

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 $\text{N}-\text{H}^+$.

Our heats of solution may be considered to occur via the following steps:

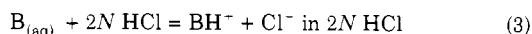
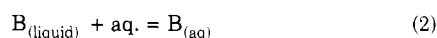


Table II. Heats of Solution, Ionization (5), and pK_a Values (1) of Bases

Base	pK_a	$-\Delta H_s$, Kcal./Mole	$-\Delta H_i$, Kcal./Mole
Pyridine	5.17	8.41	5.70
3-Picoline	5.68	9.27	6.70
2-Picoline	5.97	10.17	6.95
4-Picoline	6.02	9.64	7.03
4-Ethylpyridine	6.02	9.57	...
2,6-Lutidine	6.75	11.99	6.15

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 2N HCl 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.

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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.

THE VOLUMETRIC properties of aqueous solutions of nonelectrolytes are of interest in the elucidation of solute-water 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 water-butanol systems were therefore selected for study, since both these effects could be examined.

To obtain the limiting solute partial molal volumes \bar{V}_2 , density data on dilute solutions must be available. As the concentration is reduced, the uncertainties in \bar{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

Table I. Densities and Apparent Molal Volumes of Aqueous Solutions of *n*-BuOH

Concentration, <i>m</i>	Density, G. per Cc.	ϕ_v , Cc. per Mole	Concentration, <i>m</i>	Density, G. per Cc.	ϕ_v , Cc. per Mole
0.5° ± 0.002°			5° ± 0.002°		
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	25° ± 0.002°		
0.03082	0.9995125	85.82	0.000000	0.997048	...
0.03625	0.9994505	85.80	0.002729	0.9970145	86.67
0.03967	0.9994105	85.80	0.005560	0.996980	86.59
0.04379	0.9993635	85.79	0.008847	0.006940	86.61
0.04774	0.9993195	85.76	0.01363	0.9968825	86.55
0.05109	0.9992805	85.76	0.01765	0.9968335	86.58
0.05109	0.9992805	85.76	0.02229	0.99677	86.63
0.05492	0.999236	85.77	0.02664	0.9967235	86.62
0.05928	0.9991875	85.74	0.03165	0.9966635	86.60
0.06265	0.9991495	85.73	0.03753	0.996593	86.58
0.06707	0.9990995	85.71	0.04337	0.996522	86.58
0.07253	0.9990385	85.69	0.04967	0.9964465	86.57
RUN 2			0.04967	0.9964465	86.57
0.000000	0.999872	...	0.05654	0.9963645	86.56
0.02312	0.999602	85.83	0.06108	0.9963105	86.54
0.03533	0.9994615	85.79	0.06835	0.996225	86.52
0.05667	0.9992185	85.72	0.07617	0.9961325	86.51
0.05667	0.9992165	85.76	40° ± 0.002°		
0.07254	0.999039	85.68	0.000000	0.992220	...
0.08555	0.9988945	85.64	0.003582	0.992174	87.85
0.10475	0.9986825	85.59	0.006424	0.992138	87.68
0.11855	0.998532	85.55	0.008678	0.992109	87.70
0.11855	0.998530	85.57	0.01411	0.9920405	87.67
0.14982	0.9981965	85.46	0.01788	0.9919935	87.60
0.16290	0.9980575	85.43	0.02612	0.9918895	87.58
0.18344	0.9978435	85.36	0.03462	0.991782	87.60
5° ± 0.002°			0.04307	0.9916775	87.55
0.000000	0.999965	...	0.05077	0.991581	87.54
0.003161	0.9999285	85.68	0.05077	0.9915785	87.60
0.006298	0.999890	86.04	0.05854	0.9914825	87.58
0.009383	0.999854	85.98	0.06647	0.9913825	87.57
0.01407	0.9997985	85.97	0.07446	0.991284	87.55
0.01861	0.9997455	85.93	0.08226	0.991188	87.54
0.02234	0.999701	85.96	0.08955	0.9910965	87.54
0.02661	0.999651	85.94	0.09705	0.991006	87.51
0.03117	0.999598	85.93			

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°, \bar{V}_2^0 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 × 10⁻⁶ ohm⁻¹ was

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

Concentration, <i>m</i>	Density, G. per Cc.	ϕ_v , Cc. per Mole	Concentration, <i>m</i>	Density, G. per Cc.	ϕ_v , Cc. per Mole
0.5° ± 0.002°			5° ± 0.002°		
0.000000	0.999872	...	0.08116	0.999015	85.91
0.002823	0.9998365	86.64	0.08836	0.998934	85.88
0.005050	0.9998115	86.13	25° ± 0.002°		
0.007149	0.9997865	86.11	0.000000	0.997048	...
0.01042	0.999748	86.04	0.002758	0.9970135	86.83
0.01446	0.9996995	86.07	0.005782	0.9969765	86.81
0.01777	0.999660	86.06	0.009130	0.9969365	86.63
0.02126	0.999619	86.06	0.01459	0.996869	86.71
0.02546	0.9995695	86.04	0.01837	0.996822	86.72
0.02850	0.9995345	86.00	0.02374	0.9967575	86.66
0.03157	0.999498	86.02	0.02804	0.9967045	86.70
0.03684	0.999435	86.03	0.03267	0.996648	86.68
0.04084	0.999389	86.00	0.03763	0.996588	86.67
0.04607	0.999328	85.99	0.04318	0.9965215	86.64
0.05012	0.999281	85.97	0.04759	0.9964665	86.67
0.05012	0.9992805	85.98	0.04759	0.9964685	86.64
0.05610	0.9992125	85.95	0.05277	0.996406	86.63
0.05964	0.999172	95.93	0.05713	0.996353	86.64
0.06442	0.9991175	85.91	0.06553	0.9962525	86.62
0.06878	0.999067	85.90	0.07432	0.9961475	86.61
0.07418	0.999007	85.87	0.08325	0.996041	86.60
0.07828	0.998960	85.86	0.09253	0.9959335	86.56
0.08258	0.998911	85.85	40° ± 0.002°		
5° ± 0.002°			0.000000	0.999965	...
0.000000	0.999965	...	0.004777	0.9999075	86.14
0.004777	0.9999075	86.14	0.007514	0.9998745	86.20
0.007514	0.9998745	86.20	0.01063	0.999837	86.18
0.01063	0.999837	86.18	0.01566	0.999777	86.13
0.01566	0.999777	86.13	0.02109	0.9997125	86.11
0.02109	0.9997125	86.11	0.02651	0.9996485	86.09
0.02651	0.9996485	86.09	0.03134	0.999592	86.06
0.03134	0.999592	86.06	0.03696	0.9995255	86.06
0.03696	0.9995255	86.06	0.04186	0.9994675	86.05
0.04186	0.9994675	86.05	0.04771	0.9993995	86.02
0.04771	0.9993995	86.02	0.05181	0.9993515	86.01
0.05181	0.9993515	86.01	0.05181	0.999353	85.98
0.05181	0.999353	85.98	0.05711	0.999291	85.98
0.05711	0.999291	85.98	0.06176	0.9992375	85.96
0.06176	0.9992375	85.96	0.06665	0.9991805	85.96
0.06665	0.9991805	85.96	0.07153	0.999125	85.94
0.07153	0.999125	85.94	0.0697	0.9990625	85.92
0.0697	0.9990625	85.92	0.10300	0.990933	87.51

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_v , are presented in Tables I through IV. ϕ_v values were calculated from the experimental densities by use of the relation

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

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 *D* and 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 V. Limiting Molal Volumes, \bar{V}_2^0 , and Normalized Slopes of $\phi_v(m)$ Isotherms for Butanols in Aqueous Solution at 0.5°

	\bar{V}_2^0 , Cc. per Mole			$-10^2 (1/\bar{V}_2^0) d\phi_v/dm$ per Mole		
	This work	Ref. (1) ^a	Ref. (5) ^b	This work	Ref. (1) ^a	Ref. (5) ^b
<i>n</i> -BuOH	85.90	85.7	85.72	3.61	2.89	1.98
isoBuOH	86.15	...	86.07	3.86	...	2.86
<i>sec</i> -BuOH	86.33	...	86.02	4.27	...	2.40
<i>tert</i> -BuOH	87.95	3.17

^a at 0° C. ^b at 1° C.

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 \bar{V}_2^0 . The agreement between the literature values of \bar{V}_2^0 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 Scheraga 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.

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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.

ACCORDING 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 $< 9 \times 10^{-9} \text{ cm.}^{-1} \text{ ohm}^{-1}$.

***n*-Hexane.** *n*-Hexane (British Drug Houses, London) was shaken several times with concentrated sulfuric acid, washed and again shaken with 0.1N KMnO_4 in 10% NaOH , washed again, and kept over P_2O_5 . 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 single-stem pycnometer made from a 28-ml. Erlenmeyer flask. The pycnometer was calibrated with water at 25° C. Four