

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

Andrea Landauer, Rüdiger N. Lichtenthaler, and John M. Prausnitz*

Chemical Engineering Department, University of California, Berkeley, California 94720

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 \times 1/8 in. stainless steel column, packed with 100–120 mesh Porapak Q. The flow rate of the carrier gas, helium, was about 60 cm³/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

Table I. Mutual Solubilities of Methyl Cellosolve (1)-Hydrocarbon (2) Systems

hydrocarbon (2)	temp, °C	wt fraction	
		1 in 2	2 in 1
<i>n</i> -heptane	30	0.086 ± 0.003	0.160 ± 0.004
	47	0.212 ± 0.003	0.238 ± 0.008
2-methylheptane	30	0.100 ± 0.012	0.154 ± 0.008
	50	0.164 ± 0.020	0.260 ± 0.013
2,5-dimethylhexane	30	0.103 ± 0.009	0.154 ± 0.006
	50	0.216 ± 0.027	0.311 ± 0.048
2-methylhexane	30	0.128 ± 0.022	0.171 ± 0.026

system studied, two calibration curves are prepared by analyzing standard solutions in the composition ranges of interest and correlating the peak area ratio with the weight fraction of solute. The standard solutions are equilibrated at a high enough temperature so that only a single liquid phase is present and are analyzed at the same conditions as those used for the sample solutions. The number of standard solutions required to define the calibration curve varied from 3 to 13, depending on the size of the concentration range investigated and on whether the relationship was linear. Each standard solution is analyzed three times, as is each phase of the sample solutions. Two or three sample solutions are prepared for each system at each temperature.

Results

Table I shows the experimental mutual solubilities for each system. At 30 °C, the solubility of methyl cellosolve in the three branched alkanes is about the same; its solubility in the straight-chain alkane is slightly lower. The solubilities of the alkanes in methyl cellosolve at this temperature are essentially equivalent, within the limits of experimental uncertainty. At approximately 50 °C, methyl cellosolve is soluble to about the same extent in *n*-heptane and 2,5-dimethylhexane; it is somewhat less soluble in 2-methylheptane. At this temperature, the solubilities of the two eight-carbon alkanes, 2-methylheptane and 2,5-dimethylhexane, in methyl cellosolve are equivalent within the experimental uncertainty; however, the solubility of the seven-carbon alkane, *n*-heptane, is slightly lower.

Discussion

The primary sources of error in the experimental mutual solubilities come from uncertainty in the calibration curves and from scatter in the peak-area ratio obtained from different sample solutions. The error in the calibration curve is estimated at the particular point of the measurement; it varied from 1% for the methyl cellosolve/*n*-heptane curves, which were linear over the entire concentration range investigated, to 5% for the methyl cellosolve/2,5-dimethylhexane system, which exhibits a region in which substantially different peak-area ratios are ob-

Table II. van Laar Parameters and Activity Coefficients at Infinite Dilution for Methyl Cellosolve (1)-Hydrocarbon (2) Systems

hydrocarbon (2)	temp, °C	van Laar parameters		activity coef at infinite dilution	
		<i>A</i>	<i>B</i>	γ_1^∞	γ_2^∞
<i>n</i> -heptane	30	1.17	1.12	14.8	13.2
	47	0.914	1.04	8.20	11.0
2-methylheptane	30	1.07	1.18	11.7	15.1
	50	0.958	1.03	9.08	10.7
2,5-dimethylhexane	30	1.06	1.18	11.5	15.1
	50	0.897	0.994	7.89	9.86
2-methylhexane	30	1.04	1.11	11.0	12.9

tained at similar concentrations.

The mutual-solubility data give information on activity coefficients γ . When liquid phase (') is in equilibrium with liquid phase (''), the equations of equilibrium are

$$(\gamma_1 x_1)' = (\gamma_1 x_1)'' \quad (\gamma_2 x_2)' = (\gamma_2 x_2)'' \quad (1)$$

where x_i is the mole fraction of component i . We assume that the variation of γ with x is given by the van Laar equation

$$\log \gamma_1 = A \left[1 + A/B \frac{x_1}{x_2} \right]^{-2}$$

$$\log \gamma_2 = B \left[1 + B/A \frac{x_2}{x_1} \right]^{-2} \quad (2)$$

where A and B are binary parameters. When eq 2 are substituted in eq 1, simultaneous solution gives parameters A and B shown in Table II, which also gives limiting activity coefficients at infinite dilution, γ^∞ . The range of activity coefficients at infinite dilution is 7–16, indicating that the systems are highly nonideal, as expected for mixtures of methyl cellosolve, which is very polar, and nonpolar hydrocarbons. The activity coefficient at infinite dilution of methyl cellosolve is lower in the branched seven-carbon alkane, 2-methylhexane, than in the corresponding straight-chain alkane, *n*-heptane; similarly, it is also lower in the doubly branched eight-carbon alkane, 2,5-dimethylhexane, than in the singly branched eight-carbon alkane, 2-methylheptane. It appears that the more bulky hydrocarbons are better solvents for methyl cellosolve. At higher temperatures, the solutions become more ideal and the activity coefficients of both components decrease.

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