The low heat of ionization of 2,6-lutidine compared with pyridine has been ascribed to the lower heat of hydration of the BH^+ species (4); in the 2,6-lutidine ion the two alpha-methyl groups prevent strong solvation of the N-H⁺. Our heats of solution may be considered to occur via

the following steps:

$$B_{(\text{liquid})} + aq. = B_{(aq)}$$
(2)

$$\mathbf{B}_{(aq)} + 2N \operatorname{HCl} = \mathbf{B}\mathbf{H}^{+} + \operatorname{Cl}^{-} \operatorname{in} 2N \operatorname{HCl}$$
(3)

Table II. Heats of Solution, Ionization (5), and pK_a Values (1) of Bases $-\Delta H_s$, $-\Delta H_i$, Base pКa Kcal./Mole Kcal./Mole5.178.41 5.70 Pyridine 3-Picoline 5.68 9.27 6.70 5.9710.17 6 95 2-Picoline 4-Picoline 6.029.64 7.034-Ethylpyridine 6.02 9.57 6.75 11.99 6.15 2.6-Lutidine

The heat evolved in Equation 1 differs from that evolved in Equation 3 mainly by the heat of dilution and it is likely that this will be similar for all of the bases in 2NHCl considered. The main difference then lies in the heat change in Equation 2-i.e., the heat of hydration of liquid base. This would be expected to be greater for 2,6-lutidine because of the larger inductive effect produced by the two methyl groups. This would explain the high value of the heat of solution of 2,6-lutidine.

LITERATURE CITED

- Brown H.C., Mihm, X.R., J. Am. Chem. Soc. 77, 1725 (1955). (1)
- Greenwood, N.N., Perkins, P.G., J. Inorg. Nuclear Chem. 4, (2)291 (1957).
- Irving, R.J., Wadso, I., Acta Chem. Scand. 18, 195 (1964). (3)Mortimer, C.T., "Reaction Heats and Bond Strengths," Chap. (4)
- IX, Pergamon, New York, 1962. Mortimer, C.T., Laidler, K.J., Trans. Faraday Soc. 55, 1731 (5)
- (1959).(6)
 - Wilson, J.W., Worrall, I.J., J. Chem. Soc. 1968 (A), 316.

RECEIVED for review March 7, 1968. Accepted May 29, 1968.

Precision Densities of Dilute Aqueous Solutions of the **Isomeric Butanols**

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The densities of aqueous solutions of the four isomeric butanols in the molal concentration range 0.003 < m < 0.2 have been determined at 0.5°, 5°, 25°, and 40° C. by means of a magnetic float technique, capable of a precision of better than 1 p.p.m. The solute apparent molal volumes have been evaluated.

 $T_{
m HE}$ VOLUMETRIC properties of aqueous solutions of nonelectrolytes are of interest in the elucidation of solutewater interactions. In conjunction with other thermodynamic properties, they provide information about the phenomena of hydrophobic hydration and specific hydrogen bonding (2). These properties are affected both by the steric configurations of alkyl groups and the relative strengths of the solute-water hydrogen bonds. The waterbutanol systems were therefore selected for study, since both these effects could be examined.

To obtain the limiting solute partial molal volumes \overline{V}_{2}° , density data on dilute solutions must be available. As the concentration is reduced, the uncertainties in \overline{V}_2 , corresponding to a given experimental error in the solution density, rapidly increase, so that at concentrations below 0.1m, density errors must not exceed ± 1 p.p.m.

EXPERIMENTAL

The magnetic float technique was selected as being capable of producing data of the required precision, and details of the apparatus and its method of operation have already been described elsewhere (3, 11). Briefly, a quartz float, containing a small bar magnet of 100 c.g.s. unit pole strength, was weighted with platinum loops until it just sank in the solution under test. Different currents, i, were then applied to a solenoid wound around the outside of the solution cell and the times, t, taken by the float to rise through a given distance were determined. From the t^{-1} (i) relationship, the extrapolated current i_0 could be evaluated for which the electrical forces balanced those due to buoyancy. Thus;

$$i_0 = \frac{(1-d/D)w}{f} + \frac{W-dV}{f}$$

where d and D are the densities of the solution and platinum, respectively, W and w are the weights of the float and the platinum loops, V is the volume of the float, and f is the solenoid constant.

The cell was constructed in such a manner that progressive solute additions could be made without disturbing the float. The apparatus was immersed in a double thermostat, the temperature of which could be controlled to $\pm 0.001^\circ$, this being essential for measurements at 25° and above. Absolute temperatures were determined to $\pm 0.002^{\circ}$ with National Physical Laboratory calibrated thermometers. Values of i were obtained by measuring the potential drop across a standard 2-ohm resistance. Since no sufficiently accurate data exist for nonelectrolytes, the

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Table I.	Densities	and	Appar	ent	Molal	Volumes
	of Aqueou	us So	lutions	of	n-BuOl	4

Concen-	Density,	ϕ_v	Concen-	Density,	ϕ_v
tration,	G. per	Cc. per	tration,	G. per	Cc. per
m	Cc.	Mole	m	Cc.	Mole
0.	$5^{\circ} \pm 0.002^{\circ}$		5°	$\pm 0.002^{\circ}$	
	Run 1			Run 2	
0.000000	0.999872		0.03533	0.999550	85.90
0.003115	0.999836	85.72	0.04032	0.9994925	85.89
0.004639	0.9998185	85.64	0.04555	0.999433	85.85
0.006392	0.9997985	85.62	0.04902	0.9993925	85.85
0.008587	0.9997715	85.86	0.05347	0.9993415	85.84
0.01079	0.999746	85.81	0.05728	0.9992985	85.81
0.01243	0.999727	85,80	0.05728	0.999299	85.81
0.01478	0.999699	85.84	0.06080	0.999259	85.80
0.01870	0.9996535	85.84	0.06513	0.999209	85.79
0.02155	0.9996205	85.82	0.07097	0.9991435	85.76
0.02408	0.999591	85.83	0.07781	0.9990665	85.74
0.02736	0.9995525	85.83			
0.03082	0.9995125	85.82	0	25° - 0.002°	
0.03625	0.9994505	85.80		$.0 \pm 0.002$	
0.03967	0.9994105	85.80	0.000000	0 997048	
0.04379	0.9993635	85.79	0.002729	0.9970145	86.67
0.04774	0.9993195	85.76	0.005560	0.996980	86.59
0.05109	0.9992805	85.76	0.008847	0.006940	86.61
0.05109	0.999280	85.77	0.01363	0.9968825	86.55
0.05492	0.999236	85.77	0.01765	0.9968335	86.58
0.05928	0.9991875	85.74	0.02229	0.99677	86.63
0.06265	0.9991495	85.73	0.02664	0.9967235	86.62
0.06707	0,9990995	85.71	0.03165	0.9966635	86.60
0.07253	0.9990385	85.69	0.03753	0.996593	86.58
			0.04337	0.996522	86.58
	Run 2		0.04967	0.9964465	86.57
0.00000	0.999872		0.04967	0.9964465	86.57
0.02312	0,999602	85.83	0.05654	0.9963645	86.56
0.03533	0.9994615	85.79	0.06108	0.9963105	86.54
0.05667	0.9992185	85.72	0.06835	0.996225	86.52
0.05667	0.9992165	85.76	0.07617	0.9961325	86.51
0.07254	0.999039	85.68			
0.08555	0.9988945	85.64	4	$40^{\circ} \pm 0.002^{\circ}$	
0.10475	0.9986825	85.59	0.000000	0.000000	
0.11855	0.998532	85.55	0.000000	0.992220	
0.11855	0.998530	85.57	0.003082	0.992174	01.00
0.14982	0.9981965	85.46	0.000424	0.992138	07.00 97.70
0.16290	0.9980575	85.43	0.000070	0.992109	97.67
0.18344	0.9978435	85.36	0.01411	0.9920400	87.60
			0.01766	0.9919933	87.59
	$5^{\circ} \pm 0.002^{\circ}$		0.02012	0.9910090	87.60
0.00000	0 999965		0.03402	0.9916775	87.55
0.000000	0.0000000	85.68	0.04007	0.001581	87.54
0.006298	0.999890	86.04	0.05077	0.9915785	87.60
0.000200	0.999854	85.98	0.05854	0.0010700	87.58
0.01407	0.9997985	85.97	0.06647	0.9913825	87.57
0.01861	0.9997455	85.93	0.07446	0.991284	87.55
0.02234	0.999701	85.96	0.08996	0.991188	87.54
0.02661	0.999651	85.94	0.08955	0.9910965	87.54
0.03117	0.999598	85.93	0.00000	0.991006	87.51
			0.00100		0,101

method was tested with dilute solutions of NaCl and KCl in the molal concentration range 0.003 < m < 0.1. Good agreement was obtained with the results of Geffcken and Price (6) and Kruis (8) which are generally considered to be the most accurate density measurements on aqueous solutions (10). Thus at 25°, $\overline{V_2}$ values for NaCl and KCl were obtained as 16.65 (16.65) and 26.90 (26.85) cc. per mole, respectively, the figures in parentheses referring to the literature data (6, 8).

The butanols were purified by refluxing over CaO for 24 hours and subsequent fractionation. Their densities were determined pycnometrically. In the purification of water, extensive fractionation had to be avoided, because of isotope separation leading to density uncertainties. Hence deionized water, having a conductivity of $< 2 \times 10^{-6}$ ohm⁻¹ was

Table II. Densities and Apparent Molal Volumes of Aqueous Solutions of isoBuOH

Concen- tration, <i>m</i>	Density, G. per Cc.	$\overset{\phi_v}{ ext{Cc. per}}$ Mole	Concen- tration, <i>m</i>	Density, G. per Cc.	$\stackrel{\phi_\iota}{ ext{Cc. per}}_{ ext{Mole}}$
	$0.5^{\circ} \pm 0.002^{\circ}$		£	$5^{\circ} \pm 0.002^{\circ}$	
0.000000 0.002823 0.005050 0.007149	0.999872 0.9998365 0.9998115 0.9997865	86.64 86.13 86.11	0.08116 0.08836 2:	$\begin{array}{c} 0.999015 \\ 0.998934 \\ 5^{\circ} \pm 0.002^{\circ} \end{array}$	85.91 85.88
$\begin{array}{c} 0.01042 \\ 0.01446 \\ 0.01777 \\ 0.02126 \\ 0.02546 \end{array}$	0.999748 0.9996995 0.999660 0.999619 0.9995695	$86.04 \\ 86.07 \\ 86.06 \\ 86.06 \\ 86.04$	0.000000 0.002758 0.005782 0.009130	0.997048 0.9970135 0.9969765 0.9969365	86.83 86.81 86.63
$\begin{array}{c} 0.02850 \\ 0.03157 \\ 0.03684 \\ 0.04084 \\ 0.04607 \end{array}$	0.9995345 0.999498 0.999435 0.999389 0.999328	86.00 86.02 86.03 86.00 85.99	$\begin{array}{c} 0.01459\\ 0.01837\\ 0.02374\\ 0.02804\\ 0.03267\end{array}$	$\begin{array}{c} 0.996869\\ 0.996822\\ 0.9967575\\ 0.9967045\\ 0.996648 \end{array}$	86.71 86.72 86.66 86.70 86.68
$\begin{array}{c} 0.04007\\ 0.05012\\ 0.05012\\ 0.05610\\ 0.05964\\ 0.05964 \end{array}$	0.999281 0.9992805 0.9992125 0.999172	85.97 85.98 85.95 95.93	$\begin{array}{c} 0.03763\\ 0.04318\\ 0.04759\\ 0.04759\\ 0.04759\\ 0.05977\end{array}$	0.996588 0.9965215 0.9964665 0.9964685	86.67 86.64 86.67 86.64
$\begin{array}{c} 0.06442\\ 0.06878\\ 0.07418\\ 0.07828\\ 0.08258 \end{array}$	$\begin{array}{c} 0.9991175\\ 0.999067\\ 0.999007\\ 0.998960\\ 0.998911 \end{array}$	85.91 85.90 85.87 85.86 85.85	$\begin{array}{c} 0.05277\\ 0.05713\\ 0.06553\\ 0.07432\\ 0.08325\\ 0.08325\\ \end{array}$	$\begin{array}{c} 0.996406\\ 0.996353\\ 0.9962525\\ 0.9961475\\ 0.996041\\ 0.9952025\end{array}$	86.63 86.64 86.62 86.61 86.60
	$5^{\circ} \pm 0.002^{\circ}$		0.09253	0.9959335 $0^{\circ} \pm 0.002^{\circ}$	86.96
$\begin{array}{c} 0.000000\\ 0.004777\\ 0.007514\\ 0.01063\\ 0.01566\\ 0.02109\\ 0.02651\\ 0.03134\\ 0.03696\\ 0.04186\\ 0.04771\\ 0.05181\\ 0.05181\\ 0.05711\\ 0.06176\\ 0.06665\\ 0.07153\\ 0.0667\end{array}$	0.999965 0.9999075 0.999837 0.999837 0.999777 0.999772 0.9996485 0.999525 0.9994685 0.9993555 0.9993515 0.9993515 0.9993515 0.999353 0.999291 0.9992375 0.9991805 0.999125 0.999125 0.999125	$\begin{array}{c}\\ 86.14\\ 86.20\\ 86.18\\ 86.13\\ 86.13\\ 86.09\\ 86.06\\ 86.06\\ 86.06\\ 86.05\\ 86.05\\ 86.02\\ 86.01\\ 85.98\\ 85.98\\ 85.98\\ 85.96\\ 85.96\\ 85.94\\ 85.94\\ 85.92\end{array}$	$\begin{array}{c} 0.000000\\ 0.003565\\ 0.008570\\ 0.01339\\ 0.01850\\ 0.02538\\ 0.03120\\ 0.03734\\ 0.04423\\ 0.05246\\ 0.05246\\ 0.06107\\ 0.06961\\ 0.07770\\ 0.08636\\ 0.09435\\ 0.10300\\ \end{array}$	$\begin{array}{c} 0.992220\\ 0.9921745\\ 0.992110\\ 0.992050\\ 0.9919865\\ 0.991888\\ 0.9918255\\ 0.9918255\\ 0.9916575\\ 0.9915575\\ 0.991557\\ 0.991557\\ 0.991557\\ 0.9913445\\ 0.9913445\\ 0.991244\\ 0.991137\\ 0.9910395\\ 0.990933\\ \end{array}$	87.69 87.77 87.64 87.55 87.62 87.58 87.60 87.57 87.59 87.60 87.55 87.55 87.54 87.52 87.52 87.52

employed throughout. The water density data of Kell (7) were used but were converted from grams per milliliter to grams per cubic centimeter (1 ml. = 1.000028 cc.).

RESULTS AND DISCUSSION

Densities and solute apparent molal volumes, ϕ_{ν} , are presented in Tables I through IV. ϕ_{ν} values were calculated from the experimental densities by use of the relation

$$\phi_v = \frac{1000}{mdd_0} \quad (d_0 - d) + \frac{M}{d}$$

where d_0 is the density of water, and M is the solute molecular weight. The effect δd on the solution density by uncertainties in W, V, D, w, and i indicated that values of d were precise to well within ± 1 p.p.m. The limiting factors determining δd were an accurate knowledge of Dand the temperature control (at 25° and above).

The accuracy of ϕ_v depends on the precision of d and m. Thus for dilute solutions,

$$\delta\phi_v = - (1000/m) \delta d$$

Table	111.	Densities	and	Appar	ent	Molal	Volumes
	of	Aqueous	Solu	utions o	of se	c-BuOl	H

Table IV.	Densities	and Apparent	Molal Volumes
of	Aqueous	Solutions of te	rt-BuOH

Concen- tration, <i>m</i>	Density, G. per Cc.	$\stackrel{\phi_v}{ ext{Cc. per}} Mole$	Concen- tration, <i>m</i>	Density, G. per Cc.	ϕ_v Cc. per Mole
	$0.5^{\circ} \pm 0.002^{\circ}$			$5^{\circ} \pm 0.002^{\circ}$	
	Run 1		<u></u>	Run 2	
0.000000	0.999872		0.01068	0.999836	86.24
0.002679	0.9998385	86.56	0.01541	0.999779	86.22
0.004914	0.9998125	86.22	0.01839	0.9997425	86.23
0.007010	0.999786	86.38	0.02268	0.999691	86.23
0.009239	0.999760	86.25	0.02725	0.9996365	86.21
0.01241	0.999722	86.23	0.03269	0.999572	86.17
0.01096	0.999078	86.91	0.03927	0.9994940	86.10 86.14
0.02439	0.9995775	86.23	0.05039	0.999365	86.09
0.02902	0.999522	86.23	0.05592	0.9992085	86.10
0.03373	0.999467	86.18	0.05592	0.999299	86.09
0.03786	0.9994165	86.20	0.06245	0.999223	86.07
0.04257	0.999361	86.18	0.06764	0.9991625	86.05
0.04711	0.9993085	86.14	0.07389	0.999091	86.03
0.05291	0.9992405	86.13	0.07912	0.999030	86.02
0.05605	0,9991925	86.12	0.08509	0.998962	86.00
0.05055	0.999192	86.12	0.09048	0.998901	95.97
0.06529	0.999095	86.10	0.09913	0.998802	85.96
0.06936	0.999048	86.08	0.00010	0.000002	00.00
0.07333	0.9990015	86.08	2	$25^{\circ} \pm 0.002^{\circ}$	
0.07762	0.998954	86.04	0.00000	0.907048	
0.08149	0.9989075	86.05	0.000000	0.997048	86.18
0.08540	0.9988645	86.02	0.006702	0.9969665	86.54
0.08877	0.9988255	86.01	0.01011	0.9969255	86.51
	Run 2		0.01378	0.996881	86.53
0 00000	0 999872		0.01820	0.996829	86.46
0.01231	0.999723	86.26	0.02223	0.996779	86.52
0.02328	0.9995815	86.20	0.02730	0.9967185	86.51
0.02974	0.999511	86.30	0.03182	0.9966643	80.49 86.51
0.04410	0.9993415	86.21	0.03069	0.9965345	86.50
0.05196	0.9992505	86.15	0.4806	0.996470	86.49
0.06114	0.999142	86.14	0.04806	0.996471	86.46
0.06673	0.999140	80.17	0.05431	0.996307	86.45
0.00015	0.999002	86.08	0.06085	0.996320	86.44
0.08768	0.998835	86.05	0.06740	0.996242	86.43
0.09535	0.998747	86.03	0.07306	0.996176	86.42
0.10843	0.998599	85.99	0.08113	0.996081	86.41
0.11885	0.998483	85.94	0.09075	0.9909000	86 38
0.12981	0.998362	85.89	0.10172	0.000041	00.00
0.14144	0.9982335	85.86		$40^{\circ} \pm 0.002^{\circ}$	
0.14144	0.9982335	85.86		0.000000	
0.16707	0.9981095	85.77	0.000000	0.992220	
0.17662	0.9978525	85.74	0.004886	0.992159	87 A9
0.18754	0.9988375	85.70	0.003007	0.992055	87.42
0.19774	0.997631	85.66	0.01964	0.9919765	87.32
0.21193	0.997481	85.62	0.02594	0.9918985	87.33
0.22790	0.9973170	85.56	0.03275	0.991814	87.33
0.22790	0.9973145	85.57	0.03903	0.991737	87.32
0.24088	0.997183	85.53	0.04604	0.991652	87.29
0.20000	0.007039	00.40 85 12	0.05211	0.9915775	87.29
0.21341 0.28574	0.9967325	85.39	0.05211	0.9919779	07.32 87.91
5.200, r	$5^{\circ} \pm 0.0020$	00.00	0.06456	0.991424	87.29
	<u> </u>		0.07545	0.991293	87.26
0.000000	0.999965		0.08588	0.991168	87.24
0.004200	0.9999145	86.16	0.09740	0.9910295	87.22
0.007604	0.9998725	86.32	0.10921	0.9908895	87.20

$$= -\frac{1000}{m^2} (d^{-1} - d_0^{-1}) \,\delta m$$

An error analysis showed that for m = 0.1, the precision of ϕ_v is ± 0.02 cc. per mole, whereas for m = 0.01, the precision is at least ± 0.1 cc. per mole, as is also the accuracy

	of Aqueo	ous Solut	ions of ferf-	BUOH	
Concen-	Density,	ϕ_v	Concen-	Density,	ϕ_v
tration,	G. per	Cc. per	tration,	G. per	Cc. per
m	Cc.	Mole	m	Cc.	Mole
0.1	E 1 0 0090			50 0 000	
	$5^{-} \pm 0.002^{-}$			$3^{\circ} \pm 0.002^{\circ}$	
0.000000	0.999872		0.06827	0.999047	87.65
0.003714	0.999821	87.85	0.07375	0.998975	87.63
0.006526	0.999782	87.93	0.08000	0.998894	87.60
0.009660	0.999739	87.89	0.08522	0.9988265	87.58
0.01287	0 9996935	88.02	0.09038	0.998760	87.56
0.01201	0.00000000	87.91	0.09640	0.9986825	87.54
0.01000	0.0000020	87.92	0 10184	0.9986125	87.52
0.02017	0.000550	97.92	0.10104	0.0000120	01.02
0.02349	0.9999330	07.01	2	$5^{\circ} \pm 0.002^{\circ}$	
0.02744	0.9994900	01.00			
0.03153	0.9994405	07.00	0.000000	0.997048	
0.03406	0.9994065	87.83	0.002923	0.9970085	87.90
0.03762	0.999358	87.84	0.005601	0.9969725	87.86
0.04119	0.9993115	87.80	0.007725	0.9969435	87.93
0.04541	0.9992535	87.80	0.01113	0.996899	87.81
0.04541	0.9992515	87.84	0.01580	0.9968375	87.74
0.04958	0.9991965	87.81	0.01957	0.996787	87 79
0.05494	0.9991255	87.79	0.02480	0.996718	87.76
0.06173	0.9990345	87.78	0.03052	0.9966425	87.73
0.06554	0.9989835	87.76	0.03508	0.006583	87.71
0.07014	0.9989225	87.75	0.03003	0.990000	07.71
0.07620	0.998843	87.73	0.04147	0.990498	01.14
0.08106	0.9987805	87.70	0.04458	0.996457	01.02
0.08510	0.998727	87.69	0.04458	0.996407	07.00
0.09185	0.998639	87.66	0.04854	0.9964065	87.69
0.09185	0.998637	87.68	0.05481	0.9963245	87.68
0.00100	0.9985415	87.65	0.06032	0.996252	87.69
0.05220	0.0084465	87.63	0.06735	0.996160	87.68
0.10002	0.9904400	87.00 87.60	0.07334	0.9960835	87.65
0.11302	0.996363	07.00	0.08013	0.995996	97.64
0.12733	0.996162	07.00	0.08623	0.9959165	87.64
			0.09797	0.995767	87.61
5	$5^{\circ} \pm 0.002^{\circ}$		4	$0^{\circ} \pm 0.002^{\circ}$	
0.000000	0.999965		0.000000	0.992220	
0.003890	0.9999115	87.84	0.001529	0.992200	88.13
0.006904	0.9998705	87.85	0.004735	0.992158	88.05
0.01028	0.9998235	87.88	0.009462	0.992094	88.28
0.01526	0.9997565	87.79	0.01484	0.992021	88.36
0.01875	0.999708	87.84	0.01794	0.9910805	88.29
0.02258	0.9996565	87.82	0.02171	0.991930	88.30
0.02726	0.9995925	87.81	0.02793	0.9918475	88.29
0.03088	0.9995435	87.80	0.03295	0.9917805	88.28
0.03486	0.999491	87.77	0.04002	0.9916875	88.27
0.03948	0.9994285	87.76	0.04552	0.991614	88.28
0.04547	0.9993485	87.73	0.05420	0,991499	88.28
0.05127	0.9992705	87.73	0.06339	0.9913775	88.28
0.05127	0.9992715	87.71	0.07369	0.991242	88.27
0.05716	0.9991936	87.69	0.08356	0.991113	88.26
0.06306	0.9991155	87.67	0.09284	0.9909925	88.24
0.00000	0.0001100	0.,01	5.00201	2.0000020	00.51

of \overline{V}_2 (11). Within the concentration range $m \leq 0.1$, ϕ_v is a linear function of m at the lower temperatures, although a limiting $d\phi_v/dm$ value of zero becomes apparent for sec-BuOH and tert-BuOH at 40°. In the one case, sec-BuOH at 0.5°, where measurements were extended to higher concentrations, a distinct curvature in the $\phi_v(m)$ plot was found at m > 0.2, in agreement with Pasfield's values for n-BuOH at 30° (9).

For the linear parts of the plots, \overline{V}_2 can be easily obtained from

 $\overline{V}_2 = \phi_v + m (d\phi_v/dm)$

but the normal procedure of extrapolating ϕ_{\circ} data from relatively high concentrations to infinite dilution has no theoretical basis, and this aspect is discussed elsewhere (4).

No other density data are available with which the results here presented can be compared. Alexander (1) and Fried-

Table V. Limiting Molal Volumes, $\overline{V_2}$, and Normalized Slopes of $\phi_c(m)$ Isotherms for Butanols in Aqueous Solution at 0.5°

	\overline{V}_2° , Cc. per Mole			$-10^2 (1/\overline{V}_2) \ d\phi_v/dm \ { m per Mole}$		
	This work	Ref. (1) ^a	$\frac{\text{Ref.}}{(5)^{\flat}}$	This work	$\frac{\text{Ref.}}{(1)^a}$	$\begin{array}{c} \operatorname{Ref.} \\ (5)^{\flat} \end{array}$
n-BuOH	85.90	85.7	85.72	3.61	2.89	1.98
isoBuOH	86.15		86.07	3.86		2.86
sec-BuOH	86.33		86.02	4.27		2.40
tert-BuOH	87.95			3.17	• • •	

man and Scheraga (5) carried out pycnometric density determinations on some of the compounds in a higher concentration range (m > 0.1). In both cases, linear ϕ_v extrapolations, based on measurements at only five concentrations, were performed to evaluate $\overline{V_2^o}$. The agreement between the literature values of $\overline{V_2^o}$ and those obtained in this study is reasonable, but this is not true for the slopes of the $\phi_v(m)$ isotherms, as is shown in Table V.

Unfortunately, Friedman and Scherega state neither the numerical values of d_0 nor the density units—i.e., grams per milliliter or grams per cubic centimeter—used in their

calculations, and this makes the comparison somewhat uncertain.

ACKNOWLEDGMENT

The work described here was carried out by H. T. Smith at the University of Bradford in partial fulfilment of his Ph.D. program.

LITERATURE CITED

- (1) Alexander, D.M., J. CHEM. ENG. DATA 4, 252 (1959).
- (2) Franks, F., Ives, D.J.G., Quart. Rev. Chem. Soc. 20, 1 (1966).
- (3) Franks, F., Smith, H.T., Trans. Faraday Soc. 63, 2586 (1967).
- (4) Franks, F., Smith, H.T., Trans. Faraday Soc., in press, 1968.
- (5) Friedman, M.E., Scheraga, H.A., J. Phys. Chem. 69, 3795 (1965).
- (6) Geffcken, W., Price, D., Z. physik. Chem. B26, 81 (1934).
- (7) Kell, G.S., J. CHEM. ENG. DATA 12, 66 (1967).
- (8) Kruis, A., Z. physik. Chem. B34, 1 (1936).
- (9) Pasfield, W.H., J. Phys. Chem. 69, 2406 (1965).
- (10) Redlich, O., Meyer, D.M., Chem. Rev. 64, 221 (1964).
- (11) Smith, H.T., Ph.D. thesis, University of Bradford, Bradford, England, 1967.

RECEIVED for review March 11, 1968. Accepted June 24, 1968.

Dielectric Constants, Densities, and Viscosities of Acetone–1-Propanol and Acetone–*n*-Hexane Mixtures at 25° C.

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The dielectric constants, densities, and viscosities of acetone–1-propanol and acetone– *n*-hexane mixtures from 0 to 100% composition (at an interval of 10%) are reported at 25° C.

 $\operatorname{A}_{\operatorname{CCORDING}}$ to Stokes' law the mobility of a given ion is inversely related to the viscosity of the medium, so that the Walden product, $\Lambda^{\circ}\eta$, in a variety of solvents should remain constant. For ions which experience specific solvation effects (short range) $\Lambda^{\circ}\eta$ generally varies in different solvents. Even in the absence of any ion-solvent interaction $\Lambda^{\circ}\eta$ varies with the dielectric constant of the medium. Fuoss (4, 10) has suggested that the inconstancy is due to an additional frictional force produced as a result of dielectric relaxation induced by the ionic motion in polar solvents. Boyd (3) and Zwanzig (18) treated this subject theoretically and found that the frictional force consequent to dielectric relaxation depends upon the dielectric constant of the solvent. More recently, Atkinson (2) examined the applicability of the Fuoss-Boyd-Zwanzig equation to ionic solutions.

It seems appropriate at this stage to study the dependence of Λ° on either of the physical properties, the viscosity or the dielectric constant, singly. In the majority of conductance studies intended to examine the continuum model hydrodynamically the Fuoss effect is to be taken into account (8), as only change in the viscosity of the solvent is usually accompanied by a change in the dielectric constant.

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Mixed solvents in which either of the two physical properties remains constant throughout the whole composition range would provide a better resolution of the factors that affect Λ° . We report data on the physical properties of two mixed solvents, acetone-1-propanol and acetone-*n*-hexane, to call attention to the utility of these solvent systems in studies involving the Fuoss-Onsager conductance theory.

EXPERIMENTAL

1-Propanol. Reagent grade 1-propanol (E. Merck, Germany) was dried over $CaCl_2$, refluxed with pieces of sodium, and fractionally distilled. Traces of water were removed as a ternary azeotrope with benzene as a third component. 1-Propanol used in the preparation of mixtures had a specific conductance of $< 9 \times 10^{-9}$ cm.⁻¹ ohm⁻¹.

n-Hexane. *n*-Hexane (British Drug Houses, London) was shaken several times with concentrated sulfuric acid, washed and again shaken with $0.1N \text{ KMnO}_4$ in 10% NaOH, washed again, and kept over P₂O₅. The decanted product was refluxed with sodium and fractionally distilled twice.

Acetone. Acetone was purified by the method described earlier (8).

Measurements. Densities were measured with a singlestem pycnometer made from a 28-ml. Erlenmeyer flask. The pycnometer was calibrated with water at 25° C. Four