Henry's Constants of 1-Alkanols and 2-Ketones in Salt Solutions

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Henry's constants of the homologous series of 2-ketones from 2-propanone to 2-heptanone were measured in aqueous solutions containing sodium chloride from (0.2 to 1.2) *m* (molal) over a range of temperatures from (313 to 363) K. In addition, Henry's constants of the *n*-alkanols from ethanol to 1-hexanol in aqueous solutions with sodium sulfate from (0.2 to 1.2) *m* were also measured over the same temperature range. The data were correlated using a model based on dilute solution theory that contains one temperature-independent salt effect parameter. A linear relationship between this parameter and the critical volume of the volatile organic compound (VOC) was found for each homologous series studied in this work.

Introduction

Henry's constants of ketones and alkanols are required to estimate volatile organic compound (VOC) emissions from paper mills and ensure compliance with thresholds set by the EPA Cluster Rules.[1] In general, VOC emissions from aqueous streams are estimated using Henry's constants of the VOC of interest in water. However, since common salts such as sodium sulfate and sodium carbonate (present in process streams in the paper industry) generally salt out VOCs from aqueous solutions, their effect on Henry's constants must be considered in order to obtain reliable estimates of VOC emissions. There is therefore a need for data relevant to VOC + water + salt systems, particularly in the case of regulated VOCs such as methanol and methyl ethyl ketone (2-butanone). However, such data are rarely available at temperatures other than 298 K. This has hampered the development of models that could be employed to minimize the need for extensive measurements.

In an effort to develop models that are applicable to VOC + salt + water systems over wide ranges of temperature, pressure, and salt concentration, we have previously reported Henry's constants of VOCs in several such systems[2−6] and correlated the data using a model based on dilute solution theory. In the present work, we report Henry's constants for 2-ketones (2-propanone to 2-heptanone) in sodium chloride solutions and 1-alkanols (ethanol to 1-hexanol) in sodium sulfate solutions at temperatures ranging from (313 to 363) K, and evaluate the applicability of the dilute solution model to these systems.

Experimental Section

Apparatus and Procedure. The relative headspace gas chromatography method of Chai et al.[5] was used to measure Henry's constants in this work. The gas chromatograph (GC) employed for vapor analysis was manufactured by Hewlett-Packard (HP-6890) and equipped with an HP INNOWAX capillary column (15 m long × 0.53 mm i.d.) with a 1 μm thick cross-linked poly(ethylene glycol) stationary phase, splitless injector port configuration, and a flame ionization detector (FID). Other GC conditions were as follows: column temperature, 333 K; injector port temperature, 523 K; helium carrier gas flow, 10.6 $\text{mL}\cdot\text{min}^{-1}$; hydrogen flow rate, 40 $\text{mL}\cdot\text{min}^{-1}$; air flow rate, 400 $\text{mL}\cdot\text{min}^{-1}$; FID temperature, 523 K.

The settings of the automated headspace sampler (HP-7694, Hewlett-Packard, Palo Alto, CA) were as follows: vial pressurization time of 0.70 min; sample loop fill time of 0.10 min; loop equilibration time of 0.05 min; and an injection time of 1.00 min. Gentle shaking of the vials for 45 min was employed for 10 and 15 mL samples and for 25 min for 5 mL and smaller samples. Ultra high purity helium (Air Products, Allentown, PA) was injected into each vial to transfer 1 mL of the vapor phase into a heated sample loop. The material in the sample loop was then transferred to the GC by flow of helium carrier gas.

Chemicals. All VOCs and salts were purchased from Aldrich (Milwaukee, WI) and used as received. The purities were as follows: 2-propanone (> 99.5 %), 2-butanone (> 99 %), 2-pentanone (> 99.5 %), 2-hexanone (> 98 %), 2-heptanone (> 99 %), ethanol (absolute), 1-propanol (> 99 %), 1-butanol (> 99.5 %), 1-pentanol (> 98 %), 1-hexanol (> 99 %), sodium chloride (> 99.5 %), calcium chloride (> 99.5 %), sodium sulfate (> 99.9 %), potassium sulfate (> 99.9 %), and sodium carbonate (> 99.9 %).

Gases employed in the headspace method were purchased from Air Products. They included ultra high purity helium (99.9995 %), ultra high purity hydrogen (99.9995 %), and ultra zero air.

Sample Preparation and Headspace Analysis. A VOC stock solution in water was prepared by adding 50 μL of each VOC to 1 L of water and stirring to obtain a homogeneous solution. Several test solutions were then prepared by adding different amounts of salt to six tared flasks containing 100 g of the stock solution each. Stock solutions were weighed on an electronic balance (Sartorius, Edgewood, NJ, model 1404), and salts were weighed on a Mettler analytical balance (AE 163). Note that although the test solutions contained different amounts of salt, the VOC concentration in each solution was identical to that in the stock solution on a salt-free basis. The concentrations for all 1-alkanol and 2-ketone solutions are listed in Table 1.

Test samples were prepared by dispensing 15.00 ± 0.06 mL of a test solution into a glass vial purchased from Agilent (Palo Alto, CA). The volume of the vial was 21.6 ± 0.1 mL, and it was immediately capped with a 20 mm diameter Teflon-faced butyl rubber septum (Agilent) after addition of the solution to

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Table 1. Experimental Parameters

VOC	VOC concn in stock soln/ppmv[a]	salt	salt concn range/m[b]
2-propanone	50	NaCl	0.2−1.2
2-butanone	50	NaCl	0.2−1.2
2-pentanone	50	NaCl	0.2−1.2
2-hexanone	50	NaCl	0.2−1.2
2-heptanone	50	NaCl	0.2−1.2
ethanol	300	Na_2SO_4	0.2−1.2
1-propanol	100	Na_2SO_4	0.2−1.2
1-butanol	100	Na_2SO_4	0.2−1.2
1-pentanol	100	Na_2SO_4	0.2−1.2
1-hexanol	100	Na_2SO_4	0.2−1.2

[a] Parts per million on a volume basis. [b] Moles of salt per kilogram of water.

prevent loss of the VOC. Three reference vials containing no salt and six vials containing salt at different concentrations were loaded on the sampling carrousel (for a total of nine vials at each temperature). Three runs were performed with new samples at six temperatures to obtain a standard deviation for each reported Henry's constant.

Reference Henry's constants $H_{i,0}$ were determined using the differential method of Chai and Zhu,[3] which employs an analysis of the headspace in two vials containing different volumes of the same stock solution. Henry's constants of the ketones were measured from (313 to 363) K, and Henry's constants of ethanol were measured from (343 to 363) K. The remaining 1-alkanol Henry's constants were obtained from Gupta et al.[6] In our work, the volumes of the two vials were 5.00 ± 0.06 mL and 0.250 ± 0.005 mL for all VOCs except ethanol, when the two volumes were 10.00 ± 0.01 mL and 0.100 ± 0.005 mL.

Time for Equilibration. The GC peak area count versus equilibration time was plotted as described previously[5] and showed that the area count approached a constant value after 45 min. This equilibration time was therefore used for both 15.00 mL and 10.00 mL samples. The 15.00 mL ketone samples were also found to equilibrate in 45 min at 313 K, whereas the 5 mL samples were found to equilibrate in 25 min at this temperature. Therefore an equilibration time of 25 min was assumed for both 5.00 mL and 0.250 mL samples.

Error Analysis. According to Chai et al.,[5] Henry's constants of a volatile compound i in water with and without salt are related to measured chromatographic peak areas as follows:

$$H_{i,\mathrm{m}} = H_{i,0}\frac{A_\mathrm{m}}{A_0} \tag{1}$$

where $H_{i,0}$ and $H_{i,\mathrm{m}}$ are Henry's constants of the VOC in water and in the salt solution and A_0 and A_m are peak areas obtained from a chromatographic analysis of the headspace above water and the salt solution, respectively. Thus, $H_{i,\mathrm{m}}$ can be obtained from two peak areas and a reference value of the Henry's constant $H_{i,0}$.

According to Halpern,[7] the overall uncertainty $\sigma_{H_{i,\mathrm{m}}}$ in Henry's constant $H_{i,\mathrm{m}}$ can be expressed in terms of the uncertainty in the reference Henry's constant $\sigma_{H_{i,0}}$ and the uncertainties in the peak areas σ_{A_m} and σ_{A_0} as follows:

Table 2. Henry's Constants for 2-Ketones in Aqueous NaCl Solutions

T	pure water		0.2 m		0.4 m		0.6 m		0.8 m		1.0 m		1.2 m	
K	H/kPa	err[a]/kPa	H/kPa	err/kPa	H/kPa	err/kPa	H/kPa	err/kPa	H/kPa	err/kPa	H/kPa	err/kPa	H/kPa	err/kPa
2-Propanone														
313	454	18	629	62	497	29	523	45	542	34	569	54	600	53
323	686	16	892	97	718	38	763	36	789	46	824	33	866	41
333	1016	22	1310	130	1089	86	1090	24	1150	40	1250	31	1301	37
343	1489	40	1500	120	1570	130	1600	130	1680	120	1830	130	1880	130
353	2086	23	2207	54	2295	71	2420	120	2496	96	2660	130	2790	140
363	2910	160	3180	260	3320	290	3500	270	3560	240	3900	280	4090	340
2-Butanone														
313	721	3	767	4	794	41	842	72	883	52	940	70	1006	73
323	1167	26	1301	52	1252	46	1362	44	1436	61	1520	41	1614	53
333	1775	30	1982	34	1906	36	1965	49	2114	48	2359	44	2480	42
343	2670	100	2740	230	2920	240	3010	250	3170	240	3510	260	3660	270
353	3733	73	3906	145	4120	200	4400	290	4590	240	4910	260	5250	310
363	4960	480	5030	580	5300	630	5640	640	5820	620	6410	700	6800	790
2-Pentanone														
313	1149	32	1243	37	1321	65	1420	98	1508	75	1619	86	1759	86
323	1819	42	1950	60	1991	54	2214	56	2371	77	2538	60	2721	71
333	2826	42	3063	67	3124	71	3207	108	3510	58	4013	98	4251	80
343	4300	130	4630	180	5020	180	5228	194	5556	196	6217	198	6580	220
353	6290	180	6640	320	7090	440	7636	571	8050	500	6640	380	7170	450
363	8690	440	9440	800	10070	880	10780	880	11240	790	12490	940	13410	1140
2-Hexanone														
313	1497	90	1630	108	1773	120	1930	160	2070	140	2240	150	2460	160
323	2429	16	2602	29	2704	25	3056	21	3322	57	3589	27	3874	31
333	3822	117	4160	220	4320	180	4440	210	4930	153	5740	220	6130	210
343	5740	570	6280	630	6900	680	7260	720	7780	780	8790	870	9420	930
353	9370	860	10020	1070	10840	1250	11800	1440	12590	1450	10440	1150	11390	1290
363	11900	1330	12930	1660	13830	1850	14910	1950	15800	1940	17760	2240	19170	2530
2-Heptanone														
313	2220	45	2340	130	2583	96	2845	81	3080	111	3340	150	3690	170
323	3630	150	3910	170	3960	180	4635	199	5120	240	5610	240	6010	260
333	5680	510	6330	590	6500	570	6417	585	7270	650	8910	780	9430	820
343	9510	1040	10510	1200	11670	1380	12385	1416	13370	1490	15250	1750	16470	1880
353	15830	1670	16660	1840	18240	1980	20019	2189	21660	2350	17950	1960	19720	2140
363	21730	1530	23310	2120	25270	2310	27396	2481	29360	2670	33250	3010	36140	3280

[a] err = experimental error determined with eq 2.

$$\frac{\sigma_{H_{i,\mathrm{m}}}}{H_{i,\mathrm{m}}} = \sqrt{\left(\frac{\sigma_{H_{i,0}}}{H_{i,0}}\right)^2 + \left(\frac{\sigma_{A_\mathrm{m}}}{A_\mathrm{m}}\right)^2 + \left(\frac{\sigma_{A_0}}{A_0}\right)^2} \qquad (2)$$

Uncertainties needed in eq 2 were estimated from standard deviations from three separate runs.

Results and Discussion

Measurements. Measured Henry's constants of 2-ketones and 1-alkanols are listed in Tables 2 and 3. Experimental uncertainties calculated using eq 2 were less than 13 % for the methyl ketones and less than 15 % for the 1-alkanols. As can be deduced from these tables, the 2-ketones and the alkanols are "salted out" by sodium chloride and sodium sulfate, respectively. Sodium chloride concentrations of 0.6 *m* lead to an increase in Henry's constants of 2-propanone by 12 % and 2-heptanone by 25 %. Henry's constants of 1-alkanols increase by similar amounts in 0.6 *m* sodium sulfate solutions. In previous work,[5] sodium sulfate concentrations of 0.6 *m* resulted in an increase in Henry's constants of 2-propanone by 50 % and of 2-heptanone by 100 %.

Correlation. Most literature data on Henry's constants involving a single VOC and a solvent have been correlated with the van't Hoff equation:[6,8,9]

$$\ln(H) = a - b/T \qquad (3)$$

in which a is the entropy and b is the enthalpy of vaporization of the VOC.[10] The linear correlation is appropriate for data over a limited range of temperature, generally no more than 40 K. Gorgenyi et al.[11] proposed an expanded van't Hoff equation that can be used over a 70 K temperature range. However, data must be available for each salt concentration of interest since their model has no independent salt effect term. In an effort to describe Henry's constants of both binary and ternary aqueous systems over large temperature ranges, Teja et al.[2] extended the dilute solution theory of Harvey[12] as follows:

$$\ln(H_{i,\mathrm{m}}) = \ln P_j^{\mathrm{sat}} + \frac{A_{ij}}{T_\mathrm{r}} + B_{ij}\frac{(1-T_\mathrm{r})^{0.355}}{T_\mathrm{r}} + C_{ij}\frac{\exp(1-T_\mathrm{r})}{T_\mathrm{r}^{\,0.41}} + Dx_k \qquad (4)$$

where P_j^{sat} is the vapor pressure of pure water (component j); A_{ij}, B_{ij}, and C_{ij} are binary parameters for the VOC + water system, x_k is the salt concentration (mol of salt/kg of water), and D is a single ternary parameter that takes account of the "salt effect". This "salt effect" parameter is assumed to be independent of temperature.[13] Equation 4 has been shown to successfully correlate[2] Henry's constants of benzene in pure water from (275 to 600) K, which are highly nonlinear with respect to temperature. It has also been applied to Henry's constants of methanol in pure water and aqueous sodium sulfate or sodium carbonate solutions.[2,13]

Table 3. Henry's Constants for 1-Alkanols in Aqueous Na_2SO_4 Solutions

T	pure water		0.2 *m*		0.4 *m*		0.6 *m*		0.8 *m*		1.0 *m*		1.2 *m*	
K	H/kPa	err[a]/kPa	H/kPa	err/kPa	H/kPa	err/kPa	H/kPa	err/kPa	H/kPa	err/kPa	H/kPa	err/kPa	H/kPa	err/kPa
Ethanol														
313	68	4	81	9	91	11	110	10	120	10	140	10	160	10
323	144	17	167	20	180	20	210	30	240	30	260	30	300	40
333	251	23	280	30	320	30	360	30	400	40	430	40	490	50
343	382	24	430	30	460	30	520	40	570	40	620	50	700	50
353	613	97	690	110	760	120	800	130	850	140	950	150	1020	170
363	950	130	1020	150	1120	160	1170	170	1230	170	1300	180	1400	190
1-Propanol														
313	126	8	15	20	180	20	220	30	250	30	310	30	360	3
323	220	20	270	26	310	30	360	40	420	40	480	50	560	60
333	382	16	440	20	515	23	599	25	690	30	770	30	910	40
343	626	16	739	21	835	27	950	50	1090	50	1230	50	1410	70
353	1070	100	1270	130	1430	140	1570	160	1720	180	1980	210	2180	240
363	2030	220	2300	250	257	290	2760	320	2990	350	3250	360	3580	400
1-Butanol														
313	184	6	230	20	280	20	350	30	420	40	520	30	631	36
323	310	30	380	40	450	40	550	50	660	60	780	80	920	100
333	624	22	742	29	888	33	1064	38	1275	47	1460	50	1760	60
343	1000	30	1221	37	1428	48	1665	80	1960	90	2284	100	2690	130
353	1730	140	2100	180	2430	200	2760	260	3110	290	3680	350	4160	400
363	2680	280	3120	330	3570	380	3910	440	4400	480	4900	510	5560	580
1-Pentanol														
313	160	10	210	20	260	20	330	30	410	40	523	39	650	50
323	369	98	455	32	550	40	690	50	850	60	1030	90	1270	110
333	683	63	830	23	1017	26	1250	30	1549	39	1820	45	2256	53
343	1180	130	1479	44	1784	62	2130	109	2570	127	3072	157	3700	200
353	2000	400	2510	180	2970	200	3480	280	4030	330	4890	390	5700	460
363	3410	580	4080	400	4780	480	5360	570	6250	623	7140	690	8380	810
1-Hexanol														
313	360	20	520	50	675	57	890	80	1130	90	1486	94	1910	120
323	620	50	768	58	945	71	1210	100	1520	120	1905	167	2400	230
333	1137	22	1374	28	1721	43	2162	43	2760	60	3340	70	4230	90
343	1840	32	2336	74	2905	110	3553	196	4291	221	5460	320	6740	390
353	3140	180	4010	265	4850	290	5890	450	7010	526	8740	630	10490	780
363	4510	400	5520	510	6660	620	7680	790	9290	860	10900	990	13210	1180

[a] err = experimental error determined with eq 2.

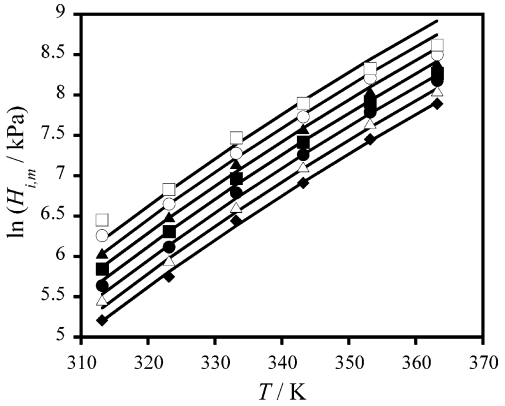

Figure 1. Henry's constants for 1-butanol in (◆) pure water and in aqueous Na_2SO_4 solutions: △, 0.2 m; ●, 0.4 m; ■, 0.6 m; ▲, 0.8 m; ○, 1.0 m; and □, 1.2 m. The solid lines are fitted using eq 4.

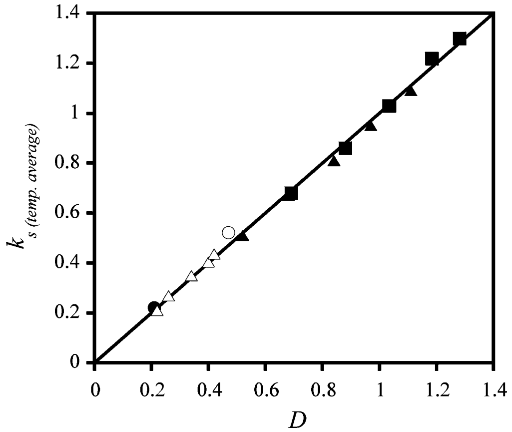

Figure 2. Comparison between temperature-averaged Setchenov constant and D on a molality basis in the system: ■, 2-ketones + Na_2SO_4 + water[5]; △, 2-ketones + NaCl + water; ▲, 1-alkanols (excluding methanol) + Na_2SO_4 + water; ○, methanol + Na_2SO_4 + water;[2] and ●, methanol + Na_2CO_3 + water.[2]

The salt effect parameter (D) in eq 4 is similar to Setchenov's constant[14] defined by:

$$\ln\left[\frac{H_{i,m}}{H_{i,0}}\right] = k_s x_k \tag{5}$$

where $H_{i,m}$ is Henry's constant of the VOC i in the salt-containing solution m, and $H_{i,j}$ is Henry's constant of the VOC in pure solvent j. Comparison of eq 4 and eq 5 shows that $k_s = D$ if the first four terms in eq 4 are obtained from data on salt-free solutions.

The data measured in the present work were fitted with eq 4 and the results for 1-butanol are shown in Figure 1. Values of Henry's constants at high salt concentrations and temperatures above 360 K were depressed because the VOC + water + salt mixtures were sensitive to small pressure fluctuations during sampling. Parameters for this system and for all 2-ketones and 1-alkanols are provided in Tables 4 and 5. The parameter D in eq 4 was determined using concentrations in terms of molality as well as ionic strength defined as

$$I = 1/2 \cdot \sum m_n \cdot z_n^{\,2} \tag{6}$$

where m_n is the molality of a salt ion, z_n is the charge number of the ion. Once A_{ij}, B_{ij}, and C_{ij} were determined from binary data, a single value of D in eq 4 proved sufficient to correlate Henry's constants of the VOCs at all salt concentrations in units of ionic strength. Table 4 shows that the maximum absolute deviation (MAD) for the 1-alkanol + sodium sulfate + water data was 4.6 %, and the average absolute deviation (AAD) did not exceed 1.3 %. Table 5 shows that the MAD for the 2-ketone + sodium chloride + water data was 4.2 %, and the AAD was less than 0.4 %. The data for 2-propanone in 0.2 m sodium chloride at 313 K and at 323 K appear to be outliers. The 2-ketone + sodium sulfate + water data are those of Chai et al.[5] The MAD did not exceed 1.0 %, and the AAD did not exceed 0.4 % for these data.

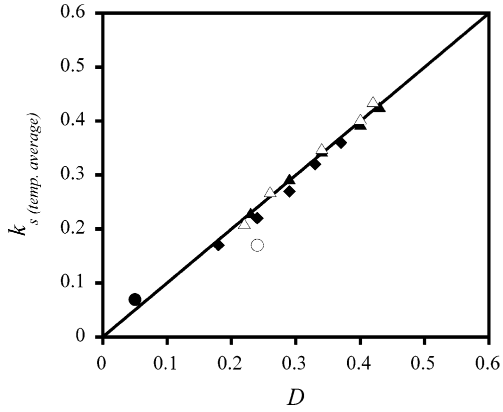

Figure 3. Comparison between temperature-averaged Setchenov constant and D on an ionic strength basis in the system: ■, 2-ketones + Na_2SO_4 + water[5]; △, 2-ketones + NaCl + water; ▲, 1-alkanols (excluding methanol) + Na_2SO_4 + water; ○, methanol + Na_2SO_4 + water;[2] and ●, methanol + Na_2CO_3 + water.[2]

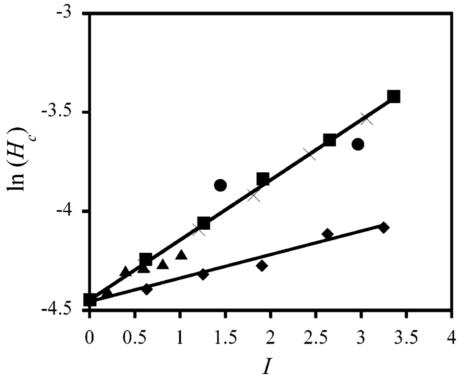

Figure 4. Salt effects for 2-propanone with ■, Na_2SO_4; ●, K_2SO_4; ×, Na_2CO_3; ▲, NaCl; and ◆, $CaCl_2$.

The parameter D was found to have approximately the same value as the temperature-averaged Setchenov constant for the system. Thus D can be replaced by literature values of the Setchenov constants, averaged over the temperature range of interest, as demonstrated in Figures 2 and 3.

The results shown for sodium chloride and sodium sulfate can easily be applied to other salts with ions of the same charge and similar size. A study using 2-propanone at 333 K with five salts having similar cations or anions showed that the salt effect is determined by the charge of the anion when the cations are similar in size. Figure 4 demonstrates that on an ionic strength basis, it is possible to model the salt effect of sodium sulfate, sodium carbonate, sodium chloride, and potassium sulfate with the same parameter. Calcium chloride requires a different salt effect parameter because its divalent cation leads to high ionic strength even though the chloride ion exhibits a weak salt effect. Only sodium sulfate and sodium carbonate can be modeled on a molality basis with the same parameter. Moreover, sodium and calcium chloride require another value of D on the molality scale.

Table 4. Constants of Equation 4 for 2-Ketones and 1-Alkanols in Na_2SO_4 Solutions

	A_{ij}	B_{ij}	C_{ij}	D (molality)	k_s (temp avg)	D (ionic strength)	k_s (temp avg)	AAD[a]	MAD[b]
2-propanone	8.03	−3.06	−3.31	0.68	0.69	0.23	0.23	0.2	0.7
2-butanone	−19.81	0.91	19.51	0.86	0.88	0.29	0.29	0.2	0.6
2-pentanone	8.58	−6.42	−0.97	1.03	1.03	0.34	0.34	0.2	0.6
2-hexanone	9.19	−7.77	−0.43	1.22	1.18	0.40	0.39	0.4	1.0
2-heptanone	9.97	−10.70	1.14	1.30	1.28	0.43	0.43	0.4	0.8
methanol[c]	9.16	−10.05	−0.15	0.47	0.52	0.24	0.17	1.3	2.8
ethanol[d]	−38.24	0.93	35.35	0.52	0.51	0.18	0.17	1.3	3.9
1-propanol[d]	13.62	−11.72	−2.74	0.68	0.67	0.24	0.22	1.2	4.6
1-butanol[d]	9.58	−11.28	0.81	0.84	0.81	0.29	0.27	1.0	3.8
1-pentanol[d]	10.04	−14.51	2.72	0.97	0.95	0.33	0.32	1.2	3.3
1-hexanol[d]	9.57	−10.61	0.64	1.11	1.09	0.37	0.36	1.0	4.5

[a] Average absolute deviation = $\Sigma\ |\ln(H_{i,\mathrm{m(expt)}}) - \ln(H_{i,\mathrm{m(calc)}})|/n$. [b] Maximum absolute deviation = max $|\ln(H_{i,\mathrm{m(expt)}}) - \ln(H_{i,\mathrm{m(calc)}})|$. [c] A_{ij}, B_{ij}, C_{ij}, and D regressed from data in Figure 2 and Table 1 of Teja et al.[2] [d] A_{ij}, B_{ij}, and C_{ij} regressed from data in Figures 2 and 3 of Gupta et al.[6]

Table 5. Constants of Equation 4 for 2-Ketones in NaCl Solutions

	A_{ij}	B_{ij}	C_{ij}	D (molality or ionic strength)	k_s	AAD[a]	MAD[b]
2-propanone	8.03	−3.06	−3.31	0.20	0.22	0.4	4.2
2-butanone	−19.81	0.91	19.51	0.23	0.26	0.3	1.0
2-pentanone	8.58	−6.42	−0.97	0.32	0.34	0.2	1.0
2-hexanone	9.19	−7.77	−0.43	0.37	0.40	0.4	0.9
2-heptanone	9.97	−10.70	1.14	0.38	0.42	0.4	0.9

[a] Average absolute deviation = $\Sigma\ |\ln(H_{\mathrm{expt}}) - \ln(H_{\mathrm{calc}})|/n$. [b] Maximum absolute deviation = max $|\ln(H_{\mathrm{expt}}) - \ln(H_{\mathrm{calc}})|$.

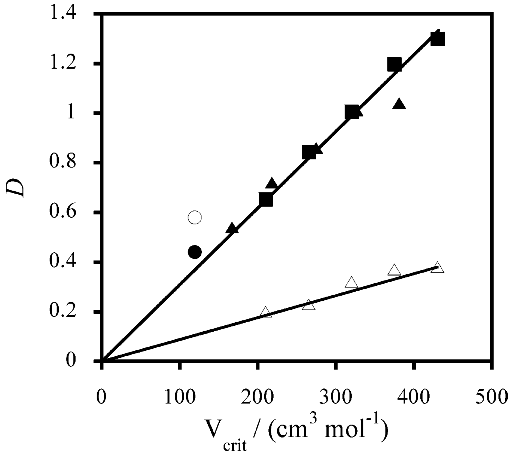

Figure 5. Correlation between D and the critical volume of ■, 2-ketones + Na_2SO_4 + water[5]; △, 2-ketones + NaCl + water; ▲, 1-alkanols (excluding methanol) + Na_2SO_4 + water; ○, methanol + Na_2SO_4 + water[2]; and ●, methanol + Na_2CO_3 + water.

Figures 2 and 3 demonstrate that a temperature-averaged Setchenov constant can be used as the salt effect parameter in eq 4. When no Setchenov constants are available, a simple linear relationship between D and the critical volume (V_{crit}) of the VOC offers an avenue to obtain the salt effect parameter. Figure 5 shows that D for a homologous series of 1-alkanols and 2-ketones varies linearly with V_{crit}, with the slope of the line depending on the salt. In the case of 2-ketones in sodium sulfate solutions, the slope was 3.3 times that for 2-ketones in sodium chloride solutions due to the stronger influence of the divalent sulfate ion, as shown in Figure 5. The two outliers in Figure 5 are likely the result of experimental error. The methanol in sodium sulfate datum in Figure 5 should have the same magnitude of the salt effect as methanol in sodium carbonate data, because both salts have the same effect on 2-propanone (see Figure 4). The 1-hexanol in sodium sulfate datum in Figure 5 is probably an outlier because ketones with six or more carbon atoms follow a linear trend.

Conclusions

Henry's constants of the 1-alkanols (ethanol to 1-hexanol) in sodium sulfate solutions and 2-ketones (2-propanone to 2-heptanone) in sodium chloride solutions were measured with an experimental uncertainty of 15 % or less. The data were fitted using a model based on dilute solution theory. In general, MADs between calculated and experimental values did not exceed 4.6 % and AADs did not exceed 1.3 %. The salt effect parameter D in this model can be obtained from literature values of temperature-averaged Setchenov constants. In addition, D varies linearly with the critical volume of the VOC for both homologous series of VOCs studied in this work. This suggests that it is possible to predict the salt effect for one compound in a homologous series from data on the other members of the series.

Notations

A_0	GC peak area in the VOC + water system
A_{m}	GC peak area in the analysis of VOC + water + salt system
A_{ij}, B_{ij}, C_{ij}	binary parameters of eq 4 from VOC + water data
a	entropy of vaporization
b	enthalpy of vaporization
D	salt parameter in eq 4
H_{c}	dimensionless Henry's constant
$H_{i,0}$	Henry's constant without salt (standard)
$H_{i,\mathrm{m(calc)}}$	Henry's constant with salt calculated from eq 4
$H_{i,\mathrm{m}}$	Henry's constant with salt
$H_{i,\mathrm{m(expt)}}$	Henry's constant determined experimentally
I	molal ionic strength
k_{s}	Setchenov's constant
m_n	salt ion concentration in molal
N	number of measurements
P_j^{sat}	saturated vapor pressure of component j
T	absolute temperature
T_{r}	reduced temperature
V_{crit}	critical molar volume
V_{l}	liquid-phase volume
x_n	individual measurement value
x_{ave}	average measurement value
x_k	salt concentration in molal
z_n	mole fraction of salt

Subscripts

crit	property at the fluid's critical point
A_0	GC peak area in the VOC + water system
A_{m}	GC peak area in the analysis of VOC + water + salt system
$H_{i,0}$	Henry's constant without salt (standard)
$H_{i,\mathrm{m}}$	Henry's constant with salt
i	volatile solute index

i,m(calc)	calculated value for mixed system
i,m(expt)	experimentally determined value for mixed system
j	solvent index
k	salt index
n	salt ion index
l	liquid phase
r	reduced quantity
temp average	average of values at all temperatures

Superscript

sat	saturated condition

Greek Symbols

$\sigma_{H_{i,\mathrm{m}}}$	uncertainty in the Henry's constant with salt
$\sigma_{H_{i,0}}$	uncertainty in the Henry's constant without salt
σ_{A_m}	uncertainty in the peak area with salt
σ_{A_0}	uncertainty in the peak area without salt

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