Solubilities of Terpenic Essential Oil Components in Aqueous Solutions

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The solubilities of the terpenic essential oil components piperitone, pulegone, and carvone were determined in aqueous solutions at 10, 20, and 30 °C. The ability of the dissolved solids to decrease the solubility of the essential oil components followed the order sodium chloride, glucose, and sucrose. Increasing concentrations of the dissolved solids decreased the solubility of the essential oil components in all cases. Piperitone and pulegone exhibited increased solubilities in the aqueous solutions as temperatures decreased from 30 to 10 °C, whereas carvone exhibited a solubility minimum near 20 °C.

Solubility measurements in liquid–liquid systems do not generally require experimentation of any great complexity; hence the variety of experimental designs for solubility measurements is not large. Classical techniques such as the volume and cloud point methods, as reviewed by Zimmerman (*25*), have been used extensively in the determination of mutual solubilities of various organic compound–water mixtures as exemplified by Hill (*14*) and Ginnings and Baum (*11*).

At the present time, instrumental methods are most widely used as analytical tools in the determination of mutual solubilities of liquids. Gas–liquid chromatography (GLC) has proven to be suitable for solubility studies. McAuliffe (*17*) obtained solubility values of paraffins, cycloparaffins, olefins, acetylene, cycloolefins, and aromatic hydrocarbons in water by using GLC. Sutton and Calder (*22*), used an extractive procedure in conjunction with GLC to find solubilities of alkylbenzenes in sea water. Massaldi and King (*16*) determined aqueous solubilities of *n*-hexyl acetate, *n*-butylbenzene, and *d*-limonene by using a GLC head space analysis.

Spectrophotometric techniques have proven useful in the determination of solubilities of various aromatic hydrocarbons in water. In particular ultraviolet (UV) spectrophotometry has been used extensively in monitoring unsaturated compounds. Andrews and Keefer (*1*), Bohon and Claussen (*5*), and Wauchope and Getzen (*23*) used UV methods to study solubilities of various aromatic hydrocarbons in aqueous solution.

A noninstrumental method worthy of mention is that developed by Sobotka and Kahn (*21*) which makes use of the water-insoluble dye, Sudan IV. As evidenced by the work of Sada et al. (*20*), this technique still finds application at the present time.

We wish to report solubility data for the essential oil components piperitone, pulegone, and carvone in aqueous solution by using a centrifugal technique to affect phase separation and ultraviolet analysis to measure solubility values. These three compounds were chosen since they are commonly used as flavoring agents in nonalcoholic beverages, ice cream, ices, etc. (*10*).

Experimental Section

Materials. The dissolved solids *d*-glucose, sucrose, and sodium chloride were reagent grade and were used as received. The flavoring components carvone (K & K), piperitone (ICN), and pulegone (Fluka) were shown to be at least 95% pure by GLC analysis and were also used as received. All solutions were prepared by using glass-distilled water.

Procedure. Saturated solutions were prepared in a Labline environmental chamber (Labline, Inc.), and temperatures are accurate to ±0.2 °C. The aqueous solution (8.0-mL aliquots) was placed in conical centrifuge tubes with screw tops. Approximately 0.1 mL of the essential oil species was added, and the centrifuge tubes were vigorously mixed on a vortex mixer for 8 min. After mixing of the sample, the tubes were centrifuged (Janetzki TS centrifuge which was placed in the Labline chamber) for as long as was required to separate excess organic phase and saturated aqueous phase. When centrifugation was completed, as determined by a totally clear aqueous phase, a 1.00-mL aliquot of the aqueous phase was extracted from the centrifuge tube. To ensure that none of the less dense organic phase entered the pipet, a gentle blowing action was applied as the pipet tip passed through the organic layer. The pipet tip was wiped to prevent possible contamination from any organic phase clinging to the outer surface of the pipet. After suitable volumetric dilution, the ultraviolet absorbance (Unicam SP1800 ultraviolet spectrophotometer) was measured, and the concentrations of the essential oil components were determined from previously prepared standard curves. Standard solutions of the essential oil components were prepared such that the range of absorbances for the standard solutions fell between 0.4 and 1.4, which has been deemed the most reliable range for double beam instruments (Willard et al. (*24*)). All solubilities were determined in triplicate.

Table I. Extinction Coefficients of Carvone, Pulegone, and Piperitone in Water and Ethanol

	solvent			
	water		ethanol	
solute	log ϵ	λ_{max}, nm	log ϵ	λ_{max}, nm
carvone	3.92	242.5	3.93[a]	235[a]
pulegone	3.80	263.0	3.97,[a] 3.85[c]	252[c]
piperitone	4.03	242.5	4.25,[a] 4.38[b]	234,[a] 236[b]

[a] Conia (*6*). [b] Dupont et al. (*8*). [c] Kuhn and Schinz (*15*).

Results

Figure 1, the standard curve for carvone, exemplifies the excellent linear relationship obtained between dissolved essential oil concentration and absorbance. In all cases, analysis of the standard curves by the method of least squares yielded correlation coefficients of 1.000 at the 95% confidence level. Values of log ϵ, the extinction coefficient, were calculated from the slopes of the standard curves and are tabulated in Table I along with previously measured values of log ϵ in ethanolic solution. Solubility data for piperitone, pulegone, and carvone in aqueous solutions of sucrose, glucose, and sodium chloride at 10.0, 20.0, and 30.0 °C are given in Tables II–IV, respectively. The solubilities are expressed in grams per liter and are precise to better than ±1% as expressed in terms of standard deviations relative to the mean.

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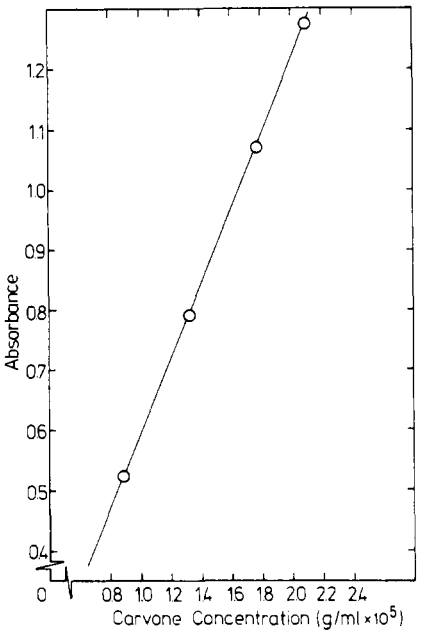

Figure 1. Standard curve for carvone at 241.5 nm.

Table II. Solubilities of Piperitone in Aqueous Solutions of Sucrose, Glucose, and Sodium Chloride at 10, 20, and 30 °C

dissolved solid	wt %	solubility, g/L 10 °C	20 °C	30 °C
sucrose	0	3.00	2.52	2.36
	10	2.82	2.40	2.34
	20	2.60	2.24	2.10
	30	2.34	2.07	1.96
	40	2.05	1.87	1.81
	50	1.71	1.65	1.64
glucose	0	2.99	2.56	2.35
	8	2.33	2.27	2.17
	16	2.09	2.00	1.94
	24	1.87	1.74	1.70
	32	1.55	1.50	1.46
	40	1.30	1.28	1.26
sodium chloride	0	3.02	2.52	2.37
	4	1.99	1.67	1.57
	8	1.31	1.11	1.03
	12	0.88	0.76	0.68
	16	0.58	0.51	0.44
	20	0.31	0.27	0.23

Discussion of Results

Various tests were performed to ensure that the above vortexing technique produced aqueous solutions saturated with essential oil component. For example, saturated solutions of an essential oil component were prepared in 30% glucose by vortexing for periods of 3, 5, 7, and 9 min. After centrifuging, extracting, and diluting of the sample, the respective measured absorbances were 0.387, 0.382, 0.377, and 0.378. On this basis, it was concluded that the 30% glucose solution was saturated with essential oil component after 3 min of vortex mixing. It was also shown that the concentration of the organic species in the aqueous phase did not increase with increased contact time between the aqueous phase and the excess organic phase. For example, at 10.0 °C the solubility of pulegone in 40% glucose was found to be 0.655 ± 0.008 g/L. These saturated pulegone solutions were then allowed to stand for a period of 48 h at 10.0 °C in contact with excess pulegone and then remixed. The saturated pulegone concentration in the 40% glucose after this period was found to be 0.659 ± 0.007 g/L. On the basis of these tests, it was concluded that the aqueous solutions were totally saturated with the organic species by the prolonged vigorous vortex mixing action.

Table III. Solubilities of Pulegone in Aqueous Solutions of Sucrose, Glucose, and Sodium Chloride at 10, 20, and 30 °C

dissolved solid	wt %	solubility, g/L 10 °C	20 °C	30 °C
sucrose	0	1.62	1.38	1.22
	10	1.49	1.29	1.15
	20	1.36	1.19	1.04
	30	1.21	1.08	0.92
	40	1.04	0.97	0.82
	50	0.87	0.85	0.77
glucose	0	1.60	1.37	1.26
	8	1.38	1.24	1.13
	16	1.17	1.10	1.01
	24	0.99	0.94	0.88
	32	0.82	0.79	0.76
	40	0.66	0.66	0.63
sodium chloride	0	1.62	1.38	1.28
	4	1.06	0.87	0.82
	8	0.68	0.55	0.52
	12	0.43	0.37	0.33
	16	0.27	0.25	0.21
	20	0.14	0.13	0.13

Table IV. Solubilities of Carvone in Aqueous Solutions of Sucrose, Glucose, and Sodium Chloride at 10, 20, and 30 °C

dissolved solid	wt %	solubility, g/L 10 °C	20 °C	30 °C
sucrose	0	1.66	1.50	1.60
	10	1.57	1.47	1.54
	20	1.46	1.40	1.47
	30	1.34	1.31	1.38
	40	1.20	1.22	1.29
	50	1.05	1.12	1.18
glucose	0	1.70	1.55	1.62
	10	1.40	1.38	1.42
	20	1.19	1.21	1.27
	30	0.99	1.04	1.15
	40	0.78	0.87	1.04
	50	0.63	0.70	0.93
sodium chloride	0	1.73	1.57	1.61
	4	1.18	1.10	1.15
	8	0.80	0.73	0.77
	12	0.54	0.50	0.49
	16	0.36	0.38	0.29
	20	0.21	0.20	0.18

By virtue of their α,β-unsaturated ketone grouping ($^{\beta}C{=}{}^{\alpha}C{-}C{=}O$), pulegone and piperitone ($C_{10}H_{16}O$ isomers) and carvone ($C_{10}H_{14}O$, i.e., possesses one more double bond than pulegone or piperitone) lend themselves very well to analysis by ultraviolet spectrophotometry. The ultraviolet spectra of these essential oil components have been fairly well characterized in ethanolic solution due mainly to the fact that ethanol does not possess any absorption bands in the ultraviolet region above 200 nm. As illustrated in Table I the absorption characteristics of these compounds in both water and ethanolic solution are similar. One difference, noticeable in all cases, is the shift toward higher wavelengths of maximum absorption in the more polar water as compared to ethanol.

Tables II–IV illustrate the variation in the solubility of the essential oil components as a function of both dissolved solids content and temperature. All compounds exhibit reduced solubility as dissolved solid content increases irrespective of the nature of the solid. Table II shows that for each of the dissolved solids at 0 wt % a solubility value is given. Since solubilities for the different dissolved solids were carried out at different times, a water solubility test was conducted with each dissolved solid to ensure that factors involving instrumentation and technique remained invariant. From Table II it is apparent that the ability of the dissolved solid to decrease the piperitone solubility follows the order sodium chloride > glucose > sucrose. Tables

III and IV show that although the solubilities of these compounds are approximately half the value obtained for piperitone, dissolved solids influence their solubilities in a similar manner.

It is well-known that the presence of a dissolved solid (ionic or nonionic) may significantly reduce the solubility of a liquid organic species in water (*16*, *18*). Many authors are currently of the opinion that this salting out effect is due to the added solute becoming hydrated in solution so that the water molecules involved in hydration of these species are no longer available for the dissolution of the second substance, thus reducing the solubility of the second substance, in this case the essential oil component. Many years ago Glasstone and Pound (*12*) questioned this concept and concluded on the basis of calculated hydration values that other more important factors are operative in this salting out effect. Ben-Naim (*2-4*) has advanced the hypothesis that hydrophilic solutes such as glucose act by decreasing the structural integrity of water which is essential for the solubilization of typically aqueous solutes (*19*).

Tables II and III show that the solubilities of piperitone and pulegone decrease with an increase in temperature. Many solutes which may be classified as typically aqueous (*19*) exhibit decreasing solubilities in water with an increase in temperature. Compounds such as ketones (*13*), *n*-butyl alcohol (*7*), butane (*18*), and isomeric pentanols (*11*) exhibit lower solubilities with higher temperatures in the range of 25 °C. In a sense the solubility characteristics of many liquid organics appear to parallel the well known solubility characteristics of gases. The "iceberg" model as first proposed by Frank and Evans (*9*) explains decreasing solubility with increasing temperature in a qualitative manner.

Carvone (Table IV) is seen to exhibit a solubility minimum between 10 and 30 °C as evidenced by the low solubility value obtained at 20 °C. The exact temperature at which carvone solubility was a minimum was not determined experimentally. Bohon and Claussen (*5*) noted a similar solubility minimum for aromatic hydrocarbons in water. The authors correlated this solubility minimum with the temperature at which the heat of solution, ΔH_s, is equal to zero.

In summation, the solubilities of various essential oil components in aqueous solution are presented as a function of the nature of the dissolved solid, dissolved solids content, and temperature. Such information is useful to the food engineer to ascertain whether or not phase separation of sparingly soluble food components may occur during food treatments such as concentration, heating, or cooling.

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Mutual Solubilities of Alkanes and Methyl Cellosolve

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Mutual solubilities are reported in the region of 30-50 °C for four binary systems containing methyl cellosolve with *n*-heptane, 2-methylheptane, 2,5-dimethylhexane, and 2-methylhexane.

For design of liquid-liquid extraction processes, it is essential to have phase equilibrium data. For multicomponent systems, phase equilibria can often be calculated from binary data (*1*). We report here experimental mutual solubilities for four binary systems containing an alkane and methyl cellosolve (2-methoxyethanol).

Experimental Section

The binary mixtures are equilibrated at the desired temperature in a water bath by vigorous agitation with a shaker for at least 24 h followed by a settling period of at least an additional 6 h. Chemicals, obtained from Aldrich Chemical Co., are analytic reagent grade (greater than 99% pure) or better and used without further purification. The glass equilibrium cell, containing 7-8 mL of solution, is covered with a layer of aluminum foil before sealing with a screw cap which has a small hole in it to allow insertion of a syringe needle. This procedure avoided the problems of solution loss through evaporation and water contamination experienced with other sealing methods.

Following the agitation period, the equilibrium cells are very quickly transferred to a second water bath which allows visual observation of the phase boundary. The temperatures of both water baths are controlled to within ±0.1 °C with a contact thermometer.

Samples from each phase are withdrawn for analysis by using a syringe; selective holdup in the syringe was negligible. The mixtures are resolved in a 7 ft × $^1/_8$ in. stainless steel column, packed with 100-120 mesh Porapak Q. The flow rate of the carrier gas, helium, was about 60 cm^3/min.

Chemical analysis is achieved with a Varian Model 1520A gas chromatograph, equipped with a Carle Model 1000 thermal conductivity detector, a Honeywell 1-mV recorder, and a Perkin-Elmer Model MZ digital integrator. Oven temperature is controlled with a Hallikainen Thermotrol controller. For each

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