Dielectric Constants of Binary Systems

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DIELECTRIC constants of liquids and gases in binary and ternary systems have become increasingly important in the evaluation of kinetic data, stability constants, and acid dissociation constants (*3, 7, 8, 11, 12, 13*). Because of the paucity of such data, the dielectric constants of 14 binary systems of common solvents were determined (Tables I and II).

Table I. Dielectric Constants of Pure Solvents at 25° C.

Pure Solvents	ε, Found	ε, Literature
p-Dioxane	2.24	2.209 (*10*)
Methanol	33.1	32.63 (*10*)
Ethanol	23.8	24.30 (*10*)
2-Propanol	19.2	19.4 (*4*)
		18.3 (*10*)
Acetone	20.5	20.7 (*10*)
2-Methyl-2-Propanol	12.5[a] (25.01°)	
	12.3 (25.92°)	

[a] Dielectric constant of supercooled liquid.

Table II. Dielectric Constants of Mixed Solvents at 25° C.

Weight % of Second Component	ε 2-Methyl-2-propanol *p*-Dioxane	ε Ethanol Acetone	ε Ethanol 2-Propanol	ε Methanol Ethanol	ε 2-Methyl-2-propanol Methanol
10.0	10.3	23.3	23.6	32.0	16.0
30.0	7.52	21.9	22.5	30.1	20.0
50.0	5.57	21.1	21.7	28.4	23.4
70.0	3.99	20.4	20.7	26.6	27.2
90.0	2.76	20.3	19.7	24.8	33.7

	2-Methyl-2-propanol Ethanol	Methanol Acetone	*p*-Dioxane Methanol	*p*-Dioxane Ethanol	*p*-Dioxane Acetone
10.0	14.8	31.9	3.90	3.27	3.96
30.0	17.6	29.4	9.17	6.61	7.56
50.0	19.6	26.9	15.9	11.1	11.3
70.0	21.5	24.2	23.0	16.1	15.0
90.0	23.3	21.7	30.2	21.3	18.6

	2-Methyl-2-propanol 2-Propanol	*p*-Dioxane 2-Propanol	Methanol 2-Propanol	2-Methyl-2-propanol Acetone
10.0	13.7	2.93	31.2	12.3
30.0	15.5	4.98	28.3	13.2
50.0	16.8	7.96	25.4	14.8
70.0	17.8	11.9	22.8	16.7
90.0	18.7	16.1	20.3	19.2

EXPERIMENTAL PROCEDURE

The heterodyne beat apparatus of Hudson and Hobbs (*5*) was employed to measure the dielectric constants of the solutions at a frequency of 550 kilocycles per second by means of the parallel substitution method. A General Radio type 722-D precision condenser was chosen as the standard condenser. It was internally calibrated by the substitution method over the entire range, 100 to 1100 micro micro farad and the appropriate correction terms were then applied to all readings. The cell consisted of two concentric platinum cylinders similar to that of Berberich (*1*). The cell constant was determined from measurements taken on nitrogen and benzene whose dielectric constants at 25° C. are 1.0005 and 2.2721 respectively. The accuracy of the measurements is between 0.5 and 1%. All measurements were performed at 24.96, ±.02° C., and the values reported are the average of ten determinations having a precision of at least 0.1%.

PURIFICATION OF SOLVENTS

Absolute ethanol, 2-propanol, and methanol were dried over magnesium ribbon for several days, then fractionally distilled in a Vigreux column (*9*). Fractions were collected at 78.34° (ethanol), 82.33–9° (2-propanol), 64.51° (methanol).

Reagent-grade 2-methyl-2-propanol was distilled from sodium and fractionally crystallized from its own melt until a melting range of 24.85° to 25.00° C. was attained (*9*).

A good grade of acetone was fractionally distilled from anhydrous copper sulfate in a Vigreux column, the fraction boiling at 56.5° C. being collected (*2*).

Reagent-grade *p*-dioxane was refluxed over sodium hydroxide for 24 hours. It was then distilled and refluxed for two days over sodium. The pure *p*-dioxane was fractionally distilled from the sodium in a Vigreux column, the 101.5° C. fraction being collected (*6*).

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