Table IV. E_A Values at Fixed Compositions

x_{CH_3COOK}	E_A, kcal/mol
1.0000	5.69
0.7947	5.56
0.5370	5.46
0.3523	5.44
0.2276	5.46
0.1263	5.45
0.000	5.50

were computed from the slopes of these plots that, in the temperature range considered, do not present a detectable curvature. The results are summarized in Table IV. The plot of these E_A values against compositions shows, contrary to any expectation, a negative deviation from ideality (Figure 5).

Acknowledgment

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Simple Technique to Determine Solubilities of Sparingly Soluble Organics: Solubility and Activity Coefficients of *d*-Limonene, *n*-Butylbenzene, and *n*-Hexyl Acetate in Water and Sucrose Solutions

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Head-space analysis by gas-liquid chromatography is used to determine solubilities of sparingly soluble substances of significant volatility. This technique is based on the analysis of the vapor phase in equilibrium with a liquid to which increasing microquantities of the solute have been fed in different flasks. The value of the pure solute vapor pressure is required. Solubility and activity coefficients of *d*-limonene, not available heretofore, are determined by this method at 0°, 5°, and 25°C in 0, 20, and 40% aqueous sucrose solutions and at 25°C in 60% sucrose. The reliability of the technique is confirmed by determining the solubility of *n*-butylbenzene and *n*-hexyl acetate at 25°C in water. Results for *n*-butylbenzene compare well with existing data, and for *n*-hexyl acetate, improved agreement with the hydrogen bond energy parameter is obtained. Activity coefficients of *d*-limonene and *n*-butylbenzene decrease with increasing sucrose concentration, whereas opposite behavior is obtained for *n*-hexyl acetate. The heats of solution of *d*-limonene in water and 40% sucrose solution are derived from the results.

Data on solubilities of relatively insoluble substances are scarce, partly because of lack of interest but mainly because of difficulties in obtaining reliable results. However, these data are increasingly needed in such diverse fields as water pollution control, biology, toxicology, and food processing. In particular, in the concentration and drying of citrus juices, an important question is how much of the substances responsible for the aroma and flavor is fully dissolved at different temperatures in solutions of varying sugar contents. *d*-Limonene, a substance critical to the aroma and flavor of citrus juices, constitutes between 70 and 90% of the essential oil present in natural citrus juices as a second phase. No data on solubility of this substance and no correlations appropriate for estimating its activity coefficient were found in the literature.

Spectrophotometry of saturated solutions was used by Andrews and Keefer (*2*), Bohon and Claussen (*4*), Klevens (*9*), and recently by Wauchope and Getzen (*14*) to determine solubilities of several liquid and solid hydrocarbons in water. Analysis by gas-liquid chromatography (glc) of liquid samples of a saturated water solution relative to a standard solution of the solute in an organic solvent was used by Buttery et al. (*5*) and McAuliffe (*11*) to determine the solubility of some slightly soluble volatiles. All these methods require separation of phases after the saturation step, by either siphoning or extraction or centrifugation. This handling of the solution can introduce error, particularly for liquid solutes or for experiments at temperatures other than ambient.

Buttery et al. (*5*) also determined air-water partition coefficients of volatile solutes by glc analysis of vapor and liquid phases in equilibrium. Activity coefficients of a number of volatiles in sucrose solutions of different concentrations were measured by Chandrasekaran and King (*7*) by use of head-space analysis.

In this work a simple technique based on head-space analysis and glc was developed to determine solubilities and/or activity coefficients of sparingly soluble organics. Saturated solutions need not be prepared in advance, thereby avoiding the problems of phase separation, nor

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do liquid samples have to be analyzed. Solubility and activity coefficients of *d*-limonene in water and sucrose solutions were determined at different temperatures. The reliability of the method was confirmed by determining the solubility in water of two other relatively insoluble substances, for which experimental data have previously been obtained in other ways.

Basis for Method

N_s moles of solute are allowed to partition between N_L and N_V moles of liquid and vapor, respectively, at a fixed temperature. At equilibrium the following mass balance holds,

$$N_s = xN_L + yN_V \tag{1}$$

where x and y are the mole fractions of solute in the liquid and vapor, respectively.

As the amount of solute fed to the system is increased, the mole fraction of solute present in the vapor can be expected to increase, in accordance with the equation

$$y = \frac{p_v}{p_T} = \gamma x \frac{p_v{}^\circ}{p_T} \tag{2}$$

where p_v is the partial pressure of the solute over the solution, p_T is the total pressure, γ is the activity coefficient of the solute in solution, and $p_v{}^\circ$ is the vapor pressure of the solute in the pure state at the system temperature. If γ is constant, Equation 2 is a form of Henry's Law, which is expected to hold well for solutes at low concentration.

When saturation of the solute in solution is reached, y and p_v will no longer increase with increasing amounts of solute fed to the system. Instead, a second phase rich in the solute will separate out. If the solubility of the original solvent in the new solute-rich phase is small, the equilibrium partial pressure of the solute over the solute-rich phase will be very nearly the same as $p_v{}^\circ$. The solvent-rich phase must have the same equilibrium partial pressure,

$$y^* = \left(\gamma x^* \frac{p_v{}^\circ}{p_T}\right)_{\text{Phase 1}} \simeq \left(\frac{p_v{}^\circ}{p_T}\right)_{\text{Phase 2}} \tag{3}$$

The asterisk refers to the compositions at saturation and to the compositions of the vapor of the solvent-rich liquid beyond the saturation point. Equation 3 shows that γx^* is close to unity.

If $N_s{}^*$ denotes the number of moles of solute added at the point where y levels off at the value y^*, and if the assumption of vanishingly small solubility of the solute in the pure solvent is made, Equations 1 and 2 may be combined to give x^* as

$$x^* = \frac{N_s{}^* - \frac{p_v{}^\circ}{p_T} N_V}{N_L} \tag{4}$$

It is possible to calculate x^* accurately by Equation 4, provided that the numerator be of the same order of magnitude as $N_s{}^*$. This can be achieved by properly selecting the values of N_V and N_L from some a priori estimation of the solubility or, if this is not available, by a preliminary determination with arbitrary values of N_V and N_L.

Two problems may arise, however, depending on the solubility and vapor pressure of the substance under study. First, the solubility may be too low, so that large values of N_L would be required in order for $N_s{}^*$ to be measurable, thereby complicating the experimental device. Secondly, precise values of $p_v{}^\circ$ may be needed if the second term in the numerator of Equation 2 is important with respect to $N_s{}^*$ (e.g., $y^* N_V > 0.20\ N_s{}^*$). However, these limitations were not restrictive to the applicability of the method within practical limits, as discussed below.

The absolute activity coefficient of the solute γ can be calculated at any dilution below saturation from Equation 2.

Experimental

Materials. *d*-Limonene and *n*-butylbenzene were Matheson Coleman & Bell Co., highest purity chemicals. *d*-Limonene was kept under N_2 atmosphere at −2°C in a dark container. Reagent-grade *n*-hexyl acetate was from Eastman Kodak Co.

Chromatograph. A Varian Aerograph Model 1740 chromatograph with a flame ionization detector was used. The column was 5-ft × 0.125-in. o.d. stainless steel, packed with 100–200 mesh Chromosorb G, coated with 1% methyl silicone oil, plus 0.05% Igepal. The column temperature was held at 150°C, and the detector at 200°C. The carrier gas was pure He at 30 ml/min, and H_2 and breathing quality compressed air were used for the detector flame. The response of the chromatograph was monitored with a Sargent Model SR-GC recorder, equipped with a Disc integrator.

Procedure. Several 250-ml Erlenmeyer flasks were chosen to have the same volumetric capacity up to the top, within 5%. The flasks were filled with a fixed amount of solvent so that predetermined vapor and liquid volumes were left in the flasks. Values of $L = 158$ and $V = 100$ ml for liquid and vapor volumes, respectively, were used throughout most of the runs. The flasks were magnetically stirred in a thermostated bath for 15 min to achieve thermal equilibrium at the desired temperature within ±0.05°C. Then, a predetermined volume (of the order of microliters) of the liquid solute was injected below the liquid level by means of a 10-μl Hamilton syringe. It was necessary to flush the syringe several times with the solute and wipe the needle carefully to ensure reproducibility.

The flasks were sealed with three layers of aluminum foil pressed tightly around the top and were placed back in the thermostat. For the lower temperature runs, a rubber stopper was placed over the aluminum foil as a further precaution in sealing the system. In either case, leakage of the volatile solute was negligible by leaving the flasks under the same conditions over 24 hr. Preliminary experiments showed that the rubber stopper could not be used as the sole seal because of the tendency of *d*-limonene to absorb in the rubber. The aluminum foil was impermeable to *d*-limonene.

Enough time (between 4 and 8 hr, depending on the temperature and sucrose concentration) was allowed for the solute to partition completely between the two phases. Head-space analysis of each flask was performed by inserting a 2-ml tight syringe through the aluminum foil, washing its cylinder four times with the vapor phase, and removing a 1-ml sample, which was readily injected in the chromatograph. A side hole needle with the tip hole blocked was used to avoid plugging the needle upon puncturing the septum injector. Peak areas were measured with the Disc integrator. Duplicate determinations were carried out for each solute feed volume.

A simultaneous calibration was performed with the vapor phase over a two-phase mixture with the solute well above the saturation level at the same conditions of temperature and sugar content, to account for any drift in the chromatograph conditions and to provide a safe basis of comparison between runs made at different times. In this way a plot of A/A_0 vs. s could be made, where A and A_0 are the peak areas for the unknown and the saturated vapor phases, respectively, and s is the volume of substance fed to the system. A slight nonlinearity of the chromatograph response in the case of *d*-limonene was previously calibrated with standard liquid solutions of the solute in ethyl acetate. Reproducibility of duplicate measurements was within 8%. Fresh sugar solutions were used since bacterial growth decreased the *d*-limonene concentration.

Vapor-pressure determinations were performed by head-space analysis of saturated solutions, with peak area calibrations made with liquid samples of standard solutions of the solute in ethyl acetate.

Results and Discussion

Figure 1 shows the experimental curve for a typical determination of the solubility of *d*-limonene. The ordinate A/A_0 is assumed to be equal to the ratio y/y^*. At the saturation point, Equation 4 holds, and x^* may be calculated, with N_V being fixed by V and the temperature, N_L being determined by L and the solvent molar density, and N_s^* being calculated from s^* and the molar density of the solute.

A slight curvature upon reaching saturation is apparent in Figure 1. The same trend was found at different temperatures and for other sucrose concentrations. However, this was not the case for *n*-butylbenzene where a fairly straight line was obtained, as shown in Figure 2. There was also no apparent curvature for *n*-hexyl acetate as solute. The curvature for *d*-limonene may be attributable to interaction (possibly dimerization) between molecules of the solute when approaching saturation.

For *d*-limonene precise knowledge of the vapor pressure was desirable for use in Equation 4. Data available from the literature were not concordant in the appropriate range of temperature. Hence, an experimental check was performed between 0° and 32°C. Figure 3 shows the previous data available and the experimental values found in this work. A close agreement with the data from Linder (*10*) can be observed. To check the accuracy of the vapor-pressure determinations, the same procedure was applied to *n*-butylbenzene at 25°C. Agreement with existing vapor-pressure data which are consistent from two sources (*1, 10*) was within 2%. For *n*-hexyl acetate the vapor pressure was estimated by the Cox-Antoine correlation. Accuracy was not critical in this case, since about 90% of the solute was in the liquid phase, even though a lower ratio of liquid to vapor was used.

In Table I are listed the measured solubilities in water, c_s, of the three substances studied, together with previous data reported in the literature. The k_M and E_H values also listed are calculated by $k_M = 1/P \log (c/c_s)$ and $E_H = 2.3\ RT[k_M P - \log (c/c_s)]$, respectively (*8*). These

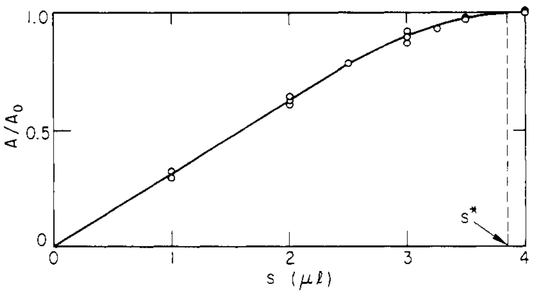

Figure 1. Relative peak area as function of *d*-limonene fed. water, 25°C. V = 100 ml; L = 158 ml

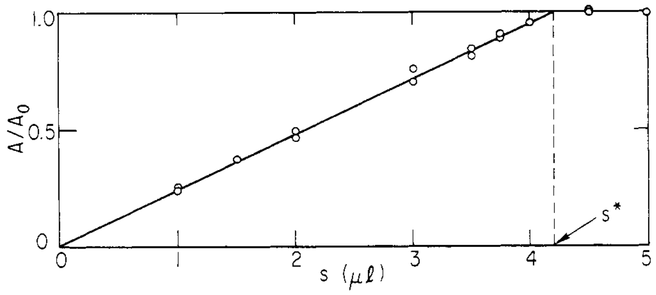

Figure 2. Relative peak area as function of *n*-butylbenzene fed. water, 25°C. V = 100 ml; L = 158 ml

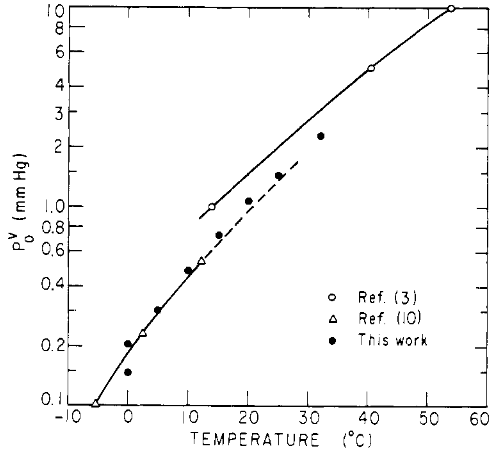

Figure 3. Vapor pressure of *d*-limonene. Range: −5° to 55°C

Table I. Comparison Between Solubility Data from This Work and Those Reported in Literature

Water, 25°C

Solute	L, ml	V, ml	c,[a] mol/l.	$c_s \cdot 10^4$, mol/l.	P[b]	k_M[c]	E_H,[d] cal/mol	Ref.
d-Limonene	158	100	6.16	1.01	375	0.0127		This work
d-Limonene	450	100	6.16	0.97	375	0.0128		This work
n-Butylbenzene	158	100	6.40	1.32	366	0.0128		This work
n-Butylbenzene			6.40	1.15	366	0.0129		(*8*)
n-Butylbenzene			6.40	3.70	366	0.0116		(*9*)
n-Hexyl acetate	50	208	6.04	35.4	375		2.24	This work
n-Hexyl acetate			6.04	89.2	375		2.81	(*8*)

[a] Molar density of the solute. [b] Parachor, estimated by group contribution method of Quayle (*13*). [c] Average value is 0.013 for hydrocarbons (*8*). [d] Average value is 2.25 for esters (*8*).

parameters are included as further criteria for comparison, in the absence of more precise experimental data. Agreement within 5% between solubility values for *d*-limonene, when using different liquid volumes, proves the technique to be consistent. Also, good correlation with the average k_M parameter is apparent.

The solubility value determined for *n*-butylbenzene is close to that reported by Deno and Berkheimer (*8*), which gives a better correlation with the average k_M parameter than the value reported by Klevens (*9*). For *n*-hexyl acetate a close agreement with the average hydrogen bond energy E_H was found, as opposed to the value reported by Deno and Berkheimer (*8*). These authors have already pointed out that solubility data should be reinvestigated for E_H values departing very far from the average. Table II shows the measured solubility of *d*-limonene in solutions of different sucrose content at the three levels of temperature.

Table II. Solubility of *d*-Limonene

$V = 100$; $L = 158$ ml

Temp, °C	Sucrose content, wt %	c_s	
		g-mol/l. × 10^4	mg/l.
25	0	1.013	13.8
	20	0.995	13.5
	40	0.979	13.3
	60	0.92	12.5
5	0	0.767	10.4
	20	0.698	9.5
	40	0.617	8.4
0	0	0.708	9.7
	20	0.637	8.7
	40	0.551	7.5

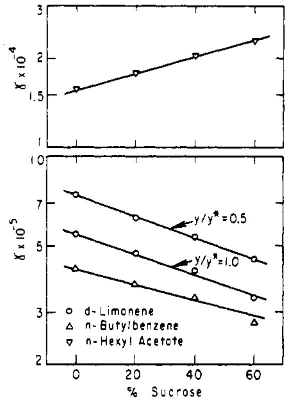

Figure 4. Variation of activity coefficient with sucrose concentration, 25°C

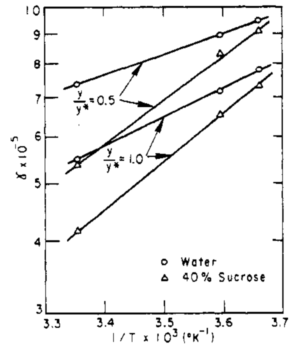

Figure 5. Variation of activity coefficient of *d*-limonene with temperature at two dilutions

Activity coefficients as a function of sucrose concentration are shown in Figure 4. For *d*-limonene absolute activity coefficients were calculated from Equation 2 at $y/y^* = 1.0$ and 0.5, in all cases. For *n*-hexyl acetate and *n*-butylbenzene, activity coefficients were calculated at $y/y^* = 1.0$ for water solutions and at $y/y^* = 0.33$ for sucrose solutions. In this last case, a complete determination of A/A_0 values vs. s was not performed. A decrease in activity coefficient with increasing sucrose concentration is observed for *d*-limonene and *n*-butylbenzene, whereas an increase is apparent for hexyl acetate.

Activity coefficients increasing with increasing sucrose content were also found by Chandrasekaran and King (*7*) for a number of other oxygenated volatiles. Chandler (*6*) reported that the solubility of limonin, a triterpenoid present in navel orange juice, increases (and consequently the activity coefficient decreases) threefold in 12% sucrose solution as compared to water. Differences between the results of Chandrasekaran and King (*7*) and those presented here for *n*-hexyl acetate arise from their having obtained the coefficient in pure water from the correlation of Pierotti et al. (*12*), rather than from experimental data, and from an improved technique in this work for solutions of high viscosity. The present results for this compound are believed to be more reliable.

Figure 5 shows the variation of the activity coefficient of *d*-limonene with temperature at two dilutions. The heat of solution calculated from the slope at $y/y^* = 1.0$ is $\Delta H_s = -2.20$ kcal/mol in pure water and $\Delta H_s = -3.72$ kcal/mol in 40% sucrose solution.

Conclusions

The simple technique described here is adequate to determine solubilities and activity coefficients of sparingly soluble organics. This method is versatile enough to allow determinations over a wide range of solubilities, provided that the pure vapor pressure of the substances is known or can be determined with sufficient accuracy, although this is not critical in many cases. The only limitation is the sensitivity of the chromatograph used for the analysis, but larger system and sample volumes could be used to circumvent this problem. However, a limit may be reached above which some practical problems, such as inefficient stirring, could offset the simplicity and relative rapidity of the technique.

Nomenclature

A = peak area of vapor sample
A_0 = peak area of vapor sample from saturated solution
c = molar density of pure solute
c_s = solubility, mol/l.
L = volume of liquid in vessel
N_L = moles of liquid in vessel
N_s = moles of solute fed to vessel
N_V = moles of vapor in vessel
p_v = partial pressure of solute in vapor phase
P = parachor
p_T = total pressure
p_v° = vapor pressure of pure solute
s = volume of solute fed to vessel
V = volume of vapor in vessel
x = mole fraction solute in liquid
y = mole fraction solute in vapor
γ = activity coefficient of solute

Superscript

$*$ = value at saturation

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Density and Partial Equivalent Volumes of Hydrated Melts: Tetrahydrates of Calcium Nitrate, Cadmium Nitrate, and Their Mixtures with Lithium, Sodium, and Potassium Nitrate

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Densities of $Ca(NO_3)_2 \cdot 4H_2O-(Li, Na)NO_3$ and $Cd(NO_3)_2 \cdot 4H_2O-(Li, Na, K)NO_3$ mixtures, as a function of temperature and alkali metal nitrate content, were determined by measuring the volume of a certain amount of melt in a precalibrated densitometer. For any pair of salts, the isotherms of equivalent volume vs. equivalent fraction of the monovalent ion were linear. The partial equivalent volume ($\bar{V}_{\text{equiv}}$) of the constituents was independent of the nature and composition of the melt at a given temperature.

The studies of concentrated aqueous electrolytes are of great importance in understanding the behavior of molten salts (*1–6*). Angell (*1–3*) postulated the existence of hydrated divalent cations in hydrated melts of calcium and magnesium nitrate and emphasized that these melts could be considered as analogs of molten salts.

Braunstein et al. (*6*), during their investigations on various aspects of some aqueous nitrate melts, measured the densities of calcium nitrate tetrahydrate–potassium nitrate mixtures at 100°C and found that the assumption of additivity in strongly concentrated aqueous solutions may be a useful approximation. This study is aimed to explore, if the additivity of equivalent volumes can be regarded as a general characteristic of hydrated melts, particularly for the mixtures containing smaller monovalent cations, e.g., lithium and sodium ions.

Experimental

Material. $LiNO_3$, $NaNO_3$, KNO_3, $Ca(NO_3) \cdot 4H_2O$ (BDH), and $Cd(NO_3) \cdot 4H_2O$ (Reanal, Hungary) of analar grade were used without further purification. (An analytical cross check for the water content was done volumetrically by use of EDTA. The results established the composition of the tetrahydrates within ±0.01 to the stoichiometric composition.) Mixtures of varying compositions were prepared separately by melting the requisite amounts of the components in a sealed glass vessel and digesting them at 60–70°C for about 6 hr.

Apparatus and procedure. The manometric densitometer used by Husband (*8*) and Cleaver et al. (*7*) was modified to allow a direct measurement of the volume of a known amount of the melt. The volume capacity of the bulb was indicated by fixed fiducial marks on both limbs and was determined at room temperature with distilled water. No correction was made for the thermal expansion of the densitometer at higher temperatures. During measurements the meniscus of the liquid in the shorter limb was kept at a fixed mark by applying pressure from a manometer, and the expansion was read on the longer capillary (calibrated to 0.01 ml). A liquid paraffin bath (10 liters) was used as constant temperature bath. The temperature was controlled and measured with a precision better than ±0.1°C.

Results and Discussion

Densities of the various mixtures tabulated in Tables I and II varied linearly with temperature and were expressed by the equation

$$\varsigma = a - bt\ (°C)$$

The linear density-temperature equations for the various mixtures investigated are presented in Tables III and IV.

Table I. Densities of $Ca(NO_3)_2 \cdot 4H_2O-MNO_3$ Mixtures

X'_{MNO_3}	Temp, °C	Density, g/cm³
	$Ca(NO_3)_2 \cdot 4H_2O-LiNO_3$	
0.0	14.5	1.7556
	23.0	1.7470
	34.3	1.7395
	39.9	1.7346
	49.2	1.7273
	60.2	1.7187
	69.2	1.7119
	79.3	1.7025
	83.7	1.6986

(Continued on page 398)