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

	$\overline{V}_2^\circ$, Cc. per Mole			$-10^2 (1/\overline{V}_2^\circ)\, d\phi_v/dm$ per Mole		
	This work	Ref. (*1*)[a]	Ref. (*5*)[b]	This work	Ref. (*1*)[a]	Ref. (*5*)[b]
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	...	...

[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 $\overline{V}_2^\circ$. The agreement between the literature values of $\overline{V}_2^\circ$ 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.

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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.

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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. 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 0.1*N* $KMnO_4$ 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

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to five fillings with the liquid of at least two samples were done and the readings (corrected to vacuum) averaged to calculate the density. The reported densities are accurate within + 0.05%.

Viscosities were measured with an Ostwald-Fenske viscometer with precautions to avoid the entrance of moisture. The viscometer was calibrated with conductivity water [$\eta = 0.8903$ (*16*)] and with Geddes data for dioxane-water mixtures (*6*). At least three readings with each sample were taken to calculate the viscosity. Kinetic energy corrections were negligible. The absolute values of the measured viscosity are better than ±1%, subject to the values used in the calibration.

Dielectric constant measurements were made with a DK 03 dekameter (Wissenschaftlich-Technische-Werkstatten). The instrument and the cells, which have been described (*8*), have been more precisely calibrated with Fuoss data on dioxane-water mixtures (*5*), since our previous paper. All measurements were done at 1.8 Mhz. The absolute values of the dielectric constant are better than 0.1%, subject to the values used in the calibration. These values, we believe, are free from systematic errors.

All mixtures were prepared in amounts of 0.4 to 0.5 kg. with an accuracy of better than ±0.01%. Despite the possibility of change in the bulk composition of the solvent mixture due to high volatility, the reported composition may be in error by not more than ±0.05%. The solvent mixing was endothermic in both cases.

All measurements were carried out in an oil bath at 25° ± 0.005° C.

RESULT AND DISCUSSION

The physical properties of acetone-1-propanol and acetone-*n*-hexane mixtures are summarized in Tables I and II, respectively. W_2 represents weight per cent acetone, X_2 its mole fraction, d density in grams per milliliter, η viscosity in centipoises, and D the dielectric constant. The tables also contain the derived physical properties of the solvent mixtures: P_{12}, the molar dielectric polarization in moles per milliliter; V_{12}, the molar volume; and δ, the deviation occurring during the volume additivity.

P_{12} of the mixtures was calculated from Kirkwood's equation (*15*),

$$P_{12} = (D - 1)(2D + 1)/9D[(X_1M_1 + X_2M_2)/d]$$

where M_1 and M_2 are the molecular weight of the two components in the mixture of mole fraction X_1 and X_2, respectively. V_{12} was calculated from

$$V_{12} = (X_1M_1 + X_2M_2)/d$$

and δ from

$$\delta = 1/d - 100/W_1d_1 - 100/W_2d_2$$

where W_1 and W_2 are the percentages of the two solvents of density d_1 and d_2, respectively.

As seen in Tables I and II, the viscosity and density of both solvent mixtures are the monotonic functions of the mole fraction composition. However, the remarkably high decrease in the viscosity of the acetone-1-propanol mixture on the initial addition of acetone indicates structure breaking in 1-propanol. Within the limits of experimental error the variation in the viscosity of acetone-*n*-hexane mixtures is in accordance with the mixture rule. As indicated by δ in Table I, contraction in volume occurs on the addition of acetone to 1-propanol throughout the whole composition range. There is an initial contraction on the addition of acetone to *n*-hexane (Table II), which becomes zero near $X_2 = 0.5$, and an initial expansion on the addition of *n*-hexane to acetone. V_{12} is a linear function of the mole fraction composition in both cases.

On the addition of acetone to 1-propanol the dielectric constant decreases, reaches a minimum near about $X_2 = 0.5$, and then increases in the acetone-rich mixtures (Figure 1). This minimum seems to be due to two conflicting effects: The addition of acetone to 1-propanol produces a considerable structure breaking and consequently a decrease in the dielectric constant, and an increase in the dielectric

Table I. Physical Properties of Acetone–1-Propanol Mixture at 25° C.

W_2	X_2	D	η	d	P_{12}	V_{12}	$10^3\delta$
0.0	0.0000	20.36[a]	1.984[b]	0.7998[c]	330.6	75.14	0.0
10.0	0.1032	19.42	1.433	0.7988	314.8	74.96	−1.4
20.0	0.2056	18.71	0.9891	0.7974	302.6	74.83	−1.8
30.0	0.3073	18.52	0.7819	0.7960	298.7	74.72	−2.0
40.0	0.4083	18.37	0.6403	0.7941	295.9	74.63	−1.0
50.0	0.5086	18.31	0.5381	0.7926	294.4	74.52	−1.0
60.0	0.6082	18.64	0.4652	0.7910	299.5	74.42	−1.4
70.0	0.7072	18.97	0.4139	0.7892	304.8	74.34	−0.8
80.0	0.8055	19.46	0.3742	0.7879	311.5	74.20	−2.0
90.0	0.9030	20.06	0.3453	0.7864	321.6	74.10	−1.3
100.0	1.0000	20.42[d]	0.3075[d]	0.7846[d]	327.1	74.02	0.0

[a] $D = 20.1$, (*1*), $D = 20.4$ (*11*). [b] $\eta = 1.93$ cp. (*7*). [c] d = 0.8008 g./cc. (*7*). [d] $D = 20.47$, $\eta = 3.040$ cp., d = 0.7846 g./cc. (*13*).

Table II. Physical Properties of Acetone–*n*-Hexane Mixture at 25° C.

W_2	X_2	D	η	d	P_{12}	V_{12}	$10^3\delta$
0.0	0.0000	1.89[a]	0.2930[a]	0.6545[a]	32.61	130.6	0.0
10.0	0.1416	2.92	0.3030	0.6699	61.34	122.7	0.0
20.0	0.2707	4.18	0.3137	0.6803	91.37	115.5	−5.4
30.0	0.3888	5.51	0.3047	0.6928	118.7	108.6	−9.1
40.0	0.4974	6.77	0.2983	0.7031	141.5	102.7	−4.8
50.0	0.5975	8.64	0.3043	0.7145	174.6	97.16	−0.0
60.0	0.6901	10.83	0.3039	0.7260	210.3	91.99	+0.8
70.0	0.7760	12.87	0.2984	0.7399	238.4	86.98	+0.8
80.0	0.8559	15.22	0.3113	0.7541	270.8	82.93	+0.4
90.0	0.9304	17.82	0.3144	0.7689	292.2	76.07	+0.5
100.0	1.0000	20.42	0.3075	0.7846	330.6	74.02	0.0

[a] $D = 1.8889$, $\eta = 0.2937$ cp., d = 0.6548 g./cc. (*17*).

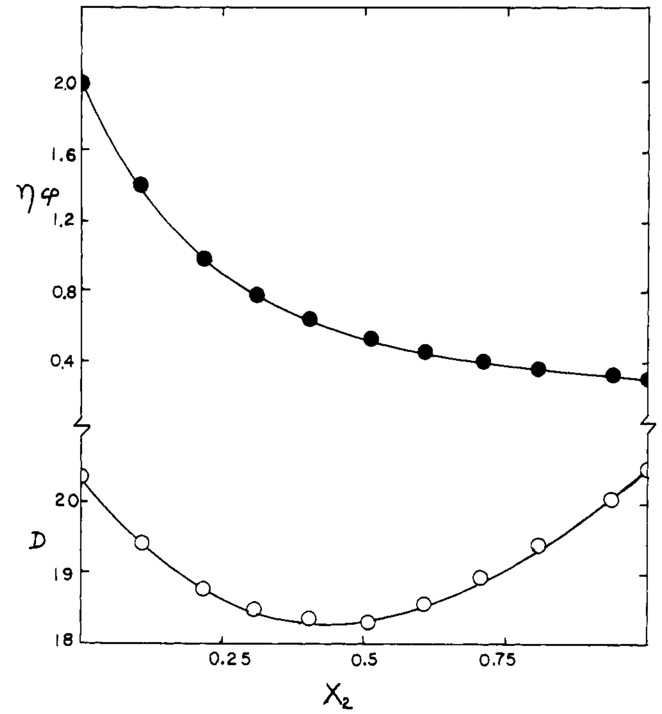

Figure 1. Dielectric constant and viscosity of acetone–1-propanol mixtures as a function of mole fraction composition

○ Dielectric constant

● Viscosity, centipoises

constant of the mixture consistent with the mixture rule. The structure breaking in hydrogen-bonded liquids, such as alcohols, is reflected as a remarkable decrease in both the dielectric constant and the viscosity. The relatively high decrease in the viscosity of 1-propanol on the initial addition of acetone, as seen in Figure 1, supports this view. The dielectric constant in acetone-*n*-hexane mixtures varies monotonically with the mole fraction composition. Evidence of changes in the intermolecular association can also be seen in the variation of Kirkwood's correlation factor, g (*9*), with composition. We calculated g by the method described by Oster (*12*). The correlation factor of acetone in *n*-hexane decreases from 1.12 in pure liquid to 0.99 in 40% acetone-60% *n*-hexane mixture. Further addition of *n*-hexane increases g. In binary mixtures of polar substances—e.g., acetone-1-propanol—it does not seem possible to calculate the correlation factor.

Acetone and 1-propanol are good solvents for several inorganic salts (*7, 13, 14*). It would be of interest to examine the conductance behavior of electrolytes in these two solvent systems to help single out the solvent's physical properties which affect Λ°.

LITERATURE CITED

(1) Akerlof, G., *J. Am. Chem. Soc.* **54**, 4125 (1932).
(2) Atkinson, G., Yori, M., *J. Phys. Chem.* **71**, 3523 (1967).
(3) Boyd, R.H., *J. Chem. Phys.* **35**, 1281 (1961).
(4) Fuoss, R.M., *Proc. Natl. Acad. Sci., U.S.* **45**, 807 (1959).
(5) Fuoss, R.M., Lind, J.E., *J. Phys. Chem.* **65**, 1001 (1961).
(6) Geddes, J.A., *J. Am. Chem. Soc.* **55**, 4832 (1933).
(7) Gover, T.A., Sears, P.G., *J. Phys. Chem.* **60**, 330 (1956).
(8) Johari, G.P., Tewari, P.H., *J. Am. Chem. Soc.* **87**, 4691 (1965).
(9) Kirkwood, J.G., *J. Chem. Phys.* **7**, 911 (1939).
(10) Lind, J.E., Fuoss, R.M., *J. Phys. Chem.* **65**, 999 (1961).
(11) Maryott, A.A., Smith, E.R., *NBS Circ.* **514** (Aug. 10, 1951).
(12) Oster, G.J., *J. Am. Chem. Soc.* **68**, 2036 (1946).
(12) Oster, G.J., *J. Am. Chem. Soc.* **68**, 2036 (1946).
(13) Reynolds, M.B., Kraus, C.A., *Ibid.*, **70**, 1709 (1948).
(14) Sears, P.G., Wilhoit, E.D., Dawson, L.R., *J. Phys. Chem.* **60**, 169 (1956).
(15) Smyth, C.P., "Dielectric Behavior and Structure," p. 28, McGraw-Hill, New York, 1955.
(16) Swindells, J.F., Snyder, C.F., Hardy, R.C., Golden, P.E., *Natl. Bur. Std., Circ. Supp.* **440**, 700 (1958).
(17) Timmermans, J., "Physico-Chemical Constants of Pure Organic Liquids,"p.42, 43, Elsevier, New York, 1950.
(18) Zwanzig, R., *J. Chem. Phys.* **38**, 1603 (1963).

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Low Temperature Heat Capacity and Entropy of Dipotassium Calcium Pyrophosphate at 10° to 310° K.

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The low temperature heat capacity of synthetic crystalline dipotassium calcium pyrophosphate, $K_2CaP_2O_7$, was measured over the temperature range 10° to 310° K. The calculated entropy at 298.15° K. is 60.91 cal. deg.$^{-1}$ mole^{-1} and the enthalpy is 9341 cal. per mole.

DIPOTASSIUM CALCIUM PYROPHOSPHATE, $K_2CaP_2O_7$, is relatively concentrated in both phosphorus and potassium, and its physical properties and ease of preparation make it a potentially useful fertilizer material. The optical properties and x-ray diffraction spectra of the crystalline material were measured by Brown *et al.* (*1*), and results of greenhouse tests of its agronomic value were reported by Lehr *et al.* (*5*). As part of a continuing program of determination of thermodynamic properties of compounds involved in fertilizer technology and in fertilizer-soil reactions, the low temperature heat capacity of dipotassium calcium pyrophosphate was measured over the range 10° to 310° K. and its entropy and enthalpy at 298.15° K. were calculated from the results.

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[1] Deceased.