Isothermal Vapor-Liquid Equilibria in Binary System Propane–Carbon Dioxide

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Isothermal vapor-liquid equilibria in the binary system propane–carbon dioxide were experimentally determined over the complete concentration range at −20 and 20 °F with a forced recirculation apparatus. The total vapor pressure determined varied from 73 to 379 psia. The lowest temperature reported in the literature which covers the complete concentration range was −4.4 °F. The data obtained were thermodynamically consistent and compared favorably with the values predicted by means of the Redlich-Kwong equation of state with a modified procedure. The average absolute deviation in *P* was less than 2.5% and in *y*, less than 0.007 mole fraction.

In recent years there has been increasing interest in the phase equilibrium studies of binary systems, particularly those containing one of the nonhydrocarbon components frequently found in petroleum or natural gas reservoirs. Information on binary systems is required for evaluating the parameters used in improved prediction of the behavior of multicomponent systems and for evaluating the binary interaction constant, k_{ij}, required in the mixing rules of an equation of state. Carbon dioxide–hydrocarbon systems have received increasing attention primarily because most natural gases contain sufficient carbon dioxide to warrant concern in processing plants, where solidified carbon dioxide can dangerously plug low-temperature equipment. Another concern is because the presence of carbon dioxide lowers the heating value of the natural gases.

Although vapor-liquid equilibrium data for the binary system propane–carbon dioxide have been reported in the literature (*1, 11–13*), they are not available over the complete concentration range below the temperature of −4.4 °F. To extend the range and smooth the correlation between the existing data, experimental points were determined in this investigation at two isothermal conditions (−20 and 20 °F).

Experimental Method

The detailed description of the equipment assembly, the equilibrium cell and the cryostat, and the experimental technique used in this work is essentially the same as that reported earlier (*3*). The equipment assembly consists of a feed measuring and charging device, a forced recirculation equilibrium cell, a closed recirculation loop, a cryostat and its temperature control system, sampling facilities, and temperature and pressure measuring devices.

The equilibrium cell was made of a 100-ml Jerguson transparent gauge. A dewar flask of 18-l. capacity was used as the cryostat. It was silvered except for two vertical strips about 1 in. wide. The windows of the equilibrium cell were centered with respect to the vertical unsilvered strips of the dewar flask to ensure clear visibility of the cell at all times using a source of illumination. A Nestlab cooling unit was used with methyl alcohol as the bath liquid. The temperature was controlled to ±0.02 °F.

Research grade propane and carbon dioxide were supplied by Phillips Petroleum Co. and Matheson of Canada Ltd., respectively, and were used without further purification. Specified minimum purities of these gases are propane, 99.99 mol %; and carbon dioxide, 99.995 vol %.

The mixtures studied were synthesized and liquefied within the equilibrium cell with propane charged first, followed by carbon dioxide. Equilibrium temperatures were measured with two thermocouples in conjunction with a Leeds and Northrup K-5 potentiometer. The thermocouples were calibrated against the vapor pressure of propane (*2, 7*), and the measured temperatures were estimated to be within ±0.2 °F. The pressure of the system was measured with two tested Heise gauges. The ranges of these two gauges are 0–200 and 0–2000 psia with 0.1% accuracy of the full scale. At the lowest experimental pressure the relative error is about 0.27%, while at the highest experimental pressure the relative error is 0.53%. A electromagnetic pump was used for recirculating the vapor through the liquid in the equilibrium cell.

After thermal equilibrium was reached in the cell, the recirculation of the vapor within the circulation loop was continued for at least 3 h at the desired temperature. Samples of the liquid and vapor phases were withdrawn from the equilibrium cell after the liquid phase was allowed to settle for 1 h and were analyzed with a Hewlett-Packard gas chromatograph Model 5700A, in conjunction with a Westronics recorder Model MT21. The output signal was fed to a Hewlett-Packard integrator Model 3373B. Pora-Pack Q (supplied by Chromatographic Specialities Co.) was used as the column packing material. Samples of prepared mixtures of known composition were used for the calibration of the chromatograph. The flow rate of helium was maintained at 30 ml/min at 40 psig. The detector temperature was kept at 150 °C, and the oven temperature at 95 °C. A retention time of 5 min was required to separate the propane–carbon dioxide mixture. At least three analyses were made for each of the samples collected. The reproducibility of the analyses was within ±0.2 mol %, and the accuracy was estimated to be ±0.3 mol %.

Results and Discussion

The vapor-liquid equilibrium data obtained at two isothermal conditions (−20 and 20 °F) are given in Table I. The data are similar in appearance to those reported by previous authors (*1, 11–13*). There exists a reversal in the curvature in the *P-y* curve for each isotherm in the region of carbon dioxide rich content. This is typical behavior for systems made up of carbon dioxide and paraffin hydrocarbons at temperatures up to and slightly above the critical temperature of the hydro-

Table I. Values of Ω_a and Ω_b

Component	T, °F	Ω_a	Ω_b
Propane	70	0.41947	0.08055
	40	0.42230	0.08111
	20	0.42522	0.08164
	−20	0.42671	0.08201
Carbon dioxide	70	0.39778	0.07702
	40	0.40754	0.07779
	20	0.41363	0.07862
	−20	0.42349	0.07973

carbon. This phenomenon is more evident as the temperature decreases as shown in Figure 1. The mixtures studied were synthesized and liquefied within the equilibrium cell with the propane being charged first, followed by carbon dioxide. A significant decrease in volume was observed during this procedure, especially in the vicinity of 170 psia at 20 °F. This behavior was not observed for the system ethane–carbon dioxide which was experimentally determined previously (*9*). This behavior may be attributed to the difference of the chemical nature of these components despite their having the same molecular weight.

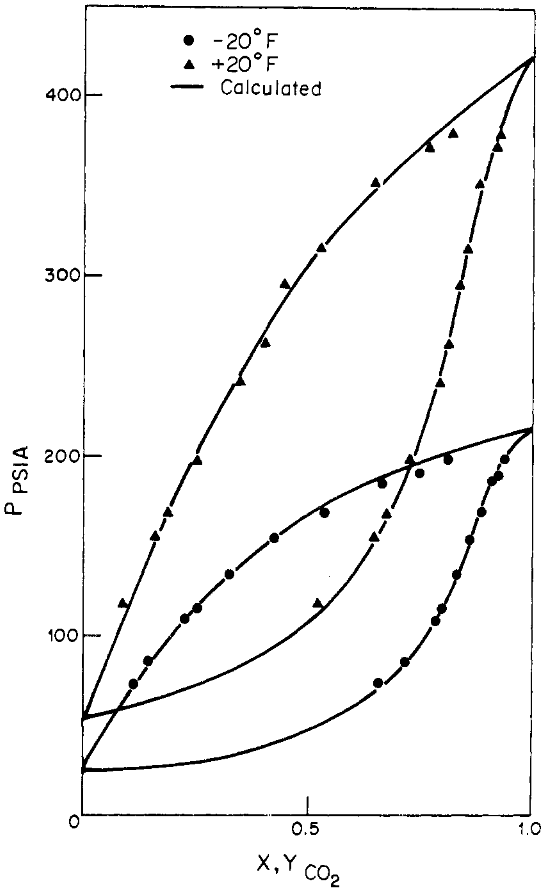

Figure 1. Comparison of calculated, experimental, and literature *P-x-y* values for binary system propane–carbon dioxide

The consistency of the experimental data was tested by the method proposed previously (*4*). The measurement errors in the calculations were set as follows: $E(P) = \pm 1.0$ psia; $E(T) = 0.2$ °F; and $E(x) = \pm 0.0005, \pm 0.001, \pm 0.002$. The experimental data are consistent within the bounds indicated by ±0.0005 mol fraction with the exception of one experimental point ($P = 351.0$ psia, $x = 0.3530$); with this point included, the data are consistent within the bounds indicated by ±0.002 mol fraction. The use of this consistency test, although developed in an approximate form, indicates the total error caused by both random and systematic errors. In the calculation the fugacities and the partial molal volumes were obtained from the Redlich-Kwong equation of state by a modified procedure (*5*). In the equation

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)} \tag{1}$$

a and b are characteristic parameters and are related to the critical properties as follows:

$$a = \Omega_a R^2 T_c^{2.5}/P_c \tag{2}$$

$$b = \Omega_b R T_c/P_c \tag{3}$$

The parameters Ω_a and Ω_b were considered temperature dependent in this study. The saturated properties, molal volumes, and vapor pressures available in the literature for propane (*2, 7, 14*) and carbon dioxide (*8, 14*) were employed in evaluating these parameters. The method of evaluation has been previously presented (*5*). The calculated values of the parameters are listed in Table II. In addition to the consistency test, the liquid activity coefficients were also evaluated. The constant-pressure, constant-temperature liquid activity coefficient for component i is defined by

$$\gamma_i(P^\circ, T, x) = \frac{\hat{\varphi}_{iV}(P, T, y)Py_i}{x_1 f^\circ_{iL}(P^\circ, T)} \exp \int_P^{P^\circ} \frac{\bar{V}_{iL}}{RT}\,dp \tag{4}$$

where $\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$.

In Equation 4, $\hat{\varphi}_{iV}(P, T, y)$ represents the fugacity coefficient of component i in the vapor phase at system temperature T and pressure P, $f^\circ_{iL}(P^\circ, T)$ represents the fugacity of

Table II. Experimental and Calculated Results for Binary System Propane(1)–Carbon Dioxide(2)

	Experimental			Calculated		Deviations	
T, °F	x_1	y_1	P, psia	P, psia	y_1	$\lvert\Delta P\rvert$	$\lvert\Delta y_1\rvert$
20	0.9114	0.4793	117.0	112.3	0.4941	4.7	0.0148
(k_{12} = 0.102)	0.8380	0.3601	155.0	155.2	0.3509	0.2	0.0092
	0.8202	0.3293	168.5	165.1	0.3281	3.4	0.0012
	0.7485	0.2747	197.5	202.5	0.2605	5.0	0.0142
	0.6536	0.2118	241.0	246.6	0.2048	5.6	0.0070
	0.6004	0.1921	262.0	268.5	0.1825	6.5	0.0096
	0.5572	0.1682	294.0	285.0	0.1674	9.0	0.0008
	0.4734	0.1477	314.5	313.6	0.1431	0.9	0.0046
	0.3530	0.1249	351.0	348.1	0.1148	2.9	0.0101
	0.2250	0.0843	371.0	378.7	0.0867	7.7	0.0024
	0.1811	0.0735	379.0	388.1	0.0761	9.1	0.0026
−20	0.8866	0.3411	73.0	69.9	0.3497	3.1	0.0086
(k_{12} = 0.099)	0.8547	0.2867	85.0	81.1	0.2969	3.9	0.0102
	0.7755	0.2180	109.0	106.4	0.2172	2.6	0.0008
	0.7505	0.2055	114.0	113.6	0.2005	0.4	0.0050
	0.6771	0.1705	133.5	132.9	0.1639	0.6	0.0066
	0.5774	0.1420	154.3	154.4	0.1318	0.1	0.0102
	0.4671	0.1172	168.0	172.8	0.1082	4.8	0.0090
	0.3328	0.0933	184.5	189.0	0.0873	4.5	0.0060
	0.2536	0.0804	190.5	196.3	0.0764	5.8	0.0040
	0.1933	0.0684	197.0	201.3	0.0673	4.3	0.0011

pure liquid *i* at the system temperature, *T*, and the reference pressure P^0. In this study, P^0 was arbitrarily taken to be 900 psia which is above the highest saturation pressure encountered in this work. The fugacity and the partial molal volume values were evaluated using Equation 1 by means of the modified procedure presented previously (*5*). The mixing rules used are identical to these reported earlier (*5*). Values of the binary interaction constant k_{ij}, assumed to be independent of temperature, pressure, and composition of the solution, were determined in such a manner that the sum of the absolute difference between the calculated and experimental *P* was a minimum. The calculated k_{ij} values are comparable to that reported by Chueh and Prausnitz (*6*). In addition, k_{ij} was obtained by minimizing the difference between the calculated and experimental values of the vapor-phase composition. The values obtained, based on the selection of either *P* or *y*, are different. Although the k_{ij} values are frequently considered to be independent of temperature, density, and composition, there is evidence that k_{ij} is not a true constant but varies with temperature (*5, 9*). The values obtained in this investigation as listed in Table IV substantiate the observation that k_{ij} does vary to some degree with temperature in spite of the fact that the values of Ω_a and Ω_b were determined individually at the temperature concerned. However, a conclusion concerning the variation of k_{ij} with temperature cannot be established at this stage, and for this reason, the average value of k_{ij}, calculated by averaging the values obtained from the minimization of the total pressure at each individual temperature, was used to recalculate the total pressure and the vapor-phase composition. The calculated results as summarized in Table IV are satisfactory and show that the use of an average value for k_{ij} did not introduce a large deviation compared to the optimum value of k_{ij}. The quantity $\hat{\varphi}_{iv}$, which is equal to $\hat{f}_{iv}/Py_i$, was evaluated using the experimental vapor composition. The experimental γ values obtained in this manner were used to obtain the excess Gibbs free energy by means of Equation 5.

$$G^E = RT \sum_i x_i \ln \gamma_i \qquad (5)$$

The calculated γ and G^E values are listed in Table III using the values of k_{ij} calculated by minimizing the deviation in *P*.

Table III. Activity Coefficients and Gibbs Free Energy of Mixing for Binary System Propane(1)–Carbon Dioxide(2)

		Experimental		Predicted		G^E, J/mol	
T, °F	x_1	γ_1	γ_2	γ_1	γ_2	Exptl	Predicted
20	0.9114	1.2143	2.6298	1.2084	2.4582	582.0	558.8
	0.8380	1.2473	2.2748	1.2180	2.3089	705.4	666.6
	0.8202	1.2440	2.3105	1.2205	2.2706	730.5	688.9
	0.7485	1.2826	2.0453	1.2417	2.1317	811.5	780.9
	0.6536	1.3082	1.8934	1.2865	1.9489	879.1	877.1
	0.6004	1.3687	1.7902	1.3245	1.8496	933.2	918.5
	0.5572	1.3919	1.8095	1.3604	1.7631	990.2	936.4
	0.4734	1.5213	1.6154	1.4742	1.6197	999.8	969.9
	0.3530	1.9215	1.4153	1.7661	1.4211	1008.9	948.8
	0.2250	2.3870	1.2256	2.4736	1.2427	783.1	824.8
	0.1811	2.7907	1.1722	2.9141	1.1915	700.2	747.2
−20	0.8866	1.1962	2.6923	1.1797	2.5490	550.8	513.1
	0.8547	1.1924	2.6157	1.1848	2.4658	589.2	560.7
	0.7755	1.2359	2.3175	1.2070	2.2679	716.8	669.7
	0.7505	1.2504	2.2012	1.2170	2.2075	740.5	700.7
	0.6771	1.3105	2.0281	1.2569	2.0353	835.7	780.5
	0.5774	1.4448	1.7926	1.3442	1.8144	932.8	859.3
	0.4671	1.6068	1.5387	1.5166	1.5937	916.3	899.5
	0.3328	2.0271	1.3210	1.9321	1.3581	854.9	860.0
	0.2536	2.4720	1.2045	2.3989	1.2419	748.3	779.1
	0.1933	2.9763	1.1442	2.9741	1.1672	648.9	681.3

Table IV. Comparison of Calculated and Experimental Total Pressure and Composition Values for System Propane(1)–Carbon Dioxide(2)

			% Absolute dev in P			Absolute dev in y		
T, °F	Press, psia	k_{ij}	Max	Av	Av abs dev in P	Max	Av	No. of points
70	125–860.9	0.094[a]	2.90	1.25	4.8	0.0129	0.0088	15
		0.100[b]	2.17	1.27	6.9	0.0164	0.0086	15
40	79–566.5	0.094[a]	4.74	1.84	4.2	0.0201	0.0102	10
		0.100[b]	3.28	1.74	5.2	0.0164	0.0088	10
20	117.0–379.0	0.102[a]	4.01	2.02	5.0	0.0148	0.0069	11
		0.100[b]	4.76	2.10	5.1	0.0181	0.0065	11
		0.096[c]	6.24	2.47	5.7	0.0248	0.0062	11
−20	73.0–197.0	0.099[a]	4.59	2.26	3.0	0.0102	0.0062	10
		0.100[b]	4.02	2.20	3.1	0.0106	0.0060	10
		0.103[c]	4.51	2.51	3.9	0.0116	0.0058	10

[a] Determined from vapor-liquid equilibrium data by minimizing the difference between the calculated and experimental *P* values. This quantity is involved in the mixing rules (*5*) and is defined by $k_{ij} = 1 - \left[\dfrac{T_{c_{ij}}}{(T_{c_i} T_{c_j})^{0.5}} \right]$. [b] Determined by averaging the values of k_{ij} obtained from the two isotherms at −20 and 20 °F using the criterion mentioned above. [c] Determined from vapor-liquid equilibrium data by minimizing the difference between the calculated and experimental *y* values.

Furthermore, the prediction method previously proposed (*10*) was used to predict the system pressure and the equilibrium vapor composition with the system temperature and liquid composition specified. The established values of Ω_a and Ω_b of Table I were used in the calculation. The predicted P and y values are listed in Table II and compared with the experimental data in Figure 1. A summary of the comparison is given in Table IV. The average absolute deviation between the predicted and experimental P values is about 2.5%. The average absolute deviation between the predicted and experimental y values is about 0.007 mol fraction. Moreover, the average value of $\dot{k}_{ij}$ was used in the modified procedure of the Redlich-Kwong equation of state to predict P-y at the conditions reported by Sage et al. (40 and 70 °F). A summary of the comparison is also listed in Table IV. The average absolute deviation in P is less than 1.25% and in y is less than 0.0088 and 0.0102 mol fraction at 70 and 40 °F, respectively. Our experience indicates that better agreement between the experimental and calculated results is obtained when the temperature dependent parameters Ω_a and Ω_b are evaluated using the saturation properties which are reported together with the vapor-liquid equilibrium data. In this case, the vapor pressure of the pure components can be predicted precisely and accurately. As a consequence, we have used the saturated properties reported by Sage et al. (*13*) for the evaluation of the parameters Ω_a and Ω_b at 40 and 70 °F. The γ and G^E values were again calculated using the predicted P and y values for the two experimental isotherms measured in this work. The results obtained, using the values of k_{ij} calculated from the minimum deviation between the calculated and experimental P criterion, are also listed in Table III. The comparison of the calculated and experimental G^E values is shown in Figure 2.

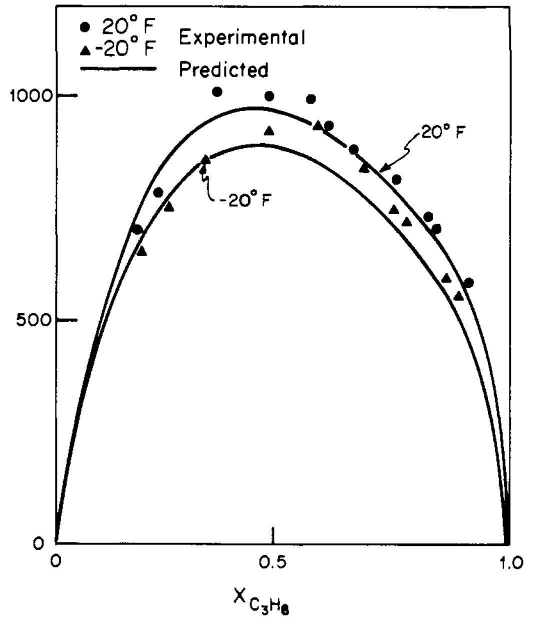

Figure 2. Comparison of calculated and experimental excess Gibbs free energy of mixing values for binary system propane–carbon dioxide

Two plots of ln P against $1/T$ were constructed from the smoothed P-x-y plot: one for constant vapor composition, the other for constant liquid composition as shown in Figures 3

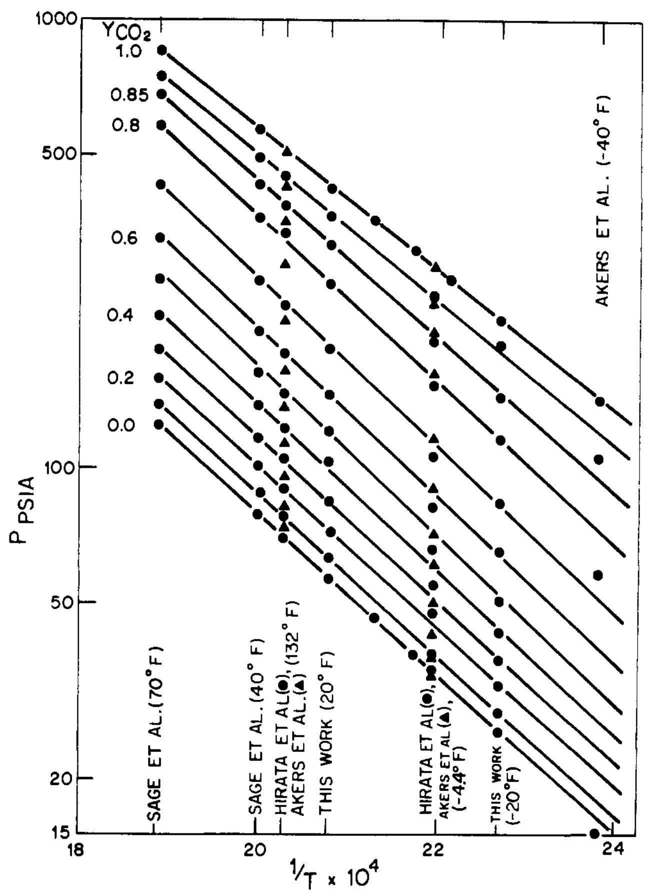

Figure 3. Plot of logarithm of experimental total pressure vs. $1/T$ at constant vapor-phase composition y

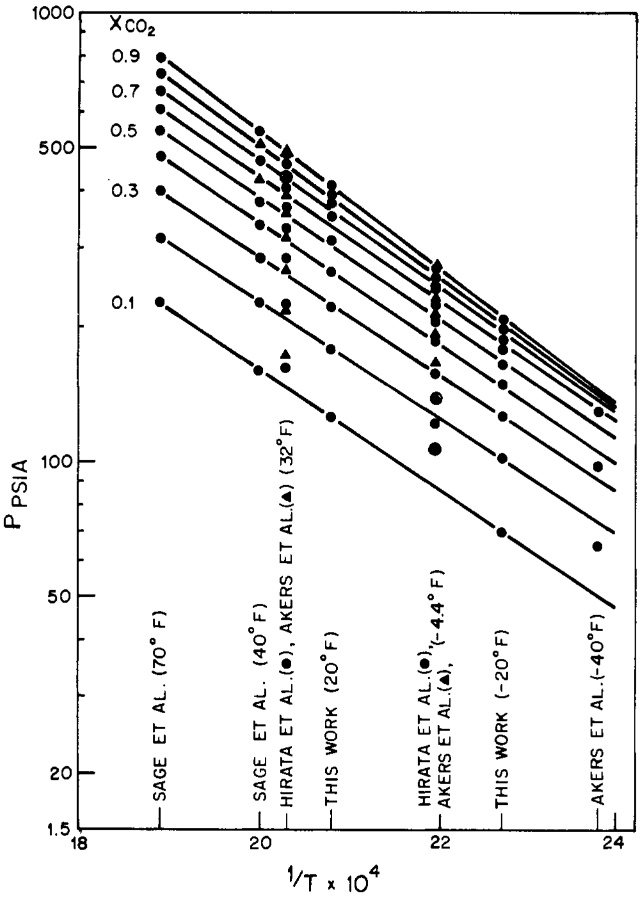

Figure 4. Plot of log of experimental total pressure vs. $1/T$ at constant liquid-phase composition x

and 4. Good agreement was obtained between the data presented in this investigation and those of Sage et al. (*13*). It appears that the data reported by Hirata et al. (*11*) and Akers et al. (*1*) do not follow the trend as shown in the graphs in the lower pressure range.

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Nomenclature

a, b = constants of the Redlich-Kwong equation of state
E = measuring error
G = molal Gibbs free energy
k_{ij} = binary interaction constant
P = total pressure
R = universal gas constant
T = temperature
V = molal volume
x = liquid-phase mole fraction
y = vapor-phase mole fraction
Ω_a, Ω_b = parameters of the Redlich-Kwong equation of state
φ = fugacity coefficient
γ = activity coefficient

Superscripts

$\hat{\ }$ = property in solution
E = excess property
$\bar{\ }$ = partial molal quantity
^{o} = standard state

Subscripts

i, j = component identification
ij = i-j pair
L = liquid phase
v = vapor phase
c = critical property

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Solubility of Butane in Water and Salt Solutions at Low Temperatures

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Additional data on the solubility of *n*-butane in water and 3.5 and 7 wt % NaCl solutions for temperatures ranging from 0 to 20 °C are presented. These data, together with those of Umano and Nakano up to 10 wt % salt, are correlated with an expected error of 3% by a single equation.

Butane has often been suggested as a refrigerant for the freezing process of desalting seawater (*2*) since it has a low solubility in water, boils at −0.5 °C at 1 atm, and is relatively inexpensive. Almost all work on the solubility of butane, however, has been for pure water at temperatures above 15 °C and not for salt solutions at lower temperatures. The notable exception is the work of Umano and Nakano (*6*) who determined the solubility of butane in water and in both 4.79 and 10 wt % NaCl solutions in the temperature range of 0–20 °C. The results reported here supplement those of Umano and Nakano at 0% salt and add butane solubility data for NaCl solutions of 3.5 and 7 wt % and for synthetic sea salt solutions of 3.5 and 7 wt %. In addition, butane solubilities were measured under different total butane pressures to check the validity of Henry's law.

Equipment and Experimental Procedure

The equipment used in these experiments consisted of an equilibrium cell in a constant temperature bath and a total carbon analyzer used to analyze the butane concentration in the liquid.

The cell was a heavy walled pyrex vessel with a volume of 1 l. The top was 1-in. thick Plexiglas with ports for sampling, pressure connection, vacuum line, and introduction of gas. The sampling port consisted of a well which extended down into the vessel below the liquid surface and had a septum for the insertion of a hypodermic syringe.

The cell was totally immersed in a constant temperature water bath controlled via a thermoregulator to ±0.02 °C. The liquid in the cell was mixed by a Teflon-coated magnetic stirring bar driven by a submersible, air operated, magnetic stirrer underneath the cell. The experimental apparatus is shown schematically in Figure 1.

At the beginning of an experiment, the reaction vessel was filled with about 700 ml of water or salt solution, sealed, and submerged in the water bath. While being stirred, the system was evacuated to the vapor pressure of water for about an hour to remove dissolved air from solution. The vessel, now devoid of air, was charged with *n*-butane of instrument purity, 99.5%.