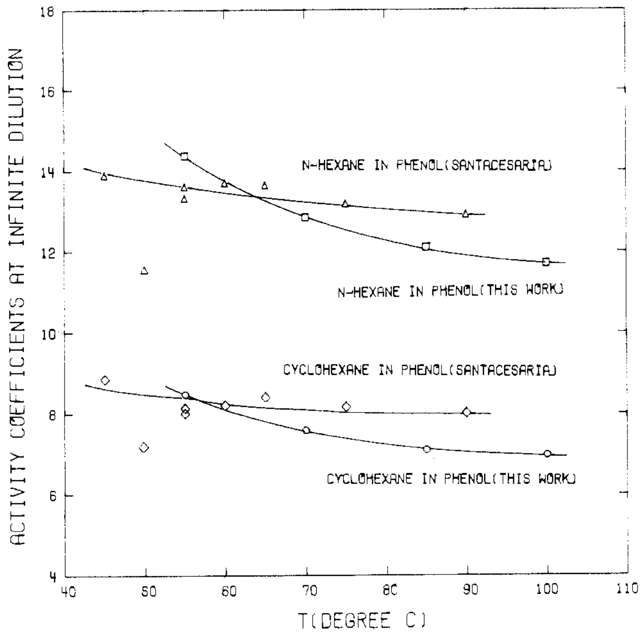

Figure 2. Comparison of γ^∞ values obtained in this work and reported by Santacesaria (*2*).

to be within the uncertainty of their data. There is as much deviation between their own data from the chromatograph method and from a transient desorption method.

Glossary

F_a	volumetric flow rate of elution gas at ambient conditions
K_i	equilibrium y_i/x_i for component i
n	moles of stationary liquid phase on column packing
p	column pressure
p_a	ambient pressure
p^0	vapor pressure
R	gas constant
t_{Ri}	retention time of solute i
t_g	retention time of hypothetical "nonabsorbed" gas
T	absolute temperature
T_a	absolute ambient temperature
$\bar{V}_{li}$	liquid molar volume of component i
z_a	compressibility factor of elution gas at ambient conditions
δ	root mean square relative deviation of the duplicates from their average γ value
$\gamma^\infty{}_i$	activity coefficient of component i in the liquid phase at T
ϕ_i	fugacity coefficient of component i in the elution gas at T and p
ϕ_i^0	fugacity coefficient of pure vapor i and T and p_i^0

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Solubility of Carbon Dioxide in Liquid Water and of Water in Gaseous Carbon Dioxide in the Range 0.2–5 MPa and at Temperatures up to 473 K

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Boiling points and dew-point pressures, as well as the isotherms $p-V$ between dew points and the pressures of 0.2 MPa of the water + carbon dioxide system, have been determined for temperatures up to 473 K. The Henry constants were calculated for the range of temperatures 323–473 K.

Introduction

The system water + carbon dioxide has caught the attention of many investigators because of technological and geothermal aspects. There are many papers concerning the liquid–vapor and gas–gas equilibria in various ranges below 350 MPa and between 298 and 623 K (*1–8*).

The system water + carbon dioxide belongs to type III of the classification introduced by Scott and van Konynenburg (*9*). The critical-temperature curve of the carbon dioxide rich phase starts at the critical temperature of pure carbon dioxide and comes to the upper critical end point. The critical-temperature curve of the water-rich phase starts with the critical temperature of pure water and reaches the area of limited solubility of gases near 539 K and 200 MPa.

This work was undertaken because of the lack of data in the range of 373–473 K below 10 MPa. The data of Takenouchi and Kennedy (*6*) and Todheide and Franck (*5*) start at 10 or 20 MPa, while those of Wiebe and Gaddy (*1–3*) cover the range of temperatures 285–373 K.

Experimental Section

Materials. Carbon dioxide was prepared by treatment of sodium carbonate with a 10% aqueous solution of sulfuric acid dried with phosphorus pentoxide and liquefied in a stainless-steel

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Table I. Isotherms for Water + Carbon Dioxide System[a]

p/MPa	V/(dm^3 mol^{-1})	p/MPa	V/(dm^3 mol^{-1})	p/MPa	V/(dm^3 mol^{-1})	p/MPa	V/(dm^3 mol^{-1})
$x_1 = 0.1210$, $T = 373.15$ K							
0.962^d	3.057^d	0.825	3.647	0.735	4.109	0.603	5.038
0.961	3.115	0.794	3.797	0.709	4.263	0.589	5.156
0.931	3.219	0.761	3.963	0.685	4.416	0.573	5.306
0.860	3.494						
$x_1 = 0.1210$, $T = 398.15$ K							
2.535^d	1.385^d	1.992	1.563	1.387	2.293	0.787	4.111
2.226	1.392	1.844	1.700	1.108	2.895	0.677	4.799
2.124	1.465	1.697	1.856	0.919	3.508	0.612	5.314
$x_1 = 0.2173$, $T = 373.15$ K							
0.507^d	5.768^d	0.431	7.065	0.330	9.251	0.286	10.707
0.502	6.038	0.395	7.720	0.297	10.288	0.254	12.087
0.467	6.506						
$x_1 = 0.2173$, $T = 398.15$ K							
1.242^d	2.509^d	1.030	3.091	0.694	4.642	0.367	8.882
1.183	2.664	0.966	3.291	0.600	5.392	0.317	10.322
1.103	2.877	0.912	3.504	0.437	7.449	0.281	11.664
$x_1 = 0.2173$, $T = 423.15$ K							
2.803^d	1.160^d	1.343	2.526	0.648	5.336	0.385	9.034
2.712	1.200	1.024	3.344	0.573	6.053	0.339	10.273
1.830	1.828	0.871	3.948	0.465	7.478	0.299	11.664
$x_1 = 0.5008$, $T = 398.15$ K							
0.466^d	6.692^d	0.341	9.497	0.302	10.770	0.244	13.363
0.385	8.394	0.319	10.179	0.256	12.721	0.215	15.240
$x_1 = 0.5008$, $T = 423.15$ K							
0.942^d	3.606^d	0.461	7.443	0.309	11.247	0.246	14.112
0.585	5.869	0.412	8.376	0.262	13.262	0.233	14.921
0.522	6.577	0.332	10.460				
$x_1 = 0.5008$, $T = 448.15$ K							
1.814^d	1.982^d	0.622	5.861	0.327	11.246	0.241	15.286
1.597	2.222	0.512	7.140	0.292	12.642	0.224	16.524
1.070	3.356	0.438	8.370	0.264	14.005	0.208	17.777
0.791	4.571	0.382	9.619				
$x_1 = 0.5008$, $T = 473.15$ K							
3.350^d	1.034^d	2.756	1.287	0.846	4.539	0.381	10.207
3.304	1.055	2.343	1.557	0.666	5.800	0.336	11.581
3.132	1.120	1.768	2.086	0.552	7.021	0.308	12.672
2.981	1.183	1.510	2.473	0.436	8.922	0.279	13.972
2.859	1.238	1.194	3.151				
$x_1 = 0.7032$, $T = 423.15$ K							
0.668^d	4.978^d	0.623	5.448	0.547	6.215	0.434	7.916
0.667	5.056	0.608	5.587	0.499	6.861	0.408	8.422
0.642	5.281	0.592	5.752	0.464	7.400	0.394	8.735
$x_1 = 0.7032$, $T = 448.15$ K							
1.307^d	2.585^d	1.066	3.334	0.611	5.921	0.433	8.430
1.278	2.737	0.927	3.860	0.525	6.915	0.415	8.807
1.247	2.818	0.743	4.847	0.491	7.418		
$x_1 = 0.7032$, $T = 473.15$ K							
2.264^d	1.536^d	1.316	2.848	0.982	3.865	0.521	7.417
2.166	1.668	1.123	3.359	0.651	5.908	0.460	8.423
2.043	1.794						
$x_1 = 0.9347$, $T = 448.15$ K							
0.933^d	3.724^d						
$x_1 = 0.9347$, $T = 473.15$ K							
1.651^d	2.098^d						

[a] d = dew point.

Table II. Boiling-Point Pressures for the Water + Carbon Dioxide System

	p/MPa					
T/K	$x_1 =$ 0.9995	$x_1 =$ 0.9984	$x_1 =$ 0.9975	$x_1 =$ 0.9970	$x_1 =$ 0.9954	$x_1 =$ 0.9924
323.15	0.154	0.488	0.762	0.892	1.441	2.505
348.15	0.237				2.100	3.591
373.15	0.356				2.701	4.560
398.15	0.527	1.145	1.773	2.138	3.235	5.389
423.15	0.769	1.556	2.124	2.499	3.609	
448.15	1.197	1.977	2.596	3.037	4.080	
473.15	1.844	2.539	3.175	3.585	4.616	

Table III. Values of Second Cross Virial Coefficient

T/K	B_{12}/(dm^3 mol^{-1})	T/K	B_{12}/(dm^3 mol^{-1})
373.15	−0.215	448.15	−0.111
398.15	−0.175	473.15	−0.089
423.15	−0.135		

Table IV. Values of Henry Constants, H_p

	H_p/MPa					
	this work	others				
T/K		ref *1-3*	ref *5*	ref *6*	ref *8*	ref *12*
323.15	303.4	296.4				
348.15	449.6	442.0				
373.15	525.6	520.9			526.9	587.4
398.15	588.9					
423.15	632.8		685.8	563.4	668.7	658.6
448.15	631.9					
473.15	593.7		672.2	490.4	648.5	600.8

container. The difference between dew and boiling points was 0.003 MPa. Water used in measurements was distilled twice. The difference between dew and boiling points was 0.002 MPa.

Method of Measurements. The static method of measurements was applied as described previously (*10*). The temperature was measured with a Tinsley 5187 SA Pt resistance thermometer calibrated on IPTS-68 at the National Physical Laboratory and controlled within ±5 mK by a proportional-integrating regulator. The volumes were determined from the heights of the meniscus in the measuring tube, with the use of a U.S.S.R.-produced KM6 cathetometer offering a precision of ±0.006 mm. The measuring tube was calibrated by means of mercury with an overall accuracy of 0.09%. The pressure was measured with a Budenberg dead-weight manometer with an overall accuracy of 0.03%. Dew and boiling points were investigated separately because of very large pressure differences between these points taken for the same composition. The pressure at the appearance of the first fog (dew point) was measured in the whole concentration range. The boiling points were determined in the vicinity of pure water only (compositions of 0.992-1 mole fraction of water). The p-V isotherms were also investigated between dew points and the lowest pressure of 0.2 MPa. We also introduced a correction due to the presence of 10^{-8} mol of air in the measuring tube. The results of the measurements are presented in Tables I and II and illustrated in Figures 1 and 2.

Results

Henry Constant. The Henry constant H_p was calculated according to eq 1. Equation 1 is valid for small values of x_2

$$\ln H_p = \ln f_2^{\mathrm{v}}/x_2 - [\bar{V}_2^{\infty}(p - p_{0,1})]/RT \qquad (1)$$

for which the change of activity coefficient with mole fraction of solute can be neglected. The second term in eq 1 is the Poynting correction arising from the compression of the liquid phase. Extrapolation of $p - p_{0,1}$ to zero produces the value of the Henry constant at each temperature. The extrapolations were performed with $\bar{V}_2^{\infty} = 0.04$ dm^3 mol^{-1} (*11*). The other values of $\bar{V}_2^{\infty}$ change the slope but not the intercept. The fugacities of carbon dioxide in the vapor phase f_2^{v} were calculated from eq 2 and 3. The second cross virial coefficients

$$f_2^{\mathrm{v}} = p y_2 \Phi_2^{\mathrm{v}} \qquad (2)$$

$$\ln \Phi_2^{\mathrm{v}} = (2/V)(B_{22} y_2 + B_{12} y_1) - \ln Z \qquad (3)$$

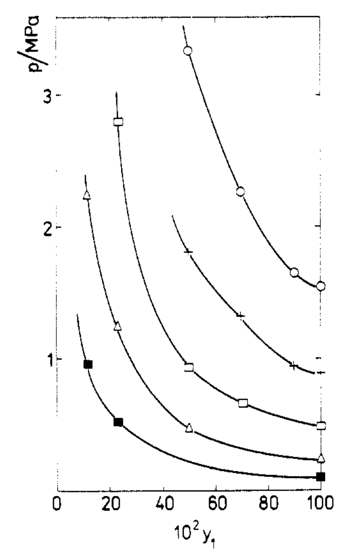

Figure 1. Isotherms of p vs. y_1 (dew points) for water + carbon dioxide system for the following temperatures (K): (■) 373.15, (△) 398.15, (□) 423.15, (+) 448.15, (○) 473.15.

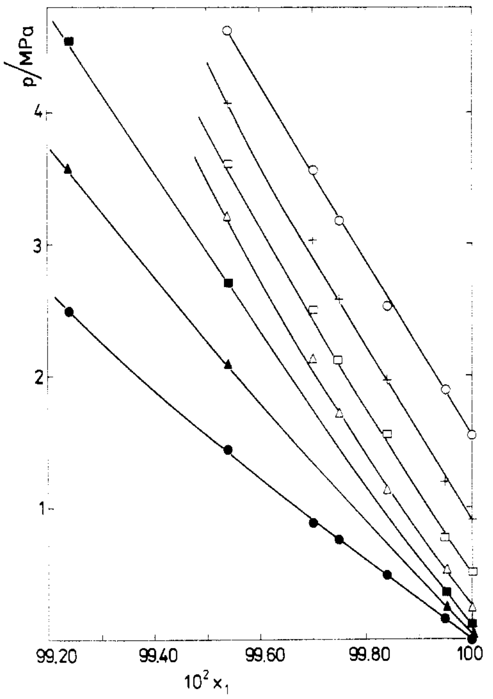

Figure 2. Isotherms of p vs. x_1 (boiling points) for water + carbon dioxide system for the following temperatures (K): (●) 323.15, (▲) 348.15, (■) 373.15, (△) 398.15, (□) 423.15, (+) 448.15, (○) 473.15.

were calculated by using the data from Table I according to eq 4. The calculated B_{12} values are given in Table III. For the

$$B_{12} = [(Z - 1)V - B_{11}y_1^2 - B_{22}y_2^2]/2y_1y_2 \qquad (4)$$

temperatures 323.15 and 348.15 K, we used the data of Coan and King (*7*). Second virial coefficients of pure substances were taken from ref *13*. The values of Henry constants calculated by means of eq 1 are given in Table IV and illustrated in Figures 3 and 4.

Discussion

Our results are in qualitative agreement with the general shape of the phase diagram for the system water + carbon dioxide. Data in the region 373–473 K were so far available only at pressures over 10 or 20 MPa as determined by Todheide and Franck (*5*) and Takenouchi and Kennedy (*6*). The plot of ln $f_2^v/x_2 - [\bar{V}^\infty(p - p_{0,1})]/RT$ vs. $p - p_{0,1}$ for pressures over 10 MPa produces some curvature which makes the extrapolation to zero pressure uncertain. Our calculations using the data for the region of pressure between 0 and 6 MPa produce the straight lines (Figure 4) which are useful for the determination of the Henry constant.

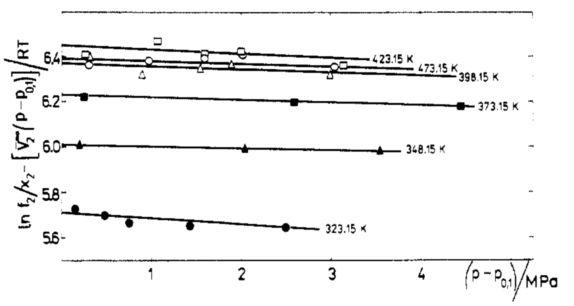

Figure 3. ln $f_2^v/x_2 - [\bar{V}_2^\infty(p - p_{0,1})]/RT$ vs. $p - p_{0,1}$ for the following temperatures (K): (●) 323.15, (▲) 348.15, (■) 373.15, (△) 398.15, (□) 423.15, (○) 473.15.

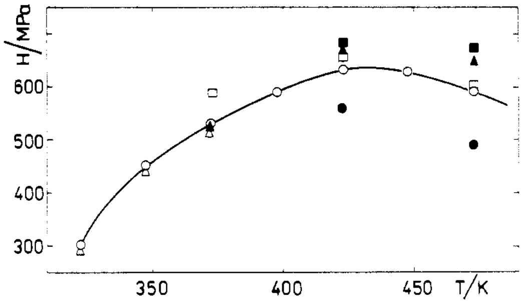

Figure 4. Henry's constant vs. temperature for the water + carbon dioxide system: (○) our data, (△) Wiebe and Gaddy (*1–3*), (■) Todheide and Franck (*5*), (●) Takenouchi and Kennedy (*6*), (▲) Ellis and Golding (*8*), (□) correlation of Heidemann and Prausnitz (*12*).

Acknowledgment

We thank Professor J. Stecki for many helpful discussions and J. Sipowska for help with the measurements.

Glossary

H_p	Henry constant, MPa
f^v	fugacity of a component in the vapor, MPa
x	mole fraction of a component in the liquid
y	mole fraction of a component in the vapor
$\bar{V}^\infty$	partial molar volume of component at infinite dilution, $dm^3\ mol^{-1}$
p	pressure of liquid and vapor in equilibrium, MPa
p_0	vapor pressure of pure component, MPa
V	volume of gas mixture, $dm^3\ mol^{-1}$
B_{12}	second cross virial coefficient in the gas mixture, $dm^3\ mol^{-1}$
B	second virial coefficient of pure component, $dm^3\ mol^{-1}$
T	temperature, K
R	gas constant, dm^3 MPa $K^{-1}\ mol^{-1}$
Z	PV/RT, compressibility factor

Greek Letters

Φ^v	fugacity coefficient of component in the vapor

Subscripts

1	water
2	carbon dioxide

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Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare-Earth Electrolyte Solutions at 25 °C. 5. $Dy(NO_3)_3$, $Ho(NO_3)_3$, and $Lu(NO_3)_3$

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The osmotic coefficients of aqueous $Dy(NO_3)_3$, $Ho(NO_3)_3$, and $Lu(NO_3)_3$ have been measured from 0.18 to 6.5–7.2 mol kg^{-1} at 25 °C with the isopiestic method. The resulting osmotic coefficients were fitted to least-squares equations, which were used to calculate water activities and mean molal activity coefficients. These data are compared to activity data for other rare-earth nitrate solutions. The lower concentration results were also fitted to Pitzer's equation.

Introduction

Activity data have been published for 14 rare-earth chlorides, 12 rare-earth perchlorates, and 9 rare-earth nitrates at 25 °C (*1–4*). The water activities of the rare-earth chlorides and perchlorates have been correlated with trends in cation hydration resulting from the lanthanide contraction (*2*). However, inner and outer sphere complexes form in rare-earth nitrate solutions, and these complexes extensively modify the hydration trends of the rare-earth cations (*5*).

In this paper isopiestic data are reported for aqueous $Dy(NO_3)_3$, $Ho(NO_3)_3$, and $Lu(NO_3)_3$ solutions. These data provide additional information about the modification of cation hydration by complex formation, and about changes in the amount of complex formation with changes in the ionic radii of the rare earths.

Experimental Section

The experimental details are nearly identical with those of the previous study (*4*). The measurements were made at 25.00 ± 0.005 °C (IPTS-68). Isopiestic equilibration times were 5–36 days, with the longer times used for lower concentrations. The isopiestic standards were $CaCl_2$ stock no. 1 and KCl; their analyses are described elsewhere (*6*). All weights were converted to mass. The molecular masses used were 348.515 g mol^{-1} for $Dy(NO_3)_3$, 350.945 g mol^{-1} for $Ho(NO_3)_3$, 360.985 g mol^{-1} for $Lu(NO_3)_3$, 110.986 g mol^{-1} for $CaCl_2$, and 74.551 g mol^{-1} for KCl.

Table I. Isopiestic Molalities of Some Rare-Earth Nitrate Solutions from Measurements with KCl Reference Solutions

$[Dy(NO_3)_3]$, m	$[Ho(NO_3)_3]$, m	$[Lu(NO_3)_3]$, m	[KCl], m	Φ(KCl)
0.185 30	0.183 87	0.181 52	0.31905	0.9047
0.192 47	0.191 02	0.188 51	0.33217	0.9041
0.301 76	0.298 55	0.293 08	0.53764	0.8986
0.315 18	0.311 75	0.305 90	0.56410	0.8982
0.413 71	0.408 73	0.399 34	0.76297	0.8968
0.517 95	0.510 46	0.498 03	0.98476	0.8972
0.527 21	0.519 43	0.506 10	1.0054	0.8974
0.597 09	0.588 11	0.571 70	1.1613	0.8985
0.677 69	0.666 63	0.646 44	1.3459	0.9005
0.755 73	0.742 80	0.718 42	1.5324	0.9031
0.841 50	0.826 77	0.796 55	1.7424	0.9065
0.936 24	0.918 68	0.882 53	1.9811	0.9110
1.045 7	1.025 4	0.981 31	2.2650	0.9169
1.068 9	1.049 2	1.003 4	2.3282	0.9183

The rare-earth nitrate solutions were prepared from pure rare-earth oxides and nitric acid and were adjusted to their equivalence concentrations. The stock solutions were analyzed by EDTA and the gravimetric sulfate method, and the concentrations were measured to at least 0.1%.

Duplicate samples were used in the equilibrations. The average molalities are known to at least ±0.1% above 0.3 mol kg^{-1} and better than 0.15% at lower concentrations. However, most equilibrations were to ±0.05% or better. The molalities at isopiestic equilibrium are reported in Tables I and II.

The higher rare-earth nitrate concentrations are for supersaturated solutions (*5*). $Dy(NO_3)_3$ was the only salt that had crystallization problems at the highest concentrations; consequently two of its points are based on single samples. After each high-concentration equilibration, the isopiestic cups were carefully examined to verify the absence of crystals.

The presence of a small amount of nitrite ions in the rare-earth nitrate solutions was indicated by a positive "brown ring" test. The rare-earth nitrate solutions were heated during their preparation from rare-earth oxides and nitric acid. Thus, any nitrite or nitrogen oxides in the nitric acid should have been decomposed or expelled. Consequently, any nitrite in the final solution was formed after preparation.

A 4.4551 mol kg^{-1} $La(NO_3)_3$ solution, prepared several years ago, was studied further. Each nitrate ion decomposing to nitrite consumes two hydrogen ions, so pH changes will result. The

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