Solubilities of *n*-Pentane and 1,3-Butadiene in Liquid Nitrogen

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The solubilities of *n*-pentane and 1,3-butadiene in liquid nitrogen are nearly two orders of magnitude smaller than those in liquid methane.

In a recent publication (*1*), we reported solubilities of several hydrocarbons in liquid methane and in liquid argon. Using the apparatus and procedure described previously, we have also measured the solubilities of *n*-pentane and 1,3-butadiene in liquid nitrogen.

Nitrogen was obtained from the Matheson Co. with a stated purity of 99.997%. *n*-Pentane and 1,3-butadiene were obtained from Phillips Petroleum Co. with stated purities of 99.90% and 99.89%, respectively.

Table I presents experimental solubilities x_2 (mole fraction of solute) along with the precision and an estimate of the parameter l_{12} in the modified Scatchard-Hildebrand equation as discussed earlier. Since the measured solubilities are extremely small, difficulties in chemical analysis are responsible for some uncertainty in the results. It is clear, however, that the solubilities of these hydrocarbons in liquid nitrogen are about one order of magnitude smaller than those in liquid argon and nearly two orders of magnitude smaller than those in liquid methane.

Table I. Solubilities in Liquid Nitrogen

Solute	T, K	$10^6 x_2$	No. of samples	Precision, rel %	Scatchard-Hildebrand l_{12}
n-Pentane	90.6	0.63	10	10	0.07
	97.2	1.45	7	4	
1,3-Butadiene	95.4	0.72	4	21	0.06

LITERATURE CITED

(1) Preston, G. T., Funk, E. W., Prausnitz, J. M., *J. Phys. Chem.*, **75**, 2345 (1971).

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Solubility of Carbon Dioxide in Aqueous Diethanolamine Solutions at High Pressures

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The solubility of carbon dioxide in aqueous solutions of diethanolamine (DEA) has been determined at temperatures between 25° and 120°C in four solutions ranging from 0.5*N* to 5*N* DEA. The partial pressures of CO_2 ranged from 0.1–827 psia. The results have been combined with previous data in the literature and smoothed values are presented. Enthalpies of solution have been calculated from the experimental results.

Aqueous diethanolamine (DEA) solutions are used extensively for the removal of the acid gas components, CO_2 and H_2S, present in gas mixtures. The proper design and operation of amine-treating units require a knowledge of the solubility behavior of the acid gases in DEA solutions.

Determinations of the solubility of carbon dioxide in aqueous diethanolamine solutions have been made by few investigators. Bottoms (*1*) presented a small-scale plot showing the solubility of CO_2 in 50% water solution at temperatures of 25°, 35°, 45° and 55°C, and partial pressures of CO_2 up to 760 mm Hg. Mason and Dodge (*4*) studied the solubility of CO_2 in 0.5, 2.0, 5.0, and 8.0*N* solutions at temperatures of 0°, 25°, 50°, and 75°C and partial pressures of CO_2 ranging from about 10 to 750 mm Hg. Reed and Wood (*6*) presented graphically a few values of the solubility of CO_2 in 2.5*N* DEA solutions at temperatures of 100° and 140°C and partial pressures of CO_2 ranging from 35 to 230 psia. The published results have been summarized by Kohl and Riesenfeld (*3*), and the reliable data available are those for partial pressures of CO_2 below atmospheric. Recently Murzin and Leites (*5*) measured the partial pressure of CO_2 over 0.5, 1.0, 2.0, 5.0, and 8.0*N* solutions at temperatures between 20° and 90°C and presented the results on small-scale plots. Mole ratios of CO_2/DEA ranged from 0.01 to 0.4 with partial pressures of CO_2 from about 0.1 to 700 mm Hg. This study was undertaken to provide data on the solubility of CO_2 in DEA solutions at high partial pressures in the range of temperatures and solution concentrations used industrially.

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EXPERIMENTAL

The amine solutions were prepared from distilled water and commercially available DEA, which had a purity of 99.8%. Nitrogen and CO_2 were also obtained from commercial suppliers and had purities of 99.997 and 99.9%, respectively. All materials were used without further treatment.

The equilibrium cell used in this work consisted of a tubular stainless steel vessel having a volume of about 500 cm^3 and equipped with a magnetic stirrer. The magnet was mounted inside the cell upon an impeller which agitated both the liquid and the vapor phases. The equilibrium pressure was measured by a Heise bourdon tube gauge which had been calibrated against a deadweight gauge. The temperature of cell was measured by duplicate 10-junction copper-constantan thermopiles which were inserted into thermowells extending into the vapor and liquid phases. The thermopiles were calibrated at the ice point and the steam point. The equilibrium cell was housed in a constant temperature air bath controlled within ±0.5°C. The chromatograph used in this work had a 10-ft long $^1/_4$-in. o.d. column packed with Chromosorb 104. It was operated isothermally at 130°C.

The DEA solution was made up to the desired strength and 100–150 cm^3 were charged into the cell, which had been purged with nitrogen. Carbon dioxide was then added to an amount determined by observation of the pressure. Nitrogen was then added to increase the total pressure. At higher partial pressures of CO_2, above 200–300 psia, no nitrogen was added so that the vapor phase was almost entirely CO_2.

Samples of the vapor were withdrawn from the top of the cell and passed to the sample loop of the gas chromatograph for analysis. From the analysis of the vapor phase, the knowledge of the gauge and barometric pressures and the vapor pressure of the amine solution, the partial pressure of the CO_2 in the vapor was calculated.

Liquid samples were withdrawn from the bottom of the cell and passed through capillary tubing into a weighed amount of 5*N* H_2SO_4 in a sample bottle. Upon contact with the sulfuric acid, the CO_2 evolved and was collected in a calibrated burette of 200 cm^3 capacity. The pressure of the evolved gases was adjusted to atmospheric, and the temperature was measured with a mercury thermometer. From the *PVT* information, the amount of CO_2 in g-mol which evolved was calculated. Analyses of the acidic solution indicated that negligible amounts of CO_2 were left in the sample bottle. The sample bottle was reweighed to determine the quantity of amine solution from which the gases evolved. From these results, the ratio of CO_2 to amine in the liquid phase was calculated.

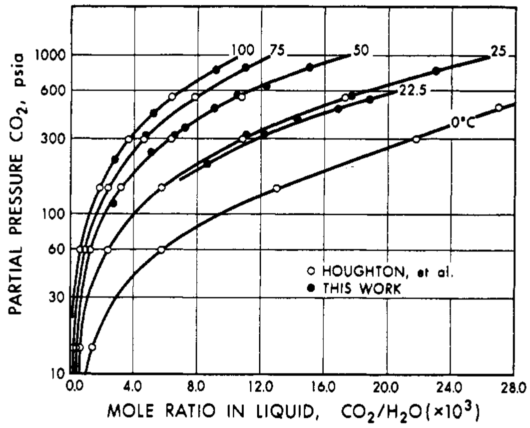

Figure 1. Solubility of carbon dioxide in water

RESULTS AND DISCUSSION

To confirm the liquid sampling and analytical procedures, the solubility of CO_2 in water was determined at 22.5°, 25°, 50°, 75°, and 100°C at partial pressures between 117 and 820 psia. A comparison of these results with values from the literature (*2*) is shown in Figure 1. The present values agree with the literature within a few per cent.

Experimental data for the solubility of CO_2 in 0.5, 2.0, 3.5, and 5.0*N* DEA solutions were obtained at temperatures of 25°, 50°, 75°, 100°, and 120°C at partial pressures of CO_2 ranging from 0.1 to 827 psia. The results are given in Table I which has been deposited with the ACS Microfilm Depository Service. A plot of the data for the 2*N* solution is presented in Figure 2 which also shows the data of Mason and Dodge (*4*). The solid lines in Figure 2 are the smoothed values determined by cross-plotting the experimental data together with the data of Mason and Dodge (*4*). Smoothing was performed with respect to temperature, pressure, and normality of the solution. The smoothed results are presented in Table II and cover the tem-

Table II. Smoothed Data for Solubility of CO_2 in DEA Solutions

Normality of DEA solution	Partial pressure of CO_2, *p* in psia		α, Mole ratio in liquid, CO_2/DEA Temp, °C						
	p	Log *p*	0	25	50	75	100	120	140
0.5	0.1	−1.0	0.680	0.475	0.302	0.098	...	...	...
	0.316	−0.5	0.776	0.580	0.418	0.212	0.058	...	...
	1.0	0.0	0.875	0.688	0.536	0.340	0.165	...	...
	3.16	0.5	0.982	0.802	0.662	0.465	0.312	0.140	0.030
	10.0	1.0	1.098	0.925	0.803	0.608	0.480	0.328	0.200
	31.6	1.5	1.350	1.065	0.963	0.767	0.665	0.545	0.420
	100.0	2.0	1.942	1.368	1.180	0.980	0.882	0.800	0.698
	316.0	2.5	...	2.080	1.680	1.361	1.240	1.165	1.080
	1000.0	3.0	...	...	2.695	2.340	2.080	1.880	1.800
2.0	0.1	−1.0	0.543	0.402	0.258	0.086	...	...	...
	0.316	−0.5	0.622	0.480	0.340	0.163	0.035	...	...
	1.0	0.0	0.708	0.568	0.440	0.248	0.112	...	...
	3.16	0.5	0.798	0.663	0.532	0.365	0.220	0.100	...
	10.0	1.0	0.892	0.765	0.638	0.486	0.348	0.212	0.093
	31.6	1.5	1.020	0.875	0.752	0.620	0.490	0.343	0.230
	100.0	2.0	1.135	1.026	0.887	0.770	0.645	0.507	0.395
	316.0	2.5	1.285	1.172	1.053	0.947	0.830	0.701	0.598
	1000.0	3.0	...	1.392	1.281	1.180	1.075	0.946	0.840

(*Continued on next page*)

Table II. *(Continued)*

Normality of DEA solution	Partial pressure of CO_2, p in psia		α, Mole ratio in liquid, CO_2/DEA Temp, °C						
	p	Log p	0	25	50	75	100	120	140
3.5	0.1	−1.0	0.513	0.387	0.243	0.085	...	...	...
	0.316	−0.5	0.588	0.453	0.314	0.160	0.027	...	...
	1.0	0.0	0.645	0.525	0.392	0.238	0.090	...	...
	3.16	0.5	0.725	0.600	0.467	0.334	0.183	0.083	...
	10.0	1.0	0.806	0.690	0.562	0.433	0.295	0.175	0.060
	31.6	1.5	0.902	0.788	0.663	0.540	0.412	0.285	0.160
	100.0	2.0	1.011	0.910	0.782	0.660	0.538	0.422	0.302
	316.0	2.5	1.133	1.030	0.920	0.800	0.678	0.568	0.455
	1000.0	3.0	...	1.190	1.082	0.983	0.855	0.752	0.650
5.0	0.1	−1.0	0.493	0.378	0.240	0.084	...	...	...
	0.316	−0.5	0.551	0.430	0.308	0.158	0.022	...	...
	1.0	0.0	0.610	0.490	0.376	0.230	0.080	...	...
	3.16	0.5	0.673	0.554	0.444	0.315	0.164	0.073	...
	10.0	1.0	0.746	0.629	0.525	0.398	0.265	0.153	0.035
	31.6	1.5	0.822	0.708	0.608	0.485	0.363	0.253	0.122
	100.0	2.0	0.920	0.818	0.702	0.580	0.460	0.355	0.241
	316.0	2.5	1.020	0.919	0.809	0.691	0.587	0.464	0.360
	1000.0	3.0	...	1.050	0.940	0.836	0.721	0.602	0.515
6.5	0.1	−1.0	0.485	0.372	0.237	0.083	...	...	...
	0.316	−0.5	0.533	0.424	0.297	0.157	0.020	...	...
	1.0	0.0	0.582	0.475	0.356	0.225	0.078	...	...
	3.16	0.5	0.638	0.524	0.419	0.290	0.160	0.065	...
	10.0	1.0	0.695	0.587	0.484	0.362	0.250	0.138	0.015
	31.6	1.5	0.758	0.650	0.555	0.440	0.338	0.222	0.090
	100.0	2.0	0.833	0.737	0.638	0.524	0.425	0.320	0.198
	316.0	2.5	0.920	0.822	0.725	0.620	0.528	0.423	0.310
	1000.0	3.0	...	0.932	0.840	0.740	0.638	0.532	0.440
8.0	0.1	−1.0	0.483	0.368	0.235	0.082	...	...	...
	0.316	−0.5	0.522	0.420	0.298	0.156	0.019	...	...
	1.0	0.0	0.568	0.472	0.355	0.221	0.077	...	...
	3.16	0.5	0.617	0.525	0.413	0.290	0.158	0.058	...
	10.0	1.0	0.668	0.580	0.479	0.362	0.245	0.126	...
	31.6	1.5	0.728	0.640	0.540	0.435	0.330	0.200	0.060
	100.0	2.0	0.782	0.702	0.615	0.520	0.402	0.290	0.169
	316.0	2.5	0.850	0.773	0.680	0.598	0.499	0.383	0.275
	1000.0	3.0	...	0.855	0.770	0.683	0.595	0.485	0.400

perature range 0–140°C, the partial pressure range 0.1–1000 psia and solutions of normality ranging from 0.5–8*N* DEA. Extrapolation of the experimental data was necessary to cover these ranges. The smoothed results include the conditions of operation of most industrial processes.

The present results are in good agreement with the results of Reed and Wood (*6*) and Mason and Dodge (*4*) in regions where comparison can be made. Figure 2 shows that the present work is generally within 3% of the data of Mason and Dodge (*4*) for the 2*N* solution.

The major sources of error in this work are associated with the measurement of the equilibrium pressure and the determination of the pressure and volume of the gases evolved from the liquid sample. Minor errors result from uncertainties in the temperature of the equilibrium cell and the gas burette, error in the determination of the normality of the solutions, and errors involved in the use of the balance for determining the amine in the liquid sample. As a result of all these factors, the present data are estimated to be accurate within 3–5% in liquid concentration at a given partial pressure of carbon dioxide.

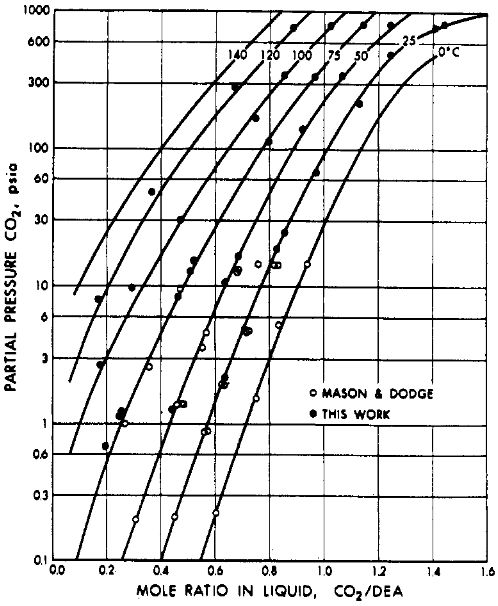

Figure 2. **Solubility of carbon dioxide in 2*N* diethanolamine solution**

Since the solvent phase is essentially nonvolatile under the conditions of these experiments, approximate values of ΔH_s, the enthalpy of solution of CO_2 in the amine solutions, can be calculated from the following equation:

$$\frac{\Delta H_s}{R} = \frac{H_1^* - \bar{H}_1^1}{R} = \left[\frac{\partial \ln f_1}{\partial(1/T)}\right]_{x_1}$$

where the subscript 1 refers to CO_2. Plots of $\ln f_1$ vs. $1/T$ were linear for all solutions except that of 0.5*N*, indicating that the enthalpy of solution was independent of temperature over the range studied here. Values of ΔH_s calculated from the

Table III. Enthalpy of Solution of CO_2-DEA Solutions

$-\Delta H_s$, kJ/g-mol CO_2

Normality of DEA solution	α, Mole ratio in liquid, CO_2/DEA 0.2	0.4	0.6	0.8	1.0	1.2	1.4
0.5	57.7[a]	53.0[a]	44.3[a]	37.3[a]	31.5[a]	27.2[a]	23.5[a]
2.0	67.2	59.5	47.5	38.8	32.0	27.2	23.5
3.5	76.3	65.4	50.3	40.0	32.4	27.3	23.5
5.0	84.3	70.5	52.6	40.9	32.7	27.4	23.5
6.5	90.7	73.7	54.2	41.5	32.9	27.4	23.5
8.0	96.2	76.3	55.5	41.8	33.0	27.4	23.5

[a] Calculated at 50°C.

smoothed data are presented in Table III. The values for 0.5*N* are those at 50°C. The enthalpy of solution depends strongly upon the loading of the CO_2 in solution and at low loadings upon the normality of the solution.

Few values of ΔH_s are available for comparison. Kohl and Riesenfeld (*3*) give a value of 653 Btu/lb_m of CO_2 for the enthalpy of solution of CO_2 in DEA solutions. This corresponds to 66.9 kJ/mol of CO_2 which agrees with the present values at low normalities and low loadings of CO_2 in the DEA solutions. Wuithier (*7*) gives a value of 262 kcal per kg which corresponds to 48.3 kJ/mol of CO_2. No information was given as to how this value was obtained. Murzin and Leites (*5*) present the results of the calculation of ΔH_s from their data and indicate that ΔH_s is independent of α in the range 0–0.2. Their results are in good agreement with the first column of Table III at the low normalities, but differ by up to 30% for the 8*N* solution.

NOMENCLATURE

α = mole ratio, CO_2/DEA
f = fugacity, psia
H = enthalpy, J mol^{-1}
p = partial pressure, y_1P, psia
P = total pressure, psia
R = gas constant
T = temperature, °C
x = mole fraction in liquid phase
y = mole fraction in vapor phase

SUPERSCRIPTS

— = partial molal quantity
* = ideal gas state
l = liquid

SUBSCRIPTS

1 = CO_2
s = solution

LITERATURE CITED

(1) Bottoms, R. R., *Ind. Eng. Chem.*, **23**, 501 (1931).
(2) Houghton, G., McLean, A. M., Ritchie, P. D., *Chem. Eng. Sci.*, **6**, 132 (1957).
(3) Kohl, A. L., Riesenfeld, F. C., "Gas Purification," Chap. 2, McGraw-Hill, 1960.
(4) Mason, J. W., Dodge, B. F., *Trans. A.I.Ch.E.*, **32**, 27 (1936).
(5) Murzin, V. I., Leites, I. L., *Zhur. Fiz. Khim.*, **45**, 2642 (1971).
(6) Reed, R. M., Wood, W. R., *Trans. A.I.Ch.E.*, **37**, 363 (1941).
(7) Wuithier, P., "Le Pétrole. Raffinage et Génie Chimique," Vol. 1, p 882, Éditions Technip, Paris, 1965.

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Excess Thermodynamic Properties of Ethylene Diamine–Ethylene Glycol Solutions at 25°C

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The excess Gibbs free energies, enthalpies, entropies, and volumes are reported for mixtures of ethylene diamine–ethylene glycol at 25°C. The refractive indices of these liquid mixtures are also reported for 25°C.

The excess thermodynamic properties have been reported for water–diethylamine solutions at 49.1°C, and ethyl alcohol–diethylamine solutions at 50°C. In both mixtures the excess enthalpies are large and negative over the entire composition range. The same is true for the Ts^E values. However, the Gibbs free energies are much smaller, and are also of opposite sign, being positive for the water–amine and negative for the alcohol–amine solutions (*2*). Investigations have shown that ethylene glycol is a suitable solvent for comparison with water, but without the eccentricities of water (*5*). It appeared to the authors that the excess thermodynamic properties of mixtures of ethylene diamine–ethylene glycol might show some unusual properties and would be worth investigating.

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