Vapor Pressure of Hexane-Soybean Oil Solutions at Low Solvent Concentrations

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THE recovery of vegetable oils from solutions obtained in solvent extraction operations is commonly accomplished by evaporation followed by steam stripping of the concentrated oil extract. Knowledge of the pressure-temperature-composition relations of the oil-solvent solutions is of importance for economical design and efficient operation of the equipment to produce an oil of acceptable quality.

The vapor pressures of Skellysolve-B solutions of cottonseed and peanut oils over a temperature range to 155°F. have been reported (3). Boiling point data have been presented recently in graphical form for trichlorethylene-soybean oil solutions (5). No vapor pressure data have been published for the important system of soybean oil and hexane. In the evaporation of hexane from soybean oil extracts, the solvent concentration can readily be reduced to about 10% at atmospheric pressure. The removal of residual solvent by steam stripping however presents a difficult problem in which adequate data can be of real value. This paper presents results of vapor pressure measurements in soybean oil solutions of hexane over a concentration range of 0 to 5 weight per cent solvent, and at temperatures from 167° to 248°F.
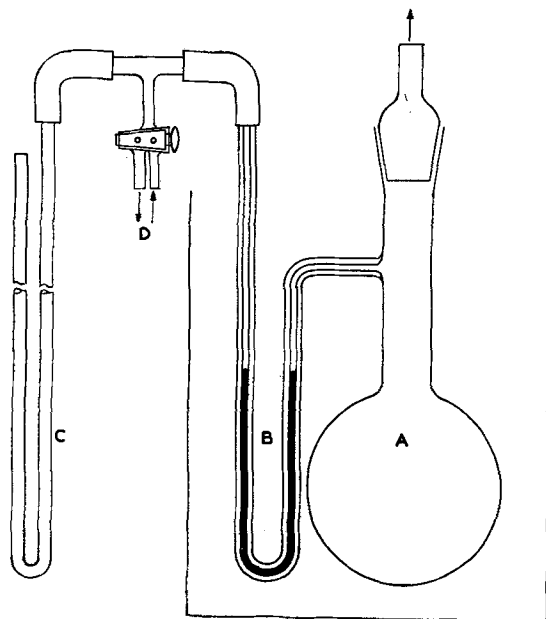

FIG. 1. Vapor pressure apparatus.

Methods available for vapor pressure measurement cannot be used satisfactorily at all concentrations and the experimental work, like the commercial operation, must be carried out in different apparatus. Dynamic, or boiling point, methods can be used conveniently when solutions contain more than about 5% solvent. Below this concentration a static method in

which known amounts of oil and solvent are brought to equilibrium is essential for reliable measurements. The choice of method is further restricted by the solvent; if it is not a single compound, as commercial hexane, it is essential that fractionation be eliminated in order to obtain results representative of the whole solvent.

The use of pure hexane is impractical, and it is impossible to select a representative hexane fraction for experimental work. The differences in boiling range of commercial hexane between suppliers, as well as between shipments from the same source, make a selection arbitrary. For this reason Eastman Kodak Company practical grade hexane was used in the

TABLE I

Vapor Pressures of Hexane-Soybean Oil Solutions

Temp. °F		167.0	185.0	203.0	221.0	239.0	248.0
Temp. °C		75.0	85.0	95.0	105.0	115.0	120.0
Hexane Concn.		Pressure, mm. Hg absolute					
Mol. Frac.	Wt. %						
0.02	0.20	12	15	19	22	28	29
0.04	0.41	24	30	37	45	54	59
0.06	0.62	36	45	55	68	81	88
0.08	0.85	47	60	73	90	108	117
0.10	1.08	58	75	92	113	135	146
0.12	1.32	70	90	111	136	162	175
0.14	1.57	81	105	129	158	189	205
0.16	1.84	93	120	148	181	218	238
0.18	2.11	104	135	166	205	249	272
0.20	2.37	116	150	185	229	281	308
0.22	2.70	127	165	203	254	310	345
0.24	3.02	138	180	221	278	341	382
0.26	3.34	150	195	241	303	373	421
0.28	3.68	162	210	261	330	409	460
0.30	4.04	173	225	281	359	444	499
0.32	4.43	185	240	303	388	481	539
0.34	4.82	197	255	325	420	521	582
0.36	5.25	208	270	348	451	561	623

work to be described. It has a nominal boiling range of 9°F.; the sample used had a normal boiling point of 155.3°F.

The soybean oil used was a crude extracted product, supplied gratis by the Central Soya Company, which had an iodine number 130; the free fatty acid content was 0.56% (oleic), and refractive index 1.4740 at 23°C. The oil was stripped with nitrogen under vacuum at 175°F. before use to remove moisture and traces of other readily volatile components and stored under vacuum.

Apparatus

A simple static apparatus and procedure were devised for the equilibrium measurements which will be described with reference to the sketch of the apparatus in Fig. 1. A sample of soybean oil was weighed into the 125-ml. flask, A, and deaerated under vacuum with heat. The oil was then cooled to room temperature, the flask opened, and weighed sample of air-free hexane sealed in a glass bulb was introduced. Mercury was then put in the manometer, B, which served as a seal, and the apparatus again evacuated through a dry ice trap. The vacuum connection to the flask was then sealed, and the glass bulb was broken by expansion of the hexane from localized heating with
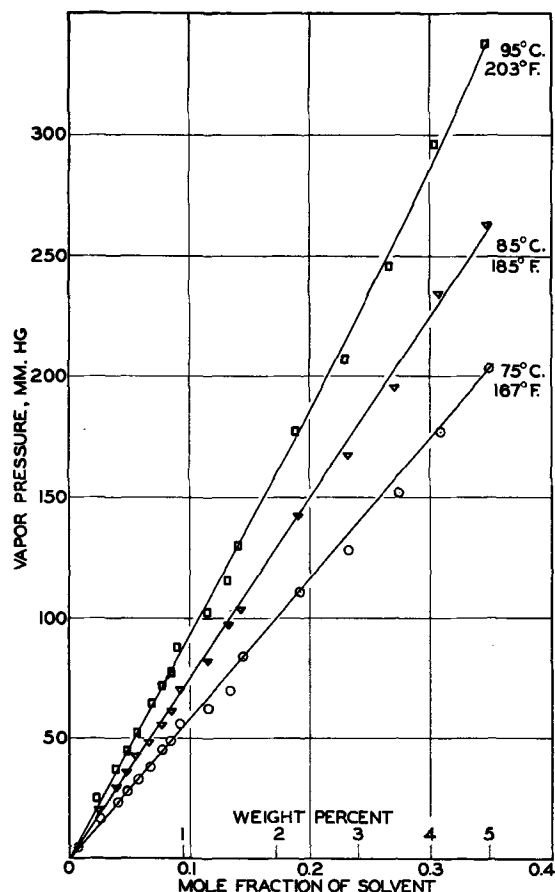
FIG. 2. Experimental vapor pressure data for soybean oil-hexane solutions.

a small flame. During this procedure pressure in the system between the seal and the measuring manometer, C, was controlled through the stopcock, D. The flask and seal were then immersed in an oil bath which was thermostatically controlled and brought to operating temperature.

Pressures were read by means of a cathetometer at a series of ascending temperatures for each oil-solvent charge. The actual concentration of solvent was obtained by correcting the weighed amount for the volume in the vapor space, assuming ideal behavior of the vapor. The flask was shaken periodically before final pressure readings were made, and equilibrium was indicated by a constant pressure. The approach to equilibrium required about 15 minutes at pressures less than 100 mm. and up to one hour at higher pressures.

Two major sources of error exist in the use of the apparatus; incomplete deaeration of the samples, and absorption of hexane by lubricant on the ground joint of the flask. The lubricant used was "Cello-grease" which is suitable for high vacuum and high temperature work, and in which no absorption of hexane vapor was measurable during exposure for four hours at room temperature. The estimated observational errors were ± 0.005 mole fraction of hexane or 0.07 weight per cent, ± 0.5 mm. and ± 0.5°C. The maximum error in the pressure reported is estimated to be ± 5% which will vary with temperature and concentration.

The experimental data were evaluated by plotting observed absolute pressure against concentration at

constant temperature. Curves drawn to smooth the data could be extrapolated to zero pressure at zero concentration at 167°, 185°, and 203°F. At higher temperatures a residual pressure was evident at zero concentration which amounted to 5, 9, and 14 mm. at 221°, 239°, and 248°F., respectively. Correlation of the original data by application of the Clausius-Clapeyron equation and by plotting activity coefficients indicated that the measured total pressure should be corrected in accordance with these residual pressures. After making these corrections, smooth curves were drawn through the points from zero pressure and concentration for the three higher temperatures.

The data given in Table I were read at uniform increments of concentration from the smooth curves of the experimental measurements at the three lower temperatures, shown in Fig. 2, and of the corrected data at the higher temperatures. The tabulated pressure data have been plotted against temperature at constant composition on a Cox type chart in Fig. 3. The unit of concentration which has been used is mole fraction of hexane in order to apply theoretical equilibrium relationships. The molecular weight of soybean oil was calculated to be 876 on the basis of an average composition in terms of the component fatty acids of glycerides (1).

Discussion of Results

An evaluation of the reliability of the experimental method and results is available by comparison with
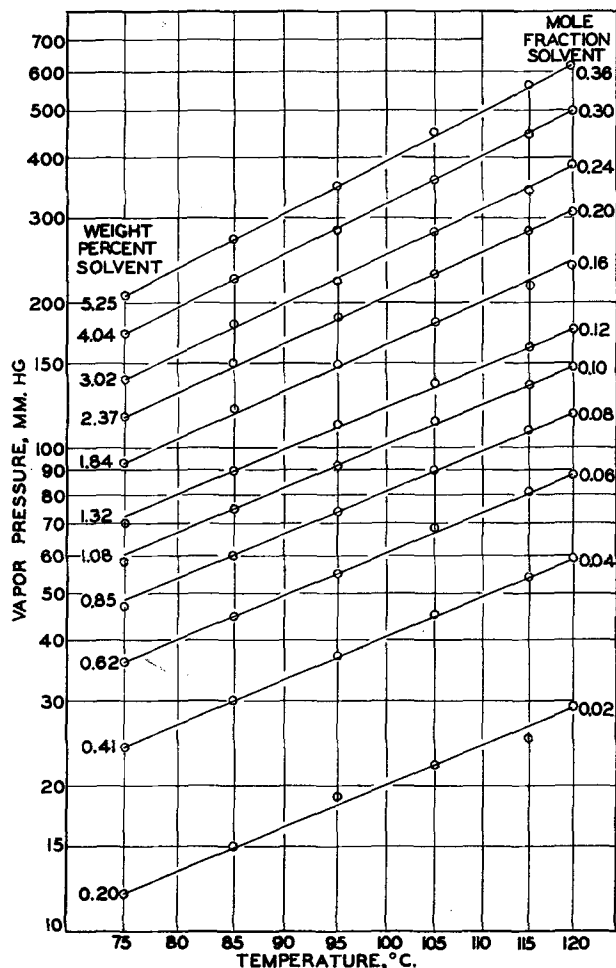

FIG. 3. Cox chart for vapor pressure of soybean oil-hexane solutions.

unpublished data (4). The latter were obtained at 171°, 216.1°, and 253.2°F. for Skellysolve B solutions of soybean oil by the method of Calingaert and Hitchcock (2). The comparison of pressure data was made for the two sets of data representing different hexane fractions by applying a factor. This was the ratio of the vapor pressures of the two solvents at the temperature of comparison. The two sets of data became comparable when the pressures of one set were multiplied by the factor at constant temperature and composition.

Comparison in the manner described indicated that the two sets of data agreed as closely as the data reported in this paper conform to smooth curves and within the estimated uncertainty of ± 5%. Between 171° and 253.2°F. the average difference in the results of the two investigations was ± 3.3%; the individual differences were ± 1.3% at 171°, ± 3.1% at 216.1°, and ± 5.4% at 253.2°F.

The relationship of pressure and concentration indicates that Henry's law, $p = HX$, is applicable to the experimental data over part of the concentration range. Henry's law commonly represents the relation between partial pressure and mole fraction of a solute in dilute solution. The partial pressure in the equation is the corrected total pressure which was measured as the oil is relatively non-volatile. In this case the solute is hexane.

Calculation of the constant, H, in the equation and its correlation with temperature facilitates the interpolation and smoothing of the experimental data. The constant should vary with temperature according to the Clausius-Clapeyron equation in the same manner as vapor pressure. Average values of the constant have been calculated and plotted on a Cox type graph in Fig. 4. The approximate upper limit of concentration below which Henry's law is applicable is also shown in the figure. Within the limiting concentration the equation $\log H = 6.045 - [997.0/(t + 230)]$ is applicable; t is temperature in °C.
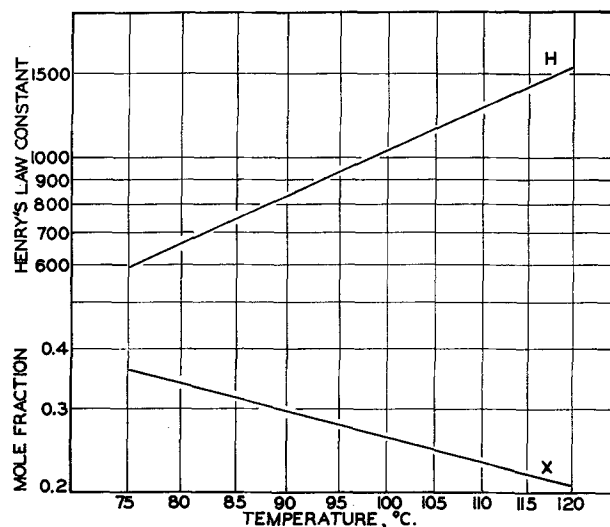

FIG. 4. Henry's law constant and concentration below which the constant is applicable in soybean oil-hexane solutions.

Acknowledgment

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Pilot-Plant Fractionation of Cottonseed: V. A Preliminary Cost Study[1,2]

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MUCH has been written on the overall economic aspects of the cottonseed industry, but comparatively little on the direct application of economic thinking to specific engineering developments. In an industry where the price of the seed and of the seed products fluctuates widely in comparison with the general price level (6), the attention of management is naturally focused on buying and selling at the right time. A mill which processes cottonseed with low efficiency can still prosper if the

seed is purchased low and the products sold high. However an increase in the process efficiency of a mill will obviously result in a saving to the mill. For instance, savings have resulted in the past from such developments as improved methods of cooking meats, the introduction of the screw-press, and the beginning of commercial continuous solvent extraction (7, 8, 9). Recently a new process for the fractionation of cottonseed meats has been reported on a pilot-plant scale (12). This process, termed differential settling, removes the whole pigment glands from the meats, producing oil, a pigment gland fraction, and a cottonseed meal essentially free of oil, hulls, and pigment glands (10, 11, 12). The purpose of this paper is to propose a technologically feasible industrial ap-