Standard Partial Molal Heat Capacities of Sodium Perchlorate in Water from 0–90°C and in Anhydrous Methanol from —5–55°C

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Heats of solution of $NaClO_4$ have been measured calorimetrically in water at several temperatures ranging from near zero to 90°C and in anhydrous methanol from —10–55°C at concentrations ranging from about 10^{-3} to 1.2×10^{-2} *m*. The data have been extrapolated to infinite dilution by means of an extended Debye-Hückel equation to obtain standard heats of solution at the various temperatures. These were treated by the integral heat method to evaluate standard partial molal heat capacities for this salt in the two solvents as a function of temperature. The heat capacity curve for $NaClO_4$ (aq) shows the characteristic maximum exhibited by other aqueous electrolytes while the heat capacity curve for the methanolic $NaClO_4$ appears to be at a maximum at the lower end of the temperature range and decreases as the temperature is increased. This suggests that the behavior of the standard partial molal heat capacities in the two solvents is similar, but that the maximum occurs in methanolic solutions at much lower temperatures.

Partial molal heat capacities at infinite dilution, $\bar{C}_{p2}^\circ$, have been extremely valuable for elucidating the structure of aqueous solutions of electrolytes (*1, 7, 18*). Within the past few years, $\bar{C}_{p2}^\circ$ data have been reported (*1, 3, 6, 9, 18*) for aqueous electrolytes over rather wide temperature ranges. The temperature dependence of $\bar{C}_{p2}^\circ$ is even more interesting, because it is very sensitive to structural changes in the solution with a change in temperature. Heat capacities of electrolytes in nonaqueous solutions should be equally useful in understanding the structure of these solutions. However, up until now only three papers (*5, 13, 15*) have reported partial molal heat capacities of solutes in nonaqueous solutions. Only in the last of these (*15*) were the data obtained at sufficiently low concentrations to give reliable values at infinite dilution.

The traditional method of obtaining $\bar{C}_{p2}^\circ$ through direct specific heat measurements is not suitable for nonaqueous solutions, because measurements must be made at high concentrations where ion-pair formation is significant and because of uncertainties in extrapolating to infinite dilution from high concentrations.

Fortunately, the integral heat method (*3*) of evaluating $\bar{C}_{p2}^\circ$ avoids the most objectionable aspects of the direct specific heat method. The method involves measuring the heat of solution of a solute at different temperatures, and since accurate calorimetric measurements can be made in the range 0.001–0.02*m*, the question of nonideality and ion-pair formation is not nearly so serious. Furthermore, application of the Debye-Hückel equation in extrapolation of heat data requires only the first derivative of the dielectric constant, which is generally known with a fair degree of accuracy. At any given temperature the heat of solution can be expressed by

$$\Delta H_s = n_1\bar{H}_1 + n_2\bar{H}_2 - n_1\bar{H}_1^\circ - n_2H_2^\circ \qquad (1)$$

where $\bar{H}_1$ and $\bar{H}_2$ are the partial molal enthalpies of the solvent and solute, respectively, $\bar{H}_1^\circ$ and H_2° the molal enthalpies of the pure solvent and pure solid solute, respectively, and n_1 and n_2 are the respective number of moles of solvent and solute. At infinite dilution, $\bar{H}_1 = \bar{H}_1^\circ$, $\bar{H}_2 = \bar{H}_2^\circ$ and for one mole of solute, $n_2 = 1$, consequently Equation 1 reduces to

$$\Delta H_s^\circ = \bar{H}_2^\circ - H_2^\circ \qquad (2)$$

where $\bar{H}_2^\circ$ is the partial molal enthalpy of the solute at infinite dilution. The difference in the standard heats of solution at two temperatures, divided by the temperature interval, is

$$\frac{\Delta(\Delta H_s^\circ)}{\Delta T} = \frac{\Delta\bar{H}_2^\circ}{\Delta T} - \frac{\Delta H_2^\circ}{\Delta T} \qquad (3)$$

which, for sufficiently small temperature differences, becomes

$$\frac{d\Delta H_s^\circ}{dT} = \frac{d\bar{H}_2^\circ}{dT} - \frac{dH_2^\circ}{dT} = \Delta C_{p2}^\circ = \bar{C}_{p2}^\circ - C_{p2}^\circ \qquad (4)$$

or

$$\bar{C}_{p2}^\circ = C_{p2}^\circ + \Delta C_{p2}^\circ$$

where ΔC_{p2}° is the change in heat capacity for the solution process and C_{p2}° is the heat capacity of the pure solute. Since the heat capacities of the common solutes have been tabulated (*14*) or can be easily estimated, a determinationof $\bar{C}_{p2}^\circ$ is essentially reduced to obtaining accurate values of ΔH_s° at two temperatures.

EXPERIMENTAL

Materials. Fisher Purified $NaClO_4$ was further purified by the method described by Perrin and Armargeo (*17*). The salt was recrystallized twice from a methanol–acetone mixture, dried first at 105° and then at 150°C in a vacuum oven fitted with a liquid nitrogen trap. One should exercise caution in recrystallizing perchlorates from organic solvents. Such mixtures are subject to violent explosions, particularly in acidic solutions at higher temperatures.

Fisher absolute methanol was distilled from CaH_2 in a dry nitrogen atmosphere. The solvent was then passed through a column containing molecular sieves (Linde 3 °A). Analysis by Karl Fischer reagent indicated less than 0.002% water before and no more than 0.009% water after a calorimetric determination.

Distilled water that had been passed through an ion exchange column was used in all calorimetric measurements.

Apparatus. An all-glass, submarine, Dewar-type solution calorimeter of about 325 ml capacity was used for all measurements. The design was such that it had a small vapor

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space, a low thermal modulus ($\sim 2 \times 10^{-3}$ cal/deg-sec) and a short equilibration time (<5 min). Precision bore tubing was used as the stirring shaft, and the calorimeter was fit with a filling tube for introducing the anhydrous solvent after the calorimeter was placed in the bath. The bath medium was controlled to better than 0.001°C over the entire temperature range.

Temperature changes in the calorimeter were measured by a thermistor placed in one arm of a Wheatstone bridge. The very slight bridge unbalance was amplified by a Keithley Model 150B amplifier and the signal recorded on a strip chart recorder. During the addition of heat, the bridge was continuously balanced and the difference in the recorded initial and final lines used to interpolate between the smallest resistance increments on the bridge. The nonlinearity of the thermistor is not significant for the small temperature changes measured ($\sim$0.02°C). A useful temperature sensitivity of approximately 3×10^{-5}°C was obtained.

Absolute temperature measurements were made with an NBS calibrated platinum resistance thermometer and an L and N G-1 type Mueller bridge, with an attached commutator.

The calorimeter contained a calibration heater of manganin wire and having a resistance of about 80 Ω. A commercially available constant current source having a stability of 0.05% was used for all calibrations. Time intervals for the electrical calibrations were measured to 1 msec by a crystal controlled electronic clock.

Procedure. Thin-walled sample bulbs of known weight and having a diameter of about 8 mm were filled with $NaClO_4$ in a drybox and weighed under anhydrous conditions. These were then evacuated and sealed by melting glass around the neck of the bulb, care being taken to avoid decomposition of the sample. These bulbs were attached to the bottom of the stirring shaft which could be pushed down at the appropriate time to break the bulb. Heats of empty bulb-breaking were negligible.

The calorimeter was electrically calibrated before and after each measurement and an average used for the calculation. This procedure eliminated most of the small error caused by the nonlinearity of the thermistor. An accuracy check of these calibrations with the recommended (*12*) reaction of tris-(hydroxymethyl)aminomethane with 0.1N HCl indicated a calibration error of <0.1%.

CALCULATIONS AND RESULTS

All data were extrapolated to infinite dilution by both the simple Debye-Hückel equation

$$\Delta H_s = \Delta H_s{}^\circ - {}^2/_3\, \delta_H\, m^{1/2} \tag{5}$$

and by an extended Debye-Hückel equation. The concentration dependence of the heats were in agreement with the limiting law within the limits of experimental error. The extended Debye-Hückel equation can be written as (*3, 11*)

$$\rho = \Delta H_s{}^\circ - 2.303\, RT^2 \left(\frac{dB}{dT}\right) \nu_+\nu_- m \tag{6}$$

where

$$\rho \equiv \Delta H_s - \frac{\nu}{2} Z_+ Z_- \delta_H I^{1/2} \alpha \tag{7}$$

$$\alpha = \left| (1 + I^{1/2})^{-1} - \frac{\sigma(I^{1/2})}{3} \right| \tag{8}$$

B is a constant at a given temperature in the extended Debye-Hückel equation, $\sigma(I^{1/2})$ is a special function of the ionic strength, values for which have been tabulated by Harned and Owen (*10*), and the other symbols have their usual meaning. At infinite dilution where $m = 0$, $\rho^\circ = \Delta H_s{}^\circ$. Values of δ_H for water were taken from a tabulation by Mitchell (*16*) and δ_H for methanol were calculated from the dielectric constant data of Albright and Gosting (*2*) and the coefficient of cubical expansion from Washburn (*20*).

Extrapolation by the latter method, in which the Debye-Hückel slope has been removed, has the advantage that the slope of the line, $d\rho/dm$, is much smaller than that in the simpler treatment. This slope is the result of deviations from the simple Debye-Hückel equation, and in the present treatment the lines were drawn such that these slopes varied smoothly with temperature even though in some cases the resultant line was not the best line that could be drawn through the points. However, in every case the lines were drawn consistent with the experimental error and within the limits of error both the simple and extended methods of extrapolation gave the same results.

Experimental results for each temperature are summarized in Table I. The limiting slopes, δ_H, are listed along wtih each

Table I. Heats of Solution and ρ Values of Sodium Perchlorate in Water and Methanol

$m \times 10^3$	$m^{1/2} \times 10^2$	ΔH_s, cal/mol	$\delta_H I^{1/2}\alpha$, cal/mol	ρ, cal/mol
Sodium Perchlorate in Water				
$t = 1.16°C$				
$\delta_H = 473$				
2.241	4.73	4147	14	4133
4.900	7.00	4160	23	4137
7.657	8.75	4173	26	4147
9.089	9.53	4161	28	4133
13.997	11.83	4159	34	4125
		$\rho^\circ = \Delta H_s{}^\circ = 4142 \pm 8$ cal/mol		
$t = 5.05°C$				
$\delta_H = 503$				
1.630	4.03	3967	13	3954
2.315	4.81	3963	16	3947
4.516	6.72	3965	22	3943
6.260	7.91	3960	25	3935
7.742	8.80	3968	28	3940
10.713	10.35	3980	32	3948
		$\rho^\circ = \Delta H_s{}^\circ = 3948 \pm 6$ cal/mol		
$t = 8.72°C$				
$\delta_H = 530$				
0.779	2.79	3762	10	3752
2.251	4.75	3806	17	3789
3.498	5.91	3811	21	3790
6.534	8.08	3818	28	3790
7.043	8.39	3817	29	3788
10.557	10.27	3833	35	3798
		$\rho^\circ = \Delta H_s{}^\circ = 3791 \pm 18$ cal/mol		
$t = 14.94°C$				
$\delta_H = 589$				
1.308	3.62	3600	14	3586
4.314	6.57	3595	23	3572
4.695	6.85	3603	26	3577
6.030	7.77	3605	29	3576
7.004	8.37	3599	31	3568
11.859	10.89	3804	38	3566
14.045	11.85	3608	43	3565
		$\rho^\circ = \Delta H_s{}^\circ = 3574 \pm 7$ cal/mol		
$t = 19.98°C$				
$\delta_H = 638$				
1.133	3.37	3450	14	3436
3.360	5.80	3462	24	3438
3.577	5.98	3445	24	3421
4.198	6.48	3462	26	3436
5.271	7.26	3439	29	3410
7.319	8.56	3458	34	3424
7.762	8.81	3474	35	3439
12.928	11.37	3481	44	3437
		$\rho^\circ = \Delta H_s{}^\circ = 3433 \pm 11$ cal/mol		

(*Continued on next page*)

Table II. *(Continued)*

$m \times 10^3$	$m^{1/2} \times 10^2$	ΔH_s, cal/mol	$\delta_H I^{1/2}\alpha$, cal/mol	ρ, cal/mol
Sodium Perchlorate in Water				
$t = 25.54$°C				
$\delta_H = 695$				
0.931	3.05	3294	14	3280
1.221	3.49	3305	16	3289
1.747	4.18	3323	18	3305
3.259	5.71	3329	25	3304
4.286	6.55	3311	29	3282
4.857	6.97	3325	31	3294
7.471	8.64	3325	37	3288
$\rho° = \Delta H_s° = 3290 \pm 10$ cal/mol				
$t = 34.91$°C				
$\delta_H = 798$				
1.324	3.64	3085	19	3066
2.320	4.82	3112	25	3087
2.365	4.86	3089	25	3064
2.464	4.96	3109	25	3084
3.764	6.14	3121	31	3090
3.802	6.17	3127	32	3095
4.028	6.35	3115	33	3082
5.704	7.55	3156	38	3118
5.796	7.61	3158	38	3120
6.835	8.27	3159	42	3117
6.958	8.34	3144	42	3102
$\rho° = \Delta H_s° = 3098 \pm 20$ cal/mol				
$t = 45.04$°C				
$\delta_H = 923$				
1.046	3.23	2911	19	2892
1.630	4.04	2944	24	2920
2.923	5.41	2984	32	2952
3.005	5.48	2973	32	2941
4.364	6.61	2944	39	2905
5.166	7.19	2973	42	2931
6.165	7.85	2975	46	2929
8.197	9.05	2990	52	2938
8.307	9.11	2991	52	2939
8.954	9.46	2983	54	2929
10.133	10.07	3032	58	2974
10.918	10.45	2996	59	2937
$\rho° = \Delta H_s° = 2933 \pm 21$ cal/mol				
$t = 54.91$°C				
$\delta_H = 1057$				
0.907	3.01	2787	21	2766
1.765	4.20	2822	29	2793
2.612	5.11	2835	35	2800
3.894	6.24	2827	42	2785
6.825	8.26	2850	51	2799
10.698	10.34	2865	68	2797
$\rho° = \Delta H_s° = 2792 \pm 12$ cal/mol				
$t = 63.45$°C				
$\delta_H = 1176$				
3.153	5.62	2683	43	2640
4.975	7.05	2711	53	2658
7.253	8.52	2736	63	2673
8.970	9.47	2732	70	2662
$\rho° = \Delta H_s° = 2656 \pm 13$ cal/mol				
$t = 74.46$°C				
$\delta_H = 1369$				
2.977	5.46	2518	48	2470
6.824	8.26	2521	72	2449
8.592	9.27	2537	79	2458
11.752	10.84	2558	92	2466
$\rho° = \Delta H_s° = 2457 \pm 10$ cal/mol				
$t = 85.64$°C				
$\delta_H = 1582$				
3.140	5.60	2264	56	2208
9.420	9.71	2322	95	2227
19.040	13.80	2349	131	2218
$\rho° = \Delta H_s° = 2218 \pm 10$ cal/mol				
Sodium Perchlorate in Water				
$t = 94.93$°C				
$\delta_H = 1778$				
1.283	3.58	2056	41	2015
2.256	4.75	2054	54	2000
3.892	6.24	2067	71	1996
6.440	8.02	2092	90	2002
7.541	8.68	2090	97	1993
$\rho° = \Delta H_s° = 2000 \pm 9$ cal/mol				
Sodium Perchlorate in Methanol				
$t = -9.93$°C				
$\delta_H = 1412$				
1.027	3.20	2916	29	2945
3.883	6.23	2900	56	2956
6.279	7.92	2887	71	2958
7.699	8.77	2869	78	2947
$\rho° = \Delta H_s° = -2956 \pm 8$ cal/mol				
$t = 0.14$°C				
$\delta_H = 1845$				
2.371	4.87	2855	58	2913
3.023	5.50	2849	56	2905
6.139	7.84	2823	91	2914
6.766	8.23	2821	95	2916
10.508	10.25	2795	117	2912
$\rho° = \Delta H_s° = -2917 \pm 6$ cal/mol				
$t = 9.67$°C				
$\delta_H = 2723$				
3.653	6.04	2758	106	2864
5.807	7.62	2712	132	2844
7.692	8.77	2716	152	2868
11.274	10.62	2677	180	2857
$\rho° = \Delta H_s° = -2866 \pm 11$ cal/mol				
$t = 19.91$°C				
$\delta_H = 3882$				
3.235	5.69	2696	142	2838
4.146	6.44	2652	160	2812
6.359	7.97	2639	195	2834
10.016	10.01	2606	241	2847
$\rho° = \Delta H_s° = -2843 \pm 19$ cal/mol				
$t = 29.38$°C				
$\delta_H = 5207$				
1.848	4.30	2741	148	2889
4.604	6.79	2594	228	2822
6.998	8.37	2558	279	2837
11.627	10.78	2488	353	2841
$\rho° = \Delta H_s° = -2866 \pm 26$ cal/mol				
$t = 39.43$°C				
$\delta_H = 6903$				
1.539	3.92	2783	180	2963
3.410	5.84	2710	264	2974
4.832	6.95	2640	310	2950
7.300	8.54	2604	377	2981
11.274	10.62	2479	461	2940
$\rho° = \Delta H_s° = -2985 \pm 17$ cal/mol				
$t = 49.70$°C				
$\delta_H = 9303$				
5.105	7.15	2722	424	3146
6.630	8.14	2687	483	3170
8.651	9.30	2553	544	3097
11.362	10.66	2501	616	3117
$\rho° = \Delta H_s° = -3164 \pm 26$ cal/mol				
$t = 54.91$°C				
$\delta_H = 10700$				
1.848	4.30	2934	298	3232
3.336	5.78	2831	401	3232
5.448	7.38	2731	507	3238
6.327	7.95	2699	542	3241
6.411	8.01	2689	547	3236
7.019	8.38	2636	571	3207
10.972	10.47	2507	701	3208
$\rho° = \Delta H_s° = -3259 \pm 13$ cal/mol				

temperature. The first two columns give the molalities and square roots of the molality, respectively, while the last three columns give the measured heats of solution, the Debye-Hückel correction terms and the ρ values, respectively. The extrapolated heats of solution are listed immediately after the data for each temperature. All uncertainties are the standard deviations of the points from the lines.

The standard heat of solution of sodium perchlorate in water at 25.54°C is 3290 ± 10 cal/mol. Correcting this to 25.00°C by the present $\bar{C}_{p_2}°$ data gives 3302 ± 10 cal/mol which is in good agreement with Vanderzee's (*19*) value of 3315 ± 7 cal/mol. The heats of solution of sodium perchlorate in methanol at 19.91° and 29.38°C give −2856 ± 23 cal/mol for $\Delta H_s°$ at 25.00°C, which differs considerably from the literature values of −2400 (*4*) and −2600 ± 100 cal/mol (*8*).

Changes in heat capacity for the solution process and partial molal heat capacities for sodium perchlorate in water and methanol are given in Table II. The heat capacities of the crystalline salt, also listed in Table II, are estimated from the known heat capacities of potassium chlorate and perchlorate and sodium chlorate as given by Kelley (*14*). Figure 1 shows the temperature dependence of $\bar{C}_{p_2}°$ for sodium perchlorate in the two solvents and Table III gives smooth $\bar{C}_{p_2}°$ values at even temperatures. We believe these smooth values are accurate to one heat capacity unit except perhaps at the extremities of the temperature range.

Table II. Partial Molal Heat Capacities of Sodium Perchlorate in Aqueous and Methanolic Solutions, Cal/Deg-Mol

t, °C	$-\Delta C°_{p2}$	$C°_{p2}$	$\bar{C}°_{p2}$
	In Water		
3.11	49.5 ± 3.6	25.5	−24.4 ± 3.6
6.89	42.8 ± 6.5	25.6	−17.2 ± 6.5
11.83	34.9 ± 4.0	25.8	−9.1 ± 4.0
17.46	28.0 ± 3.6	26.0	−2.0 ± 3.6
22.76	25.7 ± 3.8	26.2	0.5 ± 3.8
30.23	20.5 ± 3.2	26.5	6.0 ± 3.2
39.98	16.3 ± 4.0	26.9	10.6 ± 4.0
49.98	14.3 ± 3.3	27.2	12.9 ± 3.3
59.18	15.9 ± 3.0	27.6	11.7 ± 3.0
68.96	18.1 ± 2.1	28.0	9.9 ± 2.1
80.05	21.4 ± 1.8	28.3	6.9 ± 1.8
90.29	23.5 ± 2.0	28.7	5.2 ± 2.0
	In Methanol		
−4.90	3.9 ± 1.4	25.1	29.0 ± 1.4
4.91	5.4 ± 1.8	25.5	30.9 ± 1.8
14.79	2.2 ± 2.9	25.9	28.1 ± 2.9
24.65	−2.4 ± 4.8	26.3	23.9 ± 4.8
34.41	−11.8 ± 4.3	26.7	14.9 ± 4.3
44.57	−17.4 ± 4.2	27.0	9.6 ± 4.2
52.31	−18.2 ± 7.5	27.3	9.1 ± 7.5

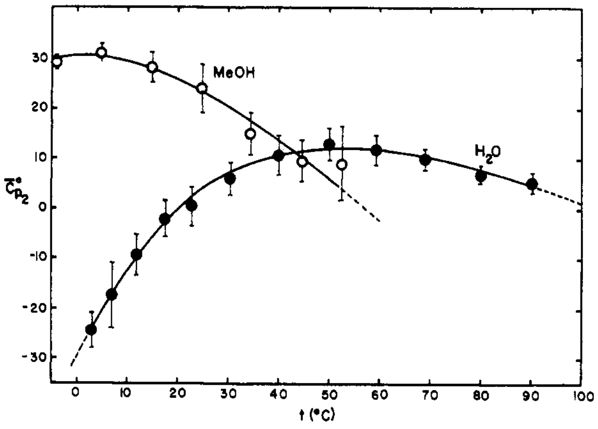

Figure 1. Partial molal heat capacities (cal/deg-mol) of sodium perchlorate in water and anhydrous methanol as function of temperature

Table III. Smoothed Values of Partial Molal Heat Capacities of Sodium Perchlorate in Water and Anhydrous Methanol, Cal/Deg-Mol

t, °C	$\bar{C}_{p_2}°$, H_2O	$\bar{C}_{p_2}°$, MeOH
−5.0	. . .	30.0
0.0	−30.0	30.4
5.0	−20.4	30.0
10.0	−12.4	29.2
15.0	−5.5	27.8
20.0	−0.2	25.5
25.0	4.2	23.0
30.0	7.1	20.2
40.0	10.7	13.7
50.0	12.0	6.0
60.0	11.6	−2.9
70.0	10.4	
80.0	7.9	
90.0	4.8	
100.0	1.2	

DISCUSSION

The most interesting feature of the data is the opposite temperature dependence of $\bar{C}_{p_2}°$ for $NaClO_4$ in the two solvents at low temperatures. While the heat capacities in water show the characteristic maximum (*1, 3, 6, 18*), those for the methanolic solutions decrease over most of the temperature range as the temperature is increased. However, the shape of the curve for the methanolic solutions indicates that it, too, may exhibit a maximum and that the curves in the two solvents may be qualitatively similar, but with the maximum in $\bar{C}_{p_2}°$ for methanol shifted to considerably lower temperatures.

These observations suggest that whatever processes are occurring in aqueous solutions are also occurring in methanolic solutions, but to a lesser extent and at lower temperatures. This is not surprising if one considers the structure of the two solvents at any given temperature. By use of the Frank and Wen (*7*) model for water, the negative heat capacities of electrolytes at lower temperatures have generally been explained by the "melting" effect that the ions have on the water structure. Because of the rupture of the normal water structure, less heat is required to increase the temperature of the solution than to increase the temperature of pure water. Presumably $\bar{C}_{p2}°$ is most negative at low temperatures where water is most structured and becomes more positive at higher temperatures because of the decreased water structure. For salts having complex ions, such as in the present case, $\bar{C}_{p2}°$ actually becomes positive at higher temperatures. For any given temperature, methanol is much less structured than water, consequently the negative contribution to the heat capacity is small and $\bar{C}_{p2}°$ is considerably larger than in water.

Above about 50°C for water and 5°C for methanol, apparently another effect predominates which causes $\bar{C}_{p_2}°$ to decrease as the temperature is increased. No satisfactory explanation has been given for this decrease, even in water.

NOMENCLATURE

B = constant in extended Debye-Hückel equation
$\bar{C}_p$ = partial molal heat capacity at constant pressure
C_p = heat capacity at constant pressure
ΔC_p = heat capacity of solution
H = enthalpy
$\bar{H}$ = partial molal enthalpy
ΔH_s = heat of solution

I = ionic strength
m = molality
n = number of moles
R = gas constant
T = absolute temperature
Z = charge on ion
α = special function defined in Equation 8
ν = number of ions
ρ = special function defined in Equation 7
$\sigma(I^{1/2})$ = special function defined in ref. *10*

Superscripts

° = standard state

Subscripts

1 = solvent
2 = solute
+ = cation
− = anion

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Ternary-Phase Diagrams for Systems Pyridine, Water, and Some C_6 Hydrocarbons

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Ternary-phase equilibrium data are reported for six liquid systems, each having pyridine and water as two of the three components. All of the measurements were made at atmospheric pressure, and the third component in the six systems was *n*-hexane, cyclohexene, 1-hexane, cyclohexene, 1-hexanol, and cyclohexanol. The solubility curve data were obtained by titrating known binary mixtures of hydrocarbon and water with pyridine to the point of homogeneity and the tie-line data were determined by titration of pyridine in hydrocarbon-, and water-rich phases with acid using an appropriate indicator.

As an extension of some previous work (*4*), we had occasion to determine phase diagrams of the ternary systems comprised of water, pyridine and *n*-hexane, cyclohexane, 1-hexene, cyclohexene, 1-hexanol or cyclohexanol as the third component. The results illustrate the effect of a double bond or a hydroxyl group on the solubility relationships among water, pyridine, and solvents listed above.

EXPERIMENTAL

Materials. Reagent-grade pyridine, cyclohexane, and cyclohexanol were obtained from City Chemical Corp. Gas chromatographic grade *n*-hexane was obtained from J. T. Baker Chemical Co. and reagent-grade 1-hexene from Matheson, Coleman and Bell. The modified methyl orange indicator used for tie-line determination consisted of equal quantities of a 0.1% methyl orange indicator solution in water and 0.25% indigo carmine indicator solution in water.

Procedure. Binodal solubility curves were determined by titrating known mixtures of hydrocarbon and water with pyridine until a homogeneous solution was obtained (*5*). The titrations were cumulative, a series of points being determined by adding water or hydrocarbon in known amount after each end point and titrating again to a clear solution. End-point sharpness varied with the ratio of components in the usual way (*3*) being poor at either end of the binodal solubility curve for

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