

DIELECTRIC CONSTANT OF METHANOL OVER A WIDE RANGE OF TEMPERATURES AND AT HIGH PRESSURES

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Abstract. The practical application of methanol in various branches of industry and energy was discussed. The apparent molar volume of aqueous and non-aqueous solutions of salts, its determination at infinite dilution, at high pressures and in a wide range of temperatures was analyzed. The necessity of thermophysical, chemical properties and especially the dielectric constant (D) of methanol for its use as a solvent in such a wide range of state parameters was discussed. The available dielectric constant (D) values of methanol available in literature were analyzed in detail. An empirical equation was developed for fitting of literature values and their deviation from fitted results was discussed.

Keywords: Methanol, dielectric constant, apparent molar volume, empiric equation, high temperature.

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1. Introduction

Methanol or methyl alcohol is the traditional chemical substance used over many centuries by various fields. In large amounts, methanol acts as an inhibitor to the transport of oil and gas to prevent hydrates from forming (Kvamme *et al.*, 2018; Bechtold *et al.*, 2007), and in the fuel industry it functions as a fuel additive (to hydrocarbons, olefins, and gasoline). The application of methanol as a fuel in an internal combustion engine (Verhelst *et al.*, 2019) has dramatically increased in recent years. Most modern fuel systems can accommodate low-level methanol blends (up to 10%) without problems (Bechtold *et al.*, 2007). Methanol is also used as a solvent, antifreeze, and for the production of different chemicals (e.g., corrosion inhibitors and descalers, functional fluids, oxidizing/reducing agents, paints and coating additives, solids separators, viscosity adjusters).

Another important application of methanol is as heat transfer fluids (HTF) in the absorption refrigeration and heat pump systems (ARMHP) in binary mixtures with an electrolyte salt (LiBr, LiCl, CaCl₂, ZnBr₂, ZnCl₂, ionic liquids, etc.) in replacement of aqueous electrolyte salt solutions. The high absorbing temperature, caused by air-cooling, requires a higher absorbent concentration of HTF to maintain a low vapor pressure in the absorber (Rockenfeller and Langeliers). HTF must be thermally stable at all ranges of working temperatures. Reactions with metals, corrosion, and consolidation materials should be minimal. The crystallization of a solution during the working time of the machine is inadmissible. During this application of methanol as a solvent, the two main problems with using conventional aqueous electrolyte salt solutions, such as HTF, are preventing crystallization and corrosion (which also depends on operating temperatures) to allow temperatures to fall below the freezing point of water.

Given their wide range, application to the design of technologies requires an understanding of the thermophysical and physicochemical properties of methanol, which has been widely investigated over the last century. During the last thirty years, our laboratory has investigated the following thermophysical properties of methanol:

- (p, ρ, T) properties at $T = (253.15 \text{ to } 468.65) \text{ K}$ and at pressures up to $p = 200 \text{ MPa}$,
- vapor pressure measurements P/Pa at $T = (274.15 \text{ to } 468.67) \text{ K}$,
- heat capacity measurements $c_{p0,s}/(\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1})$ at $T = (253.15 \text{ to } 468.67) \text{ K}$, ambient and saturated vapor pressures,
- viscosity measurements $\eta_{0,s}/(\text{mPa} \cdot \text{s})$ at $T = (253.15 \text{ to } 468.67) \text{ K}$, ambient and saturated vapor pressures etc.

The important parameters throughout the investigation of thermophysical and physicochemical properties of binary methanol and electrolyte salts as HTF are the analysis of apparent molar volume and compressibility, application of the Pitzer equation, analysis of Debye–Hückel limiting slopes (for the electrolyte salts), and evaluation of the infinite–dilution apparent molar volume of electrolyte salts.

The apparent molar volume of electrolyte solutions (V_ϕ) is the difference between solution volume and the volume of the pure solvent per mole of solute:

$$V_\phi = \frac{V - n_1 V_1^0}{n_2}, \quad (1)$$

where V is the volume of the solution, n_1 and n_2 are the number of moles of pure solvent and solute, respectively, and V_1^0 is the molar volume of pure solvent. It is possible to calculate V_ϕ from the density measurements, and using related mathematical equations, one can define the limiting value of the apparent molar volume (which is equal to the standard partial molar volume). The apparent molar volumes of aqueous and non–aqueous salt solutions in the solvent are defined as:

$$V_\phi = 1000 \left(\frac{\rho_1 - \rho}{m \cdot \rho \cdot \rho_1} \right) + \frac{M_2}{\rho}, \quad (2)$$

where ρ_1 and ρ are densities of the solvent and solution ($\text{g} \cdot \text{cm}^{-3}$), respectively, m is the solution molality ($\text{mol} \cdot \text{kg}^{-1}$), and M_2 is the molar mass of the dissolved salt ($\text{g} \cdot \text{mol}^{-1}$).

The apparent molar volume of investigated aqueous and non–aqueous salt solutions, at infinite dilution (V_ϕ^0) and constant temperature and pressure, can be obtained from the Pitzer–Debye–Hückel limiting slope equation:

$$V_\phi = V_\phi^0 + A_v m^{1/2} + B_v m \quad (3)$$

where V_ϕ^0 is the apparent molar volume of salt at infinite dilution (which is the same as the partial molar volume of salt at infinite dilution), $A_v/(\text{cm}^3 \cdot \text{kg}^{1/2} \cdot \text{mol}^{-3/2})$ is the Debye–Hückel limiting slope, m is molality ($\text{mol} \cdot \text{kg}^{-1}$), and $B_v/(\text{cm}^3 \cdot \text{kg} \cdot \text{mol}^{-2})$ is an adjustable parameter.

Redlich *et al.* attempted to prove the Masson hypothesis for deriving A_v by using Debye–Hückel theory (Debye and Hückel):

$$A_v = k_v w^{3/2} \quad (4)$$

where k_v and w are expressed as:

$$k_v = N_A^2 e^3 \left(\frac{8\pi}{1000 D^3 R T} \right)^{1/2} \left[\left(\frac{\partial \ln D}{\partial p} \right) - \frac{\kappa_T}{3} \right] \text{ and } w = 0.5 \sum_i v_i z_i^2, \quad (5)$$

Archer and Wang calculated the values of k_v for 1:1 electrolytes ($w = 1$):

$$k_v = -4RT \left(\frac{\partial A_\phi}{\partial p} \right)_T = 6RTA_\phi \left[\left(\frac{\partial \ln D}{\partial p} \right) - \frac{\kappa_T}{3} \right], \quad (6)$$

$$A_\phi = \frac{1}{3} \cdot (2\pi N_A \rho)^{1/2} \left(\frac{e^2}{4\pi \epsilon_0 D k T} \right)^{3/2}, \quad \text{or} \quad (7)$$

$$A_\phi = \frac{1}{3} \cdot \left(\frac{2\pi N_A \rho_w}{1000} \right)^{1/2} \left(\frac{e^2}{D k T} \right)^{3/2}, \quad (8)$$

where $N_A = 6.02214199 \cdot 10^{23} \text{ mol}^{-1}$ is Avogadro's number, $e = 1.6021773 \cdot 10^{-19} \text{ Coulomb}$ (Equation 5.3.42) or $4.803242 \cdot 10^{-10}$ (Equation 5.3.43) is the electron charge, D is the dielectric constant of solvent, $R = 8.31441 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ is the universal gas constant, T is the absolute temperature (K), p is the absolute pressure (MPa), κ_T is the isothermal compressibility of the pure solvent (MPa^{-1}), v_i is the number of ions of species (i), z_i is valency formed by one molecule of electrolyte, ρ is the solvent density, $\epsilon_0 = 8.8541878 \cdot 10^{-12} \text{ F} \cdot \text{m}^{-1}$ is the permittivity of vacuum, and $k = 1.3806503 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$ is the Boltzmann constant. The value $w = 3$ was used for 2:1 electrolytes.

According to equations (4–8), for an electrolyte of a fixed valence type, w is constant and the limiting slope (A_v) depends only on temperature and the physical properties of the solvent (ρ , D , $(\partial \ln D)/\partial p$, and κ_T). As a rule, this relationship is applied at a fixed pressure and temperature in all experimental parameter intervals. For the methanol solutions of electrolyte salts, the following properties were taken:

- density of methanol, at $T = (253.15 \text{ to } 468.65) \text{ K}$ and $p = (0.101 \text{ to } 200) \text{ MPa}$, were measured in our laboratories and compared with available literature results;
- the isothermal compressibility of methanol at these state parameters was calculated from the investigated density values;
- the various literature results for the dielectric constant (D) of methanol at these state parameters were analyzed.

Given the aforementioned conditions, it is necessary to analyze previous literature on dielectric constant (D) values of methanol to ensure proper, future calculations (at concrete pressures and temperatures).

The dielectric constant (DC) is a property of a dielectric material that is equal to the ratio of the capacitance of a capacitor filled with the given material to the capacitance

of an identical capacitor in a vacuum without the dielectric material. The study of dielectric properties provides more insight into their structural properties. An analysis of the temperature and pressure dependence of the equilibrium dielectric permittivity of hydrogen-bonded liquids appears to be an important method (Dannhauser *et al.*). Three methods are used to study the DC of substances: the bridge method, the resonance method, and the beat (or superposition) method.

Born calculated the electrostatic interaction energy of a spherical ion with a surrounding dielectric, but limited with ions with spherically symmetrical charge distribution. Kirkwood, in 1934, published a theory of solutions, in which he leads an extension of Born's relationship to spherical molecules with arbitrary charge distribution. The application of these theories to calculate solvation volumes requires knowledge of the DC pressure dependence of the solvents.

The hydrogen bond is a polar bond and dielectric polarization is a vectorial quantity; dielectric measurements must be able to discriminate, to some extent, between the specific interactions due to hydrogen bonds and other nonspecific interactions (for example, van der Waals forces). In addition, the vectorial nature of hydrogen bonds makes it possible to obtain the average degree of association and to analyse temperature and concentration dependence. The lower aliphatic alcohols provide an ideal compound for such a study: their molecular structure and dipole moments are well known; they are thermally stable and have an extremely large liquid range (Dannhauser *et al.*).

The DC pressure dependence (p, D, T) of liquids and liquid mixtures is also of interest for both analytical investigations and for the determination of phase equilibria in chemical reaction systems (Schadow & Steiner). The experimentally generated pressures in highly condensed liquid systems are generally moderate with respect to the internal pressures (the van der Waals forces); it depends on the generation of possible high pressures and accurate dielectric properties measurements on pronounced dipole liquids (Kyropoulos). These values also allow one to distinguish between the influences of isothermal density changes and isochoric temperature changes (Ledwig and Würflinger).

To ensure accuracy when determining the DC of polar liquids, a low-frequency bridge method can be used. In case two, however, sources of error can be controlled by eliminating the end effects by using a three-terminal (guarded) electrode system and a means for evaluating the capacitance component in the resistors used to balance the conductance of polar liquids (Srinivasan *et al.*). Using this method, it was also possible to make measurements at high pressures (up to $p = 300$ MPa). However, the assumption of a single equilibrium constant is difficult to reconcile with spectroscopic measurements on the alcohol systems; Srinivasan *et al.* tried to analyze this important moment. Due to the close relationship between the pressure dependence of the dielectric constant and the density, it was possible to calculate the corresponding DC from density values for different pressures and, conversely, to calculate corresponding density values from DC measurements by means of the Danforth relationship (Schadow & Steiner).

This part of our work investigates the field of thermophysical and physicochemical properties of methanol (Safarov) at wide temperature ranges and at high pressures. We use methanol regularly as a solvent in binary electrolyte solutions, where analysis of the apparent molar volume is very important. As noted above, the DC values of methanol at a wide range of temperatures and high pressures are necessary for such an analysis. In this case, this work involves a fundamental literature review of DC analysis and fitting found results using an empiric equation (Table 1).

Table 1. Literature values of dielectric constant D of methanol

First Author	Year	Temperature, T/K	Pressure, p/MPa	Uncertainty $\Delta D/D$, %
Kyropoulos	1927	292.15	0.098 to 294.2	± 2
Hückel	1957	293.15	0.098 to 294.2	± 1
Dannhauser	1964	298.15 to 513.15	0.1	± 0.5
Hartmann	1965	293.15 to 323.15	0.098 to 176.6	$\pm(1 \text{ to } 2)$
Jhon	1967	298.15 to 503.15	0.1	
Schadow	1969	303.15	1 to 110.8	± 0.1
Srinivasan	1975	283.15 to 313.15	0.1 to 300	± 0.05
Frank	1978	305.15 to 525.15	0.1 to 200	± 1.5
Ledwig	1982	223.10 to 305.10	0.1 to 250	± 0.5
Diguet	1987	323 and 398	50 to 200	± 1.5

In 1927, Kyropoulos measured the DC of methanol at $T = 292.15$ K and pressures $p = (0.098 \text{ to } 294.2)$ MPa using undamped oscillations of $\lambda \sim 350$ m. The dependence of the Lorenz-Lorentz relation in this pressure range was calculated. In 1957, Hückel and Ganssaue presented the DC of methanol at $T = 293.15$ K and pressures up to $p = 294.2$ MPa. The obtained experimental values were correlated using the Owen and Brinkley, and Tait equations. The authors indicated that the volume contraction of the solvent per ion pair in a "model electrolyte solution" can be calculated for sufficiently dilute solutions from Born's approach for the partial free hydration enthalpy per ion pair.

In 1964, Dannhauser *et al.* investigated the ambient pressure DC values at temperatures $T = (298.15 \text{ to } 511.15)$ K of methanol. New, precision-bore capillary tubing constructed dilatometers were used during the measurements, which had a thick wall bulb blown on one end and was examined using the water DC measurements at a wide range of temperatures, up to $p = 5$ MPa and $\Delta D/D = \pm 0.5$ % APD was obtained. The Kirkwood-Fröhlich equation was analysed on the basis of the experimental values. In 1965, Hartmann *et al.* determined the DC of methanol and other liquids at $T = (293.15, 308.15 \text{ and } 323.15)$ K and in a pressure range of $p = (0.098 \text{ to } 176.52)$ MPa, using the installation attributed to a capacitance measurement. The frequency was chosen so low that the area of anomalous dielectric dispersion was not reached. The uncertainty of DC values were estimated between $\Delta D/D = \pm(1 \text{ to } 2)$ % dependence of low or high polar liquids.

In 1967, Jhon *et al.* calculated eight DC values for methanol at ambient pressure and temperatures $T = (298.15 \text{ to } 503.15)$ K, using their own proposed domain model in conjunction with the significant-structure theory of liquids. The investigations constituted a validity check of the Hobbs, Jhon, and Eyring's theory. The authors indicated that the significant-structure theory – by introducing the concept of solid-like and gas-like molecules – explains the observed temperature coefficient of the DC in alcohols. In 1969, Schadow and Steiner constructed a high-pressure apparatus in the pressure range up to 147.1 MPa using the resonant circuit method for the experimental and theoretical investigation of the relationship between the DC and density of liquids at such pressures. An uncertainty of DC values of methanol was estimated to be $\Delta D/D = \pm 0.1\%$. Based on the obtained values, they demonstrated that both the Danforth and Owen-Brinkley functions are well suited for describing the pressure dependence of the dielectric constant.

In 1975, Srinivasan *et al.* reported the precise static DC for methanol, ethanol, and n-propanol at $T = (283.10 \text{ to } 313.10)$ K and pressures up to 300 MPa. The measurements were carried out by a low-frequency bridge method using a three-terminal, all-glass cell. The authors tried to reconcile the difficulty of taking spectroscopic measurements on the

alcohol systems. An uncertainty of DC measurements of methanol were estimated as $\Delta D/D = \pm 0.05\%$. The obtained average values at high pressures were fitted to the Tait type equation and used to analyze the Kirkwood correlation factor g_K , which can be obtained from the Fröhlich equation.

In 1978, Frank and Deul studied the DC of methanol at $T = (305.15 \text{ to } 525.15) \text{ K}$ and pressures $p = (0.1 \text{ to } 200) \text{ MPa}$ by measurement of the capacitance $C(T, p)$ of a capacitor mounted inside an autoclave, which was filled with the fluid sample at temperature T and pressure p . The capacitance without the fluid $C(T, p = 0)$ was measured independently at the same temperature, and the ratio of these parameters determined the DC of methanol. Due to an unavoidable, small electrolytic conductivity (caused by impurities at high temperatures), an alternating electric field of 300 kHz was applied. The DC values of methanol were estimated as $\Delta D/D = \pm 1.5\%$.

In 1982, Ledwig and Würflinger determined the DC and density ρ data of liquid methanol at a wide range of temperatures $T = (223.10 \text{ to } 305.10) \text{ K}$ and pressures up to $p = 250 \text{ MPa}$. The high-pressure autoclave, made of a copper-beryllium alloy, was used during the DC measurements. The breakdown capacitance of various cylindrical condensers in a three-pole measuring arrangement was measured up to frequencies of 10 MHz. At the same time, the conductivity or loss angle was registered. The Kirkwood correlation factor g_K was calculated from the data using the Kirkwood-Fröhlich-Onsager theory; a remarkable negative temperature dependence under isochoric conditions of the g_K -factor was discussed. The uncertainties of the obtained DC values of methanol were estimated to be $\Delta D/D = \pm 0.5\%$ and density measurements as $\Delta \rho/\rho = \pm 0.1\%$. The dependence of permittivity on density, together with previous literature findings, were analysed.

After the analysis of literature values collected in the Table 1, they were fitted to the correlation equation (9):

$$D = \sum_{i=0}^3 (p/\text{MPa})^i \sum_{j=0}^3 d_{ij} (T/\text{K})^j, \quad (9)$$

where d_{ij} are the adjustable parameters and tabulated in the Table 2.

Table 2. Adjustable parameters d_{ij} in the eqn. (9)

$d_{00} = 175.0627226$	$d_{20} = -0.3818507652 \cdot 10^{-3}$
$d_{01} = -0.8604276164$	$d_{21} = 0.2290794936 \cdot 10^{-5}$
$d_{02} = 0.1637148868 \cdot 10^{-2}$	$d_{22} = -0.1835327707 \cdot 10^{-8}$
$d_{03} = -0.117977269 \cdot 10^{-5}$	$d_{23} = -0.7678680053 \cdot 10^{-11}$
$d_{10} = 0.2087365317$	$d_{30} = 0.4782028861 \cdot 10^{-6}$
$d_{11} = -0.1275468809 \cdot 10^{-2}$	$d_{31} = -0.3571309768 \cdot 10^{-8}$
$d_{12} = 0.2559584403 \cdot 10^{-5}$	$d_{32} = 0.1929480437 \cdot 10^{-11}$
$d_{13} = -0.8039780625 \cdot 10^{-9}$	$d_{33} = 0.181290638 \cdot 10^{-13}$

The average percent deviation between literature and fitted results of the DC of methanol is $\Delta D/D = \pm 0.0.689 \%$.

The developed equation was checked using the comparison of calculated values of dielectric constant D of methanol and fitted values using the eqn. (9). A deviation plot between literature and experimental DC values of methanol versus pressure, at various temperatures, is shown in Figure 1. The seven DC measurements of methanol at $T = 292.15 \text{ K}$ and high pressures of Kyropoulos were compared with fitted results using a

constructed eqn. (9) and $\Delta D/D = \pm 0.715\%$ APD was obtained. These literature values are higher than the results calculated from eqn. (9). The APD of seven DC values of methanol, presented by Hückel and Ganssaue at $T = 293.15$ K and high pressures, was approximately $\Delta D/D = \pm 0.234\%$. The presented data of Hückel and Ganssaue are mostly higher than the results calculated using eqn. (9). The 14 DC values published by Dannhauser *et al.* have an APD of $\Delta D/D = \pm 1.406\%$ with present fitted results using an eqn. (9). The 36 experimental DC values reported by Hartmann *et al.* at $T = (293.15$ to $323.15)$ K and $p = (0.098$ to $176.520)$ MPa, have a $\Delta D/D = \pm 0.451\%$ from present calculations. The minimum deviation of this comparison is $\Delta D/D = \pm 0.954\%$, at $T = 323.15$ K and $p = 39.227$ MPa. The eight calculated DC values for methanol at ambient pressure and temperatures $T = (298.15$ to $503.15)$ K provided by Jhon *et al.* has APD in $\Delta D/D = \pm 0.969\%$, which have both positive and negative deviations from the fitted eqn. (9). The 11 DC values for methanol at $T = 303.15$ K, provided by Schadow and Steiner have a $\Delta D/D = \pm 0.543\%$ compared with present values, showing a good deviation; the minimum deviation is $\Delta D/D = -0.777\%$, at $p = 91.398$ MPa.

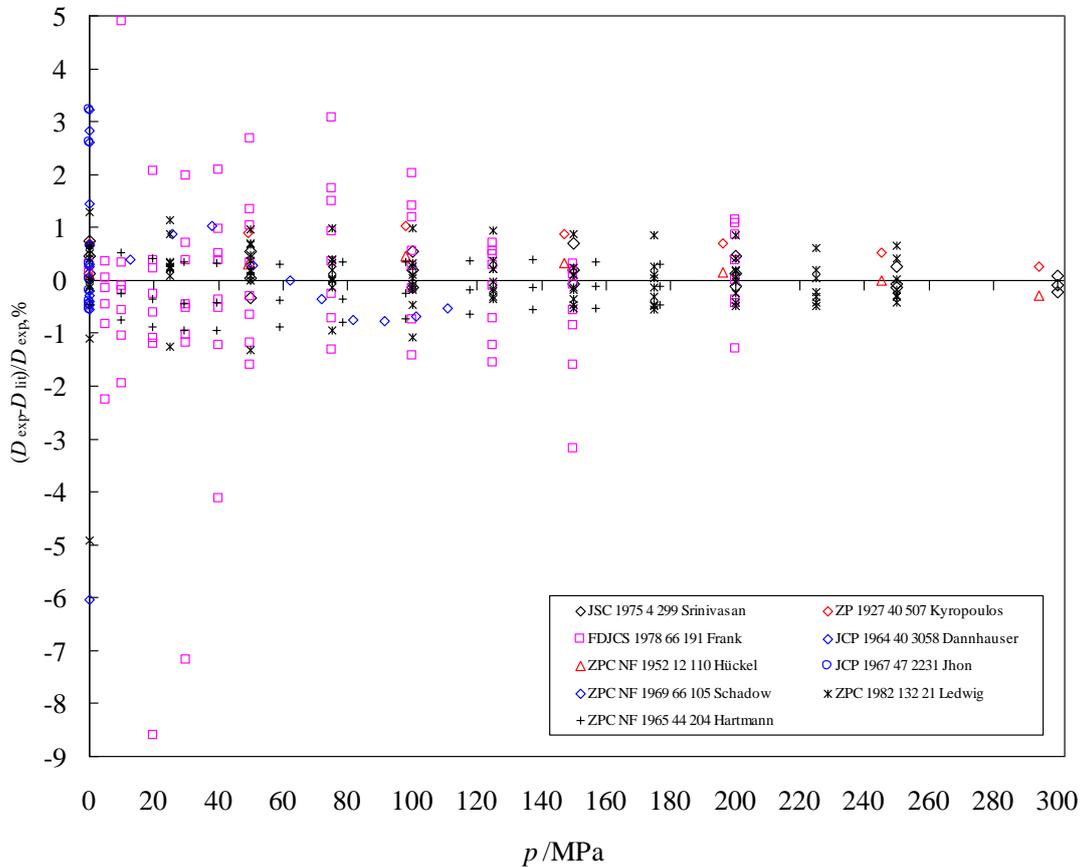


Fig. 1. Plot of deviation between literature experimental $D_{exp.}$ and fitted $D_{cal.}$ dielectric constant D values of methanol versus pressure p/MPa at various temperatures

The 16 DC values published by Srinivasan *et al.* at $T = (283.15$ to $313.15)$ K and $p = (0.1$ to $300)$ MPa, have a $\Delta D/D = \pm 0.27\%$ to calculated results, using eqn. (9). The maximum deviation is $\Delta D/D = \pm 0.745\%$ (at $p = 0.1$ MPa and $T = 283.15$ K). A comparison of the 88 DC values from Frank and Deul at $T = (305.15$ to $525.15)$ K and $p = (0.1$ to $200)$ MPa, showed a $\Delta D/D = \pm 1.103\%$ average deviation. The minimum deviation between the experimental and fitted DC values was $\Delta D/D = -0.943\%$ (at $T = 525$ K and $p = 20$

MPa). A comparison of calculated DC values with the 100 values from Ledwig and Würflinger has a $\Delta D/D = \pm 0.432\%$ APD, with a minimum deviation of $\Delta D/D = -4.923\%$, at $T = 283.1\text{ K}$ and $p = 0.1\text{ MPa}$. The fitted DC of methanol was used to define the infinite-dilution values of apparent molar volumes, which were obtained by extrapolating eqn. (9) to zero molality of solution ($m = 0$).

2. Conclusion

An application of methanol in the various branches of industry were widely discussed. Literature dielectric constant (D) investigations of methanol was analyzed and tabulated. The empiric equation for the fitting of literature values were developed. The deviation of literature values from calculated equation was discussed.

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