copper tubing. Refined, bleached, and deodorized soybean oil (Riceland Foods, Stuttgart, IA) was coated on Chromasorb G, 45/60 mesh, that had been washed with acid and treated with DMCS. Coating was affected by concentrating a hexane solution of the oil with a rotary evaporator. The coated packings were carefully transferred into three-foot-long columns, and

conditioned overnight using flowing carrier gas at the highest experimental temperature used in these studies. The percentage oil loading on the packing was determined by weight difference after calcination of the support in a muffle furnace. A small correction to the recorded weight loss due to pyrolysis of the silane coating and adsorbed water was determined by independent pyrolysis of the uncoated support. Columns were prepared at the following soybean oil loadings: 5.200%, 9.834%, 12.60%, 17.02%, and 20.56% by weight. Pyrolysis of the coated packings before and after use revealed a negligible weight loss (0.3-0.5%), consistent with the thermal stability of vegetable oils in non-oxidative atmospheres (13).

The injected solutes were selected from literature citations (1,2) reporting their use as extraction solvents for vegetable oils. Solute classes included n-alkanes, aromatic hydrocarbons, alcohols, chlorinated solvents, and n-alkanoic acids. All solutes were reagent grade chemicals, and used without further purification. Injections were made by taking up approximately one microliter of the solute mixture into the syringe barrel and then pumping the plunger back and forth so as to produce a "vapor state" injection. This technique assures the injection of an infinitely dilute plug of sample vapor into the chromatographic column, thereby producing a very dilute solution of the solute in the coated solvent (oil). The chromatographic profiles obtained by this method are symmetrical, and the peak maximum retention time is invariant with respect to its concentration in the column mobile phase or the presence of the other solutes in the injected mixture. Solute mixtures were made up according to chemical classes, 4-5 solutes per mixture, and injected as described above. The instrumental and column dead volume was determined by injecting a methane sample before and after the injection of the solute mixtures.

RESULTS

The fundamental parameter upon which all of the IGC derived-thermodynamic data are based is the specific retention volume, V_g^o given by Equation 1 as:

$$V_g^o = \frac{(t_r - t_a)(273.16/T_o)(760/p_o)(1 - p_w/p_o)(j)(F_o)}{w_2} \quad [1]$$

where t_r, t_a = retention time of solute (r) and nonsorbed solute (a); F_o = flow rate at ambient conditions; P_o = atmospheric pressure under ambient conditions; P_w = vapor pressure of water; j = James-Martin compressibility factor; T_o = temperature at ambient conditions; and w_2 = weight of the stationary phase (2).

Further details on derivation of this equation and its constituent parameters can be found in standard texts (14,15). The experimentally measured parameters in Equation 1—column and ambient temperatures, inlet pressure, and ambient flow rates—were averages of 4-5 determinations on the day that the data were accumulated. The average variance in the column (oven) temperature was determined to be ±0.2°C. Recorder chart speed was varied, depending on the magnitude of the retention times, to improve the accuracy in the retention volume measurement.

Inspection of the experimental specific retention volumes for all five soybean columns revealed excellent agreement between the values for each solute determined on the three columns having the highest oil loadings. Specific retention volumes determined on columns having less than 10% by weight coatings appeared to be influenced by interfacial adsorption at the support surface (16). Therefore, these retention volumes were not used in computing the average specific retention volume at each of the four averaged temperatures.

The resultant V_g^o data are shown in Table 1 as a function of temperature for six generic solute classes. The trends in V_g^o with temperature are similar to those found in many other thermodynamic gas chromatographic studies (17,18); namely, there was an exponential decrease in retention volume with increasing column temperature. Likewise, within a solute class, the retention volume increases with solute carbon number in a homologous series at a given temperature. This trend is partially due to the lower vapor pressure encountered as the molecular weight of solute is increased.

Activity coefficients at infinite dilution, utilizing both the mole and weight fraction convention (7,19), can be computed from the above specific retention volumes using Equations 2 and 3:

$$\ln_w^\infty = \ln \frac{273.16 \, R}{V_g^o M_1 p_1^o} - \frac{p_1^o (B_{11} - \overline{V}_1)}{RT} \quad [2]$$

and

TABLE 1

Specific Retention Volumes (mL/g) for Solute/Soybean Oil Systems at Selected Temperatures

Solute	Temperature (°C)			
	58.7	79.0	100.9	123.4
n-Hexane	63.4	34.4	20.1	12.2
n-Heptane	154	77.9	41.9	23.9
n-Octane	219	113	60.9	35.0
n-Decane	380	177	86.1	45.8
Cyclohexane	127	69.3	38.4	22.7
Benzene	179	94.3	51.0	30.0
Toluene	462	223	110	59.9
Ethylbenzene	1010	451	207	106
Methylene chloride	61.4	34.6	20.1	12.1
Carbon tetrachloride	159	82.1	45.4	26.3
Trichloroethylene	257	129	67.2	37.4
Acetone	35.9	20.4	12.4	7.68
Methyl ethyl ketone	91.5	50.1	27.1	16.1
Methyl isobutyl ketone	322	152	75.1	41.0
Furfural	1120	484	215	108
Methanol	18.8	10.5	6.37	4.14
Ethanol	33.8	19.4	11.1	6.82
Isopropanol	51.8	27.3	15.0	9.14
n-Butanol	254	116	56.9	30.6
Acetic acid	360	141	62.9	30.8
Propionic acid	920	327	133	60.0
Butyric acid	2130	726	264	112

$$\gamma_x^\infty = \frac{\gamma_w^\infty M_1}{M_2} \qquad [3]$$

where γ_w^∞ = weight fraction-based activity coefficient at infinite dilution; γ_x^∞ = mole fraction-based activity coefficient at infinite dilution; R = gas constant (6.236 × 10^4 mL − mm Hg/°K − mole); M_1 = molecular weight of the solute (1); M_2 = molecular weight of the solvent (2); p_1^0 = saturated vapor pressure of the solute; B_{11} = second pure virial coefficient of the solute; $\overline{V}_1$ = molar volume of the solute; and T = column temperature.

Solute vapor pressures for Equation 2 were computed using the well-known Antoine equation, where p_1^0 is given by:

$$\log p_1^0 = A - B/(T + C) \qquad [4]$$

and A, B, and C are constants available from several standard sources (20,21). Pure second virial coefficients for each solute were calculated using the equation derived by McGlashan and Potter from corresponding states theory (19), where B_{11} is:

$$\frac{B_{11}}{V_c} = 0.430 - 0.866(T_c/T) - 0.694(T_c/T)^2$$
$$- 0.0375(n - 1)(T_c/T)^{4.5} \qquad [5]$$

and T_c and V_c are the critical temperature and volume of the solute, respectively.

The value for n in Equation 5 is the hypothetical number of carbon atoms for a given solute that yields a vapor pressure equivalent to that for a corresponding n-alkane solute. This parameter was estimated using the procedure of Guggenheim and Wormald (22), where the vapor pressure parameter A is determined with the aid of Equation 6:

$$A = \frac{T(P_c/p_1^0)}{T_c - T} \qquad [6]$$

and P_c is the critical pressure of the solute. The calculated value of A is then matched with an n-alkane that yields an equivalent value for A. If an equivalent value for A could not be found, then the alkane yielding the closest value to the solute's A was used.

Required critical constant data was obtained from several sources (20,23–29). The critical volume for furfural was estimated by using Equation 7:

$$V_c = \frac{Z_c R T_c}{P_c} \qquad [7]$$

using a value of 0.26 for critical compressibility factor, Z_c.

Castells and Mazza (30) have cautioned against using pure virial coefficient values derived from Equation 5 for solutes exhibiting intermolecular hydrogen bonding. Therefore, the values derived from Equation 5 for each solute were checked against the experimentally determined data in Dymond and Smith's compendium (31). Agreement was satisfactory for all of the solutes except the alcohols. For the purposes of this study, the actual

experimental B_{11} values for n-butanol were taken from Dymond and Smith (31). The second virial coefficients for methanol, ethanol, and isopropanol were calculated using the empirical formula given by Kretschmer and Wiebe (32).

The molar volume data required in Equation 2 was derived by dividing the solute's density into the corresponding molecular weight. Some of the required density data was derived from interpolation on plots of solute density as a function of temperature (33). Alternatively, the procedure advocated by Al-Saigh and Munk (34), based on the law of rectilinear diameters, was used, as given in Equation 8:

$$\varrho_L = a + bT - \varrho_v \qquad [8]$$

where ϱ_L and ϱ_v are the liquid and vapor densities of the solute, respectively, and a and b are constants available from standard sources (20,24). Values for ϱ_v were obtained from the ideal gas law.

For some applications, the mole fraction-based activity coefficient is preferred over γ_w^∞, since this thermodynamic parameter can be related to its value for an ideal solution (γ_x^∞ = 1.0). Computation of γ_x^∞ requires a knowledge of the solvent molecular weight as shown in Equation 3. Natural oils, such as soybean, are complex mixtures of triglycerides and therefore only a average molecular weight can be used to characterize the solvent in this case. A similar problem arises in the use of IGC for studies of solute-solvent interaction in molten polymers (7). Despite this uncertainty in the solvent molecular weight, values of γ_x^∞ can be of considerable value in interpreting the solution thermodynamics of the soybean oil/solute systems.

Values of M_2 for the soybean oil triglycerides were determined from lipase hydrolysis data (35,36) and the 1-3 random, 2 random theory advanced by Coleman and Fulton (37) and VanderWal (38). Soybean triglycerides were incubated with pancreatic lipase at 40°C, and the 2-monoglycerides isolated from the hydrolyzate mixture by liquid-liquid chromatography on silicic acid (39). The fatty acid composition of the complete triglyceride and the 2-monoglyceride were used to calculate the average molecular weight of the soybean oil, 870 a.m.u. Interestingly, this average value is very close to the molecular weight of the principal triglyceride in soybean oil, trilinolein (874 a.m.u.).

Table 2 lists the derived weight fraction activity coefficients computed from Equation 2. There are several interesting trends in the data contained in Table 2—within each class of solutes, between classes of solutes, and as a function of temperature. For example, n-octane and n-decane exhibit a decreasing escaping tendency (lower γ_w^∞) from solution as the temperature is increased. This is consistent with the increased miscibility of these oil and solvent mixtures with increasing temperature as reported in the literature (40). A similar trend is also noted for the alcohols used in this study. However, inspection of the γ_w^∞ values for the lower alkanes, the aromatic solutes, and the chlorinated hydrocarbons reveals a limited dependence, if any at all, on the solution temperature.

Weight fraction activity coefficients appear to be largest for the alcohol moieties when compared to values exhibited by other solute classes at the same temperature.

TABLE 2

Weight Fraction Based Activity Coefficients for Solute/Soybean Oil Systems at Selected Temperatures

Solute	Temperature (°C)			
	58.7	79.0	100.9	123.4
n-Hexane	5.94	5.91	5.73	4.77
n-Heptane	5.64	5.47	5.26	5.19
n-Octane	9.28	7.98	7.01	6.33
n-Decane	30.0	23.4	18.9	15.8
Cyclohexane	4.40	4.26	4.18	4.17
Benzene	3.33	3.26	3.34	3.24
Toluene	3.07	2.99	3.02	2.99
Ethylbenzene	3.07	2.98	2.99	2.96
Methylene chloride	2.41	2.43	2.48	2.60
Carbon tetrachloride	1.68	1.72	1.72	1.76
Trichloroethylene	1.73	1.75	1.79	1.84
Acetone	10.2	9.70	8.99	8.82
Methyl ethyl ketone	7.11	6.55	6.44	6.24
Methyl isobutyl ketone	5.22	5.03	4.87	4.73
Furfural	10.9	8.88	7.73	6.82
Methanol	48.9	41.0	33.4	27.6
Ethanol	33.8	25.3	20.2	16.6
Isopropanol	20.5	16.2	13.1	10.7
n-Butanol	16.6	12.9	10.3	8.42
Acetic acid	9.22	10.1	10.4	10.6
Propionic acid	9.42	9.63	9.35	9.14
Butyric acid	11.6	10.5	9.89	9.15

TABLE 3

Mole Fraction Based Activity Coefficients for Solute/Soybean Oil Systems at Selected Temperatures

Solute	Temperature (°C)			
	58.7	79.0	100.9	123.4
n-Hexane	0.588	0.585	0.568	0.572
n-Heptane	0.649	0.630	0.606	0.597
n-Octane	1.22	1.05	0.920	0.831
n-Decane	4.90	3.83	3.09	2.58
Cyclohexane	0.426	0.412	0.404	0.404
Benzene	0.299	0.293	0.300	0.291
Toluene	0.325	0.317	0.320	0.317
Ethylbenzene	0.374	0.363	0.365	0.361
Methylene chloride	0.235	0.237	0.242	0.254
Carbon tetrachloride	0.297	0.304	0.303	0.311
Trichloroethylene	0.262	0.264	0.270	0.278
Acetone	0.683	0.648	0.600	0.589
Methyl ethyl ketone	0.589	0.543	0.533	0.517
Methyl isobutyl ketone	0.601	0.579	0.560	0.545
Furfural	1.21	0.980	0.854	0.753
Methanol	1.80	1.51	1.23	1.02
Ethanol	1.79	1.34	1.07	0.881
Isopropanol	1.42	1.12	0.908	0.736
n-Butanol	1.42	1.10	0.876	0.718
Acetic acid	0.636	0.697	0.715	0.732
Propionic acid	0.802	0.820	0.796	0.778
Butyric acid	1.18	1.07	1.00	0.927

This is not surprising considering the substantial polarity difference between the alcohols and the non-polar triglyceride solvent. Additional rationalization of trends in solute classes is difficult to discern when the activity coefficient is expressed on a weight fraction basis; however a high escaping tendency is exhibited by carboxylic acids, while the aromatic and chlorinated hydrocarbons seem to prefer partitioning into the triglyceride matrix.

The weight fraction activity coefficient data in Table 2 suggests that there are both subtle and regular trends in the γ_w^∞ values as a function of molecular structure within classes of solutes. For example, the n-alkane data indicates that higher molecular weight homologues have higher γ_w^∞ at all temperatures studied, with the exception of an inversion in this trend between n-hexane and n-heptane. Conversely, addition of methylene groups to an alcohol moiety increases the non-polar nature of the solute resulting in a decrease of γ_w^∞ for the higher homologues. This suggests that methylene-methylene interactions between the triglyceride chains and the solutes are crucial to enhancing solubility of the solute in the oil phase.

Mole fraction-based activity coefficients derived from Equation 3 are tabulated in Table 3. As noted previously, the γ_w^∞ values can be compared to a reference γ_w^∞ of unity, the value expected if an ideal solution existed for a given solute/solvent system. Utilizing this criterion, it is apparent that many of the solutes listed in Table 3 form solutions at infinite dilution that exhibit negative deviations from Raoult's Law ($\gamma_w^\infty < 1.0$). This trend is exhibited by all of the aromatic and chlorinated hydrocarbons listed in Table 3. In addition, γ_w^∞ less than unity is also recorded for n-hexane, n-heptane, cyclohexane, and for three of the

ketones in Table 3 at all of the listed experimental temperatures.

Based on the activity coefficient trends in Table 3, it is apparent that many solutes exhibit a transition from positive to negative deviation from Raoult's Law as temperature is increased. Examples of this trend are found in the activity coefficient data for the higher alcohols and furfural. In general, the mole fraction-based activity coefficients for each specific solute in Table 3 as a function of temperature exhibit a similar pattern to the activity coefficient data in Table 2. One notable exception to this observation is the inversion in the relative values of γ_w^∞ for n-hexane and n-heptane compared to the γ_w^∞ values recorded in Table 2.

It is interesting to note that the mole fraction activity coefficient is a particularly sensitive diagnostic parameter with which to measure solute-solvent interactions as the molecular structure of the solute or solvent is varied. For example, the polar alcohols at lower temperatures exhibit positive deviations from Raoult's Law, a trend that is in accordance with solubility data (2). Likewise, many of the solute/solvent systems, the n-alkanes and chlorinated hydrocarbons, have activity coefficients less than unity, a fact that is not too surprising in lieu of their widespread use as extraction solvents. Negative deviations from Raoult's Law are also exhibited by acetic and propionic acids despite their polar nature. This indicates that factors other than polarity (e.g., vapor pressure, molecular size) are responsible for the resultant solution thermodynamic patterns. This trend for the acidic solutes would not have been observed if only weight fraction activity coefficients had been considered.

TABLE 4

Henry's Law Constants (atm) for Solute/Soybean Oil Systems at Selected Temperatures

Solute	Temperature (°C)			
	58.7	79.0	100.9	123.4
n-Hexane	4.28	8.06	14.2	24.5
n-Heptane	1.48	2.98	5.66	10.2
n-Octane	0.906	1.77	3.34	5.93
n-Decane	0.416	0.897	1.85	3.52
Cyclohexane	2.15	4.00	7.38	12.8
Benzene	1.64	3.15	5.93	10.4
Toluene	0.533	1.11	2.29	4.28
Ethylbenzene	0.211	0.474	1.04	2.07
Methylene chloride	4.52	8.23	14.7	25.4
Carbon tetrachloride	0.942	1.85	3.41	6.06
Trichloroethylene	0.676	1.36	2.66	4.90
Acetone	11.2	20.0	33.7	56.6
Methyl ethyl ketone	3.48	6.44	12.2	21.1
Methyl isobutyl ketone	0.703	1.50	3.08	5.76
Furfural	0.209	0.484	1.09	2.19
Methanol	38.4	69.7	117	186
Ethanol	14.7	26.0	46.3	78.2
Isopropanol	7.37	14.2	26.5	45.2
n-Butanol	1.20	2.63	5.46	10.3
Acetic acid	1.04	2.67	6.03	12.5
Propionic acid	0.330	0.930	2.31	5.16
Butyric acid	0.120	0.352	0.972	2.31

The Henry's Law constant which has many applications in applied chemical engineering can be directly derived from the activity coefficient data. For the purposes of this study, we have defined a Henry's Law constant based on the weight fraction activity coefficient convention (15) as defined by Equation 9 as:

$$H_w^\infty = p_1 (a_1/w_1) \qquad [9]$$

where p_1 is the partial vapor pressure of the solute above the solution, a_1 is the activity of solute, and w_1 is the weight fraction of the solute in the solution. Knowledge of the Henry's Law coefficient permits the calculation of the solute vapor pressure above the oil phase at the limit of infinite dilution where the sorption isotherm is linear. Equation 9 neglects the previously cited gas imperfection term used in the activity coefficient calculations and the small sorption of helium carrier gas in the oil phase.

The Henry's Law constants calculated from Equation 9 are presented in Table 4. As would be expected, the H_w^∞ values increase with increasing temperature, a trend that is a reflection of the increase in solute vapor pressure. Solute volatility differences are also apparent within a solute class, the lower molecular weight compounds having larger H_w^∞ values than the higher molecular weight species. Such data can then be used in design calculations to estimate the size requirements for desolventizing units.

DISCUSSION

The activity coefficient data presented in Tables 2 and 3 can be used to assess the solubilizing potential of many solvents for soybean oil. For example, 14 of the 22 listed

solute/solvent mole fraction activity coefficients at 58.7°C have activity coefficients less than unity. This implies that they deviate negatively from Raoult's Law and that solute-solvent interactions predominate over solute-solute or solvent-solvent interactions. Both the chlorinated and aromatic hydrocarbons consistently have the lowest activity coefficients of the listed solutes, which supports their documented capability as excellent vegetable oil extraction solvents (2). Unfortunately, their potential carcinogenic nature limits their application for the processing of oils or by-product meals intended for food use. The tragic consequences of using trichloroethylene as an extraction solvent have been cited in the literature (41). Other organic solvents, such as the ketones, which exhibit low activity coefficients in soybean oil, may have potential in processing oils that are intended for industrial applications, such as paints or lubricants (42).

The effect of temperature on the limiting activity coefficients reported in Tables 2 and 3 correlates well with observed solubility phenomena that have been reported for various solvent/vegetable oil systems. Mole fraction activity coefficients for the alcohol/soybean oil systems in Table 3 become less than unity at temperatures approaching 100°C. This trend correlates well with studies on model alcohol/triglyceride systems (43) in which negative deviations from Raoult's Law occur at slightly under 100°C. Such data is important, particularly for conventional desolventization schemes utilizing steam. In addition, the increase for alcohol/soybean oil activity coefficients at lower temperatures supports their observed phase separation from the oil at these temperatures (2). The dependence of solubilizing power on chemical structure is also apparent in the alcohol/soybean oil activity coefficient data. For instance, Baker and Sullivan (44) have noted the superiority of isopropanol over ethanol in soybean oil extraction, an observation that is supported by the relative values of the activity coefficients for ethanol and isopropanol at 58.7°C.

A more thorough analysis of the dependence of the solute activity coefficients on temperature allows additional conclusions to be drawn on the basic solution thermodynamics accompanying the dissolution process. For this analysis, we must invoke the Van't Hoff relationships, where the heat of solution, $\Delta \overline{H}_s^\infty$, for the solute dissolving in soybean oil is given by:

$$\Delta \overline{H}_s^\infty = R(\partial \ln V_g^0 / \partial 1/T) \qquad [10]$$

and the corresponding heat of mixing between solute and solvent, $\Delta \overline{H}_m^\infty$, is calculated by:

$$\Delta \overline{H}_m^\infty = R(\partial \ln \gamma_w^\infty / \partial 1/T) \qquad [11]$$

The heat of solution is composed of enthalpy of vaporization for the solute molecule and the above-defined heat of mixing. The former quantity represents the energy required to overcome solute-solute interactions, thereby permitting solute-solvent interactions to be determined, as represented by heat of mixing term in Equation 12:

$$\Delta \overline{H}_s^\infty = \Delta \overline{H}_v^\infty + \Delta \overline{H}_m^\infty \qquad [12]$$

This "excess" enthalpy of solution, $\Delta \overline{H}_m^\infty$, is a measure of the specific interactions between the solute and the
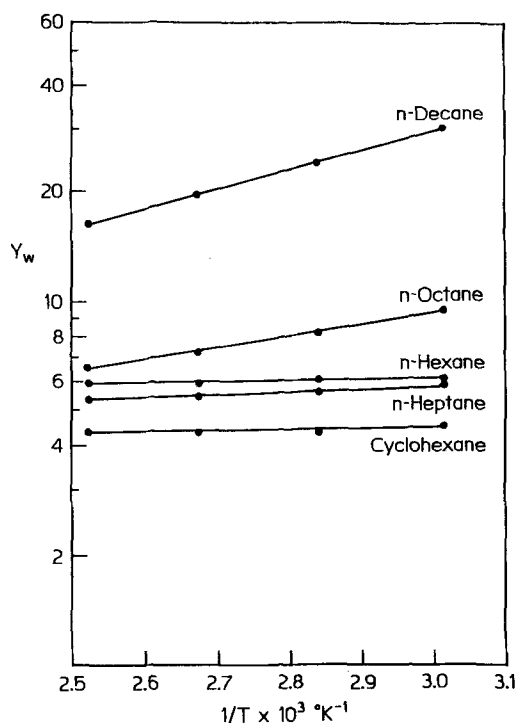
FIG. 1. Weight fraction activity coefficient vs reciprocal temperature for alkane/soybean oil system.

TABLE 5

Heats of Solution and Mixing for Solute/Soybean Oil Systems

Solute	$\Delta\overline{H}_S^\infty$ (kcal/mole)	$\Delta\overline{H}_m^\infty$ (kcal/mole)
n-Hexane	−6.64 ± 0.08	0.14 ± 0.06
n-Heptane	7.53 ± 0.07	0.35 ± 0.04
n-Octane	−7.41 ± 0.04	1.55 ± 0.06
n-Decane	−8.55 ± 0.07	2.60 ± 0.07
Cyclohexane	−6.96 ± 0.02	0.22 ± 0.06
Benzene	−7.24 ± 0.06	0.8 ± 0.09
Toluene	−8.28 ± 0.06	0.58 ± 0.05
Ethylbenzene	−9.14 ± 0.07	0.12 ± 0.05
Methylene chloride	−6.54 ± 0.01	−0.31 ± 0.09
Carbon tetrachloride	−7.24 ± 0.08	−0.17 ± 0.05
Trichloroethylene	−7.79 ± 0.02	−0.24 ± 0.04
Acetone	−6.20 ± 0.07	0.63 ± 0.08
Methyl ethyl ketone	−7.06 ± 0.07	0.5 ± 0.1
Methyl isobutyl ketone	−8.35 ± 0.09	0.399 ± 0.009
Furfural	−9.45 ± 0.09	1.9 ± 0.1
Methanol	−6.1 ± 0.2	2.32 ± 0.08
Ethanol	−6.48 ± 0.04	2.9 ± 0.1
Isopropanol	−7.0 ± 0.1	2.63 ± 0.03
n-Butanol	−8.6 ± 0.1	2.75 ± 0.05
Acetic acid	−9.9 ± 0.2	−0.5 ± 0.1
Propionic acid	−11.0 ± 0.2	0.1 ± 0.1
Butyric acid	−11.9 ± 0.2	0.94 ± 0.05

solvent, and permits certain conclusions to be drawn about the solution thermodynamic behavior of the system which is under study.

The variance in the logarithm of the weight fraction activity coefficient as a function of the reciprocal of absolute temperature was subjected to linear regression analysis to calculate the heat of mixing. The coefficients of regression (all at least 0.999) indicated an excellent fit of the experimental data to Equation 10. Figure 1 shows the Van't Hoff relationship for the n-alkanes and cyclohexane in soybean oil over the temperature range employed in this study. The slopes of the curves in Figure 1 are proportional to the heats of mixing of the aliphatic solutes in the soybean oil matrix. Figure 1 suggests that this enthalpic interaction is very weak for the lower alkanes and cyclohexane, but takes on finite values for n-octane and n-decane.

The resultant heats of solution and mixing from the linear regression analyses are listed in Table 5. The tabulated heats of solution for all of the solutes with soybean oil are negative, implying that the enthalpic component of the solution process favors dissolution. The error in the heats of solution presented in Table 5, computed as the standard deviation of the slope, is between 1-2%, testimony to the high precision of the experimental data. The heats of solution tabulated for the members of homologous series in Table 5 show increasingly negative values, a trend reported in many IGC studies (45).

The heats of mixing data in Table 5 are extremely interesting. The absolute magnitudes of the $\Delta\overline{H}_m^\infty$'s are small for all of solutes, with the exception of n-octane, n-decane, furfural, and the alcohols. Inspection of the Van't Hoff plots of the other solutes indicates a high

conformity to linear relationships, each having a slope effectively equal to zero. This suggests that their overall solution behavior is athermal, and that the free energy of solution is dominated by the entropy of mixing. Hence, the high error associated with these particular heats of mixing is a reflection of the solution process and not the error in the measurement. This is borne out by the standard deviations associated with the heats of mixing for the higher alkanes, alcohols and furfural, which are typical of the relative error associated with the heats of solution. The fact that the heats of mixing for many solutes with soybean oil are approximately zero should not be too surprising, considering that many of the chosen solutes are excellent solvents for this particular vegetable oil.

As noted previously, there is limited data in the literature to compare with the results derived in this study. For this reason, the data presented in Tables 1-5 are quite unique and should find wide application in engineering processes, such as oil deodorization. In such a unit process, the level of extractable residues is in the range where Henry's Law is applicable. Smith and coworkers (4) in the 1950's determined vapor pressures above hexane-soybean oil solutions at weight fractions approaching infinite dilution using a static equilibrium apparatus. The data in Smith's study affords a potential comparison between the H_w^∞ values derived from IGC and the static vapor pressure measurements.

The H_w^∞ values derived from Smith's data were taken from the limiting slopes of solute vapor pressure-weight fraction relationship. The Henry's Law constants derived by this procedure were 9.30 (77.2°C), 15.5 (102.2°C) and 28.1 (122.9°C) atmospheres. These values are of a

similar magnitude to constants reported in Table 4 for n-hexane, despite the subtle difference in experimental temperatures. The H_w^∞'s derived from the IGC method are consistently lower then those derived from the static vapor pressure study. This trend may be due to the fact that the IGC-derived H_w^∞'s are obtained under more dilute solution conditions, i.e., at a lower solute concentration range, than that utilized in the older, classical technique. The slight concavity of the vapor pressure-weight fraction plot toward the concentration axis in the Smith study suggests that perhaps the range of "infinite dilution" has not been reached.

The activity coefficient data presented in this study can have additional applications in the oil processing field. For example, the relative activity coefficient values listed in Tables 2 and 3 can be used as a basis for entrainer selection in supercritical fluid extraction. Solutes exhibiting negative deviations from Raoult's Law are the most preferred solvents for the soybean oil; hence they should be attractive co-solvents in combination with a dense gas, for the extraction of a vegetable oil. Several reported supercritical fluid extraction studies (46,47) utilizing compressed carbon dioxide in combination with n-hexane, acetone, methylene chloride, benzene, and others support the above hypothesis.

ACKNOWLEDGMENTS

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