J. Chem. Eng. Data **1988**, *33*, 477-479 **477**

Isopiestic Measurements of the Osmotic and Activity Coefficients for the System $NaClO_4–Ba(ClO_4)_2–H_2O$ at 25 °C

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Isopiestic measurements of the osmotic coefficients are presented for the system $NaClO_4–Ba(ClO_4)_2–H_2O$. Parameters obtained from these results are used to calculate values of the osmotic and activity coefficients of each component.

This paper is the fourth in a series on the Gibbs energies of mixed perchlorate solutions. The first paper (*1*) reported the results of isopiestic measurements on mixtures of univalent perchlorates. The second paper (*2*) reported the results of isopiestic measurements of $HClO_4$ and $NaClO_4$ with $UO_2(ClO_4)_2$. The third paper (*3*) presented the results of such measurements on mixtures of $HClO_4$ and $Ba(ClO_4)_2$. This paper presents the results for mixtures of $NaClO_4$ and $Ba(ClO_4)_2$.

Experimental Section

The experimental work described in this paper was performed in 1970. The delay in analysis and presentation of the results was caused by a change in work assignment for the author.

Materials. The stock solutions of H_2SO_4, NaCl, and $Ba(ClO_4)_2$ were the same as described previously (*3*).

The stock solution of $NaClO_4$ was prepared by neutralizing concentrated reagent grade $HClO_4$ with solid reagent grade NaOH to a pH of 4.5. The solution was analyzed by evaporation of a sample to dryness, heating at 110 °C, and weighing as $NaClO_4$. Analysis by dilution, measurement of the density to 5 parts in 100 000, and comparison with the data of Wirth et al. (*4*) gave a molality 0.02% lower than that obtained by evaporation to dryness. The concentration was monitored by measuring the density to 5 parts in 100 000. The maximum change in molality from the value used previously as indicated by these measurements was 0.04% over the course of these experiments.

Solutions of the various perchlorate mixtures were prepared by weight from the above solutions. Distilled water, passed through a mixed-bed ion-exchange column, was used for the preparation of all solutions.

Apparatus and Procedure. The apparatus and procedure have been described previously (*5*). The temperature of the bath varied 0.02 °C or less during the course of an equilibration. The temperature of the bath at equilibrium varied from one equilibration run to another within the range of 24.99–25.00 °C.

Following the weighing of the 12 dishes, the first dish was weighed again; the difference between the two weighings was less than 0.02% of the weight of the solution.

For each set of equilibrations there were at least two dishes containing the same solution. The maximum difference in concentration among the replicate dishes was 0.11%.

The reference material was NaCl up to the limit of its solubility and H_2SO_4 for higher concentrations. The osmotic coefficients for these electrolytes were taken from the tables given by Robinson and Stokes (*6*). The values used for the osmotic coefficient of NaCl differ from those derived from the results of Gibbard et al. (*7*) with an average deviation without regard to sign of 0.0012 and a maximum deviation of 0.0021. The values used for the osmotic coefficient of H_2SO_4 differ from those derived from the report of Staples (*8*) with an average deviation without regard to sign of 0.0045 and a maximum deviation of 0.0077.

Table I. Isopiestic Concentrations and Osmotic Coefficients for $NaClO_4$ with H_2SO_4 as Reference Material

	$NaClO_4$	
m_{ref}, mol/kg	m, mol/kg	ϕ_{obsd}
7.4910	14.881	1.2346
7.3146	14.401	1.2298
6.4418	12.124	1.1989
6.0946	11.244	1.1852
5.2655	9.2380	1.1476
4.6265	7.7710	1.1122
4.1682	6.7725	1.0856
3.4156	5.2200	1.0375
3.1322	4.6705	1.0177
2.3958	3.3224	0.9747
2.3468	3.2391	0.9717
1.6856	2.1569	0.9421
1.2040	1.4516	0.9259

Table II. Isopiestic Concentrations and Osmotic Coefficients for the System $NaClO_4$ (A)–$Ba(ClO_4)_2$ (B)–H_2O with NaCl as Reference Material

m_{ref}, mol/kg	I, mol/kg	y_B	ϕ_{obsd}
4.8791	6.0333	0.2491	1.0919
	6.6347	0.4993	1.1585
	7.3716	0.7515	1.2533
4.2605	5.2115	0.2491	1.0600
	5.7635	0.4993	1.1183
	6.4494	0.7515	1.2012
3.1778	3.8171	0.2491	1.0052
	4.2735	0.4993	1.0476
	4.8551	0.7515	1.1083
2.2088	2.6139	0.2491	0.9607
	2.9676	0.4993	0.9873
	3.4315	0.7515	1.0262
1.4716	1.7246	0.2491	0.9308
	1.9830	0.4993	0.9445
	2.3328	0.7515	0.9650
0.9848	1.1476	0.2491	0.9164
	1.3328	0.4993	0.9206
	1.5895	0.7515	0.9278
0.6688	0.7766	0.2491	0.9099
	0.9084	0.4993	0.9075
	1.0940	0.7515	0.9057

Results

The concentrations at isopiestic equilibrium and the observed osmotic coefficients are given in Tables I–III. Concentrations are given as molality, m, and ionic strength on the molality scale, I. The composition of the mixtures is given as the fraction of ionic strength contributed by $Ba(ClO_4)_2$, y_B. The observed osmotic coefficients, ϕ_{obsd}, were calculated from the isopiestic concentrations and the osmotic coefficients of the reference materials noted above. All reported values are the average of duplicate measurements.

Treatment of Results

The results were analyzed by using the neutral-electrolyte treatment. This approach is based on Scatchard's 1961 paper (*9*) and was discussed in our previous publications (*1*, *2*) and

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Table III. Isopiestic Concentrations and Osmotic Coefficients for the System $NaClO_4$ (A)–$Ba(ClO_4)_2$ (B)–H_2O with H_2SO_4 as Reference Material

m_{ref}, mol/kg	I, mol/kg	y_B	ϕ_{obsd}
7.4910	15.777	0.2491	1.3301
	16.728	0.4993	1.4636
	17.811	0.7515	1.6523
7.3146	15.259	0.2491	1.3258
	16.217	0.4993	1.4555
	17.286	0.7515	1.6413
6.4418	12.926	0.2491	1.2845
	13.800	0.4993	1.4037
	14.817	0.7515	1.5714
6.0946	11.996	0.2491	1.2690
	12.855	0.4993	1.3816
	13.846	0.7515	1.5418
5.2655	9.9255	0.2491	1.2201
	10.701	0.4993	1.3204
	11.621	0.7515	1.4613
4.6265	8.3835	0.2491	1.1776
	9.1025	0.4993	1.2654
	9.9636	0.7515	1.3895
4.1682	7.3457	0.2491	1.1432
	8.0123	0.4993	1.2229
	8.8230	0.7515	1.3348
3.4156	5.7035	0.2491	1.0847
	6.2875	0.4993	1.1480
	7.0077	0.7515	1.2380
3.1322	5.1255	0.2491	1.0593
	5.6711	0.4993	1.1170
	6.3538	0.7515	1.1984
2.3958	3.6819	0.2491	1.0046
	4.1293	0.4993	1.0451
	4.7006	0.7515	1.1035
2.3468	3.5946	0.2491	1.0001
	4.0332	0.4993	1.0400
	4.5970	0.7515	1.0967
1.6856	2.4186	0.2491	0.9597
	2.7539	0.4993	0.9834
	3.1964	0.7515	1.0184
1.2040	1.6413	0.2491	0.9353
	1.8907	0.4993	0.9474
	2.2291	0.7515	0.9658

Table IV. Parameters for the Two-Component Systems

	$NaClO_4$[a]	$Ba(ClO_4)_2$[b]
a	1.5	1.673
$a(1)$	0.00894	0.04414
$a(2)$	0.01102	0.004816
$a(3)$	−0.000950	−0.000356
$a(4)$	0.0000236	0.0000070
$\sigma(\phi)$	0.0030	0.0033
max I, mol/kg	17.9	19.0

[a] Taken from Table VII of ref *1*. [b] Taken from Table VI of ref *3*.

Table V. Parameters for the Three-Component System $NaClO_4$–$Ba(ClO_4)_2$–H_2O

$b(01)$	0.03061	$b(12)$	−0.000780
$b(02)$	−0.003033	$b(13)$	0.0000507
$b(03)$	0.0000831	$\sigma(\phi)$	0.0022

Table VI. Values of the Osmotic and Activity Coefficients for the System $NaClO_4$ (A)–$Ba(ClO_4)_2$ (B)–H_2O

			log $\gamma_\pm$	
I, mol/kg	y_B	ϕ	A	B
1.0	0.0	0.9167	−0.1962	−0.3479
	0.2	0.9153	−0.1929	−0.3462
	0.4	0.9123	−0.1895	−0.3444
	0.6	0.9068	−0.1861	−0.3427
	0.8	0.8976	−0.1827	−0.3410
	1.0	0.8823	−0.1792	−0.3392
2.0	0.0	0.9364	−0.2104	−0.3473
	0.2	0.9416	−0.2051	−0.3459
	0.4	0.9458	−0.1997	−0.3444
	0.6	0.9485	−0.1941	−0.3428
	0.8	0.9486	−0.1884	−0.3413
	1.0	0.9444	−0.1825	−0.3396
4.0	0.0	0.9939	−0.1972	−0.2779
	0.2	1.0106	−0.1897	−0.2780
	0.4	1.0284	−0.1815	−0.2779
	0.6	1.0470	−0.1727	−0.2777
	0.8	1.0662	−0.1633	−0.2773
	1.0	1.0854	−0.1532	−0.2767
6.0	0.0	1.0583	−0.1651	−0.1818
	0.2	1.0851	−0.1562	−0.1832
	0.4	1.1154	−0.1461	−0.1843
	0.6	1.1498	−0.1348	−0.1852
	0.8	1.1887	−0.1222	−0.1855
	1.0	1.2334	−0.1081	−0.1852
8.0	0.0	1.1182	−0.1281	−0.0828
	0.2	1.1541	−0.1181	−0.0841
	0.4	1.1966	−0.1063	−0.0853
	0.6	1.2466	−0.0926	−0.0860
	0.8	1.3062	−0.0767	−0.0857
	1.0	1.3786	−0.0585	−0.0843
12.0	0.0	1.2020	−0.0633	0.0891
	0.2	1.2554	−0.0499	0.0928
	0.4	1.3208	−0.0340	0.0961
	0.6	1.4015	−0.0148	0.1003
	0.8	1.5031	0.0082	0.1065
	1.0	1.6358	0.0357	0.1160
16.0	0.0	1.2455	−0.0164	0.2249
	0.2	1.3158	0.0017	0.2365
	0.4	1.4002	0.0220	0.2461
	0.6	1.5053	0.0460	0.2567
	0.8	1.6423	0.0751	0.2712
	1.0	1.8309	0.1108	0.2924

also in publications describing other results obtained in this laboratory (*10*, *11*). In this approach the concentration is expressed in terms of the ionic strength fraction of the component electrolytes ($NaClO_4$ and $Ba(ClO_4)_2$) and the total ionic strength of the mixture. The excess free energy is expressed as a sum of contributions from the limiting two-component systems and a contribution from the three-component system. Equations for the osmotic coefficient and the activity coefficients are obtained by appropriate differentiation of the excess free energy equation. The resulting equations are given in the initial paper in this series (*1*). The value used for the Debye–Hückel limiting slope (S) was −1.17082.

Discussion

***NaClO*$_4$.** Solutions of $NaClO_4$ alone were included in several of the equilibration runs as a check on previous results. The results are shown in Table I. The parameters for $NaClO_4$ derived from earlier investigations (*1*) are given in Table IV. Comparison of the observed osmotic coefficients shown in Table I with values calculated by using the parameters in Table IV gives an average deviation without regard to sign of 0.0022 and a maximum deviation of 0.0050. This was considered sufficiently close agreement to warrant the use of the earlier parameters (Table IV) without modification.

***Ba(ClO*$_4$*)*$_2$.** The parameters for $Ba(ClO_4)_2$ derived from the previous investigation (*3*) are given in Table IV. No additional observations were made as a part of this investigation.

***NaClO*$_4$*–Ba(ClO*$_4$*)*$_2$ *Mixtures*.** Values for the b parameters for this three-component system are given in Table V. The parameters were obtained by a least-squares fit to all the data (Tables II and III). Fits to the data were obtained by using fewer than five b parameters; in all cases the standard deviation was significantly higher.

As with previous systems investigated, it is apparent that the equations given by Scatchard provide an adequate and convenient means of representing the osmotic coefficients of three-component mixtures. The Scatchard equations also provide a simple method for calculating the activity coefficients that is not dependent on an integration to zero concentration, as is the case with the McKay–Perring method (*12*). Values for the osmotic coefficient and the activity coefficients for various mixture compositions are given in Table VI.

Acknowledgment

The author expresses his deep appreciation to J. S. Johnson, Jr., for invaluable advice and patient understanding. He also expresses his appreciation to Donna C. Michelson for valuable technical assistance.

Glossary

A	symbols subscripted A refer to $NaClO_4$
B	symbols subscripted B refer to $Ba(ClO_4)_2$
m	molal concentration, mol/kg
I	total ionic strength, mol/kg
y	ionic strength fraction
ϕ	molal osmotic coefficient
$\gamma_\pm$	mean molal activity coefficient
$a(n)$	parameters (n = 1-4) in Scatchard equations for single electrolytes, see ref *1*
$b(pq)$	parameters (pq = 01, 02, 03, 12, 13) in Scatchard equations for electrolyte mixtures, see ref *1*
$\sigma(\phi)$	standard deviation for osmotic coefficients

Registry No. $NaClO_4$, 7601-89-0; $Ba(ClO_4)_2$, 13465-95-7.

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Received for review November 30, 1987. Accepted March 26, 1988. Research sponsored by the U.S. Department of Energy under Contract No. DE-AC-05-84OR21400 with Martin Marietta Energy Systems, Inc.

Binary Gaseous Diffusion Coefficients. 7. Tetrachloroethene and 1,1,1-Trichloroethane with Methane and Tetrafluoromethane at 100 kPa and 283–343 K

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Binary gaseous diffusion coefficients D_{12} for tetrachloroethene diffusing in methane and tetrafluoromethane and for 1,1,1-trichloroethane diffusing in tetrafluoromethane were measured at about 283, 298, 313, 328, and 343 K and at 100 kPa by the capillary-tube method of Stefan. In addition, D_{12} for tetrachloromethane in methane and in tetrafluoromethane were determined at 283 and 298 K, respectively. The experimental results are compared with diffusion coefficients calculated via the first-order Chapman–Enskog approximation. For the gases, effective Lennard-Jones [6,12] pair potential parameters were taken from recent literature; for the heavy chlorinated hydrocarbons the parameters were obtained from semitheoretical extended-corresponding-states correlations. Agreement is satisfactory throughout.

Introduction

The measurements reported in this paper are a sequel to our recent study of diffusion in air of chlorinated hydrocarbons of practical, industrial importance (*1*), and continue our systematic investigations of binary gaseous diffusion coefficients D_{12} via the Stefan capillary-tube method (*1–6*). Specifically, we now report D_{12} of tetrachloroethene (C_2Cl_4) diffusing in methane (CH_4) and tetrafluoromethane (CF_4) and of 1,1,1-trichloroethane (1,1,1-$C_2H_3Cl_3$) diffusing in tetrafluoromethane. All experiments were conducted at atmospheric pressure in the temperature range 283–343 K. In addition, D_{12} was determined for tetrachloromethane (CCl_4) diffusing in methane at 283 K and in tetrafluoromethane at 298 K, respectively. The results are compared with diffusion coefficients calculated via the first-order Chapman–Enskog approximation (*7*, *8*) in conjunction with effective pair-potential parameters from two popular extended-corresponding-states correlations (*1*, *6*, *9*, *10*).

Experimental Section

The apparatus and procedure for measurements by the capillary-tube method have been described in detail in our earlier papers (*1–6*). Each solvent/gas pair was run in duplicate at a pressure of approximately 100 kPa at 283, 298, 313, 328, and 343 K, with the exception of CCl_4/CH_4 and CCl_4/CF_4, which were investigated only at 283 and 298 K, respectively. Temperature was controlled to better than ±0.01 K over the entire measurement periods and was measured with a calibrated platinum resistance thermometer on IPTS-68. The total system pressure was controlled to better than ±0.5 kPa by a mercu-

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0021-9568/88/1733-0479$01.50/0