Nomenclature

A^* = solubility of gas in electrolyte solution, g-mol/l.
A_w^* = solubility of gas in water, g-mol/l.
c_i = concentration of ions in solution, g-ion/l.
i_+, i_-, i_g = contributions of positive ion, negative ion, and dissolved gas, l./g-ion or l./g-mol
I = ionic strength of solution defined by Equation 2, g-ion/l.
k_s = salting-out parameter for single electrolyte, l./g-ion
K_s = overall salting-out parameter for mixed electrolytes, l./g-ion
R = carbonation ratio, ratio of concentration of bicarbonate ion to that of carbonate ion in solution
z_i = valency of ions

Subscripts

1 = electrolyte 1 ($NaHCO_3$)
2 = electrolyte 2 (Na_2CO_3)

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Phase-Equilibria Behavior of System Carbon Dioxide-*n*-Decane at Low Temperatures

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Pressure, composition, and molar volume data of the two coexisting liquid phases for the system CO_2-*n*-decane are presented as a function of temperature along the three-phase (L_1-L_2-V) curve. Also, pressure, composition, and molar volume data on the S_1-L_1-V curve and the *P-T* profile of the S_1-L_2-V curve are presented. The termination points of these loci are located and characterized.

Although extensive vapor-liquid equilibria information is available on the binary system CO_2-*n*-decane as reported by Reamer and Sage (*7*), to our knowledge no information is available on its partial miscibility behavior. For this reason, a study has been completed of the above system describing the partial miscibility regimes. Our study of the system CO_2-*n*-decane involves the P-$\bar{V}$-T-X equilibrium data on the S_1-L_1-V and L_1-L_2-V loci, *P-T* profile of the S_1-L_2-V locus, and the invariant points such as the *Q*-points, as well as the upper critical solution temperature of L_1 and L_2.

The partial miscibility of various CO_2-normal alkane binary systems has been studied by several different workers: Im and Kurata (*5*), CO_2-*n*-heptane; Stewart and Nielsen (*9*), CO_2-*n*-tetradecane and CO_2-*n*-hexadecane; Schneider (*8*), CO_2-*n*-octane, CO_2-*n*-undecane, CO_2-*n*-tridecane, and CO_2-*n*-hexadecane; Francis (*2*), CO_2-*n*-tetradecane, CO_2-*n*-hexadecane, CO_2-*n*-octadecane, and CO_2-*n*-eicosane; Huie (*3*) and Huie et al. (*4*) CO_2-*n*-eicosane. However, only Huie has reported detailed P-$\bar{V}$-T-X information over the entire immiscibility range for the system he studied. Kurata has reported *P-T-X* information over the entire immiscibility range for CO_2-*n*-heptane. The Kurata study would seem to indicate that CO_2 is partially miscible with all normal alkanes from *n*-heptane up to the high-molecular-weight alkanes. Francis has reported L_1-L_2 compositions at room temperature on the systems he studied. Only *P-T* projections of loci are reported by Schneider.

The authors feel that an extensive study of CO_2-*n*-decane partial miscibility phenomena, along with previously cited detailed studies, would lead to further insight into the partial miscibility behavior of CO_2 mixtures with normal alkanes, as a family, when considered in concert with the studies cited earlier. Furthermore, economically attractive methods of separation along the solid-liquid-vapor and liquid-liquid-vapor three-phase surfaces are presently being developed requiring detailed data of this nature for design purposes.

Experimental

A detailed description of the experimental equipment and procedure is given elsewhere (*3, 4, 6*). Briefly, a known amount of *n*-decane was placed in a 10-cc glass equilibrium cell. During the experimental runs, measured amounts of pure CO_2 gas were added to the thermostated equilibrium cell from a high-pressure bomb, through use of a positive displacement mercury pump. By a mass balance, the moles of CO_2 added to the liquid phase or phases were then determined. In the case of the L_1-L_2-V runs, the moles of CO_2 in the individual liquid phases were determined by making separate runs in which one or the other of the two phases is present in a trace amount.

In the case of the S_1-L_1-V system, S_1 crystals (assumed to be pure n-decane) were maintained in trace amounts; hence, composition in the liquid phase is easily calculated. However, this technique of determining com-

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positions was not successful in the S_1-L_2-V experiments. This is because the CO_2-rich phase L_2 is heavier than the CO_2-lean phase L_1. During the course of an experiment, repeated crystallizations and meltings can form an impervious S_1 layer on top of L_2, which makes the attainment of equilibrium between vapor and L_2 impossible.

This problem was avoided by carefully freezing *n*-decane in the bottom of the equilibrium cell at the start of an experiment; being present in the form of a large mass of crystals, it remains at the bottom of the equilibrium cell throughout the run. Liquid carbon dioxide (L_2) was then allowed to form on the top of the solid, and vigorous stirring allowed the liquid to leach out an equilibrium amount of *n*-decane from the solid at the bottom, while still in equilibrium with the vapor. The authors felt that sampling of L_2 would not lead to precise results owing to the low amount of *n*-decane in the L_2 phase; therefore, compositions are not reported for the S_1-L_2-V locus.

Procedures for determining the *UCST* point and the Q_1 point (coexistence of the four phases V-L_1-L_2-S_1) are rather routine and discussed elsewhere (*3, 4, 6*). The determination of Q_2 (coexistence of the four phases V-L_2-S_1-S_2) required careful observational techniques. Preliminary experiments were performed to get a sense of the physically visible differences between S_1 and S_2 crystals. Careful observations of the pure CO_2 triple point indicated that S_2 crystals settle quickly in L_2 and tend to cluster, whereas S_1 crystals settle more slowly and appear somewhat needle shaped.

Temperature was measured with a Pt-resistance thermometer to an estimated accuracy of ±0.15°C. Pressure was measured with Bourdon tube gages, which were frequently calibrated against an accurate dead-weight gage to an estimated accuracy of ±0.07 atm. The viewable glass cell was marked, carefully calibrated, and judged to give volumetric readings to an estimated accuracy of ±0.02 cc.

Materials

The CO_2 used in this study was obtained from the Matheson Co. as "Coleman grade" material with a stated minimum purity of 99.99%. Oxygen, nitrogen, carbon monoxide, and hydrogen were the major impurities.

The CO_2 was prepared for use by flashing it from the cylinder at room temperature to the 3000-cc storage reservoir maintained at 0°C. In doing this, it was hoped that the resulting liquefaction of the CO_2 would make it free from impurities, the impurities remaining in the vapor space. Subsequent venting of the vapor phase in the reservoir would then remove these impurities.

The Kuenen criterion of purity (the difference between the bubble point and the dew-point pressure divided by the critical pressure) was less than 0.01. The properties vapor pressure, sublimation pressure, and critical and triple point were within 0.3 atm and 0.1°C of the literature values (*1*).

The *n*-decane used in this study was a Humphrey-Wilkinson product labeled as having 99% minimum purity. The melting point of *n*-decane was observed to be −29.60°C. It was used without further purification.

Results

Table I presents smoothed composition, pressure, temperature, and molar volume data on the CO_2-*n*-decane binary system along the L_1-L_2-V locus.

The immiscibility range in this system extended approximately 13.1°C above the Q_1 point. The upper critical solution temperature was determined as −24.41°C by observing the appearance and disappearance of the second liquid phase.

The depression in freezing point of *n*-decane upon CO_2 pressurization (S_1-L_1-V locus) is reported in Table II along with composition and molar volume information. The locus extends from the melting point of *n*-decane at −29.6°C to the Q_1 point at −37.5°C.

The *P-T* data for the S_1-L_2-V locus extending from the Q_1 point to the Q_2 point are reported in Table III. The quadruple point (the peritectic point) at the lower end of S_1-L_2-V locus was at −56.23°C.

The *P-T* projections of the phase behavior given in Figure 1 illustrate all the above loci. The vapor-pressure data of pure CO_2 are also plotted in Figure 1.

In Figure 1 the S_1-L_1-L_2 locus, which should meet the other three loci at the Q_1 point, is not shown. Because of experimental difficulties, data could not be obtained ac-

Table I. Smoothed Values of Pressure, Temperature, Compositions, and Liquid Molar Volumes of Liquid 1-Liquid 2-Vapor Locus for System Carbon Dioxide-*n*-Decane

Temp, °C	Press, atm	CO_2 mole fraction		Liquid molar vol, cc/g-mol		Comment
		L_1	L_2	$\bar{V}_1$	$\bar{V}_2$	
−37.5	10.44	0.577	0.974	103.2	44.1	Q_1(S_1-L_1-L_2-V)
−37.0	10.60	0.582	0.973	102.7	44.2	L_1-L_2-V
−35.0	11.36	0.602	0.970	100.3	44.8	L_1-L_2-V
−33.0	12.17	0.627	0.965	97.1	45.7	L_1-L_2-V
−31.0	13.01	0.659	0.960	92.6	47.3	L_1-L_2-V
−29.0	13.95	0.695	0.954	87.1	49.0	L_1-L_2-V
−27.0	14.89	0.734	0.942	80.8	51.0	L_1-L_2-V
−25.0	15.89	0.783	0.916	73.4	54.4	L_1-L_2-V
−24.41	16.16	0.850[a]	0.850[a]	63.9[a]	63.9[a]	*UCST* (L_1 with L_2)

[a] Estimated.

Table II. Smoothed Values of Pressure, Temperature, Composition, and Molar Volume of Solid 1-Liquid 1-Vapor Locus for System Carbon Dioxide-*n*-Decane

Temp, °C	Press, atm	CO_2 mole fraction L_1	Liquid molar vol, cc/g-mol	Comment
−29.6	1.0	...	189.6	*n*-Decane, mp
−30.0	2.15	0.034	184.4	S_1-L_1-V
−32.0	5.42	0.159	163.7	S_1-L_1-V
−34.0	7.90	0.283	142.5	S_1-L_1-V
−36.0	9.58	0.436	120.5	S_1-L_1-V
−37.5	10.44	0.577	103.2	Q_1(S_1-L_1-L_2-V)

Table III. Smoothed Values of Pressure and Temperature of Locus Solid 1-Liquid 2-Vapor for System Carbon Dioxide-*n*-Decane

Temp, °C	Press, atm	Comment
−37.5	10.44	Q_1(S_1-L_1-L_2-V)
−38.0	10.22	S_1-L_2-V
−40.0	9.45	S_1-L_2-V
−42.0	8.78	S_1-L_2-V
−44.0	8.12	S_1-L_2-V
−46.0	7.52	S_1-L_2-V
−48.0	6.97	S_1-L_2-V
−50.0	6.40	S_1-L_2-V
−52.0	5.90	S_1-L_2-V
−54.0	5.39	S_1-L_2-V
−56.0	4.89	S_1-L_2-V
−56.23	4.86	Q_2(S_1-S_2-L_2-V)

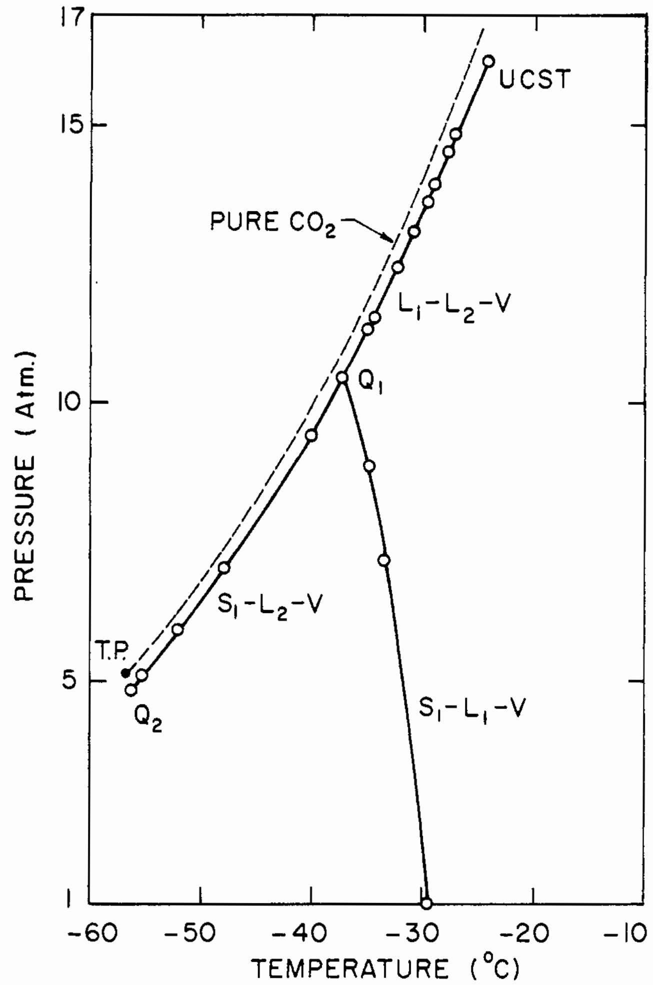

Figure 1. Phase equilibria in system CO_2-*n*-decane (*P-T* projection). Pure CO_2 data denoted by dashed line

curately along this locus. The authors feel that this locus should rise from Q_1 with a slight positive slope.

The raw data were smoothed by plotting them on a large scale graph paper. The standard deviations of the raw data from the smoothed values of pressure, composition, and liquid molar volume are ±0.2 atm, ±0.002 mole fraction, and ±0.2 cc/g-mol, respectively.

Nomenclature

L_1 = CO_2 lean liquid phase
L_2 = CO_2 rich liquid phase
P = pressure, atm
Q_1 = quadruple point 1 (coexistence of the four phases V-L_1-L_2-S_1)
Q_2 = quadruple point 2 (coexistence of the four phases V-L_2-S_1-S_2)
S_1 = solid *n*-decane
S_2 = solid CO_2
T = temperature, °C
UCST = upper critical solution temperature of L_1 and L_2
V = vapor phase
$\bar{V}$ = molar volume, cc/g-mol
X = composition

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Stability of First Dissociable Proton of Uric Acid

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The stability constant of the first dissociable proton of uric acid was measured at 20°, 25°, 38°, and 45°C by two different techniques—solubility and spectrophotometric titration—with good agreement of results. The spectrophotometric data indicated a p*K*a of 5.468 at 38°C and an enthalpy of ionization of −5.22 kcal/mol. On the basis of observations of sodium acid urate solubility and the internal consistency of the stability measurement data, it was concluded that the sodium urate complex is negligible in biological systems.

The currently accepted (and only reported) value of the p*K*a of uric acid is that of Bergmann and Dikstein (2). It was determined at room temperature by plotting the trajectory of the optical absorbance maximum as a function of pH in uric acid in solutions containing various sodium salt buffers. An algorithm for reducing the trajectory data was not given either by Bergmann and Dikstein or by Robinson and Pekrul (5), whom they cited. The optical absorbance maximum trajectory as presented by Bergmann and Dikstein had the characteristic shape of a titration curve, and the midpoint of the trajectory or its inflection point was probably used to identify the p*K*a (the two points, for practical purposes, appear to be the same).

Use of the midpoint of the trajectory to identify the p*K*a requires that the molar optical absorbance dispersion curves of uric acid and acid urate have facing shoulders that are mirror images of each other. Absorbance dispersion data on uric acid were not presented. Intrepretation of Bergmann and Dikstein's observation is further complicated by the possibility that a sodium acid urate complex is present in significant concentration. Analysis of sodium acid urate solubility data by Hammarsten (3) suggests

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