

# Deviation of Dielectric Constant from Ideality for Certain Binary Solvent Systems

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**Abstract** □ An equation was derived which relates the dielectric constant of mixtures of a binary solvent system to the mole fraction of the polar and nonpolar components of the system. The coefficients of the formula are readily calculated from the dielectric constant and the molar volume of the pure components of the binary solvent system. These calculated values are employed in graphical representations of the theoretical relationship of the dielectric constant of the binary solvent system and the mole fraction of the polar component of the solvent system. Experimental measurements are employed to demonstrate deviations from ideality.

**Keyphrases** □ Dielectric constant—binary solvent systems, deviation from ideality, equation developed □ Binary solvent systems—deviation of dielectric constant from ideality, equation developed □ Solvents—binary systems, deviations from ideality, equation developed relating the dielectric constant to mole fraction

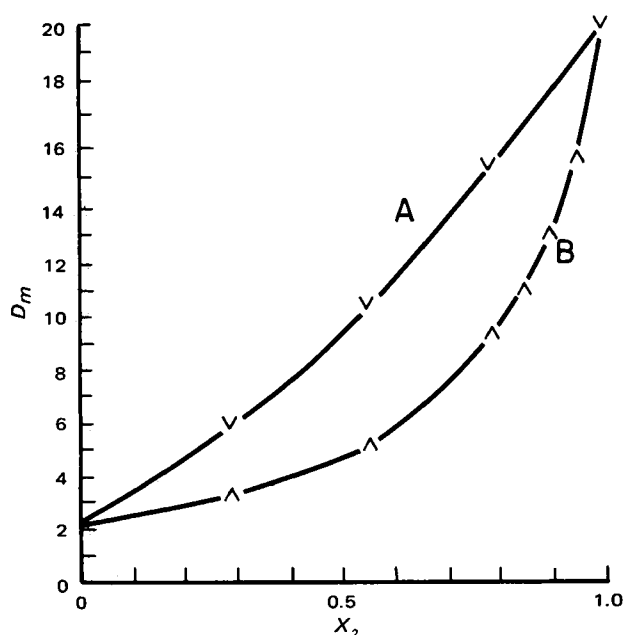
For solutions of polar solutes in nonpolar solvents, the following equation applies (1):

$$P_M = [(D - 1)/(D + 2)](M/\rho) \quad (\text{Eq. 1})$$

By using this equation, the dielectric constant of a binary solvent mixture ( $D_m$ ) was related to the mole fractions of the nonpolar solvent ( $X_1$ ) and the polar solvent ( $X_2$ ):

$$D_m = (aX_1 + bX_2)/(cX_1 + dX_2) \quad (\text{Eq. 2})$$

The coefficients  $a$  and  $b$  are summations of the molar volume and molar polarization of pure nonpolar and polar solvents, respectively;  $c$  and  $d$  represent the



**Figure 1**—Relationship of the dielectric constant ( $D_m$ ) and the mole fraction of acetone ( $X_2$ ) for the benzene–acetone binary solvent system. A is the experimental curve, and B is the theoretical curve.

**Table I**—Theoretical Values of  $a$ ,  $b$ ,  $c$ , and  $d$  for Benzene–Acetone and Benzene–Methyl Isobutyl Ketone Binary Solvent Systems

Coefficient	Benzene–Acetone	Benzene–Methyl Isobutyl Ketone
$a$	142.40	142.40
$b$	201.80	325.50
$c$	61.90	61.90
$d$	9.64	25.25

difference between the molar volume and molar polarization of the nonpolar and the polar solvents, respectively (2). These coefficients can be derived and represented as:

$$a = \bar{V}_1 + 2[(D_1 - 1)/(D_1 + 2)]\bar{V}_1 = \bar{V}_1[(3D_1)/(D_1 + 2)] \quad (\text{Eq. 3})$$

$$b = \bar{V}_2 + 2[(D_2 - 1)/(D_2 + 2)]\bar{V}_2 = \bar{V}_2[(3D_2)/(D_2 + 2)] \quad (\text{Eq. 4})$$

$$c = \bar{V}_1 - [(D_1 - 1)/(D_1 + 2)]\bar{V}_1 = \bar{V}_1[(3)/(D_1 + 2)] \quad (\text{Eq. 5})$$

$$d = \bar{V}_2 - [(D_2 - 1)/(D_2 + 2)]\bar{V}_2 = \bar{V}_2[(3)/(D_2 + 2)] \quad (\text{Eq. 6})$$

where  $\bar{V}_1$  and  $\bar{V}_2$  are the molar volumes and  $D_1$  and  $D_2$  are the dielectric constants of the nonpolar and polar components of the binary solvent system, respectively.

## EXPERIMENTAL

Benzene was selected as the nonpolar component of the non-aqueous binary solvent system. The polar component was methyl isobutyl ketone in one system and acetone in the other. These reagents, of the highest purity grades available, were used without further purification.

The benzene–methyl isobutyl ketone solvent system had a dielectric constant range of 2.29 for pure benzene to 12.80 for pure methyl isobutyl ketone (3). The dielectric constant range for the benzene–acetone solvent system was 2.29 for pure benzene to 20.97 for pure acetone. The Heterodyne-Beat apparatus and procedure (2) were employed in determining the dielectric constants of the different mixtures of the two binary solvent systems. All measurements were performed at 25°.

## RESULTS AND DISCUSSION

The theoretical values for the coefficients of Eq. 2 are calculated from the molar volumes ( $\bar{V}_1$  and  $\bar{V}_2$ ) and dielectric constants ( $D_1$  and  $D_2$ ) of the pure solvents. The  $\bar{V}_1$  and  $\bar{V}_2$  values are readily determined from the molecular weight and the density of the pure solvents. The  $D_1$  and  $D_2$  values were determined experimentally and approximated those reported in the literature (3).

The theoretical values of  $a$ ,  $b$ ,  $c$ , and  $d$  for benzene–acetone and benzene–methyl isobutyl ketone are reported in Table I. By using these values and Eq. 2, the theoretical dielectric constant of any mixture at any given mole fraction of the two components can be calculated. These values are reported in Table II.

Mixtures of definite composition were prepared, and their dielectric constants were measured. The results for benzene–acetone and benzene–methyl isobutyl ketone are also reported in Table II. The theoretical and experimental values for the benzene–acetone binary solvent system are plotted in Fig. 1. The experimental curve shows definite deviations from the theoretical (the same is observed when the results for the benzene–methyl isobutyl ketone

Table II—Theoretical, Experimental, and Computer-Calculated Values of  $D_m$  for Benzene–Acetone and Benzene–Methyl Isobutyl Ketone Binary Systems

Benzene–Acetone $D_m$				Benzene–Methyl Isobutyl Ketone $D_m$			
$X_2$	Theoretical	Experimental	Computer Calculated <sup>a</sup>	$X_2$	Theoretical	Experimental	Computer Calculated
0.000	2.30	2.30	2.19	0.000	2.30	2.30	2.27
0.284	3.39	5.83	5.85	0.190	3.22	4.28	4.23
0.549	5.24	10.42	10.20	0.420	4.72	6.66	6.63
0.784	9.37	15.65	15.14	0.690	7.33	9.59	9.50
0.850	11.02	—	—	0.800	8.88	—	—
0.900	13.18	—	—	0.900	10.62	—	—
0.950	16.19	—	—	0.950	11.67	—	—
1.000	20.90	20.90	20.98	1.000	12.89	12.90	12.86

<sup>a</sup>Based on computer-determined values of the coefficients. (See Ref. 2.)

system are plotted), because the ideal conditions under which the relationship was derived were not satisfied in real mixtures.

For example, the molar volumes of the two solvents change upon mixing. The electrical forces of the surrounding molecules exert an appreciable effect on each other. Consequently, the molar polarizations of the solvents also change upon mixing. Hence, the  $D_m$  values calculated from theoretical values of  $a$ ,  $b$ ,  $c$ , and  $d$  are significantly different from the experimentally determined  $D_m$  values. Therefore, it becomes necessary to measure the  $D_m$  values experimentally and subject them, along with the  $X_1$  and  $X_2$  values, to computer analysis to determine the values of the coefficients that will produce the best fit of the relationship to the experimental data.

The best values of the  $a$ ,  $b$ ,  $c$ , and  $d$  coefficients were determined by computer analysis (2) based on a series of laboratory experiments. The dielectric constant for any mixture of the benzene–acetone or the benzene–methyl isobutyl ketone binary solvent system can thus be predicted with the use of these values and Eq. 2. As reported in Table II, the predicted values (computer calculated) for  $D_m$  compare favorably with the experimentally determined values.

This finding supports the usefulness of Eq. 2 for predicting  $D_m$  values of the binary solvent systems of the type studied here.

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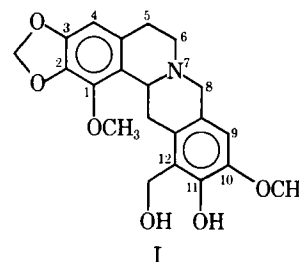
## Alkaloids of *Papaver orientale* and *Papaver pseudo-orientale*

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**Abstract** □ Dry latex of *Papaver orientale* was shown to contain 20% oripavine and 9% thebaine. Dry latex of *Papaver pseudo-orientale* contained two major alkaloids, isothebaine (11.7%) and orientalidine (0.5%), and the minor alkaloids bracteolin, salutaridine, Or<sub>1</sub>, Or<sub>2</sub>, PO-4, alborine (PO-5), and a novel alkaloid aryapavine.

**Keyphrases** □ *Papaver* alkaloids— isolation and identification from *P. orientale* and *P. pseudo-orientale* □ Aryapavine— isolation, identification from *Papaver pseudo-orientale*

As part of a broad study of the *Papaver* genus in Iran (1–3), the chemotaxonomy of *Papaver bracteatum*<sup>1</sup>, *Papaver orientale*<sup>1</sup>, and *Papaver pseudo-orientale*<sup>1</sup> has been studied.



Contradictory results exist in the literature with regard to the alkaloids of *P. bracteatum* and *P. orientale*. In addition to thebaine, other alkaloids have been reported in *P. bracteatum* (4–7). However, the present authors and others have demonstrated the existence of only thebaine (1, 3, 8) or a small amount of alpinigenine in addition to thebaine (2, 9–11) in *P. bracteatum*. Similar contradictory results have been reported for *P. orientale*. In addition to isothebaine,

<sup>1</sup> The plants were identified by P. Goldblat, Missouri Botanical Garden, St. Louis, Mo. Herbarium samples have been deposited in the Missouri Botanical Garden.