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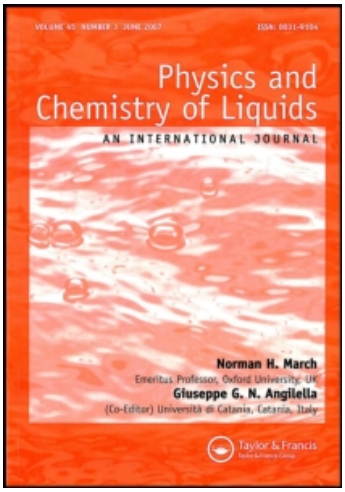

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Nikos G. Tsierkezos [a]; Ioanna E. Molinou [b]
[a] Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic [b] Physical Chemistry Laboratory, Department of Chemistry, University of Athens, Athens, Greece

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An investigation on ion association and ion solvation of potassium acetate in alcohol solutions

Nikos G. Tsierkezos[a]* and Ioanna E. Molinou[b]

[a]*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic;* [b]*Physical Chemistry Laboratory, Department of Chemistry, University of Athens, Athens, Greece*

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The molar conductivities (Λ) of potassium acetate in methanol (MeOH), ethanol (EtOH), 1-propanol (PrOH), 2-propanol (isoPrOH), 2-methyl-1-propanol (MPrOH), 1-butanol (BuOH), 1-pentanol (PeOH), and benzyl alcohol (BeOH) were measured at 293.15 K. The concentration dependence of Λ was analysed by means of the Lee–Wheaton conductivity equation in the form proposed by Pethybridge and Taba. From the analysis of the experimental Λ values, the limiting molar conductivities (Λ_o) and the association equilibrium constants (κ_α) were determined. The centre-to-centre distance (a) of the formed ion pairs were assumed to be equal to the Bjerrum's distance of closest approach. Furthermore, the ultrasonic velocities (u) and the densities (ρ) were measured in order to determine the limiting partial molar volume (V_φ^o) and the limiting apparent isentropic compressibility ($k_{S\varphi}^o$). The results provide information regarding the association and solvation of the ions of the investigated electrolyte.

Keywords: alcohol; apparent isentropic compressibility; apparent molar volume; association constant; Lee–Wheaton model; molar conductivity; potassium acetate

1. Introduction

As pointed out in previous studies [1,2], molar conductivities, apparent molar volumes and apparent isentropic compressibilities give valuable information regarding the behaviour of the electrolytes in different solvent media. These techniques were proven to be sensitive to the ion solvation as well as the ion association. In the past, much research has been carried out in extensive investigations on the effect of the structure of the solvent medium and the nature of the ions on the ion association [3–5]. The concept of ion association is widely used in solution chemistry. As is well known, there are two different mechanisms of ion association in electrolytes. The first, proposed by Bjerrum [6], is electrostatic ion association, in which the association process is due to strong Coulomb interactions. According to Bjerrum, when the distance between two oppositely charged ions is smaller than a critical value (which called the distance of closest approach), the ions can be considered as paired. The distance of closest approach depends on the charge of the ions as well as on the relative permittivity of the solvent medium. The distance of closest

*Corresponding author. Email: nikos.tsierkezos@gmx.de

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approach is larger and consequently the extent of ion association is greater for multiply charged electrolytes dissolved in solvents of fairly low dielectric constant. It has been proven that aqueous solutions of 2:2 electrolytes are electro-statically equivalent to solutions of 1:1 electrolytes in a solvent medium of low dielectric constant [7,8]. The second mechanism of ion association is the chemical association in which a real chemical bond between the ions is formed. This is the case of weak acids in water as well as the formation of complex ions [9]. Alcohols are strongly self-associated in the pure state through hydrogen bonding to form short-lived aggregates [10]. The alcohol complexes represent an important class of hydrogen-bonded solvents, for which the degree of association is very sensitive to the influence of temperature and the presence of electrolytes [11,12]. However, the association between alcohol molecules cannot be compared with the high degree of association which occurs in liquid water. The hydroxyl group of alcohol participates in two hydrogen bonds, acting as a proton donor and at the same time as a proton acceptor. Consequently, in alcohols one observes the presence of cyclic and open dimers in methanol [13] and the coexistence of open dimers and monomers in higher alcohols [14,15]. The last observation can be attributed to the unfavourable steric effect of the alkyl group on the hydrogen bonding [16]. Although less structured than water and with lower solvation ability [17], alcohols have drawn much attention as a solvent medium for electrochemical studies [18–22]. It has been reported that in alcoholic solutions of electrolytes, the ion association is more pronounced compared with corresponding aqueous solutions. Potassium acetate is a particularly useful material in the manufacture of penicillin. This material can be used as a drug to prevent or to treat a potassium deficiency. Conductivity measurements of potassium acetate in dimethyl sulfoxide have been recently reported by Barthel *et al.* [23]. The lack of electrochemical and ultrasonic data on potassium acetate in alcohols caused us to investigate this system. The present work reports the limiting molar conductivities (Λ_o), the association equilibrium constants (K_A), the limiting apparent molar volumes (V_φ^o), and the limiting apparent isentropic compressibilities ($k_{S\varphi}^o$) of potassium acetate in methanol (MeOH), ethanol (EtOH), 1-propanol (PrOH), 2-propanol (isoPrOH), 2-methyl-1-propanol (MPrOH), 1-butanol (BuOH), 1-pentanol (PeOH) and benzyl alcohol (BeOH) at the temperature of 293.15 K.

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2. Experimental section

2.1. *Materials*

Methanol (Merck, 99.8%), ethanol (J.T.Baker, 99.9%), 1-propanol (Lab-Scan, 99.5%), 2-propanol (Merck, 99.7%), 2-methyl-1-propanol (Merck, 99.0%), 1-butanol (Merck, 99.5%), 1-pentanol (Fluka, 99.0%) and benzyl alcohol (Fluka, 99.0%) were stored over 4 Å molecular sieves and used without further purification. The specific conductivities of the solvents were found to be sufficiently small ($0.10\,\mu s\,cm^{-1}$). The purity of the solvents was assessed by comparing the experimental values of density (ρ), viscosity (η), and speed of sound (u) with the available literature values at 293.15 K [24–33] (Table 1). The agreement between the experimental and the literature ρ, η, u values was found to be satisfactory. The relative permitivities (ε) of the alcohols were all taken from the literature [24]. Anhydrous potassium acetate (Fluka, 99.5%) and potassium chloride (Merck, 99.8%), needed for calibration, were dried before their use at 383.15 K for 24 h.

Table 1. Densities (ρ), viscosities (η), speeds of sound (u) and relative permittivities (ε) of methanol (MeOH), ethanol (EtOH), 1-propanol (PrOH), 2-propanol (isoPrOH), 2-methyl-1-propanol (MPrOH), 1-butanol (BuOH), 1-pentanol (PeOH) and benzyl alcohol (BeOH) at 293.15 K.

	ρ (g cm^{-3})		η (mPa s)		u (m s^{-1})		
Solvent	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	ε[a]
MeOH	0.79135	0.7912[b] 0.7912[c]	0.587	0.597[a]	1120	1119[c]	33.66
EtOH	0.78950	0.7893[b] 0.7893[c]	1.204	1.200[a]	1162	1160[c]	25.00
PrOH	0.80362	0.8039[d] 0.8034[c]	2.222	2.256[a] 2.144[d]	1222	1223[c]	20.81
isoPrOH	0.78509	0.7862[d] 0.7849[c]	2.458	2.301[d]	1156	1156[c]	18.95
MPrOH	0.80191	0.8017[e]	4.118	4.02[e]	1204	1209[f]	18.47
BuOH	0.80985	0.80984[a] 0.8095[c]	2.995	2.948[a]	1268	1257[c]	17.80
PeOH	0.81466	0.81480[g] 0.8142[c]	4.030	3.700[h]	1292	1292[c]	14.27
BeOH	1.04574	1.0452[i]	6.536	5.800[a] 5.735[i]	1543	1541[j]	13.10

Notes: References [a][24], [b][25], [c][26], [d][27] (interpolated values), [e][28], [f][29] (interpolated values), [g][30], [h][31] (interpolated values), [i][32] (interpolated values), and [j][33].

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2.2. *Solutions*

A stock solution of potassium acetate (~0.0100 mol L^{-1}) was prepared by mass (±0.0001 g, Sartorius, AG 204) and the dilute solutions, in the concentration range from 0.0001 to 0.0015 mol L^{-1}, were obtained by diluting the stock solution. The conversion of molality to molarity was done using the density values. The molarities were obtained with an accuracy ±0.0001 mol L^{-1}.

2.3. *Apparatus and procedures*

The density was measured with a digital precision densimeter (Anton Paar, model DMA 58, Austria) with a built-in solid-state thermostat and a capacity of *ca.* 5.0 cm^3. The densimeter was calibrated with dry air and distilled water at 293.15 ± 0.01 K. The estimated uncertainty of the measured density was ±0.00005 g cm^{-3}.

The speed of sound was measured with an Anton Paar (model DSA 48, Austria) sound analyser. The sound analyser was calibrated with dry air and doubly distilled water at 293.15 ± 0.01 K. The uncertainty of the speed of sound was ±1 m s^{-1}.

The kinematic viscosity was measured with a viscosity-measuring unit (Schott Geräte, model AVS 310, Germany) equipped with an Ubbelohde capillary viscometer. The viscometer was calibrated with doubly distilled water at 293.15 K. The uncertainty in the viscosity was ±0.1%.

The conductance was measured with a digital bridge-type conductivity meter (Metrohm, model 712, Switzerland). A conductance cell (dipping type) with electrodes

of platinum black was used. The cell constant ($0.814 \pm 0.001\,\mathrm{cm}^{-1}$) was determined by measuring aqueous solutions of potassium chloride in the concentration range 0.0010–0.1000 mol L^{-1} at 293.15 K. The electrode was cleaned first with nitric acid solution, then with distilled water, and finally was dried with acetone. The cell was thermostatised at 293.15 ± 0.01 K using a water bath. All data were corrected with the specific conductivity of the solvent medium. The correction was made by subtracting the specific conductivity of the solvent medium from those of the salt solutions. The molar conductivities (Λ) were calculated from the experimental specific conductivities (k) and the concentrations (c) of the solutions using the equation: $\Lambda = 10^3\, k\, c^{-1}$. The accuracy of the measured conductivity values was ±0.3%.

3. Results and discussion

3.1. *Limiting molar conductivity and association equilibrium constant*

The experimental molar conductivities (Λ) were analysed by means of the Lee and Wheaton [34–36] conductivity equation in the form suggested by Pethybridge and Taba (Equations (1–5)) [37], which includes the mass action law for the ion association (Equation (6)) and the Debye–Hückel limiting law (Equation (7)):

$$\Lambda_{\mathrm{Calc.}} = \gamma \Lambda_i, \tag{1}$$

$$\Lambda_i = \Lambda_o\left[1 + C_1(\beta\kappa) + C_2(\beta\kappa)^2 + C_3(\beta\kappa)^3\right] - \partial\kappa/(1+\kappa\alpha) \times \left[1 + C_4(\beta\kappa) + C_5(\beta\kappa)^2 + \kappa\alpha/12\right], \tag{2}$$

$$\beta = \frac{|z|^2 e^2}{(\varepsilon_0 \varepsilon k_B T)}, \tag{3}$$

$$\kappa = \left(\frac{8\pi N_A e^2 |z|^2 \gamma c}{1000 \varepsilon_0 \varepsilon k_B T}\right)^{1/2}, \tag{4}$$

$$\partial = \frac{F\xi e|z|}{3\pi\eta}, \tag{5}$$

$$K_A = \frac{(1-\gamma)}{\gamma^2 f_\pm^2 c}, \tag{6}$$

$$f_\pm^2 = \exp\left[\frac{-\beta\kappa}{(1+\kappa\alpha)}\right], \tag{7}$$

where C_1–C_5 are functions of the product $(\kappa \cdot \alpha)$, K_A the association equilibrium constant, γ the degree of dissociation, c the salt concentration, $f_\pm$ the mean ion activity coefficient of the dissociated species, e the electronic charge, $z_\pm$ the ion charge, ε_0 the permittivity of vacuum, ε the relative permittivity of the solvent medium, η the absolute viscosity of the solvent, F the Faraday constant, k_B the Boltzmann's constant, N_A the Avogadro's number, and T the absolute temperature; the symbol ξ is equal to 1/299.79. The parameter a

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represents the centre-to-centre distance between the ions in the ion pairs formed and in the present work, it was assumed to be equal with the Bjerrum's distance [38]:

$$a = \frac{z_+ z_- e^2}{8\pi\varepsilon_0 \varepsilon k_B T}. \quad (8)$$

The derived values of limiting molar conductance Λ_o (±0.3%), association constant K_A (±5%) and Bjerrum's distance (a) for potassium acetate in MeOH, EtOH, PrOH, isoPrOH, MPrOH, BuOH, PeOH and BeOH at 293.15 K are reported in Table 2. The Λ_o and K_A values are presented graphically in Figures 1 and 2, respectively.

As can be observed in Figure 1, the Λ_o values of the electrolyte diminish with the following order: MeOH > EtOH > PrOH > isoPrOH > BuOH > PeOH > MPrOH > BeOH. The results demonstrate that the rise of the viscosity of the solvent medium ongoing from MeOH (0.587 mPa s) to BeOH (6.536 mPa s) is one of the factors which causes the progressive diminishing of the ion mobilities and thus the decrease of Λ_o. However, the

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Table 2. Limiting molar conductances (Λ_o), association constants (K_A) and SDs (σ_Λ) of potassium acetate in methanol (MeOH), ethanol (EtOH), 1-propanol (PrOH), 2-propanol (isoPrOH), 2-methyl-1-propanol (MPrOH), 1-butanol (BuOH), 1-pentanol (PeOH) and benzyl alcohol (BeOH) at 293.15 K.

Solvent	Λ_o (S cm^2 mol^{-1})	K_A (L mol^{-1})	a (Å)	$W = (\eta\,\Lambda_o)$	σ_Λ (S cm^2 mol^{-1})
MeOH	86.5 ± 0.3	50 ± 2	8.5	51	0.048
EtOH	60.6 ± 0.2	164 ± 7	11.4	73	0.032
PrOH	31.6 ± 0.2	596 ± 28	13.7	70	0.031
isoPrOH	27.3 ± 0.2	804 ± 38	15.1	67	0.002
MPrOH	9.80 ± 0.04	908 ± 43	15.4	40	0.005
BuOH	19.63 ± 0.06	990 ± 46	16.0	59	0.011
PeOH	10.33 ± 0.04	1399 ± 68	20.0	42	0.002
BeOH	3.90 ± 0.01	1497 ± 72	21.8	25	0.002

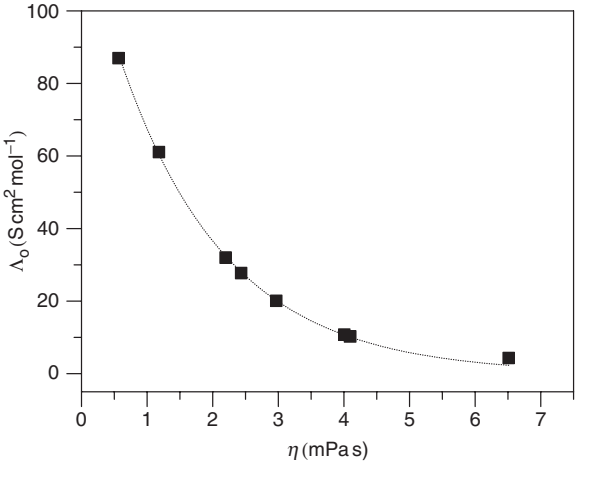

Figure 1. Limiting molar conductance (Λ_o) of potassium acetate *vs.* the viscosity (η) of the solvent medium at 293.15 K.

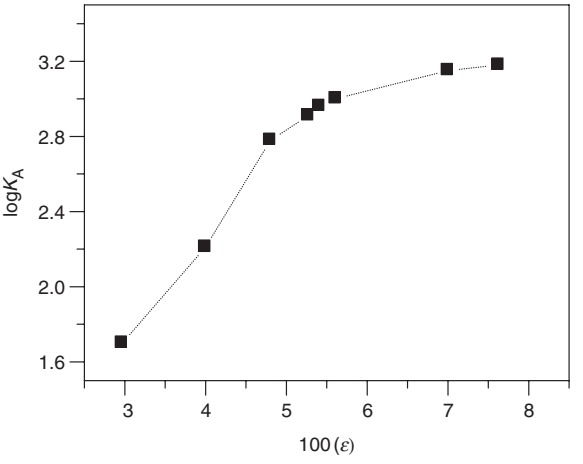

Figure 2. Logarithm of the association constant ($\log K_A$) of potassium acetate *vs.* the inverse dielectric constant ($100/\varepsilon$) of the solvent medium at 293.15 K.

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Walden product W ($W = \eta \cdot \Lambda_o$) changes remarkably, demonstrating that the viscosity of the medium is not the only factor which negatively affects the mobility of the ions. The divergence of the W values can be attributed to the different degrees of solvation of the ions in the investigated alcohols. Another factor which contributes to the decrease of Λ_o is the amplification of the ion pair formation of the electrolyte and the conversion of the conductive free ions to non-conductive neutral ion pairs, which, according to the determined K_A values, follows the sequence: MeOH < EtOH < PrOH < isoPrOH < MPrOH < BuOH < PeOH < BeOH. The increase of K_A ongoing from MeOH to BeOH can be explained in terms of the decrease with this sequence of the relative permittivity (ε) of the alcohol ($\varepsilon_{MeOH} = 33.66, \varepsilon_{BeOH} = 13.10$ at 293.15 K). The amplification of the ion pair formation with the decrease of the permittivity of the medium has been also confirmed by many other researchers, using electrochemical methods [39]. However, the plot of $\log K_A$ *versus* the inverse relative permittivity of the medium ($1/\varepsilon$) was found to be non-linear (Figure 2), demonstrating that K_A depends not only exclusively on the relative permittivity but also on other properties of the solvent molecule (e.g. shape, size, dipole moment). According to the relation proposed by Fuoss [40], the association constant is a product of two terms: $K_A = K_R (1 + K_S)$, where the term K_R depends on the relative permittivity of the solvent medium and the term K_S, on the short-range ion–ion and the ion–solvent interactions, which are related to the 'electrostriction' effect [41]. In large and branched alcohols the ions are not strongly solvated and the 'electrostriction' effect is insignificant (see V_φ^o, $k_{S\varphi}^o$ results). Consequently, ion–ion interactions become stronger and the salt forms predominantly contact ion pairs.

3.2. *Limiting apparent molar volume and apparent isentropic compressibility*

The partial molar volume (V_ϕ) of potassium acetate in a solvent medium is given as the difference between the volume of the solution and the volume of the solvent divided by the mole of potassium acetate:

$$V_\varphi = V - n_1 V_1 / n_2, \tag{9}$$

where V is the volume of the solution, n_2 the moles of the solute, and n_1, V_1, the moles and the molar volume of the solvent medium, respectively. The V_ϕ values can be calculated from the experimental density values (ρ) by using the following equation [42, 43]:

$$V_\varphi = M_2/\rho_1 - (\rho - \rho_1)/m\rho\rho_1, \tag{10}$$

where m represents the concentration of the solute expressed in number of moles per kilogram of solution (molonity), M_2 the molar mass of solute, and ρ, ρ_1 the densities of the solution and solvent, respectively. The variation of the calculated V_φ values with the $m^{1/2}$ values was found to be linear in the investigated concentration range, and consequently, the determination of the limiting apparent molar volume (V_φ^o) of the solute can be calculated by using the Masson empirical equation [44]:

$$V_\varphi = V_\varphi^o + S_V m^{1/2}, \tag{11}$$

where S_V is the experimental slope. The isentropic compressibility (k_S) of the solution, which is defined as the product of the inverse volume of the solution (1/V) multiplied with the variation of the volume (V) with the pressure (P) under constant entropy (S):

$$k_S = -1/\mathrm{V}(\partial \mathrm{V}/\partial \mathrm{P})_\mathrm{S}, \tag{12}$$

is related with the experimental values of density (ρ) and speed of sound (u) of the solution by means of the Laplace equation:

$$k_S = \left(\frac{1}{u^2\rho}\right). \tag{13}$$

Accordingly, the apparent isentropic compressibility ($k_{S\varphi}$) of the solute in a solvent medium can be determined by means of the following equation:

$$k_{S\varphi} = (k_S\rho_1 - k_{1S}\rho)/m\rho\rho_1 + M_2 k_{1S}/\rho_1, \tag{14}$$

where k_S and k_{1S} are the isentropic compressibility of the solution and the solvent, respectively. Given that the variation of $k_{S\varphi}$ with $m^{1/2}$ was found to be linear, the limiting apparent isentropic compressibility ($k_{S\varphi}^o$) of the solute can be calculated by fitting the $k_{S\varphi}$ values to the following equation:

$$k_{S\varphi} = k_{S\varphi}^o + S_K m^{1/2}, \tag{15}$$

where S_K represents the experimental slope. The determined values of V_φ^o and $k_{S\varphi}^o$ of potassium acetate in the investigated alcohols are given in Table 3.

As can be observed in Table 3, the V_φ^o and $k_{S\varphi}^o$ values of potassium acetate increase in the following order: MeOH < EtOH < PrOH < isoPrOH < MPrOH < BuOH < PeOH < BeOH. The results indicate that from BeOH to MeOH, the strength of the solute–solvent interactions increases, leading to the amplification of the 'electrostriction' effect, and resulting, therefore, in the contraction of the volume and the enhancement of the 'elasticity' of the solution [45–47]. The lowest V_φ^o and $k_{S\varphi}^o$ values which have been obtained in MeOH can be explained in terms of the more pronounced 'electrostriction' effect which occurs in this medium [48]. In addition to the 'electrostriction' effect, the size of the alcohol and consequently the degree of steric hindrance of the poles of the dipole of the molecule are additional factors which affect the V_φ^o and $k_{S\varphi}^o$ values [49]. As the alcohol size increases, the steric-hindering effect becomes more significant, and

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Table 3. Limiting apparent molar volumes (V_φ^o) and limiting apparent isentropic compressibilities ($k_{S\varphi}^o$) of potassium acetate in methanol (MeOH), ethanol (EtOH), 1-propanol (PrOH), 2-propanol (isoPrOH), 2-methyl-1-propanol (MPrOH), 1-butanol (BuOH), 1-pentanol (PeOH) and benzyl alcohol (BeOH) at 293.15 K.

Solvent	V_φ^o ($cm^3\,mol^{-1}$)	$10^2 k_{S\varphi}^o$ ($TPa^{-1}\,mol^{-1}\,m^3$)
MeOH	26.2 ± 0.3	-24.3 ± 0.1
EtOH	41.7 ± 0.5	-13.8 ± 0.1
PrOH	53.6 ± 0.6	-5.50 ± 0.03
isoPrOH	55.0 ± 0.5	-2.20 ± 0.02
MPrOH	56.0 ± 0.6	-1.90 ± 0.01
BuOH	55.2 ± 0.6	-1.24 ± 0.01
PeOH	60.0 ± 0.7	-0.90 ± 0.01
BeOH	61.7 ± 0.7	0.55 ± 0.01

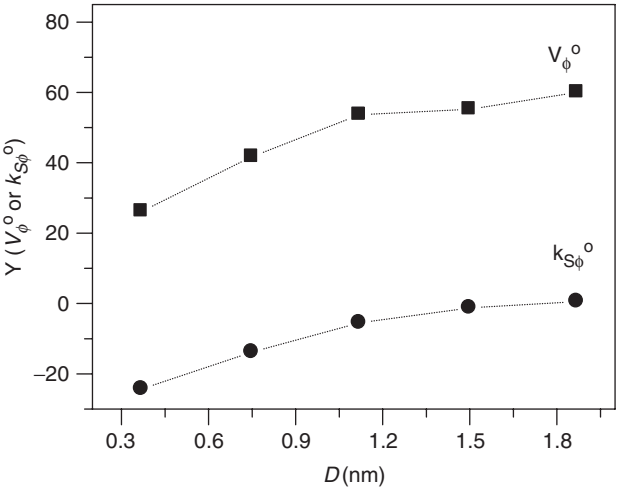

Figure 3. Limiting apparent molar volume (V_φ^o) and limiting apparent isentropic compressibility ($k_{S\varphi}^o$) of potassium acetate *vs.* the chain-length (D) of MeOH ($D = 0.37$ nm), EtOH ($D = 0.75$ nm), PrOH ($D = 1.12$ nm), BuOH ($D = 1.50$ nm), and PeOH ($D = 1.87$ nm) [50].

the solvation capacity of the alcohol weakens, leading finally to greater V_φ^o and $k_{S\varphi}^o$ values. The dependence of V_φ^o and $k_{S\varphi}^o$ on the chain length of the *n*-alkanol molecule is presented graphically in Figure 3. The estimated values of the chain-length (D) for the *n*-alkanols were taken from the literature ($D_{MeOH} = 0.37$ nm, $D_{EtOH} = 0.75$ nm, $D_{PrOH} = 1.12$ nm, $D_{BuOH} = 1.50$ nm, $D_{PeOH} = 1.87$ nm) [50]. This curve reveals a unique examination of the influence of the chain length of the alcohol molecule on the V_φ^o and $k_{S\varphi}^o$ values.

4. Conclusions

The present article presents the experimental values of limiting molar conductivity (Λ_o), association constant (K_A), limiting apparent molar volume (V_φ^o) and limiting apparent

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isentropic compressibility ($k^o_{S\varphi}$) of potassium acetate in methanol (MeOH), ethanol (EtOH), 1-propanol (PrOH), 2-propanol (isoPrOH), 2-methyl-1-propanol (MPrOH), 1-butanol (BuOH), 1-pentanol (PeOH), and benzyl alcohol (BeOH) at 293.15 K. The results provide information on solvation and association of potassium acetate in the investigated alcohols. The V^o_φ and $k^o_{S\varphi}$ values reveal the weakening of the solute–solvent interactions. Consequently, the diminution of the 'electrostriction' effect around the ions is related to the increase of the size of the alcohol molecule. Therefore, the V^o_φ and $k^o_{S\varphi}$ values increase in the following order: MeOH < EtOH < PrOH < isoPrOH < MPrOH < BuOH < PeOH < BeOH. The K_A values were found to increase in the same order, as with V^o_φ and $k^o_{S\varphi}$, indicating that the ion association of the solute is somehow more favourable when the 'electrostriction' effect is less significant. Furthermore, the enhancement of K_A from MeOH to BeOH can be also attributed to the diminishing of the relative permittivity of the medium. The Λ_o values tend to decrease with the increase of the viscosity of the solvent medium, as well as with the enhancement of K_A.

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