ARCHIVES OF ACOUSTICS
14, 3–4, 217-229 (1989)

MOLAL VOLUME AND COMPRESSIBILITY OF AQUEOUS NON-ELECTROLYTE SOLUTIONS

ADAM JUSZKIEWICZ

Faculty of Chemistry, Jagiellonian University
(30-060 Kraków, Karasia 3)

The measurements of ultrasonic velocity and of density in aqueous solutions of 20 non-electrolytes were carried out. From the obtained results isentropic compressibility, apparent molal volumes and apparent molal compressibilities were calculated. The changes of these parameters with the change of concentration of the non-electrolytes confirm the model of hydration of non-electrolytes suggested previously on the basis of ultrasonic velocity measurements in binary and ternary systems.

1. Introduction

Physico-chemical properties of aqueous solutions of non-electrolytes are subject of numerous papers published in recent years. The reason for such great interes in this group of substances are their anomalous concentration dependent changes of a number of physico-chemical parameters such as: molal volume, heat capacity, viscosity coefficient, activity coefficient, diffusion coefficient, ultrasonic velocity and compressibility, ultrasonic absorption coefficient and others. In spite of very many data collected in this subject there has not been so far a uniform theory describing all these phenomena.

In previous studies [1 – 4] of hydration of non-electrolytes, in which the measurements of the ultrasonic velocity in binary and ternary aqueous systems were applied, a model of the hydration of these substances in aqueous solutions was presented. It is assumed in this model that molecules of non-electrolytes are built into the structure of water in such a way that hydrophobic groups of these molecules occupy cages (voids) of this structure, and hydrophilic groups of these molecules occupy nodes of the lattice of water where they replace a certain number of water molecules. It is also assumed in this model that hydrophilic groups such as —OH, $-NH_2$, $-CONH_2$, =CO, —O— and others have a negative contribution to the total hydration of a non-electrolyte and that this contribution is expressed by a number of water

---

This work was partially financed by the Polish Academy of Sciences Problem CBBP.02.03.

molecules replaced by these groups at nodes of the lattice. Hydrophobic groups (alkyl groups), on the other hand, have a positive contribution to the total hydration and this contribution is expressed by a number of water molecules that surround an alkyl group. The total hydration is an algebraic sum of the both contributions.

The results obtained with other techniques such as: volumetric, calorimetric, viscosimetric, dielectric, NMR, IR and Raman spectroscopy confirm the above described model. On the basis of these results it may be concluded that with the hydrophobic (positive) hydration of alkyl groups of alcohols, ketones, amines, amides and their N-alkyl derivatives are connected the following effects: egzothermic effect of dissolving of a non-electrolyte, negative excess of partial molal volume, positive excess of partial molal heat capacity, positive excess of viscosity coefficient, positive excess of activity coefficients of a non-electrolyte and water, negative excess of diffusion coefficients, and others. Negatively hydrated molecules e.g. molecules of urea and formamide show the effects opposite to the above listed ones i.e. endothermic effect of dissolving, positive excess of partial molal volume of a non-electrolyte, negative excess of heat capacity and the others. In many cases the concentrations of non-electrolytes at extrema are comparable with those obtained from ultrasonic velocity measurements. In the paper [4] a qualitative analysis of literature data on this subject was carried out, for it was impossible to make a quantitative comparison of the obtained values of hydration numbers with the values obtained with the other techniques i.e. to verify the suggested model of hydration, because of the lack of numerical data for some of the examined substances.

This paper is one of the attempts undertaken to verify the suggested model of hydration of molecules of electrolytes, non-electrolytes as well as macromolecules. It presents the results of measurements of apparent molal volumes and compressibilities of 20 non-electrolytes showing either positive or negative hydration.

2. Relations between density and/or ultrasonic velocity and partial molal thermodynamic parameters of solute

Any partial molal quantity is expressed with:

$$\mathbf{F}_1 = \left(\frac{\partial F}{\partial n_i}\right)_{p,T,n_1,\ldots,n_k} \tag{1}$$

In the case of a binary solution, partial molal quantities of a solute and of a solvent are expressed by the following partial derivatives:

$$\mathbf{F}_2 = \left(\frac{\partial F}{\partial n_2}\right)_{T,p,n_1} ; \quad \mathbf{F}_1 = \left(\frac{\partial F}{\partial n_1}\right)_{T,p,n_2} \tag{2.3}$$

In order to determine partial molal quantities it is necessary to know apparent molal quantities, and these can be obtained experimentally.

In generally any apparent molal quantity of a solute is defined by the following equation:

$$\Phi F_2 = (F - n_1 \mathbf{F}_1^0)/n_2 \tag{4}$$

where F is an extensive quantity for a solution, $\mathbf{F}_1^0$ is a respective molal quantity for a solvent, n_1 and n_2 are numbers of moles of a solvent and of a solute, respectively. The relation between ΦF_2 and F_2 can be obtained by differentiating eq. (4) with respect to n_2:

$$\mathbf{F}_2 = \Phi F_2 + \left(\frac{\partial F_2}{\partial \ln n_2}\right)_{n_1} = F_2 + \left(\frac{\partial F_2}{\partial \ln m}\right) \tag{5}$$

where m is a molality (m/kG solvent).

For dilute solutions molal concentration can be replaced by molar concentration, c, and then eq. (5) changes into:

$$\mathbf{F}_2 = \Phi F_2 + \left(\frac{\partial F_2}{\partial \ln c}\right). \tag{6}$$

At the limiting concentration, when $c \to 0$

$$\mathbf{F}_2^0 = \Phi F_2^0. \tag{7}$$

Some researchers are of the opinion that no physical sense can be ascribed to the partial molal quantities and that these are only mathematical quantities because for example negative partial molal volume has no physical sense. According to the author it is not the right opinion. Physical sense can be ascribed to these quantities when molecules of a solute are considered together with molecules of a solvent solvated with a solute. Then, for example negative partial molal volume is a measure of a decrease in the volume of solvent molecules in solvation sheath as compared to the volume of solvent molecules which are not influenced on by solute molecules.

Apparent molal volume of the solute ΦV_2 is defined by:

$$\Phi V_2 = (V - n_1 \mathbf{V}_1^0)/n_2, \tag{8}$$

where V is a volume of the solution containing n_1 moles of the solvent and n_2 moles of the solute. $\mathbf{V}_1^0$ is a partial molal volume of the solvent.

Apparent molal compressibility of the solute ΦK_2 is expressed by:

$$\Phi K_2 = \left(\frac{\partial \Phi V_2}{\partial p}\right)_S = (\beta_s V - n_1 \beta_{s0} V_1^0)/n_2, \tag{9}$$

where β_s and β_{s0} are isentropic compressibilities of a solution and of solute, respectively.

Using experimental results, ΦV_2 and ΦK_2 can be calculated from the following relations:

$$\Phi V_2 = \frac{1000}{mdd_0}(d_0 - d) + \frac{M_2}{d}, \tag{10}$$

$$\Phi K_2 = \frac{1000}{md_0}(\beta_s - \beta_{s0}) + \beta_s \Phi V_2, \tag{11}$$

$$\beta_s = \frac{1}{du^2}, \tag{12}$$

where d and d_0 are densities of the solution and of the solvent, respectively, u is the velocity of ultrasound, m is the molality (m/kG solvent), and M_2 is the molecular weight of the solute.

In liquid binary systems the principle of additivity of the above parameters is not always fulfilled: the expression $(\Phi F_2 - \Phi F_2^0)$ is a measure of the deviation from this principle.

3. Experiment

All the examined substances: methanol, ethanol, n-propanol, tert.-butanol, ethylene glycol, 1,2-propylene glycol, 1,3-butylene glycol, 2,3-butylene glycol, glycerol, acetone, 1,4-dioxane, etylene glycol monoacetate, methoxyethanol, formamide, hydrazine, N-methylformamide, acetamide, dimethylformamide, dimethylsulphoxide and urea were of analar grade. Triple-distilled water was used throughout.

Density measurements were carried out with use of a pycnometer and of a vibrating tube densimeter [5, 6]. Ultrasonic velocity measurements were carried out by the pulse-phase method [7] and by the "sing around" method [8–10]. The temperature of measurements was 25°C. For the density measurements with the vibrating tube densimeter as well as for ultrasonic velocity measurements with the "sing around" gauge the solutions were thermostated to an accuracy of ±0.001°C, for the other measurements to ±0.02°C.

The results of the measurements are presented in Fig. 1–13 and in Table 1.

4. Discussion

The results of the density measurements of the examined substances in solutions of the water are presented in Fig. 1–4 in the form of dependences of $(\Phi V_2 - \Phi V_2^0)$ on molar fractions of the non-electrolytes.

For the majority of the examined non-electrolytes typical curves with minima were obtained. Only for urea, formamide, hydrazine and glycerol these dependences have no minima and within the studied concentration range the values of $(\Phi V_2 - \Phi V_2^0)$ are positive. The measured densities and the calculated values of $(\Phi V_2 - \Phi V_2^0)$ at different

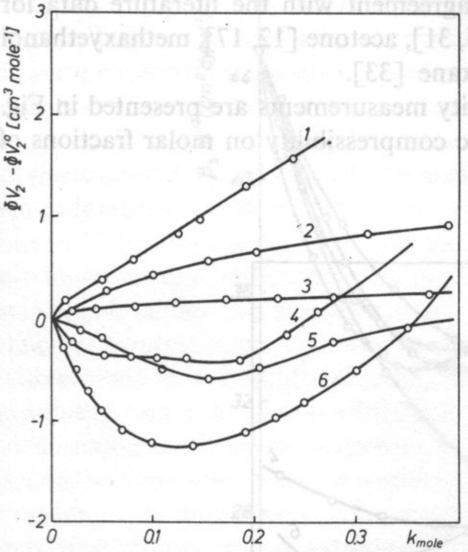

Fig. 1. Dependence of excess of the apparent molal volume of non-electrolytes $\Phi V_2 - \Phi V_2^0$ on the molal fraction of solute: *1* – urea, *2* – formamide, *3* – hydrazine, *4* – *N*-methylformamide, *5* – acetamide, *6* – dimethylformamide

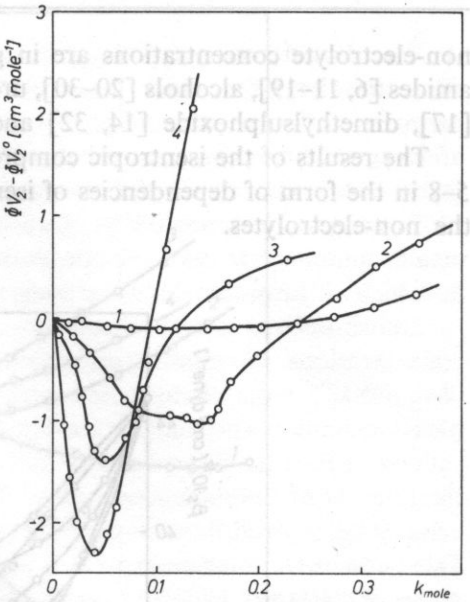

Fig. 2. Dependence of excess of the apparent molal volume of non-electrolytes $\Phi V_2 - \Phi V_2^0$ on the molal fraction of solute: *1* – methanol, *2* – ethanol, *3* – *n*-propanol, *4* – *t*-butanol

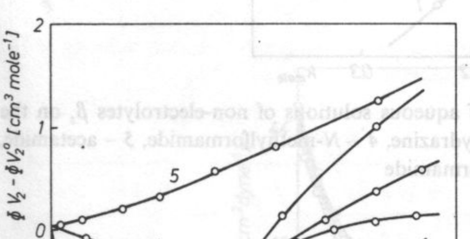

Fig. 3. Dependence of excess of the apparent molal volume of non-electrolytes $\Phi V_2 - \Phi V_2^0$ on the molal fraction of solute: *1* – ethylene glycol, *2* – 1,2-propylene glycol, *3* – 2,3-butylene glycol, *4* – 1,3-butylene glycol, *5* – glycerol

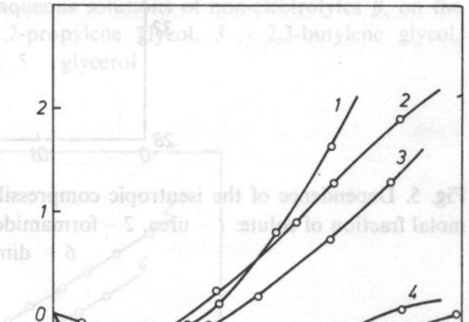

Fig. 4. Dependence of excess of the apparent molal volume of non-electrolytes $\Phi V_2 - \Phi V_2^0$ on the molal fraction of solute: *1* – acetone, *2* – 1,4-dioxane, *3* – methoxyethanol, *4* – etylene glycol monoacetate, *5* – dimethylsulphoxide

non-electrolyte concentrations are in good agreement with the literature data for amides [6, 11–19], alcohols [20–30], urea [15, 31], acetone [12, 17], methaxyethanol [17], dimethylsulphoxide [14, 32] and dioxane [33].

The results of the isentropic compressibility measurements are presented in Fig. 5–8 in the form of dependencies of isentropic compressibility on molar fractions of the non-electrolytes.

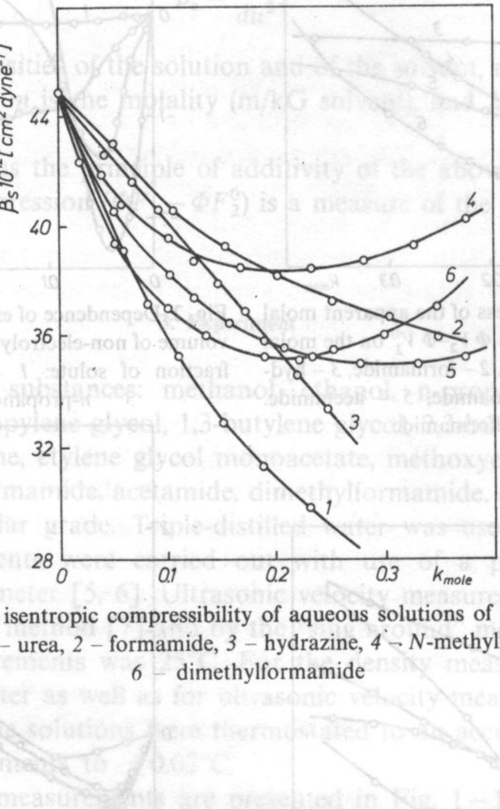

Fig. 5. Dependence of the isentropic compressibility of aqueous solutions of non-electrolytes β_s on the molal fraction of solute: *1* – urea, *2* – formamide, *3* – hydrazine, *4* – *N*-methylformamide, *5* – acetamide, *6* – dimethylformamide

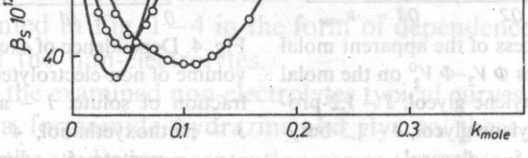

Fig. 6. Dependence of the isentropic compressibility of aqueous solutions of non-electrolytes β_s on the molal fraction of solute: *1* – methanol, *2* – ethanol, *3* – *n*-propanol, *4* – *t*-butanol

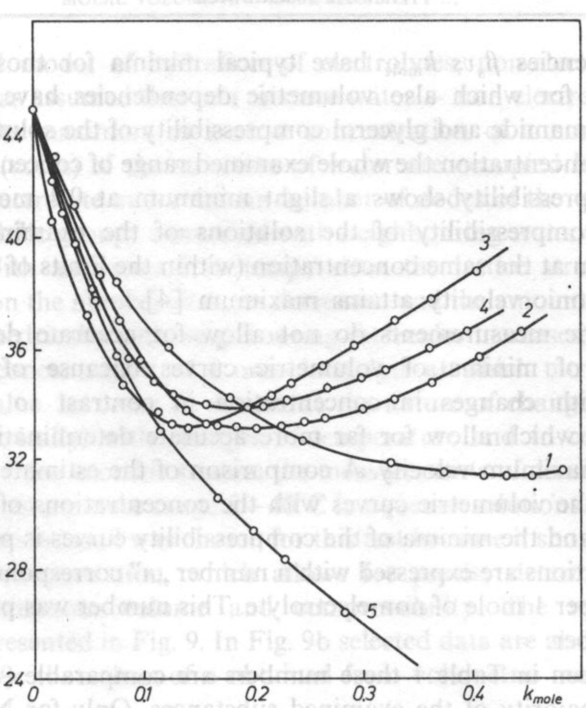

Fig. 7. Dependence of the isentropic compressibility of aqueous solutions of non-electrolytes β_s on the molal fraction of solute: 1 – ethylene glycol, 2 – 1,2-propylene glycol, 3 – 2,3-butylene glycol, 4 – 1,3-butylene glycol, 5 – glycerol

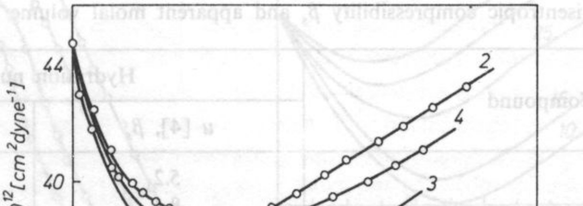

Fig. 8. Dependence of the isentropic compressibility of aqueous solutions of non-electrolytes β_s on the molal fraction of solute: 2 – 1,4-dioxane, 3 – methoxyethanol, 4 – ethylene glycol monoacetate, 5 – dimethylsulphoxide

The dependencies β_s *vs* k_{mole} have typical minima for those of the examined non-electrolytes for which also volumetric dependencies have minima. For hydrazine, urea, formamide and glycerol compressibility of the solutions decreases with an increase in concentration the whole examined range of concentration; for ethylene glycol the compressibility shows a slight minimum at 0.4 molar fraction.

Isentropic compressibility of the solutions of the examined non-electrolytes attains minimum at the same concentration (within the limits of experimental error), at which ultrasonic velocity attains maximum [4].

Densitometric measurements do not allow for accurate determination of the concentrations of minima of volumetric curves bacause of small changes in $(\Phi V_2 - \Phi V_2^0)$ with changes in concentration in contrast to ultrasonic velocity measurements , which allow for far more accurate determination of the concentrations of the maximum velocity. A comparison of the estimated concentrations of the minima of the volumetric curves with the concentrations of the maxima of the velocity curves and the minima of the compressibility curves is presented in Table 1. These concentrations are expressed with a number „*n*” corresponding to a number of moles of water per 1 mole of non-electrolyte. This number was previously defined as hydration number.

As can be seen in Table 1 these numbers are comparable (within experimental error) for the majority of the examined substances. Only for N-methylformamide, methoxyethanol and acetone the difference between the numbers are higher than the experimental error.

Table 1. Values of hydration numbers *n* obtained from measurements of ultrasonic velocity *u* [4], isentropic compressibility β_s and apparent molal volume ΦV_2

Compound	Hydration number *n*	
	u [4], β_s	ΦV_2
methanol	5.2	5±2
ethanol	8.4	8.5±2
n-propanol	19.9	19±2
tert-butanol	22.6	24±2
ethylene glycol	1.4 (β_s)	4±2
1,2-propylene glycol	4.4	9.5±4
1,3-butylene glycol	3.8	9.5±4
2,3-butylene glycol	6.9 (β_s)	11.5±4
N-methylformamide	4.5	13±4
acetamide	2.4	5.5±2
N,*N*-dimethylformamide	3.8	6.5±2
acetone	10.7	17±4
methoxyethanol	6.5	25±4
1,4-dioxane	8.7	7±2
ethylene glycol monoacetate	10.5	10±2
dimethylsulphoxide	3.4	4±2

In the presented model of hydration of electrolytes, non-electrolytes and of macromolecules it was assumed that in a mixture water – non-electrolyte velocity of ultrasound attains its maximum at such a concentration of a non-electrolyte at which all the cages (voids) of the structure of water are occupied by hydrophobic groups of the non-electrolyte and a certain number of nodes of the water lattice are occupied by hydrophilic groups connected with neighbouring water molecules with hydrogen bonds. With an increase in temperature the lattice structure of water undergoes destruction the number of cages decreases, and the amount of "free" water not connected tetrahedrically with neighbouring molecules increases. This results in an decrease of the concentration of a non-electrolyte at which ultrasonic velocity attains maximum value. In order to determine the nature of changes of parameter *n* (obtained volumetrically) with changes of temperature and to compare it with values of *n* obtained from acoustic studies, the measurements of density and velocity of ultrasound in the temperature range 5 – 40°C in aqueous solutions of tert.-butanol were carried out. Tert.-butanol was chosen for this test because it shows considerably big changes in its concentration, which allows for precise determination of the concentration of minimum volume and compressibility. The results of these measurements are presented in Fig. 9. In Fig. 9b selected data are also given [23]. As can be seen in Fig. 9c the values of *n* obtained from volumetric measurements are

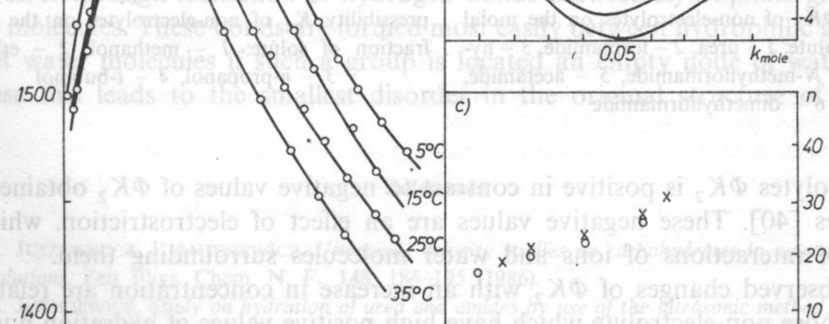

Fig. 9. Temperature dependence of ultrasonic velocity a) excess of the apparent molal volume $\Phi V_2 - \Phi V_2^0$ b) and hydration number c) from the aqueous solution of *t*-butanol

similar to those obtained from acoustic measurements. Also the nature of the changes with temperature is similar. This constitues a very good confirmation of the assumed model of hydration since there is no other interpretation of the effect that the non-electrolyte concentration at which certain physical parameters attain extrema decrease in temperature. Similar values of n at different temperarures obtained with two different techniques also confirm that the assumptions are correct. A similar opinion on the interpretation of this effect can be found in many other papers [16, 21, 34–39].

In Fig. 10–13 the dependences of apparent molal compressibility of solute on molar fraction of a non-electrolyte are presented. For all the examined non-electrolytes ΦK_2 is positive in contrast to negative values of ΦK_2 obtained for electrolytes [40]. These negative values are an effect of electrostriction, which is a result of interactions of ions and water molecules surrounding them.

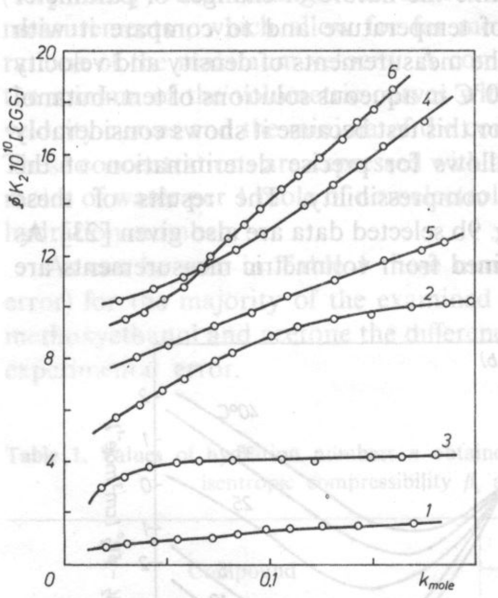

Fig. 10. Dependence of the apparent molal compressibility ΦK_2 of non-electrolytes on the molal fraction of solute: 1 – urea, 2 – formamide, 3 – hydrazine, 4 – N-methylformamide, 5 – acetamide, 6 – dimethylformamide

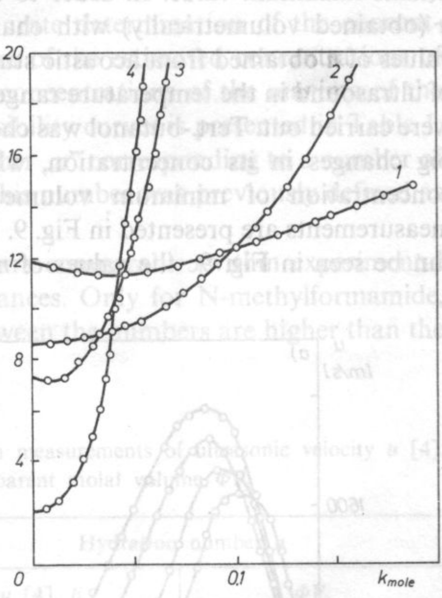

Fig. 11. Dependence of the apparent molal compressibility K_2 of non-electrolytes on the molal fraction of solute: 1 – methanol, 2 – ethanol, 3 – n-propanol, 4 – t-butanol

The observed changes of ΦK_2 with an increase in concentration are relatively high for those non-electrolyte which have high positive values of hydration number n, which results from hydrophobic hydration of a non-electrolyte. For urea, hydrazine, formamide, ethylene glycol and glycerol the changes of ΦK_2 with concentration are considerably lower, and at higher concentrations ΦK_2 for urea, hydrazine and formamide are practically constant. This prove once more that

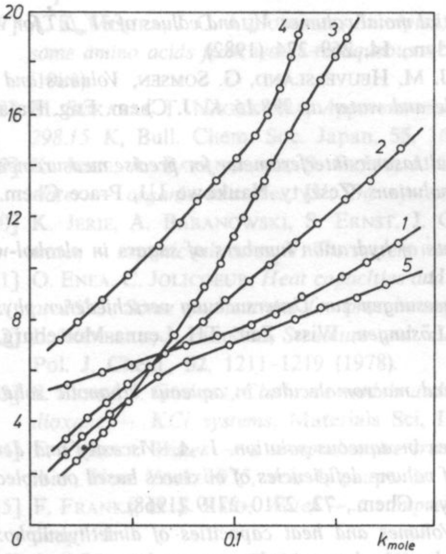

Fig. 12. Dependence of the apparent molal compressibility K_2 of non-electrolytes on the molal fraction of solute: *1* – ethylene glycol, *2* – 1,2-propylene glycol, *3* – 2,3-butylene glycol, *4* – 1,3-butylene glycol, *5* – glycerol

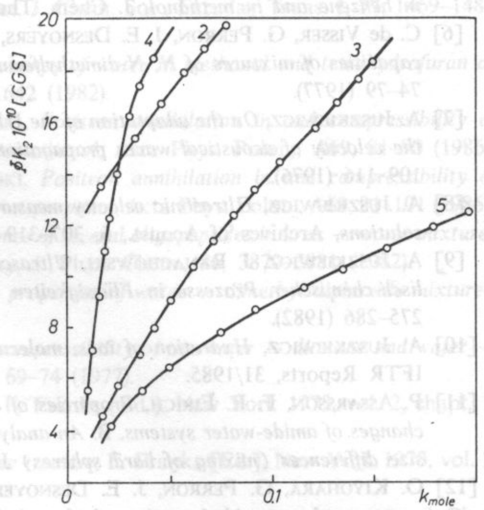

Fig. 13. Dependence of the apparent molal compressibility K_2 of non-electrolytes on the molal fraction of solute: *2* – 1,4-dioxane, *3* – methoxyethanol, *4* – ethylene glycol monoacetate, *5* – dimethylsulphoxide

physico-chemical properties of this group of substances are different from those of the rest of the non-electrolytes. This difference in physico-chemical properties was among others a basis for assuming that these substances exhibit negative hydration.

The above listed substances are counted into the group of substances named after FRANKS [34] hydrophilic substances in which hydrophilic interactions have a decisive influence on the properties of whole molecules. The hydrophilic interactions manifest themselves through formation of hydrogen bonds between hydrophilic groups and water molecules. These bonds are formed most easily between hydrophilic group and closest water molecules if such a group is located an empty node of water lattice, because this leads to the smallest disorder in the original structure of water.

References

[1] A. JUSZKIEWICZ, J. ANTOSIEWICZ, *Ultrasonic velocity studies on carbohydrates in aqueous ethanolic solutions*, Zeit Phys. Chem. N. F., **148**, 185–195 (1986).

[2] A. JUSZKIEWICZ, *Study on hydration of urea and amides by use of the ultrasonic method*, Zeit. Phys. Chem. N. F., **158**, 87–98 (1988).

[3] A. JUSZKIEWICZ, *Ultrasonic studies on hydrophobic and hydrophilic hydration of non-electrolytes*, J. Solution Chem. – in press.

[4] A. JUSZKIEWICZ, *Ultrasonic studies of hydration of non-electrolytes*, Ultrasonics – **27**, 131–139 (1989).

[5] M. SAKURAI, T. NAGAKAWA, *Densities of dilute solutions of water in benzene and in methanol at*

278.15, 288.15, 298.15, 308.15 and 318.15 K. *Partial molal volumes* V_w *and values of* $\partial V_w/\partial T$ *for water in benzene and in methanol*, J. Chem. Thermodyn., **14**, 269–274 (1982).

[6] C. de Visser, G. Perron, J. E. Desnoyers, W. J. M. Heuvelsland, G. Somsen, *Volumes and heat capacities of mixtures of N, N-dimethylformamide and water at 298.15 K*. J. Chem. Eng. Data, **22**, 74–79 (1977).

[7] A. Juszkiewicz, *On the adaptation of the UI–11 ultrasonic interferometer for precise measurements of the velocity of acoustical waves propagation in solutions.* Zeszyty Naukowe UJ, Prace Chem., **21**, 109–116 (1976).

[8] A. Juszkiewicz, *Ultrasonic velocity measurements of hydration numbers of sugars in alcohol-water solutions*, Archives of Acoust., **6**, 307–319 (1981).

[9] A. Juszkiewicz, J. Ranachowski, *Ultraschallmessungen zur Untersuchung verschiedener physikalisch-chemischer Prozesse in Flüssigkeiten und Lösungen*, Wiss. Zeit. TH Leuna-Merseburg, **24**, 275–286 (1982).

[10] A. Juszkiewicz, *Hydration of ions, molecules and macromolecules in aqueous ethanolic solutions*, IFTR Reports, 31/1985.

[11] P. Assarsson, F. R. Eirich, *Properties of amides in aqueous solution. I. A. Viscosity and density changes of amide-water systems. B. An analysis of volume deficiencies of mixtures based on molecular size differences (mixing of hard spheres)* J. Phys. Chem., **72**, 2710–2719 (1968).

[12] O. Kiyohara, G. Perron, J. E. Desnoyers, *Volumes and heat capacities of dimethylsulphoxide, acetone and acetamide in water and of some electrolytes in these mixed aqueous solvents* Can. J. Chem., **53**, 3263–3268 (1975).

[13] C. de Visser, P. Pel, G. Somsen, *Volumes and heat capacities of water and N-methylformamide in mixtures of these solvents*, J. Solution Chem., **6**, 571–580 (1977).

[14] C. de Visser, W. J. M. Heuvelsland, L. A. Dunn, G. Somsen, *Some properties of binary aqueous liquid mixtures*, J. Chem. Soc., Faraday Trans. I, **74**, 1159–1169 (1978).

[15] C. de Visser, G. Perron, J. E. Desnoyers, *Volumes and heat capacities of ternary aqueous systems at 25°C. Mixtures of urea, tert.-butyl alcohol dimethylformamide and water* J. Am. Chem. Soc., **99**, 5894 5898 (1977).

[16] F. Kawaizumi, M. Ohno, Y. Miyahara, *Ultrasonic and volumetric investigation of aqueous solutions of amides*, Bull. Chem. Soc. Japan, **50**, 2229–2233 (1977).

[17] G. Roux, G. Perron, J. E. Desnoyers, *The heat capacities and volumes of some low molecular weight amides, ketones, esters and ethers in water over the whole solubility range*, Can. J. Chem., **56**, 2808 2814 (1978).

[18] N. M. Murthy, K. V. Sivakumar, E. Rajagopal, S. V. Subrahmanyam, *Excess thermodynamic functions of the systems water + N-methylformamide and water + N,N,-dimethylformamide*, Acustica, **48**, 341–345 (1981).

[19] K. Subbarangaiah, N. M. Murthy, S. V. Subrahmanyam, *Excess thermodynamic functions of the system: water + formamide*, Acoustica, **58**, 105–108 (1985).

[20] K. Nakanishi, *Partial molal volumes of butyl alcohols and of related compounds in aqueous solution*, Bull. Chem. Soc. Japan, **33**, 793–797 (1960).

[21] F. Franks, J. G. Ives, *Alcohol-water mixtures*, Quart. Rev., **20**, 1–50 (1966).

[22] H. Hoiland, E. Vikingstad, *Partial molal volumes and additivity of group partial molal volumes of alcohols in aqueous solution* at 25 and 35°C, Acta Chem. Scand., **A30**, 182–186 (1976).

[23] C. de Visser, G. Perron, J. E. Desnoyers, *The heat capacities, volumes and expansibilities of tert.-butyl alcohol — water mixtures from 6 to 65°C*, Can. J. Chem., **55**, 856–862 (1977).

[24] A. Hvidt, R. Moss, G. Nielsen, *Volume properties of aqueous solutions of tert.-butyl alcohol at temperatures between 5 an 25°C*, Acta Chem. Scand., **B32**, 274–280 (1978).

[25] G. C. Benson, O. Kiyohara, *Thermodynamics of aqueous mixtures of non-electrolytes. I. Excess volumes of water — n-alcohol mixtures at several temperatures*, J. Solution Chem., **9**, 791–804 (1980).

[26] R. V. Jasra, J. C. Ahluwalia, *Entalpies of solution, partial molal heat capacities and apparent molal volumes of sugars and polyols in water*, J. Solution Chem., **11**, 325–338 (1982).

[27] A. K. Mishra, J. C. Ahluwalia, *Entalpies, heat capacities and apparent molal volumes of transfer of some amino acids from water to aqueous t-butanol*, J. Chem. Soc., Faraday Trans. I, **77**, 1469–1483 (1981).

[28] M. Sukarai, T. Nagakawa, *Apparent molar volumes of water in methanol and tetrahydrofuran at 298.15 K*, Bull. Chem. Soc. Japan, **55**, 1641–1642 (1982).

[29] K. Jerie, A. Baranowski, S. Ernst, J. Gliński, *Positron annihilation in and compressibility of water – organic mixtures*. IV. *The system water-ethanol*, Acta Phys. Polon., **A69**, 81–90 (1986).

[30] K. Jerie, A. Baranowski, S. Ernst, J. Gliński, *Positron annihilation in and compressibility of water – organic mixtures*. V. *The system water – n-propanol*, Acta Phys. Polon., **A69**, 91–101 (1986).

[31] O. Enea, C. Jolicoeur, *Heat capacities and volumes of several oligopeptides in urea – water mixtures at 25°C. Some implications for protein unfolding*, J. Phys. Chem., **86**, 3870–3881 (1982).

[32] L. Werblan, J. Lesiński, *Structure and selected properties of water – dimethylsulphoxide mixtures*, Pol. J. Chem., **52**, 1211–1219 (1978).

[33] S. Ernst, J. Gliński, *Clathrate models and the compressibility of the water – dioxane and water – dioxane – KCl systems*, Materials Sci, III/3, 69–74 (1977).

[34] F. Franks, *Water – a comprehensive treatise*, F. Franks [Ed.], New York 1973, vol. 2, chapt. 1; ibid., New York 1975, vol. 4, chapt. 1.

[35] F. Franks, D. S. Reid, *Water – a comprehensive treatise*, F. Franks [Ed.], New York 1973, vol. 2, chapt. 5.

[36] E. K. Baumgartner, G. Atkinson, *Ultrasonic velocity in nonelectrolyte – water mixtures*, J. Phys. Chem., **75**, 2336–2340 (1971).

[37] J. Lara, J. E. Desnoyers, *Isentropic Compressibilities of alcohol – water mixtures at 25°C*, J. Solution Chem., **10**, 465–478 (1981).

[38] G. D'Arrigo, O. Conde, *Acoustic properties of water – ethanol mixtures at low temperatures*, J. Phys., Colloque **C7**, 185–193 (1984).

[39] G. D'Arrigo, A. Paparelli, *Sound propagation in water – ethanol mixtures at low temperatures*. I. *Ultrasonic velocity*, J. Chem. Phys., **88**, 405–415 (1988).

[40] J. Stuehr, E. Yeager, *Physical Acoustics*, vol. II, part A, New York-London 1965.

Received November 7, 1988.