s^E = excess entropy
v^* = molar volume
x = mole fraction in liquid phase
y = mole fraction in vapor phase

Greek Letters

γ = activity coefficient
δ_{ij} = deviation quantity defined in Equation 6
δ_g = deviation quantity in Equation 7
μ^E = excess chemical potential

Subscripts

1 = acetonitrile
2 = benzene
3 = carbon tetrachloride
i, j, k = component i, j, k

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Molecular Associations in 2-Butanone

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Association in solutions of 2-butanone with the solutes 4-hydroxy benzaldehyde, 4-hydroxy-3-methoxy benzaldehyde, 4-hydroxy benzoic acid, and 4-hydroxy-3-methoxy benzoic acid was studied by ebulliometric measurements to about 1*m* concentration. Association numbers for solutes and observed equilibrium constants for solute dimerization reactions at 79.5°C + ΔT_b at 1-atm pressure were calculated.

The solvent 2-butanone is particularly useful for polar solutes which may not be appreciably soluble in nonpolar solvents. Most previous studies of nonaqueous solution association have been with inert solvents to minimize solute–solvent association (*1, 2, 8*). However, one object of this present work has been to study the effect of solute–solvent interaction on solute–solute association as a function of concentration in 2-butanone, as well as to investigate the effect of intramolecular hydrogen bonding on solute–solute and solute–solvent association.

The association of the hydroxy compound solutes with the ketone solvent 2-butanone described in this study is of especial interest because both the solute–solute and solute–solvent interactions may be assumed to be primarily owing to hydrogen bonding (*8–12*). In dilute solution the solute–solute equilibrium reactions which predominate in these systems may be assumed to be dimerization (*1, 18*). In this study the effect of solute intramolecular hydrogen bonding on the dimerization reactions and the concentration dependence of dimerization have been studied by ebulliometric measurements of association numbers and by determination of the observed equilibrium constants for the solute dimerization reactions.

Experimental

Chemicals. All chemicals used were reagent grade. The 2-butanone was obtained from Aldrich Chemical Co. and was dried with $CaCl_2$, decanted, and fractionally distilled twice, by use of a Todd distillation column following standard procedures (*17*). The 4-hydroxy-3-methoxy benzaldehyde was obtained from Matheson Coleman & Bell; 4-hydroxy benzaldehyde, 4-hydroxy benzoic acid, and 4-hydroxy-3-methoxy benzoic acid were obtained from Aldrich Chemical Co. Solid reagents were desiccator-dried and stored and were used soon after their receipt without further purification. Table I compares determined solute melting points with literature values.

Apparatus and procedures. An improved Washburn-Read (*16*) modification of the Cottrell ebullioscope (*3*) was used for measurements. A platinum wire heating coil was sealed into the bottom of the apparatus, and a constant current was maintained. Temperatures were corrected for pressure fluctuations by use of a barometer and applying the temperature coefficient of pressure (*17*) and also by use of a second apparatus with solvent only. A minimum of 2 hr was allowed for all temperature equilibrations.

The apparatus was carefully shielded from drafts and was assembled with standard tapers and protected from moisture with a drying-agent tube; standard measurement procedures (*5, 14*) were followed. Apparatus reliability was determined by measuring the true molecular weight of benzoic acid in methanol where single molecules are stabilized by the solvent. The overall reliability of data has been determined to be no more uncertain than ±1 molecular-weight unit. Uncertainty in calculated values of Kx (obs) is ±0.05.

Table I. Solute Melting-Point Data

Solute	Mp, °C Exp	Mp, °C Lit
4-Hydroxy benzaldehyde	116	116 (*15*)
4-Hydroxy-3-methoxy benzaldehyde	81	81.5 (*15*)
4-Hydroxy benzoic acid	214	214–215 (*15*)
4-Hydroxy-3-methoxy benzoic acid	212	213–215 (*6*)

Results and Discussion

Calculation of association numbers. The equation which was used for the calculation of the association number, *i*, of the solute was not restricted to dilute solutions. The equation can be derived by use of standard procedures from the thermodynamic relation which applies to liquid-vapor equilibrium:

$$[\partial \ln x_1/\partial T]_P = -\Delta H_v/RT^2$$

For calculation of *i*, it was assumed that ΔH_v and K_b were constant, that solutions were ideal, and that solutes were nonvolatile.

$$i = W_2M_1/W_1M_2\,[e^{\Delta T_b M_1/1000\,K_b} - 1]^{-1}$$

The value of K_b used was 2.28 (*7*). Association numbers as a function of solute molality are shown in Figures 1-4 and are tabulated in Table II. Table II also includes the measured values for ΔT_b.

Calculation of equilibrium constants for solute dimerization. The monomer-dimer equilibrium reaction can be represented as:

$$2\,M \rightleftarrows D$$

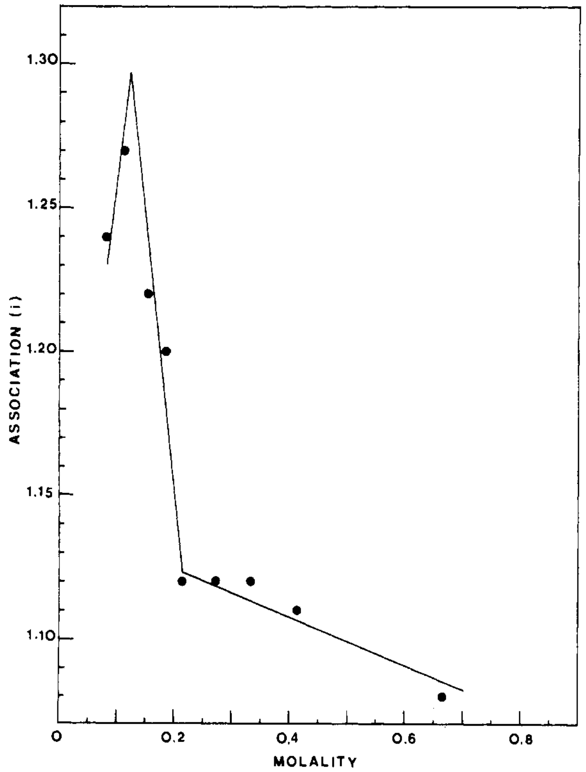

Figure 1. Association number-concentration curve for 4-hydroxy benzaldehyde in 2-butanone

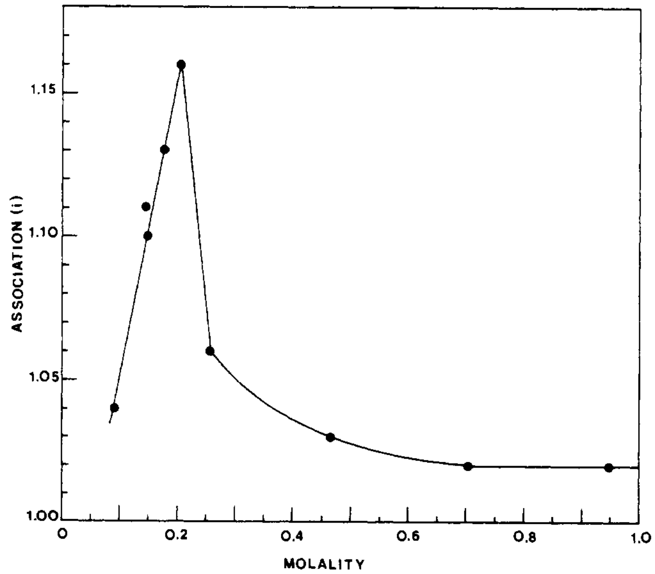

Figure 2. Association number-concentration curve for 4-hydroxy-3-methoxy benzaldehyde in 2-butanone

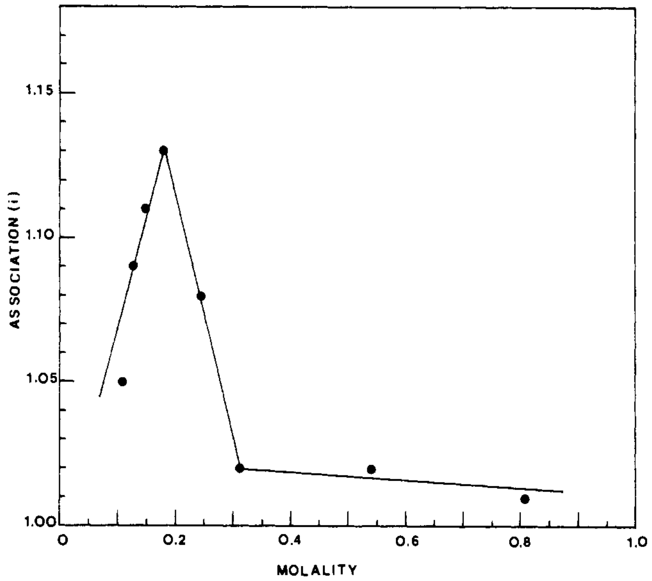

Figure 3. Association number-concentration curve for 4-hydroxy benzoic acid in 2-butanone

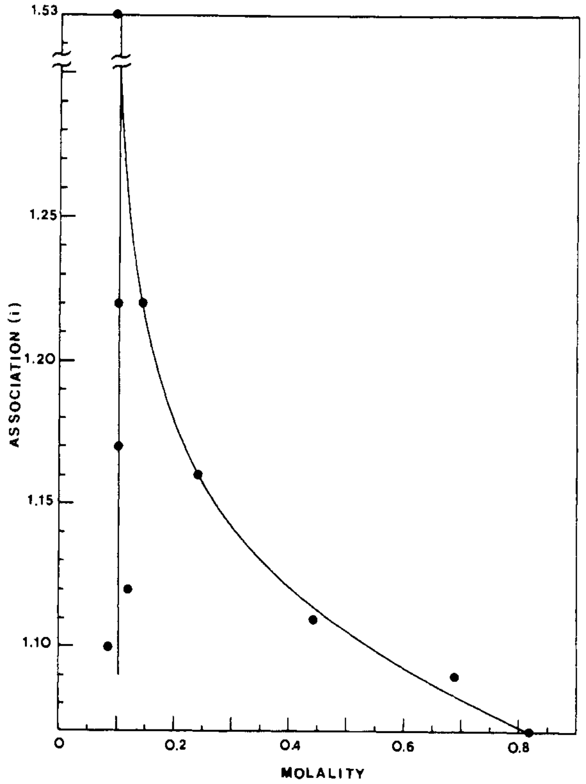

Figure 4. Association number-concentration curve for 4-hydroxy-3-methoxy benzoic acid in 2-butanone

Table II. Association Number and Observed Dimerization Equilibrium Constant Data for Solutes in 2-Butanone at 79.5°C + ΔT_b and 1-Atm Pressure

Molality	ΔT_b	i	K_x (obs) × 10
	4-Hydroxy benzaldehyde		
0.081	0.150	1.24	4.15 ± 0.05
0.112	0.199	1.27	5.04
0.153	0.283	1.22	3.63
0.183	0.346	1.20	3.10
0.215	0.435	1.12	1.54
0.271	0.550	1.12	1.54
0.331	0.667	1.12	1.54
0.413	0.840	1.11	1.39
0.662	1.372	1.08	0.94
	4-Hydroxy-3-methoxy benzaldehyde		
0.092	0.198	1.04	0.43
0.145	0.298	1.11	1.39
0.149	0.306	1.10	1.24
0.179	0.358	1.13	1.72
0.204	0.400	1.16	2.27
0.258	0.552	1.06	0.68
0.466	1.019	1.03	0.32
0.703	1.539	1.02	0.21
0.948	2.057	1.02	0.21
	4-Hydroxy benzoic acid		
0.110	0.239	1.05	0.55
0.128	0.269	1.09	1.08
0.150	0.311	1.10	1.24
0.181	0.364	1.13	1.72
0.248	0.521	1.08	0.94
0.312	0.687	1.02	0.21
0.541	1.189	1.02	0.21
0.807	1.767	1.01	0.10
	4-Hydroxy-3-methoxy benzoic acid		
0.088	0.181	1.10	
0.097	0.144	1.53	
0.102	0.174	1.33	
0.103	0.194	1.22	
0.103	0.197	1.17	
0.121	0.245	1.12	
0.145	0.268	1.22	3.63
0.241	0.473	1.16	2.27
0.443	0.896	1.11	1.39
0.688	1.414	1.09	1.08
0.817	1.692	1.07	0.81

and the reaction equilibrium constant for mole fraction concentrations, K_x (eq), can be represented as:

$$K_x\text{ (eq)} = a_D/a_M^2 = \gamma_D/\gamma_M^2\, x_D/x_M^2 = \gamma_D/\gamma_M^2\, K_x\text{ (obs)}$$

where K_x (eq) is concentration independent, and K_x (obs), the observed equilibrium constant, is concentration dependent. For dilute solutions and especially for infinitely dilute solutions, activity coefficients approach unity, and K_x (obs) approaches K_x (eq). For dilute solutions of this study, the magnitude of K_x (obs) indicates the degree of dimerization. Values of K_x (obs) for solute dimerization reactions as a function of concentration have been calculated by use of the equation (*13*):

$$K_x\text{ (obs)} = \frac{\alpha/2(1-\alpha/2)}{(1-\alpha)^2}$$

Values for α were obtained from the experimentally determined values for i, with the relation (*4*):

$$\alpha = 2(i-1)/i$$

Values of K_x (obs) for the solute 4-hydroxy-3-methoxy benzoic acid for molalities below 0.145 were not calculated because of the almost vertical shape of the curve in this region; however, a maximum in K_x (obs) of 2.40 is estimated at 0.097*m*. Calculated K_x (obs) values are tabulated in Table II.

For substituted benzaldehyde solutes, it is assumed that hydrogen bonding for dimerization is primarily between aldehyde and hydroxy functional groups for both solutes and that the methoxy group ortho to the hydroxy group is intramolecularly hydrogen bonded to this hydroxy group (*11*), thereby causing a decrease in dimerization. This conclusion is supported by a decrease in the maximum value of i from 1.30 at 0.120*m* to 1.16 at 0.204*m* for 4-hydroxy benzaldehyde, as compared with 4-hydroxy-3-methoxy benzaldehyde. If dimerization involved hydroxy functional groups only, the methoxy group could also be expected to decrease dimerization by intramolecular hydrogen bonding.

For substituted benzoic acid solutes, it is assumed that hydrogen bonding for dimerization is primarily between the relatively strongly hydrogen-bonded carboxyl groups (*11*). For these solutes, therefore, intramolecular hydrogen bonding between the hydroxy and methoxy groups may be expected to decrease solvation involving hydrogen bonding between the solvent and the hydroxy group, with a subsequent increase in dimerization. This conclusion is supported by an increase in the maximum value of i from 1.13 at 0.181*m* to 1.53 at 0.097*m* for 4-hydroxy benzoic acid, as compared with 4-hydroxy-3-methoxy benzoic acid.

For all solutes in this study, the decrease in i at concentrations greater than the maxima in i may be due to an auto-solvation effect at these higher concentrations caused by the hydroxy functional group. The hydroxy group, common in all solutes of the study, may at higher concentrations stabilize the monomer, similar to the monomer stabilization observed for hydroxylic solvents (*4*). Decrease in i observed in this study at higher concentrations is contrary to the usual simple dimerization cases where i continuously increases to a maximum with increase in concentration.

Nomenclature

i (association number of solute) = ratio of the apparent to the true molecular weight
x_1 = mole fraction of solvent
M_1 = molecular weight of solvent
M_2 = molecular weight of solute
W_1 = weight of solvent in grams
W_2 = weight of solute in grams
ΔT_b = elevation of boiling point
ΔH_v = molar heat of vaporization of solvent
K_b = molal ebulliometric constant
m = molality
a_i = activity of component i
γ_i = activity coefficient of component i
x_i = mole fraction of component i
α = fraction of dimerized molecules

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Phase-Equilibria Behavior of Systems Carbon Dioxide-2-Methylnaphthalene and Carbon Dioxide-*n*-Decane-2-Methylnaphthalene

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The phase-equilibria behavior of the binary system CO_2–2-methylnaphthalene was studied for liquid-vapor, solid-liquid-vapor, and liquid-liquid-vapor systems. The liquid-liquid-vapor equilibria of the ternary system CO_2–2-methylnaphthalene–*n*-decane were studied in detail. As well as locating where the liquid-liquid-vapor loci exist in pressure-temperature space, the distribution of hydrocarbons in the individual liquid phases was measured. The ternary liquid-liquid-vapor locus exhibited either *UCST* or *K*-type termination at the upper end of the locus, depending upon initial mole ratio of hydrocarbons. Furthermore, the CO_2-richer phase (L2) preferred selectively *n*-decane. Also presented are the data on the depression in the freezing point of 2-methylnaphthalene upon the addition of *n*-decane at 1 atm and on the elevation in the freezing point of 2-methylnaphthalene owing to pressurization.

The ability of CO_2 to induce partial miscibility in hydrocarbons suggests separation processes with liquid CO_2 as a selective solvent. Its potential utility in this respect is attractive because of its availability and other desirable properties like low toxicity and noncorrosiveness. Moreover, the recovery of CO_2 from the hydrocarbons by mere depressurization, which eliminates the need of expensive distillation processes, makes the use of CO_2 particularly attractive.

To make full use of CO_2 as an extractive solvent, it is desirable to understand the ability of CO_2 to separate different chemical groupings such as lower vs. higher (i.e., with respect to molecular weight) alkanes, aromatics vs. alkanes, and single-ring aromatics vs. multiple-ring aromatics. For this reason, well-defined ternary prototype systems are being studied in detail. These studies would also provide accurate data for correlative purposes. The data obtained on the ternary system are such as to facilitate modeling these systems by solution models. Since most models use binary interactions in describing the ternary data, the binary systems constituting the ternary system are also studied. It is hoped that a model based only on binary interaction forces, obtained from relatively simple experiments such as solubility limits or freezing-point depressions, can a priori determine the types of systems to which this process might find application. As more systems are studied and their data analyzed, a model or models should evolve that will serve this purpose and, furthermore, aid in the design of the separation process.

Huie and coworkers (*4, 5*) studied in detail the system CO_2–*n*-decane–*n*-eicosane. One of the goals of the Huie study was to answer questions regarding the selectivity of CO_2 for lower vs. higher alkanes. Huie's results show that CO_2 can separate lower alkanes from the higher alkanes. These results are in agreement with other studies (*3*).

The Huie study is being extended to systems containing CO_2, alkanes, and aromatics. Of interest here is the selectivity of CO_2 for alkanes vs. aromatics. The study on the prototype system CO_2–*n*-decane–2-methylnaphthalene is now completed. Two out of the three components of this ternary system are the same as that of Huie's system. The third component, namely, 2-methylnaphthalene, has a similar melting point to that of *n*-eicosane. Work on other prototype systems which are parallel to this system and extend Huie's work is also being done (*17*). Furthermore, efforts are being made to correlate the phase-equilibria behavior of these systems by use of well-known solution models.

Phase-equilibria studies on a variety of CO_2–alkane systems have been conducted by a large number of investigators (*1, 6, 10–16*). However, there are little data on the systems of CO_2 and aromatics. The authors believe that the only study done on the systems of CO_2 and aromatics is by Francis (*2*). The partial miscibility characteristics of CO_2 in a variety of hydrocarbon solvents, including aromatics, have been investigated by Francis in an extensive scanning study. He has presented only compositional data on these systems in the form of triangular diagrams at room temperature. In view of the lack

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