Osmotic Coefficients of Aqueous Solutions of NaBr, NaI, KF, and $CaCl_2$ Between 0° and 90°C

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New data are reported on the osmotic coefficients of aqueous solutions of NaBr, NaI, KF, and $CaCl_2$ over a broad temperature range at moderate to high concentrations. Nonlinear least-square fits, suitable for interpolation, or (in favorable cases) modest extrapolation, are given. These empirical fits are compared with similar ones to literature data which have previously been reported for NaCl, KCl, CsCl, and Na_2SO_4 solutions.

In connection with our program for determining solvent isotope effects on the thermodynamic properties of selected aqueous solutions (*7, 26*), it was necessary to determine the vapor pressure lowering of H_2O solutions of a series of common electrolytes over broad temperature and concentration ranges (moderate to high concentration solutions). The ultimate application of the isotope effect data will be to test certain theories about the structure of aqueous solutions via the pathway of cell model calculations for the condensed phase. However, we feel that the measurements of the osmotic coefficients themselves are of sufficient intrinsic interest to warrant reporting.

There is a surprising lack of data on the thermodynamic activity of water solutions at temperatures other than 25°C. For example, a standard reference in the field [Robinson and Stokes (*28*)] quotes very little data except at 25°C, and even there the data are mostly limited to concentrations below those which are in isopiestic equilibrium with nearly saturated sodium chloride solutions (6*m*). Isopiestic measurements at high concentration are possible by using $CaCl_2$ (*37*) or H_2SO_4 reference solutions (*30, 36*) at lower water activity, but there are not a large number of studies in the very high concentration region. In the moderate to high concentration region and between room temperature and one to several hundred degrees, Soldano and coworkers (*24, 33, 34*) and Caramazza (*4, 5*) among others, most recently Braunstein and Braunstein (*3*), have reported data on a number of different salt solutions. The available data for solutions of NaCl, KCl, CsCl, and LiCl (*26*) and on Na_2SO_4 (*6*) have been summarized by Pupezin et al. (*26*) and by Chan (*6*). These authors report nonlinear least-square fits suitable for interpolation and/or modest extrapolation. Their empirical equations are quoted in Table II. In the present paper we report new measurements on the systems NaBr, NaI, KF, and $CaCl_2$. Our interest throughout is restricted to concentrations above about 1*m*, and in the temperature range between 0° and 90°C.

EXPERIMENTAL

The measurements were made on our differential vapor pressure apparatus which has already been described (*16, 27*). In this apparatus the samples are held in a large copper block thermostated to ±0.001°C at any desired temperature between −15° and 100°C. The pressure difference between the two samples is measured with a differential capacitance manometer (Datametrics, Inc., Watertown, MA) to four-figure precision, temperature by resistance thermometery using a Leeds and Northrup G-2 Mueller bridge. The maximum pressure difference which can be allowed in our apparatus is 100 torr. The limiting factor on pressure measurements in the apparatus is neither the pressure measurement itself, nor the temperature control, but rather the precise history of how each individual sample is handled. Thus, it is necessary to take elaborate precautions to degas the samples properly before each run, and it is equally important to avoid the formation of any spurious condensate drops in any portion of the apparatus except the bottom of the sample cell itself (parasitic condensation). We have observed that the data obtained with salt solutions are superior to those obtained on the pure solvents. In our opinion this is due to the drying action of the saline solutions which efficiently remove parasitic microdrops from the (hotter) upper surface of the sample cell and the connecting lines.

The majority of the data reported here were obtained by measuring the differential pressure developed between the solution of stated concentration and pure H_2O, but sometimes for the more concentrated solutions, we have elected to determine differential pressures between solutions of different concentrations with an ultimate reference to pure water. This technique was necessary because our maximum pressure difference of 100 torr would be exceeded when comparing high concentration solutions at high temperatures with pure water.

The salts used in this study were reagent-grade materials recrystallized and then exhaustively dried under vacuum to constant weight. The excellent agreement with earlier workers seems to indicate that this was sufficient except for $CaCl_2$ where we apparently have a small amount of residual water (0.2 wt %, see below). The solutions were made up gravimetrically with doubly distilled water. A sample of the same water was used in the reference side of the apparatus.

RESULTS

The original object was to obtain interpolative equations to determine solution vapor pressures which, in turn, are combined with measurements of isotopic pressure difference ($P_{H_2O} - P_{D_2O}$) to give the desired isotopic pressure ratios P_H/P_D. The requirement on accuracy and precision here translates to ±0.01 or even 0.02 on ϕ, the osmotic coefficient, over most of the range of interest. We have therefore not made the elaborate precautions necessary to determine osmotic coefficients to ±0.001 or better. Nonetheless, comparison of the present data with literature data (where available) and tests of our data for internal consistency and precision allow us to place uncertainty limits of 0.005–0.01 ϕ unit on most of the data reported in this paper except at the highest concentrations *and* lowest temperatures where the uncertainty may be larger.

We have chosen to report the data directly in terms of the

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Table I. Experimental Osmotic Coefficients of Some Aqueous Salt Solutions

Sodium Bromide

$2m$[a]

t_m, °C[b]	$P^\circ - P_{2m}$	ϕ_{2m}
19.45$_5$	1.209	1.026
24.49$_5$	1.673	1.043
34.79$_2$	2.999	1.033
39.78$_3$	3.954	1.038
44.78$_0$	5.142	1.038
49.95$_0$	6.674	1.037
54.97$_0$	8.565	1.041
60.11$_1$	10.97	1.046
64.08$_2$	13.10	1.042
69.21$_5$	16.52	1.047
73.98$_5$	20.28	1.047
78.66$_1$	24.64	1.046
83.44$_5$	30.09	1.053
88.91$_7$	37.27	1.053

$7m$

t_m, °C	$P^\circ - P_{7m}$	ϕ_{7m}
−0.48$_8$	1.355	1.451
1.09$_7$	1.528	1.459
3.65$_9$	1.835	1.461
7.78$_2$	2.444	1.461
10.95$_1$	3.040	1.470
15.98$_9$	4.228	1.472
21.34$_0$	5.924	1.476
29.63$_0$	9.719	1.479
34.80$_2$	12.99	1.476
40.13$_0$	17.40	1.480
44.90$_6$	22.34	1.480
50.24$_0$	29.22	1.477
54.89$_8$	36.65	1.476
63.37$_4$	54.22	1.469
69.29$_5$	70.40	1.465
74.12$_6$	86.34	1.460
77.51$_3$	99.34	1.458
35.0[d]		1.495
45.0		1.485
55.0		1.480
65.0		1.473
75.0		1.463
85.0		1.447
95.0		1.426

$5m$

t_m, °C	$P^\circ - P_{5m}$	ϕ_{5m}
49.95$_4$	19.53	1.314
59.86$_9$	31.40	1.312
69.21$_3$	47.81	1.312
78.62$_8$	71.03	1.308
19.87$_1$	3.585	1.279
29.85$_7$	6.544	1.287
39.80$_3$	11.42	1.294
51.54$_2$	21.01	1.306
54.95$_0$	24.78	1.305
59.93$_5$	31.37	1.306
69.20$_0$	47.55	1.304
74.07$_1$	58.58	1.304
79.04$_4$	71.82	1.299
83.77$_1$	86.81	1.298
87.10$_8$	99.13	1.297
1.0[c]		1.267
11.0		1.282
21.0		1.294
31.0		1.302
41.0		1.308
51.0		1.311
61.0		1.310
71.0		1.306
81.0		1.299
91.0		1.288
101.0		1.273

$5m$ vs. $7m$

t_m, °C	$P_{5m} - P_{7m}$
0.15$_3$	0.478
4.18$_3$	0.637
8.01$_7$	0.832
11.55$_1$	1.052
15.46$_2$	1.357
19.56$_5$	1.755
19.74$_8$	1.781
29.58$_4$	3.170
39.54$_7$	5.476
48.82$_0$	8.799
58.54$_9$	14.01
69.12$_0$	22.43
78.49$_3$	33.03
88.74$_9$	49.15

Sodium Iodide

$4m$[a]

t, °C	$P^\circ - P_{4m}$	ϕ_{4m}
1.00$_2$	0.887	1.378
3.79$_6$	1.068	1.357
8.26$_4$	1.434	1.335
12.10$_7$	1.841	1.324
15.32$_6$	2.257	1.316
19.75$_5$	2.954	1.300
29.43$_5$	5.290	1.304
39.74$_6$	9.438	1.313
48.84$_3$	15.23	1.324
59.81$_0$	26.01	1.333
69.16$_3$	39.80	1.339
78.53$_2$	59.30	1.342
88.79$_6$	89.27	1.344

t, °C	ϕ_{8m}[e]	ϕ_{10m}[f]
0	1.831	2.124
5	1.805	2.081
10	1.787	2.050
15	1.776	2.027
20	1.770	2.010
25	1.768	1.998

$4m$[a] *(contd)*

t, °C	ϕ_{8m}[e]	ϕ_{10m}[f]
30	1.767	1.989
35	1.768	1.981
40	1.769	1.975
45	1.770	1.969
50	1.771	1.963
55	1.772	1.957
60	1.771	1.950
65	1.770	1.943
70	1.767	1.935
75	1.764	1.926
80	1.759	1.917
85	1.754	1.908
90	1.748	1.898

$8m$

t, °C	$P_{4m} - P_{8m}$
−0.21$_7$	1.031
3.83$_6$	1.380
8.13$_1$	1.855
11.72$_9$	2.357
15.42$_7$	2.997
19.61$_5$	3.902
29.66$_3$	7.106
39.61$_8$	12.32
49.86$_4$	20.86
59.85$_3$	33.41
69.16$_1$	50.51
78.56$_9$	74.68
85.07$_2$	96.43

$10m$

t, °C	$P_{8m} - P_{10m}$
1.07$_9$	0.613
4.24$_7$	0.759
8.23$_8$	0.986
11.82$_3$	1.234
15.45$_6$	1.547
19.73$_1$	1.989

$10m$ *(contd)*

t, °C	$P_{8m} - P_{10m}$
29.53$_4$	3.482
39.64$_5$	5.967
49.87$_5$	9.896
59.95$_0$	15.59
69.24$_4$	23.31
78.65$_0$	34.13
88.49$_8$	49.61

Potassium Fluoride

$3m$[a]

t, °C	$P^\circ - P_{3m}$	ϕ_{3m}
3.40$_4$	0.612	1.023
11.68$_1$	1.096	1.041
15.68$_1$	1.438	1.053
19.65$_9$	1.840	1.048
29.66$_1$	3.351	1.049
39.71$_1$	5.864	1.050
44.69$_9$	7.631	1.052
49.82$_9$	9.889	1.051
59.77$_1$	15.76	1.037
69.12$_4$	23.87	1.030
78.51$_8$	35.44	1.027

$6m$

t, °C	$P^\circ - P_{6m}$	ϕ_{6m}
3.90$_0$	1.456	1.272
8.03$_8$	1.947	1.277
11.59$_9$	2.479	1.281
15.56$_3$	3.210	1.281
19.68$_6$	4.166	1.282
29.72$_4$	7.557	1.275
39.78$_3$	13.10	1.263
44.59$_6$	16.83	1.259
49.90$_0$	21.89	1.251
59.87$_4$	34.87	1.231
69.17$_9$	52.40	1.215
74.04$_4$	63.99	1.202
78.62$_0$	77.03	1.196
84.18$_2$	95.55	1.184

$9m$

t, °C	$P^\circ - P_{9m}$	ϕ_{9m}
19.933	7.237	1.648[g]
24.681	9.511	1.614[g]
29.621	12.49	1.578[g]
34.585	16.31	1.550[g]
39.569	21.17	1.527
44.689	27.40	1.506
49.880	35.26	1.485
54.902	44.60	1.466
59.972	56.06	1.446
66.633	74.78	1.420
69.821	85.43	1.408
73.091	97.90	1.401

$12m$

t, °C	$P^\circ - P_{12m}$	ϕ_{12m}
19.49$_8$	9.368	1.851[g]
24.58$_3$	12.59	1.811[g]
29.68$_3$	16.77	1.779[g]
34.69$_8$	22.06	1.751[g]
39.70$_9$	28.66	1.723
44.67$_6$	36.81	1.695
50.01$_2$	47.65	1.666
54.85$_4$	59.77	1.642
59.80$_4$	74.67	1.616
64.07$_5$	89.97	1.595
66.61$_7$	100.42	1.586

Calcium Chloride

2.957$_3m$[a,h]

t, °C	$P^\circ - P_{2.9573}$	$\phi_{2.9573}$
23.98$_1$	5.510	1.769
29.60$_9$	7.621	1.755
34.64$_9$	10.04	1.736
39.78$_8$	13.20	1.723
44.91$_5$	17.10	1.704
49.91$_9$	21.92	1.694
55.26$_2$	28.15	1.673
59.87$_0$	34.72	1.658
64.11$_4$	41.68	1.636
69.19$_8$	51.81	1.621
74.04$_8$	63.37	1.609
78.68$_4$	76.10	1.590

t, °C	$P_{7.8767}$[i]	$\phi_{7.8767}$
21.816	5.343	3.051
26.132	7.071	3.002
29.917	8.994	2.954
35.318	12.50	2.895
39.921	16.39	2.844
45.028	21.93	2.787
50.844	30.23	2.720
55.457	38.60	2.671
60.138	49.09	2.622
64.503	61.04	2.577
68.511	74.07	2.538
68.471	73.99	2.536
72.605	89.69	2.502

t, °C	$P_{2.9573} - P_{5.4185}$
19.70$_2$	5.241
24.78$_3$	7.054
29.76$_3$	9.317
34.86$_4$	12.25
40.23$_1$	16.16

t, °C	$\phi_{5.4185}$[j]
21	2.739
26	2.692
31	2.648
36	2.605
41	2.563

(Continued on next page)

Table I. *(Continued)*

2.9573*m*[a,h] *(contd)*			
t, °C	$P_{2.9573} - P_{5.4185}$	*t*, °C	$\phi_{5.4185}$[j]
45.13_1	20.63	46	2.522
50.09_6	26.14	51	2.480
55.16_0	33.01	56	2.439
60.36_1	41.52	61	2.397
64.38_7	49.23	66	2.355
69.32_2	60.37	71	2.313
74.13_5	73.14	76	2.269
79.99_2	91.25	81	2.226
		86	2.182
		91	2.137
		96	2.093
		101	2.048

t, °C	$P_{5.4185} - P_{7.8767}$	*t*, °C	$\phi_{7.8767}$[k]
24.77_4	4.176	26	3.010
29.84_7	5.517	31	2.944
34.71_0	7.197	36	2.884
39.72_1	9.448	41	2.830
45.07_8	12.38	46	2.778
50.17_3	15.93	51	2.727
54.91_6	19.94	56	2.676
59.88_6	25.09	61	2.626
64.16_0	30.36	66	2.576
69.24_5	37.80	71	2.525
74.03_6	46.13	76	2.474
78.92_6	56.15	81	2.423
83.76_1	67.86	86	2.372
88.92_9	82.36	91	2.322
		96	2.272
		101	2.222

[a] All concentrations reported ±0.0002. [b] 1968 IPTS. [c] Points from here down calculated from smoothed $(P^\circ - P_{7m})$ and $(P_{5m} - P_{7m})$ at rounded temperatures. [d] Points from here down calculated from smoothed $(P^\circ - P_{5m})$ and $(P_{5m} - P_{7m})$ at rounded temperatures. [e] These points calculated from smoothed $(P^\circ - P_{4m})$ and $(P_{4m} - P_{8m})$ points. [f] These points calculated from smoothed $(P^\circ - P_{4m})$, $(P_{4m} - P_{8m})$, and $(P_{8m} - P_{10m})$ at rounded temperatures. [g] These points not included in least squaring as per text. [h] Concentration is corrected as per text. Solutions had nominal concentrations of 3.0, 5.5, and 8.0*m*. [i] Data reported in this run referenced to vacuum. [j] These points calculated from smoothed $(P^\circ - P_{2.9573})$ and $(P_{2.9573} - P_{5.4185})$ at rounded temperatures. [k] These points calculated from $(P^\circ - P_{2.9573})$, $(P_{2.9573} - P_{5.4185})$, and $(P_{5.4185} - P_{7.8768})$ at rounded temperatures.

observed pressure differences together with the associated temperatures [1968 scale (*2*, *8*)], and finally the osmotic coefficients as calculated from the data points themselves (Table I). To convert the observed pressure differences to the osmotic coefficients, it is necessary to know the pressure of the reference. In the cases where the reference was water itself, we have used the equation given by Goff (*11*) to obtain the absolute vapor pressure of H_2O from the temperature. The Goff equation,

$$P_{H_2O}(\text{mm}) = 760 \exp 2.302585 \left\{ 10.79586 \left(1 - \frac{273.16}{T}\right) - 5.02808 \log \frac{T}{273.16} + 1.5047 \times 10^{-4} \left[1 - \exp 19.10436 \times \left(1 - \frac{T}{273.16}\right)\right] + 0.42873 \times 10^{-3} \left\{ \exp \left[10.98229 \times \left(1 - \frac{273.16}{T}\right)\right] - 1 \right\} - 2.2195983 \right\} \quad (1)$$

was selected because of the excellent agreement between its predictions and the recent high precision data of Stimson (*35*) between 25° and 100°C. Since our original work-up of this data, Wexler and Greenspan (*41*) have suggested a new and improved equation which would have served equally well. Below 100°C the osmotic coefficient is given to sufficient precision by Equation 2:

$$\phi = \frac{-55.508}{\nu m} \left[\ln \frac{P}{P^\circ} + \frac{B(T)}{RT}(P - P^\circ) + \frac{\bar{V}_1}{RT}(P^\circ - P) \right] \quad (2)$$

Here ν is the number of ions per formula, m is the molality, P and P° are the solution and solvent pressures, respectively, and $B(T)$ is the second virial coefficient of the vapor. $B(T)$ was evaluated from the relationship obtained by Keyes (*17*) as quoted by Eisenberg and Kauzmann (*9*), P° from Equation 1, and P from the relationship, $P^\circ - P = \Delta P$. The last term in Equation 2 is negligibly small for aqueous solutions below 100°C but was approximated using 0.018 liter for $\bar{V}_1$, the partial molal volume of the solvent condensed phase. In those cases where the pressures over a solution of concentration c_x were being compared with those at c_y (followed with a comparison between c_y and c_0), we fitted the raw data $P^\circ - P_y$ and $P_x - P_y$ with empirical least-square relationships of the form:

$$\ln (P_x - P_y) = A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3} \quad (3)$$

finally combining the parameters for the different runs to obtain a value of $P^\circ - P_x$ at each experimental temperature. This method, of course, has the drawback of accumulating errors, but this is perhaps offset by the advantage of being able to measure samples at high concentrations and high temperatures. On the other hand, as we gained experience, we found generally smooth temperature coefficients and in most of the later measurements elected to reference against pure solvent and stop the measurements at a somewhat lower temperature, implicity preferring those errors arising from a short extrapolation of the interpolative fits to the accumulating errors of several solution measurements.

We have fitted the data in Table I by nonlinear least squares (*19*) to the semiempirical extended Debye-Hückel equation.

$$\phi = 1 - \frac{S}{A^3 I} \left[(1 + AI^{1/2}) - 2 \ln [1 + AI^{1/2}] - \frac{1}{1 + AI^{1/2}} \right] + Bm + Cm^2 + \ldots \quad (4)$$

In this equation, S is the limiting slope, I the ionic strength, m the molality, B, C . . . are parameters, and A is given by $50.29 (\epsilon T)^{-1/2} a$. Parameter a enters the Debye theory as a characteristic length and ϵ is the dielectric constant.

Following Stoughton and Lietzke (*38*, *39*), we have assigned $A = 1.5$ for all of the salts studied [except Na_2SO_4 where A was set as 2.2 (*20*)] and assumed a temperature dependence for the coefficients B, C, . . . , of the general form

$$B = \frac{B_1}{T} + B_2 \ln T + B_3 + B_4 T + \ldots . . \quad (5)$$

Finally, the limiting slope, S, in Equation 4 is given by

$$S = 1.17202 \left(\sum_i m_i Z_i^2 \Big/ \sum_i m_i \right) \rho^{1/2} (\epsilon_{25} T_{25} / \epsilon T)^{3/2} \quad (6)$$

where ϵ is taken from Akerlöf and Oshry (*1*),

$$\epsilon = 5321/T + 233.76 - 0.9297\,T + 0.001417\,T^2 - 8.292 \times 10^{-7}\,T^3 \quad (7)$$

and the density of water, ρ, is given by ref *18*

$$\rho = 1.00157 - 1.5609 \times 10^{-4}\,t - 2.69691 \times 10^{-6}\,t^2 \quad (8)$$

The parameters derived from the least-square fits are reported in Table II to sufficient precision to allow the calculation of osmotic coefficients to 0.0001 followed by rounding to 0.001. Estimates of the reliability and precision of the fits can be found

Table II. Osmotic Coefficients as Fitted to

$$\phi = 1 - \frac{S}{A^3 I}\left\{(1 + A\sqrt{I}) - 2\ln(1 + A\sqrt{I}) - \frac{1}{1+\sqrt{A}}\right\} + Bm + Cm^2 + Dm^3$$

where $A = 1.5$ and B, C, and D take the form $B = \frac{B_1}{T} + B_2 \ln(T) + B_3 + B_4 T$

S is the Debye-Hückel Limiting Slope

Salt	NaBr	NaI	KF	$CaCl_2$	Na_2SO_4	KCl	CsCl	NaCl
Reference	This work	This work	This work	This work	*(6, 14, 15, 24, 33, 34, 37, 39)*	*(4, 5, 12, 21, 24, 26, 31, 32, 33, 37, 39)*	*(4, 5, 24, 26, 33, 34)*	*(38)*
Concentration range	~1–9*m*	~2–10*m*	~1–12*m*	~2–8*m*	~0–3*m*	~1–5*m*	~1–7*m*	~1–6*m*
Temperature range	~0–90°C	~0–90°C	~0–90°C	~0–90°C	~0–100°C (A = 2.2)	~0–100°C	~0–100°C	~0–100°C
B_1	473.59	2325.8	−1409.1	238.63	−5137.6	−1438.0	−4385.9	−330.33
B_2	3.4728	13.498	−7.6681	4.0422	−28.463	−7.6311	−24.518	0.9094
B_3	−19.605	−78.857	45.376	−20.805	167.22	45.263	144.104	6.3145
B_4	−0.00578	−0.01931	0.01028	−0.00966	0.03958	0.01008	0.03435	...
C_1	−6.5724	−35.653	23.349	154.09	19.749	100.9	5.064	32.681
C_2	−0.04635	−0.10154	0.05178	0.2518	...	0.2929	...	0.0790
C_3	0.29436	0.70082	−0.36497	−1.8727	0.09338	−1.9820	0.00348	−0.5537
C_4	...	...	...	...	...	...	...	...
D_1	−0.24433	0.55408	−0.21393	−6.0926	1.966	−0.497	0.142	...
D_2	...	...	...	...	...	...	...	...
D_3	0.00031	−0.00196	0.00035	0.01246	−0.02645	−0.00167	−0.00204	...
D_4	...	...	...	...	...	...	...	...
Variance	2.3×10^{-5}	9.0×10^{-5}	2.6×10^{-5}	1.3×10^{-5}	6.8×10^{-5}	2.5×10^{-5}	1.6×10^{-5}	...
$(\phi_{exp} - \phi_{calcd})_{max}$	1.4×10^{-2}	2.9×10^{-2}	1.3×10^{-2}	0.8×10^{-2}	...	1.0×10^{-2}	1.0×10^{-2}	...

Table III. Osmotic Coefficients at Rounded Temperatures and Concentrations as Calculated from Table II

		Concentration (molality)										
	Temp, °C	1	2	3	4	5	6	7	8	9	10	12
NaBr	10	0.957	1.021	1.099	1.186	1.278	1.372	1.466	1.555	1.636		
	25	0.961	1.031	1.112	1.200	1.293	1.386	1.478	1.564	1.642		
	50	0.967	1.043	1.128	1.217	1.307	1.396	1.482	1.560	1.630		
	75	0.968	1.048	1.133	1.219	1.304	1.385	1.461	1.528	1.585		
NaI	10		1.110	1.217	1.328	1.441	1.557	1.676	1.798	1.923	2.051	
	25		1.099	1.204	1.312	1.423	1.536	1.651	1.766	1.882	1.998	
	50		1.099	1.207	1.318	1.430	1.543	1.654	1.762	1.866	1.964	
	75		1.106	1.220	1.335	1.450	1.561	1.668	1.767	1.856	1.934	
KF	10	0.934	0.977	1.037	1.109	1.191	1.280	1.373	1.470	1.566	1.661	1.833
	25	0.939	0.987	1.049	1.120	1.200	1.285	1.373	1.462	1.551	1.636	1.788
	50	0.938	0.985	1.044	1.110	1.181	1.255	1.331	1.407	1.480	1.550	1.670
	75	0.929	0.972	1.024	1.081	1.142	1.205	1.268	1.330	1.390	1.446	1.540
$CaCl_2$	10	1.037	1.393	1.822	2.272	2.688	3.018	3.21	3.20	(3.20)	(3.20)	
	25	1.041	1.383	1.782	2.193	2.568	2.859	3.02	3.00	(3.00)	(3.00)	
	50	1.036	1.353	1.706	2.060	2.376	2.617	2.74	2.72	(2.72)	(2.72)	
	75	1.018	1.305	1.615	1.917	2.184	2.384	2.49	2.47	(2.47)	(2.47)	

in the last two columns where we report the variance of fit (its square root is approximately the average root mean square deviation) and the magnitude of the single worst deviation from the calculated line. We regard these fits as purely empirical in spite of the relationship to the reasonably well accepted semi-empirical extended Debye-Hückel theorey as pointed out above. Thus, we are not willing to ascribe any theoretical significance to the values of any of the derived parameters. In fact, our motive behind the fitting procedure was just the opposite, we wanted good interpolative formulas, not good parameters. Therefore, we have not experimented in trying to find either the best theoretical form to fit the data, or the minimum number of parameters for a given quality of fit, and the standard errors on the parameters are large (often above 20% of the parameter itself) even though the uncertainty in the linear combination of interest is small (the parameters are highly correlated). Thus, we have elected not to report either the error matrices for the least-square fits, or the standard errors on the parameters as obtained from their diagonal elements. Similarly, we feel that temperature derivatives of the osmotic coefficients [the excess enthalpies of solution (*10, 26*)] from our data are best obtained numerically (from Table III, for example).

At the end of Table II we also quote interpolative formulas for aqueous solutions of four other salts over the same temperature and concentration range in order to place all of the available data together. The data which were fitted (*26, 38, 39*) to obtain formulas for these last salts were of very good quality for the systems NaCl, KCl, and Na_2SO_4, but those for CsCl were available only for a few temperatures and concentrations and therefore this particular equation is not so reliable as those for the other seven entries in the table. It is to be emphasized that the regions of reliability for the fits in Table II are strictly delineated with respect to both temperature and concentration. In the latter instance they never extend below approximately 1*m*.

In Table III values for the calculated osmotic coefficients for the new data reported in this paper are given. These are cited at close enough intervals to suffice for crude interpolation ($\Delta\phi \approx 0.01$).

Sodium Bromide. The experimental points and the

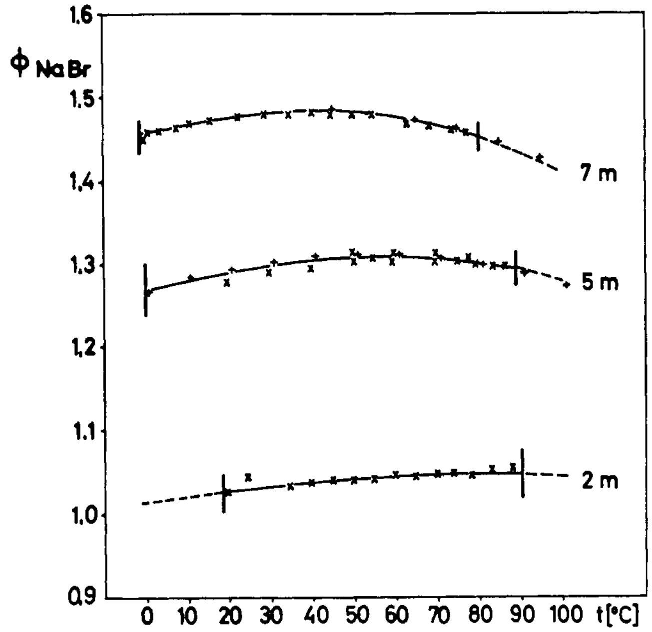

Figure 1. Experimental osmotic coefficients and least-square lines for NaBr

× Referenced directly to solvent
+ Referenced indirectly to solvent

Table IV. 25°C Comparisons of Osmotic Coefficients

NaBr

m	Robinson and Stokes (*28*)	Penciner and Marcus (*25*)	Makarov et al. (*22*)	This work
2	1.028	1.023		1.031
3	1.107	1.097	1.107	1.112
4	1.199	1.192	1.199	1.200
5		1.287	1.291	1.293
6		1.382	1.384	1.386
7		1.465	1.471	1.478
8		1.538	1.553	1.564
9		1.615	1.633	1.642
9.19	1.660	1.639	1.651	1.665

NaI

m	Robinson and Stokes (*28*)	Miller and Sheridan (*23*)	Makarov et al. (*22*)	This work
2	1.079	0.921		1.099
3	1.188	1.180	1.187	1.204
4		1.274	1.301	1.312
5		1.358	1.416	1.423
6		1.443	1.534	1.536
7		1.523	1.692*	1.651
8		1.597	1.764	1.766
9		1.667	1.870	1.882
10		1.736	1.972	1.998

KF

m	Robinson and Stokes (*28*)	Tamas and Kosza (*40*)	This work
2	0.984	0.984	0.987
3	1.048	1.048	1.049
4	1.124	1.116	1.120
5		1.204	1.200
6		1.291	1.285
7		1.373	1.373
8		1.449	1.462
9		1.526	1.551
10		1.608	1.636
12		1.681	1.716

$CaCl_2$

m	Robinson and Stokes (*28*)	This work
1	1.046	1.041
2	1.376	1.383
3	1.779	1.782
4	2.182	2.193
5	2.574	2.568
6	2.891	2.856
7	3.081	3.020
8	3.151	3.003

* In error? See text.

calculated lines are compared in Figure 1. Both the temperature and concentration dependence are smooth and well behaved. Comparison with other workers is possible only at 25°C. Such comparisons are shown in Table IV against Robinson and Stokes (*28*, *29*), Penciner and Marcus (*25*), and Makarov et al. (*22*). The present data average less than 0.5% different from either Robinson and Stokes or Makarov et al. where comparisons can be made. The results of Penciner and Marcus are between $^1/_2$ and $1^1/_2$% lower and the difference is worse at the higher concentrations. It thus appears that the present data are reliable to about 0.005 osmotic unit over the whole concentration range at 25°C, and the well-behaved nature of the least-square fits indicates that this degree of reliability is to be expected over the whole temperature range. Note that the temperature dependence of the sodium bromide data is small.

Sodium Iodide. The experimental points and the least-square lines are compared in Figure 2. The temperature dependence is very small. The concentration dependence is smooth and well behaved. The error in the fitting is about twice that observed for the NaBr system. This is partly due to the fact that we were forced to compare 4*m* and 8*m*, and 8*m* and 10*m* solutions with an ultimate reference to solvent through the 4*m* solution and therefore accumulated errors. Thus, the $(\text{variance})^{1/2}$ = 0.009 while for the NaBr data it was only 0.005 unit. To have at least a few low concentration points in the input data to the least squaring, we included four points from Robinson and Stokes (*28*) with the data reported in Table I. Since these were all at one temperature, they actually received very little weight in the routine (addenda to Table I: 25°C; m = 1.0, 2.0, 3.0, 3.5; ϕ = 0.991, 1.079, 1.188, 1.243).

Comparison with other workers (again possible only at 25°C) is shown in Table IV. The agreement with Makarov et al. (*23*) is within about 0.01 unit, with the present work lying higher. This holds except at 7*m* where the Russian point is 0.04 unit above ours. In view of the fact that the present data lie on a smooth curve, we think it likely that the Russian point is in error (typographical?). The data of Miller and Sheridan (*23*) appear between 3% (at 4*m*) and 13% (at 10*m*) lower than either Makarov et al. or us, and are apparently in error. We conclude that the present fits are reliable to about 0.01 osmotic unit or better between 4 and 10*m* although the uncertainty may be somewhat larger toward the lowest temperatures of the measurements. The uncertainty is also somewhat larger (as much as 0.02 unit) in the extrapolated (2 and 3*m*) portion reported in Table III.

Potassium Fluoride. The experimental points and calculated lines are compared in Figure 3. The temperature dependence is rather more marked than for the sodium bromide or iodide. The concentration dependence appears well behaved. The data at 9 and 12*m* extend only to about 20°C because of the solubility limit. Also, they do not extend to as high a temperature as is common in this paper because the capacity of our gauge was exceeded by their large vapor pressure depression with respect to the reference pure solvent. (At this late point in our experimental series, we were consistently electing reference to solvent to avoid accumulating errors. For one criticism of this approach, see below.) The four lowest temperature points at 9 and 12*m* have been discarded from the least-square fit. In each of these runs a systematic error apparently developed at the lower temperatures, no doubt due to a drop of

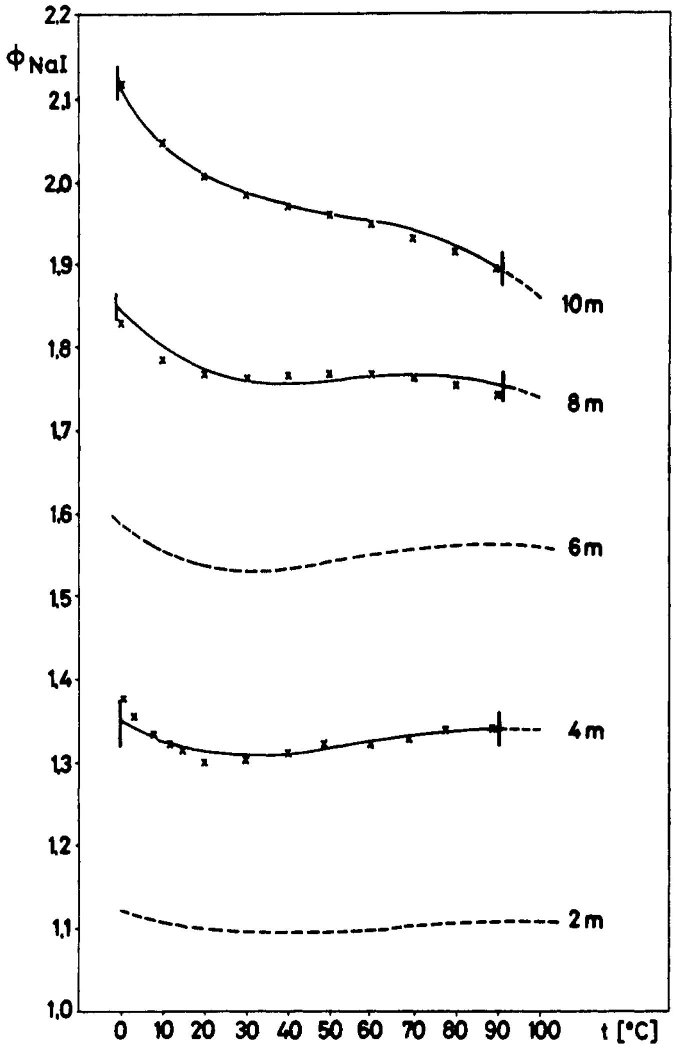

Figure 2. Experimental osmotic coefficients and least-square lines for NaI

parasitic condensate. Such drops tend to form on the pure solvent side as discussed in the experimental portion above. If the eight points under discussion be included in the analysis, we find an increase in the variance of a factor of six, the development of what are apparently spurious minima between 80 and 100°C for all concentrations, and that the agreement with other workers at 25°C worsens markedly. We therefore feel that the dropping of these eight points is justified from both the statistical and the experimental analysis of the measurements.

Comparison (Table IV) with the data of Robinson and Stokes (*28*) and Tamas and Kosza (*40*) is possible at 25°C. [Wu and Hamer (*42*) have considered these 25°C data also and have reported smoothed values for them.] The agreement is very good [within 0.5% (0.005 osmotic unit)] up to 7*m*. Above that concentration it worsens slightly, becoming as large as 2.2% at 12*m* which is our highest concentration. Both sets of data appear smooth and well behaved and we do not wish to choose between them. In summation, it is our judgment that the fit reported in this paper is good to 0.01 unit or better except for the higher concentrations (>7*m*) at the lower temperatures (<40°C) where it worsens.

Calcium Chloride. The experimental points and least-square lines for this system are compared in Figure 4. Both the temperature and concentration dependencies are by far the largest of any of the salts yet encountered. The data at 5.5*m* and 8*m* (nominal concentrations) are referenced through

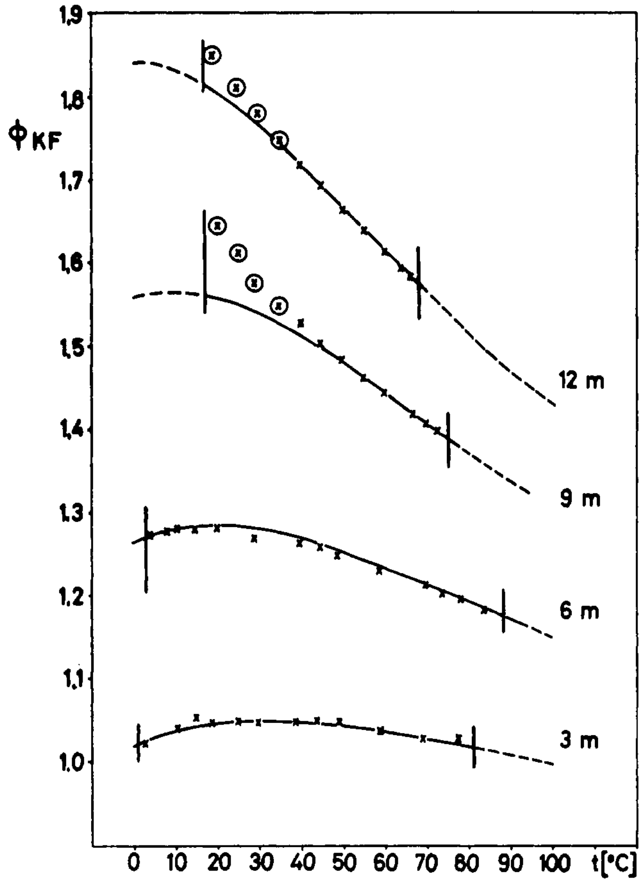

Figure 3. Experimental osmotic coefficients and least-square lines for KF

Circled points not included in the least squaring

the other solutions, ultimately to the solvent, but we also made one run with the 8*m* in which we referenced directly to vacuum. The data for this salt does not extend below 20°C.

Our original work-up of the data at 3 and 5.5*m* showed marked discrepancies with the standard values (*28*, *37*). It appears that there can be little or no error in the standards at these concentrations (which have been very carefully checked), and we concluded that our data were in error. The probable cause of the error was assumed to be the presence of a small amount of water in the material used to make up the solutions. On this assumption, we found that the application of a correction for 1.35 mol % (0.221 wt %) water brought the data at both 3 and 5.5*m* into excellent agreement with the literature (0.5%). In view of the fact that the correctiion is markedly concentration dependent, we consider it unlikely that the cause for the deviations could lie elsewhere. The corrected concentrations are the ones quoted in Table I. It is unfortunate that we made up these solutions gravimetrically and neglected to analyze them before they were destroyed.

A further word of explanation is in order. The recommended procedure for $CaCl_2$ solutions (*36*) involves preparation of concentrated stock solutions whose concentration is then determined by AgCl precipitation. Dilution to the desired concentrations then follows. We elected not to use this technique because we are preparing both D_2O and H_2O solutions simultaneously. We wished to use identical techniques for each, and thought that the standard method would not be convenient for the heavy solvent. After the fact, it appears clear that the method which we selected, carefully vacuum drying at elevated temperatures to constant weight followed by gravimetric solution preparation, was not a good one. However, the correction for 0.2% residual water is a small one, and its application

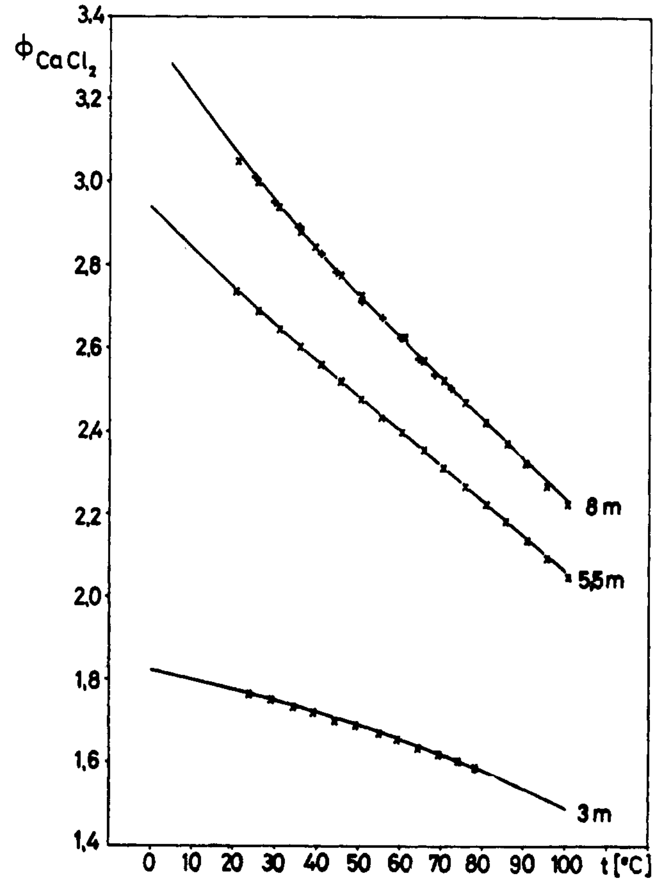

Figure 4. Experimental osmotic coefficients and least-square lines for $CaCl_2$

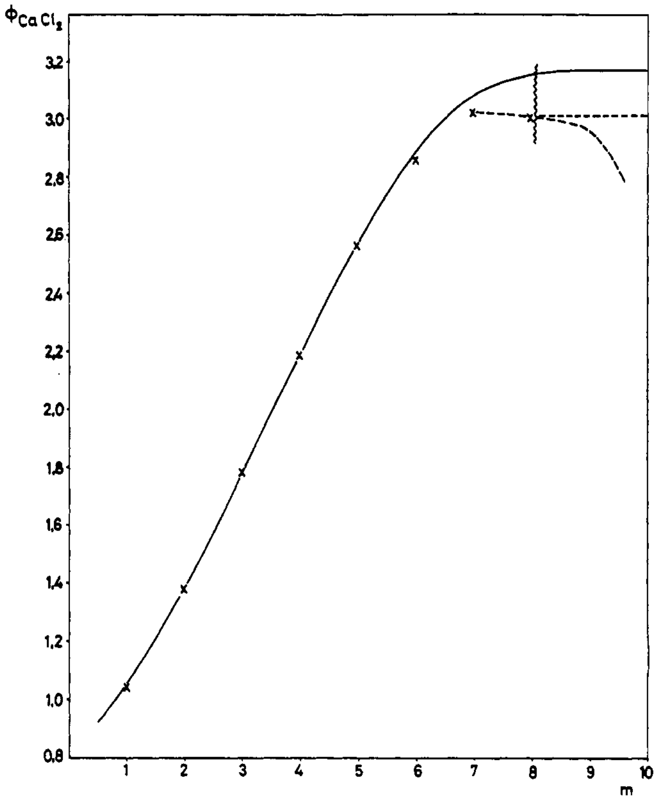

Figure 5. Osmotic coefficients for $CaCl_2$ solutions at 25°C

——— From Robinson and Stokes (*28*)
X X X ----- Calculated from Table II

enables us to report data on a more rational basis at temperatures other than 25°C. In our further defense we wish to note that judging from the agreement (3 and 5.5*m*, 25°C) between the present data and Robinson and Stokes (*28*), that the reliability of the present data (with or without the correction under discussion) was sufficient for our purposes. Those purposes were to determine the pressure of the HOH solution, P_H, in solvent isotope effect studies (*7*, *26*), so that the ratio P_H/P_D could be evaluated from the measured differential pressures within the precision of those differential pressure measurements.

The comparison with the literature values is again possible only at 25°C. It is shown in Table IV and also in Figure 4. With the correction the agreement at 3 and 5.5*m* is satisfactory (within 0.5%) but it worsens at 8*m*. The point here is almost 5% below the literature value, but at this higher concentration the accepted value has a larger associated uncertainty than it does below 7*m*.

In view of the fact that $CaCl_2$ solutions are suggested as isopiestic standards under some conditions, it is worthwhile to review their history. The ultimate references (25°C) at present appear to be NaCl up to 6*m* (3*m* $CaCl_2$) and H_2SO_4. There is no question that the data up to 3*m* must be nearly identically correct. They have been intercompared with NaCl and H_2SO_4 and have a very high degree of reliability. Above 3.0*m*, the $CaCl_2$ and the H_2SO_4 scales are not independent. The salt data are derived from the acid through isopiestic comparison. The acid data have been established as reliable by the vapor pressure measurements of Shankman and Gordon (*30*) and the bithermal equilibration measurements of Stokes (*36*), but the latter measurements extend only as far as 11*m* H_2SO_4 (7*m* $CaCl_2$) and there appears to be a significant and growing discrepancy between refs. *30* and *36* as the concentration increases. Above 11*m* sulfuric acid, the recommended standard reverts to the differential vapor pressure measurements of Shankman and Gordon (*30*). These authors certainly experienced all of the experimental difficulties which plagued us during the present series of measurements, and these difficulties were no doubt exacerbated by their considerably less convenient experimental apparatus. The other experimental information on this system goes back to the emf data of Harned and Hamer (*13*). These authors used two different cells, comparing a hydrogen electrode with a $PbSO_4/PbO_2/Pt$ electrode (0–7*m*) and with a Hg_2SO_4/Hg electrode (0–17.5*m*). The agreement with the vapor pressure data is excellent up to 3*m*, but at 5 and 7*m* the discrepancy is serious. However, at 10*m* the agreement has improved (0.7% on γ, Table IV, ref *30*). If one makes a Gibbs-Duhem integration of the Harned and Hamer data above 10*m* (using the Robinson-Stokes, Shankman-Gordon reference at 10*m*), the derived osmotic coefficients are found to lie several percent above the presently accepted reference line.

The net result of these considerations is definitely to question the reliability of the H_2SO_4 isopiestic reference standard (and by implication the $CaCl_2$ reference which is based on it) in the higher concentration regions; that is, above 10*m* H_2SO_4 (7*m* $CaCl_2$). It is our opinion that the Shankman-Gordon-Stokes line is presently the best to use, but we feel that new measurements are definitely called for in the high concentration region.

The concentration dependence of ϕ ($CaCl_2$) is interesting (Figure 5). It rises smoothly up to 6 or 7*m* and then rather abruptly flattens to an apparently constant value. The abrupt change in slope results in the prediction of a spurious maximum in the least-square fit (Table II) which is therefore not all reliable for even modest extrapolation. Values above the last observed point are probably best estimated by using the values calculated for the 8*m* solution, and we have in fact so indicated this estimate up to 10*m* in Table III.

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RECEIVED for review January 26, 1972. Accepted May 9, 1972. This work was supported by the U.S. Department of the Interior, Office of Water Resources Research, A-012 TN, and the Petroleum Research Fund, American Chemical Society. Computing time was donated by the University of Tennessee computing center which has been generously supported by the National Science Foundation.

Solubility of Oxygen in Selected Organic Solvents

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The solubility of oxygen was measured in four organic liquids of high dielectric constant at 25°C by the method of Morrison and Billett. The measurements, expressed as Bunsen coefficients, were γ-butyrolactone 0.0499, propylene carbonate 0.0153, dimethyl sulfoxide 0.0342, and *N*-nitrosodimethylamine 0.0605. No salting-in or salting-out effects were observed in $LiClO_4$ (up to 1*M*) solutions in the first two solvents. The data were correlated with the liquids' surface tensions using the Uhlig cavity model.

The solubility of oxygen was measured in four organic solvents of high dielectric constant as part of an investigation of the oxygen electrode in aprotic electrolytic solutions. The four organic solvents were dimethyl sulfoxide, *N*-nitrosodimethylamine, propylene carbonate, and γ-butyrolactone. Their dielectric constants are given. In the last two solvents, the solubility was also measured in $LiClO_4$ solutions (up to 1*M*) to determine any salt effects.

APPARATUS AND MATERIALS

The apparatus and method of Morrison and Billett were employed (*5*). In this method, gas saturation is achieved by the liquid's flowing in a thin film down a spiral column which, in our apparatus, consisted of six turns of 10-mm glass tubing with an equivalent length of 1.8 m. A flow rate of 2-3 ml/min was maintained and, in a typical run, 100 ml of saturated liquid was collected. The reproducibility of this method is ±0.5% and, according to Morrison and Billett, the results are slightly low. For example, they reported a Bunsen coefficient of 0.0280 for

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