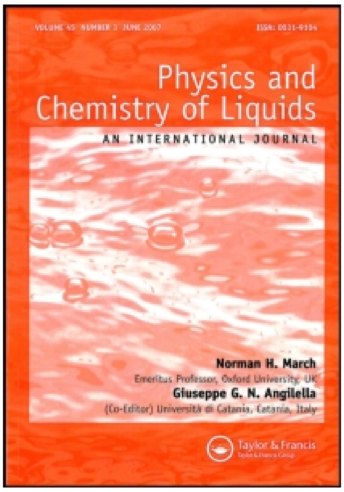

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Kinart, Cezary M. and Kinart, Wojciech J.(2000) 'Physicochemical Methods Used to Study Internal Structures of Liquid Binary Mixtures', Physics and Chemistry of Liquids, 38: 2, 155 — 180

To link to this Article: DOI: 10.1080/00319100008030266

URL: http://dx.doi.org/10.1080/00319100008030266

Phys. Chem. Liq., 2000, Vol. 38, pp. 155-180
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Review Article

PHYSICOCHEMICAL METHODS USED TO STUDY INTERNAL STRUCTURES OF LIQUID BINARY MIXTURES

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(Received 10 September 1998)

Different methods, based on application of studies of intensive physicochemical properties of liquid binary mixtures and ^{1}H-NMR spectral measurements, used in the analysis of intermolecular interactions and estimation of the internal structure of these mixtures are here reviewed.

Keywords: Physicochemical properties; intermolecular interactions; liquid binary mixtures

INTRODUCTION

Recently there has been considerable progress in studies on intermolecular interactions and the internal structure of liquid one-, two- and three-component systems. This is linked with the possibility of application of these results for interpretation of problems connected with interactions of the ion-ion and ion-solvent type within the liquid system. Such results are necessary for interpretation of data obtained from thermochemical, electrochemical, biochemical and kinetic studies. Some splendid monographs devoted to this subject

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have appeared previously as published in 1988 "Ionic Solvation" by Y. Marcus and "Solvent and Solvent Effects in Organic Chemistry" by Ch. Reichardt. Regarding structural studies, review of the literature shows that for the analysis of this type of effect in liquid solvent mixtures it is possible to apply both a wide range of spectral methods, thermochemical methods as well as studies on intensive macroscopic properties of solutions (such as density, viscosity, dielectric permittivity, surface tension, *etc.*) carried at different temperatures. Different conclusions, not always consistent, have been drawn from these studies particularly regarding binary mixtures. However, authors of numerous physicochemical works used to limit their studies to determination of the composition range characterized by the strongest intermolecular interactions or to the suggestion of the stoichiometry of intermolecular complexes formed in these systems. Little effort has hitherto been devoted to explain how molecules are bound in intermolecular complexes and which of them are the most stable. It is fair to say that researchers sometimes have not paid sufficient attention to the fact that it is not indifferent which way of expressing the concentration is chosen, while determining the stoichiometry of intermolecular complexes and probable interactions in the studied system on the base of the analysis of changes of deviations from additivity of the physicochemical property studied. This results from the fact that for each additive property of the ideal system it is possible to attribute only one physically consistent way of expressing the concentration. Inappropriate choice of the concentration can lead to flawed interpretation of the experimental data. To our knowledge, there is no available work analysing and systemizing deeply the above-mentioned problem. This has motivated us to prepare this review of physicochemical methods useful in these studies and it is natural enough then to select the most substantially justifiable procedures. We have also included methods of application of ^{1}H-NMR studies for determination of the internal structure of binary liquid mixtures, proposed in our previous studies.

I. INTERMOLECULAR INTERACTIONS IN LIQUID BINARY MIXTURES BASED ON STUDIES OF PHYSICOCHEMICAL PROPERTIES

Studies on different physical properties (macroscopic) of liquid binary mixtures within wide ranges of composition and temperature are valuable sources of information that may be used to examine the relation between the internal structure of the system and its physical properties. These data are very often essential for explanation of the solvent influence, one or two component, on chemical, electrochemical and biochemical processes occurring in the system. The experimental values of physical properties are often applied for calculations of other parameters characterising binary mixtures. Different theoretical, empirical and semiempirical methods have been extensively applied for this purpose. Many of them are based on well-founded physical dependences, *e.g.*, between molecular and macroscopic parameters. In other methods, mathematical dependences between experimentally measured values of physical properties are derived. In semiempirical methods also correlations between different parameters, which are theoretically justified, are accounted for. Next, the appropriate empirical parameters are chosen to achieve consistency with an experiment. Such parameters are often available in tabulated form. In this article some basic physical characteristics of binary mixtures applicable in the analysis of intermolecular interactions will be discussed. It has been found, on the basis of extensive studies on binary liquid mixtures, that in case of the appearance within them weak intermolecular interactions (*e.g.*, in mixtures of two liquid hydrocarbons or two non-polar, or weakly polar components not able to interact specifically with each other) the additive character of some of their physical properties, as the refractive index, dielectric permittivity and so on, is frequently observed. However, in liquid binary mixtures characterised by stronger intermolecular interactions (*e.g.*, of dipole–dipole or specific type) distinct deviations from additivity have often been observed. Those are sometimes termed deviations from linearity, $\Delta p_{\text{add.}} - \Delta p_{\text{linear}} \neq 0$ (where p indicates a studied intensive physical property of the liquid system). Finlay [1] and Denison [2] at the beginning of the 20-th century expressed their view that it is possible to study the nature and composition of possible "complexes" formed in real solutions by finding that composition for which the maximum deviation of *e.g.*, viscosity from the ideal curve is observed. Kendall and Monroe [3] in 1917 expressed some criticism of this view. They found this rule limited as long as the definition of the "normal" curve is not precise. They proved that in order to find the composition of a binary complex it is necessary to analyse the position of the maximum at the curve illustrating the course of the value Δp_{ideal}

(measuring deviations from ideality) plotted as a function of the concentration of the studied mixture expressed in different units:

$$\Delta p_{\mathrm{ideal}} = (p_{12})_{\mathrm{expected}} - (p_{12})_{\mathrm{ideal}} \tag{1.1}$$

Assuming the stability of the external pressure and temperature, the first term of the Eq. (1.1) refers to a directly measured chosen intensive physical property of the binary mixture, whereas the second term refers to the same property of this mixture assuming that it behaves as an ideal one. Monroe [3] has also defined the conception of the ideality assuming that the system may be regarded as ideal if mixing of components does not result in any change of their molecular state. It means that no association, dissociation as well as formation of new chemical individuals should be observed. All components of such system should be also mutually miscible and no thermal effects and changes of volume should be observed while mixing solvents. The analogous conclusions regarding the examination of properties of binary liquid mixtures using Eq. (1.1) are also contained in works of other authors [4, 5]. According to them, the value of the heat of mixing equal to zero and total volume being a sum of volumes of both components at chosen temperature is required for the system to be treated as ideal. The solution under investigation must also obey the Raoult's law. Such two component binary liquid mixtures should obey the equation given below:

$$\Delta u = \Delta h - p\Delta V$$

Assuming that $\Delta h_{\mathrm{ideal\,mixture}} = 0$ and $\Delta V_{\mathrm{ideal\,mixture}} = 0$ one obtains $\Delta u_{\mathrm{ideal}} = 0$. This indicates that in case of ideal solutions their internal energies (u) do not change while mixing components. However, other thermodynamic functions of these systems such as free energy (g) and entropy (s) must change while mixing of components. The dependences given below must always fulfilled for the spontaneous process as mixing of components.

$$\Delta g_{\mathrm{ideal\ mixture}} < 0$$

$$\Delta s_{\mathrm{ideal\ mixture}} > 0$$

The difference between values of thermodynamic functions of mixing for the studied solution and the ideal solution is called the excess thermodynamic function $Z^E = Z_{\text{expected mixture}} - Z_{\text{ideal mixture}}$. On the grounds of the definition of molar excess functions of mixing, G^{0E}, H^{0E}, S^{0E} and V^{0E} are equal to zero for the molar fractions of components equal respectively to $x_1 = 1$ ($x_2 = 0$), it means for pure components. Also from the definition, for positive deviations from Raoult's law $G^{0E} < 0$, whereas for negative deviations $G^{0E} > 0$. Hildebrand [6] found the new class of solutions known as regular solutions for which $S^{0E} = 0$, whereas G^{0E} and H^{0E} are different from zero. The implication is that two components are randomly distributed in the solution as if they were ideal, although the interaction energies of molecules of the same and different types are different. Finally, in case of an athermal solution $\Delta H^{0E} = 0$, although ΔS^{0E} and ΔG^{0E} are not necessarily equal to zero. This situation may occur with components of similar chemical nature but of very different molecular sizes. There is some statistical thermodynamic basis for the supposition that for a solution to be an ideal one the molar volumes of the components should be nearly the same and Raoult's law may in fact be less general, even as a limiting law, than is customarily thought.

The property p_{12} or its function of a binary liquid mixture may be only treated as an additive one if for a two component mixture it behaves as a linear function of the analytical composition of the mixture.

$$(p_{12})_{\text{additive}} = p_1 c_1 + p_2 c_2$$

$$[f(p_{12})] = f(p_1)c_1 + f(p_2)c_2$$

Very often, the logarithm of the studied property displays linearity.

$$\log(p_{12}) = c_1 \log(p_1) + c_2 \log(p_2)$$

The nonadditive properties do not fulfil the given above equations regardless of the method of expressing the concentration. In principle the "ideal" term in Eq. (1.1) is unknown and therefore it is commonly assumed that it may be calculated in the additive way. The approximation of Eq. (1.1) is carried according to the following (assuming p, T = const.):

$$(\Delta p)_{\text{ideal}} \cong (\Delta p)_{\text{additive}} = (p_{12})_{\text{expected}} - (c_1 p_1 + c_2 p_2) \qquad (1.2)$$

where:

p_1 and p_2 – the intensive properties of pure liquid components 1 and 2 of the system studied.

p_{12} – the reference property of the binary liquid system, *e.g.*, density (d_{12}) or specific volume ($1/d_{12}$), viscosity or fluidity, dielectric permittivity (ε_{12}), surface tension (σ_{12}), the refractive index of monochromatic light (n_{12}), rate of sound propagation (u_{12}) and so on.

c_1 and c_2 – concentration expressed most often as molar fraction. Though, sometimes without any substantiation volume or weight fractions happen to be used.

Indexes 1 and 2 correspond to pure components, whereas the index 12 refers to the two component mixture. The choice of the method of expressing the concentration plays an important role in the determination of the stoichiometry of complexes (adducts) and possibly the type of interactions between components of the liquid system based on the physicochemical analysis. Only one physically justifiable way of expressing the concentration of components is possible to be ascribed to each additive property of the ideal system. For example, density of the ideal two component system is additive only when the composition of the solution is expressed as a volume fraction. The analogous situation for molar volume is observed when the composition of the solution is expressed as a molar fraction [7]. The changes of shapes of curves at appropriate graphs with going from one method of expressing concentrations to other was very throughly and precisely discussed by Anosov [7]. The analytically-geometrical analysis of graphs for ideal two component systems shows that if a certain property is additive, when using a given method of expressing the concentration, then it assumes a hyperbolic shape with transition into another method. For example, if a given property p_{12} is additive (it means linear) when the concentration is expressed as a molar fraction, which means $(p_{12})_{\text{additive}} = p_1 x_1 + p_2 x_2$, then with a change into, *e.g.*, weight fraction, it assumes a hyperbolic shape (and *vice* *versa*) and it is given by the following equation:

$$p_{12} = \frac{M_1 \cdot M_2}{M_1 w_1 + M_2 w_2} \cdot \left(\frac{p_1}{m_1} \cdot w_1 + \frac{p_2}{m_2} \cdot w_2 \right)$$

Usually rather the deviation of the isotherm of the given property from additivity than a parent isotherm is selected for a precise characterisation of the type and energy of interactions occurring in the regular system. Such choice has its physical justification if the given property is additive for the reference ideal system. The analysis of Eq. (1.2) indicates that if the extreme is observed at the curve given by equation $(p_{12})_{\text{experimental}}$ *vs.* c_1, then it is very often present at curve given by the equation $(\Delta p_{12})_{\text{additive}}$ *vs.* c_1. In general, the positions of these two extremes will not coincide [4]. Whereas for $(p_{12})_{\text{exp.}}$ and $(1/p_{12})_{\text{exp.}}$ as a function of c_1 expressed as molar, volume or weight fraction, the extremes correspond to the same value of c_1. If specific intermolecular interactions, leading to formation of intermolecular complexes (adducts) are present in the studied liquid mixture then molar mass of a mixture is given by the equation including real molar fractions of N components reflecting interactions occurring in this system. For a two component system obtained by mixing components A and B in which the following intermolecular interactions are present:

$nA + nB \rightleftarrows A_nB_n$ (the molecular complex or the labile compound)

where the equilibrium constant: $K = [A_mB_n]/[A]^m \cdot [B]^n$ the real molar mass is equal to:

$$M_{\text{real}} = M_A N_A + M_B N_B + M_{A_mB_n} \cdot N_{A_mB_n}$$

Molar properties (referred to one mole of the mixture) calculated using the real molar masses are called as real molar properties. Whereas, molar properties referred to the additive molar masses ($M_{\text{additive}} = M_A x_A + M_B x_B$) are termed as pseudomolar [4]. x_A and x_B indicate analytical concentrations of components estimated as it is shown below.

$$x_A = \frac{\frac{m_A}{M_A}}{\frac{m_A}{M_A} + \frac{m_B}{M_B}} \qquad x_B = \frac{\frac{m_B}{M_B}}{\frac{m_A}{M_A} + \frac{m_B}{M_B}} \qquad x_A + x_B = 1$$

In purpose to precisely determine the stoichiometry of specific interactions in a multicomponent liquid system it necessary to apply pseudomolar properties or more precisely their deviations from additivity. It makes possible to determine the stoichiometry of intermolecular complex without knowledge of the equilibrium constant (K). Besides, molar additive properties considered usually in the physicochemical analysis occur in general to be pseudomolar due to the fact that the knowledge of equilibrium concentrations of components is necessary for determination of the real molar mass of the liquid mixture. However, the procedure of determination of real properties even for a two component mixture is very complex. The term molar properties will further indicate pseudomolar properties which is in agreement with suggestions of Anosov [5]. Therefore, it is necessary to use modified values of additive ideal properties. For example, if the composition is expressed obligatorily as weight or volume fraction, such modified values must be additive in the molar fraction scale. This subject has been thoroughly discussed by Anosov [5]. For the given ideal property $(p^{(w)})_{\text{ideal}}$ which is additive when the composition is expressed as weight fraction (for a multicomponent system) the following equation must be obeyed.

$$p_{\text{ideal}}^{(w)} = \sum_i p_i^{(w)} \cdot w_i$$

As the result of a mathematical transformation [5] the additive derivative in the molar fraction scale is obtained.

$$[p_{\text{ideal}}^{(w)} \cdot M_{12}]_{\text{additive}}^{x} = \sum_i p_i^{(w)} \cdot M_i \cdot x_i$$

where:

$$M_{\text{additive}} = \sum_i x_i M_i$$

Whereas, for a two component ideal system, for which $M_{12} = M_1 \cdot x_1 + M_2 \cdot x_2$, the given below equation can be obtained:

$$[(p_{12}^{(w)})_{\text{ideal}} \cdot M_{12}]_{\text{additive}}^{x} = p_1^{(w)} \cdot M_1 \cdot x_1 + p_2^{(w)} \cdot M_2 \cdot x_2$$

In case of the ideal volume additive property of the binary system for which $V_{12} = V_1 \cdot x_1 + V_2 \cdot x_2$ the following dependence can be derived:

$$[(p_{12}^{(w)})_{\text{ideal}} \cdot M_{12}]_{\text{additive}}^{x} = p_1^{(w)} \cdot M_1 \cdot x_1 + p_2^{(w)} \cdot M_2 \cdot x_2$$

The extreme of the isotherm $p_{12}^{(w)}$ always corresponds to the stoichiometry of the studied reaction, it means to the same value of abscissa x_1, being independent of a value of the equilibrium constant K. The decrease of the K results only in decrease of the absolute value of $p_{12}^{(x)}$, without any impact at the position of the extreme. However, if deviations from additivity are observed (for properties $(p_{12})_{\text{experimental}}$, for which reference ideal properites $(p_{12})_{\text{ideal}}$ are either volume additive, it means $(p_{12}) = p_1 v_1 + p_2 v_2$, or weight additive, it means $(p_{12}) = p_1 w_1 + p_2 w_2$, then deviations of extremes of isotherms Δp_{12}^{v} or Δp_{12}^{w} with the increase of the value of the equilibrium K are noticeable. Only for $K \Rightarrow \infty$, it means when the complexation is complete, the position of the extremes of three isotherms corresponds to the same searched stoichiometry of (product, chemical individual) A_mB_n. Therefore, it occurs that the physicochemical analysis of isotherms $p_{12}^{(x)}$ as a function of x_1 gives the best result. It may be explained as the result of the fact that the scale of the shift of the equilibrium of complexation in the studied binary liquid system is usually unknown.

I.a. Density of Binary Liquid Mixtures

Density (d) belongs to the group of most useful intensive physicochemical properties widely applied in studies of pure liquids and liquid solutions. The knowledge of density of these systems is also necessary for calculations of other properties as for example of kinematic viscosity. Results of many experimental works [8–11] show that the analysis of deviations from ideality of density as a function of the composition of the mixture is more useful for studies of intermolecular interactions in liquid binary mixtures than the analogous examination of changes of density. Anosov and Ozierowa [5] and others [12] proved that density behaves as an additive volumetric property for reference ideal solutions:

$$(d_{12})_{\text{ideal}} = v_1 d_1 + v_2 d_2$$

Thus, isotherms of deviations of experimental densities from ideality for binary solutions must be calculated from the given below dependence:

$$\Delta(d_{12})^{v}_{\text{ideal}} = \Delta(d_{12})^{(v)}_{\text{add.}} = (d_{12})_{\text{exp.}} - (v_1 d_1 + v_2 d_2) \qquad (1.3)$$

or from a more precise equation [12]:

$$\Delta(d_{12})^{(x)}_{\text{ideal}} = (d_{12})_{\text{exp.}} - \frac{x_1 M_1 + x_2 M_2}{x_1 \cdot \frac{M_1}{d_1} + x_2 \cdot \frac{M_2}{d_2}} \qquad (1.4)$$

In purpose to apply Eq. (1.3) it is necessary to represent appropriate isotherms in the coordinate system of the type $\Delta(d)^{(v)}_{\text{ideal}}$ *vs.* v_1. Whereas, application of Eq. (1.4) requires use of the coordinate system of the type $\Delta(d_{12})^{(x)}_{\text{ideal}}$ *vs.* x_1.

It results from Eq. (1.4) that the (imaginary) deviations from ideality calculated from the equation given below:

$$\Delta(d_{12})^{(x)}_{\text{add.}} = (d_{12})_{\text{exp.}} - (x_1 d_1 + x_2 d_2)$$

have no sound theoretical explanation and should not be taken into consideration. Therefore, priority should be given to Eq. (1.4) and to appropriate isotherms of the type $\Delta(d_{12})^{(x)}_{\text{ideal}}$ *vs.* molar fractions x_1. It seems also worth mentioning that the positions of extremes at figures $\Delta(d_{12})^{(v)}_{\text{ideal}}$ *vs.* v_1 and $\Delta(d_{12})^{(x)}_{\text{ideal}}$ *vs.* x_1 will correspond to the same compositions of binary mixtures only if equilibrium constants of complex formation in these systems achieve very large values.

Apparent volume is an alternative physicochemical property applied in the analysis of intermolecular interactions of liquid binary mixtures. Earlier works [4, 5] have shown that apparent volume for reference ideal systems is a weight additive property. Thus, it is theoretically justifiable to apply the equation given below for calculations of deviations from ideality:

$$\Delta\left(\frac{1}{d}\right)^{(w)}_{\text{ideal}} = \Delta\left(\frac{1}{d}\right)^{(w)}_{\text{add.}} = \left(\frac{1}{d_{12}}\right)_{\text{exp.}} - \left[w_1 \cdot \left(\frac{1}{d_1}\right) + w_2 \cdot \left(\frac{1}{d_2}\right)\right]$$

and then the appropriate isotherms should be represented as a function $\Delta(1/d_{12})^{(w)}_{\text{add.}}$ *vs.* w_1.

Experimentally measured values of density can be also used for calculations of molar volumes of liquid binary mixtures [13], *viz.*

$$(V_{12})^{(x)}_{\mathrm{ideal}} = x_1 \cdot V_1 + x_2 \cdot V_2$$

where:

$$V_1 = \frac{M_1}{d_1};\quad V_2 = \frac{M_2}{d_2}$$

Thus, deviations from ideality for nonideal binary solutions should be calculated from the Eq. (1.5) and the appropriate isotherms should be represented as a function of $\Delta(V_{12})^{(x)}_{\mathrm{add.}}$ *vs.* x_1.

$$\Delta(V_{12})^{(x)}_{\mathrm{ideal}} = \Delta(V_{12})^{(x)}_{\mathrm{add.}} = (V_{12})_{\mathrm{exp.}} - (x_1 \cdot V_1 + x_2 \cdot V_2) \qquad (1.5)$$

If the contraction of volume and the exothermic effect accompany mixing of pure components then isotherms of the type $\Delta(V_{12})^{(x)}_{\mathrm{add.}}$ *vs.* x_1 exhibit always a minimum which may point to the formation of a complex of the composition corresponding to this minimum.

I.b. Viscosity of Binary Liquid Mixtures

Many authors [8–11] underlined the existing relationship between experimental data of viscosity of liquids and their internal structure. Usually dynamic viscosity is applied for studies of liquid systems. The coefficient of viscosity being its measure is given by Newton's equation.

$$F = \eta \cdot A \cdot \frac{dv}{dx}$$

where F is force required to shift a layer of liquid of area A with velocity dv with reference to an other layer separated by a distance dx.

In many works in parallel with dynamic viscosity other physicochemical properties happen to be used, such as dynamic fluidity $\Phi = 1/\eta$, kinematic fluidity (d/η), kinematic viscosity $\nu = \eta/d$ as well as molar viscosity $\eta_M = \eta \cdot V_M^{1/3}$.

It seems worth mentioning that viscosity of binary liquid mixtures is not a simple additive property. Kendall and Monroe [3] found that a simple linear law of mixing $d\eta/dc = k =$ const. (where c represents the composition of the mixture expressed as volume or weight fraction or most logically justified molar fraction [5]) is never precisely obeyed even for liquid mixtures of two saturated hydrocarbons. Up to now, there is no satisfactory theory allowing one to calculate the ideal term η_{12}(ideal) from Eq. (1.2). Moelwyn-Hughes in his monograph [14] simply states that derivation of the precise equation of viscosity of liquids is beyond present capacities since such theory should be linked in extremely complex way with local thermal and density fluctuations occurring on the microscopic scale. In spite of this, some authors attempted to approximate Eq. (1.2) by introduction, instead of p (property), dynamic viscosity (η), fluidity ($1/\eta$) or kinematic viscosity (η/d). Such an approach was based on the assumption that the ideal term in Eq. (1.2) can be empirically approximated by introduction of the value found by the additive method. Therefore, in different works, approximate equations given below were applied.

$$\Delta(\eta_{12})^{(x)}_{\text{ideal}} \cong \Delta(\eta_{12})^{(x)}_{\text{add.}} = (\eta_{12})_{\text{exp.}} - (x_1 \cdot \eta_1 + x_2 \cdot \eta_2) \qquad [5, 15-17]$$

$$\Delta(1/\eta)^{(x)}_{\text{ideal}} \cong \Delta(1/\eta)^{(x)}_{\text{add.}} = (1/\eta)_{\text{exp.}} - (x_1 \cdot 1/\eta_1 + x_2 \cdot 1/\eta_2) \qquad [5, 18-20]$$

$$\Delta(\eta_{12}^{1/3})^{(x)}_{\text{ideal}} \cong \Delta(\eta_{12}^{1/3})^{(x)}_{\text{add.}} = (\eta_{12}^{1/3})_{\text{exp.}} - (x_1 \cdot (\eta_1)^{1/3} + x_2 \cdot (\eta_2)^{1/3}) \qquad [5, 19]$$

However, Herms [21] and co-workers expressed their opinion that for ideal liquid binary mixtures the analysis of intermolecular interactions should be based on the idea of molar viscosity $\eta_M \equiv \eta \cdot V^{1/3}$. Such systems should obey the following dependence:

$$(\eta_{M_{12}})_{\text{ideal}} = x_1 \cdot \eta_{M_1} + x_2 \cdot \eta_{M_2}$$

It allows to calculate deviations from expected ideality of solutions from the given below equation (at constant temperature):

$$\Delta(\eta_{M_{12}})^{(x)}_{\text{ideal}} \cong \Delta(\eta_{M_{12}})^{(x)}_{\text{add.}} = \eta_{M_{12}}{}^{(x)}_{\text{theor.}} - \eta_{M_{12}}{}^{(x)}_{\text{exp.}} = $$
$$= (x_1 \cdot \eta_1 \cdot V_1^{1/3} + x_2 \cdot \eta_2 \cdot V_2^{1/3}) - (\eta_{12} \cdot V_{12}^{1/3}) \qquad (1.6)$$

where: $V_{12} = x_1 \cdot V_1 + x_2 \cdot V_2$.

The idea of molar viscosity was introduced on the base of theoretical considerations [22]. It is a theoretical property independent from the type of molecules and the state of aggregation. Hafez and Sadek [73] carried analysis of graphs for several liquid mixtures (*e.g.*, dioxane–water and dimethyl sulfoxide–water) based on Eq. (1.6) and they expressed an opinion that the depth of minimum at the graph $\Delta(\eta_{M_{12}})^{(x)}_{\text{add.}}$ *vs.* x_1 may be treated as a measure of intermolecular forces present in the mixture. However, our review of the literature shows that a growing number of authors seem to support the view that the approximation of the ideal term in Eq. (1.2) requires application of Arrhenius [19] equation in its corrected and general form given by Kendal [5]:

$$(\eta_{12})^{(x)}_{\text{ideal}} \cong (\eta_1)^{x_1} \cdot (\eta_2)^{x_2}$$

The dependences given below derived from the above equation are quite often used for calculations of deviations from ideality for real solutions (at constant temperatures):

$$\Delta(\eta_{12})^{(x)}_{\text{ideal}} \cong (\eta_{12})_{\text{exp.}} - [(\eta_1)^{x_1} \cdot (\eta_2)^{x_2}] \qquad (1.7)$$

$$\Delta[\log(\eta_{12})]^{(x)}_{\text{ideal}} \cong \Delta[\log(\eta_{12})]^{(x)}_{\text{add.}} =$$
$$= [\log(\eta_{12})]_{\text{exp.}} - [x_1 \cdot \log(\eta_1) + x_2 \cdot \log(\eta_2)] \qquad (1.8)$$

$$\Delta[\log(1/\eta_{12})]^{(x)}_{\text{ideal}} \cong \Delta[\log(1/\eta_{12})]^{(x)}_{\text{add.}} =$$
$$= [\log(1/\eta_{12})]_{\text{exp.}}$$
$$- [x_1 \cdot \log(1/\eta_1) + x_2 \cdot \log(1/\eta_2)] \qquad (1.9)$$

Fialkow, Anosow and other suggested that it is possible to apply the above equations only if $\eta_1/\eta_2 \leq 6$ [4, 5].

The analysis of values of kinematic fluidity (d_{12}/η_{12}) and kinematic viscosity (η_{12}/d_{12}) leads occasionally to better results than those obtained on the basis of Eq. (1.7). Deviations from ideality are calculated from the following dependences [23, 24]:

$$\Delta\left(\frac{d_{12}}{\eta_{12}}\right)^{(v)}_{\text{ideal}} \cong \Delta\left(\frac{d_{12}}{\eta_{12}}\right)^{(v)}_{\text{add.}} = \left(\frac{d_{12}}{\eta_{12}}\right)_{\text{exp.}} - \left[v_1 \cdot \left(\frac{d_1}{\eta_1}\right) + v_2 \cdot \left(\frac{d_2}{\eta_2}\right)\right] \tag{1.10}$$

$$\Delta\left(\frac{\eta_{12}}{d_{12}}\right)^{(x)}_{\text{ideal}} \cong \left(\frac{\eta_{12}}{d_{12}}\right)_{\text{exp.}} - \left[\left(\frac{\eta_1}{d_1}\right)^{x_1} \cdot \left(\frac{\eta_2}{d_2}\right)^{x_2}\right] \tag{1.11}$$

The second ideal term in Eq. (1.11) is given by the exponential equation of the Arrhenius type. Francks [11] recommended for studies of internal structures of binary liquid mixtures the analysis of another property of these solutions calculated from values of experimental dynamic viscosity. This method is based on studies of the course of the derivative $d\eta_{12}/dx$ plotted as a function of x_1 as has been shown for mixtures of ethanol – water and 1, 4-dioxane – water. These systems are characterized by the appearance of the maximum at graphs of viscosity (η_{12}) plotted as the function of molar fraction x_1. Simultaneously graphs of the function $\Delta\eta_{12}/\Delta x_1$ differ considerably for both mixtures. The maximum is observed only in case of the ethanol – water mixture. According to Francks [11] this difference may be treated as a result of "ordering" of the water structure by a small addition of ethanol and its disruption by the analogous addition of 1, 4-dioxane.

I.c. Dielectric Permittivity of Binary Liquid Mixtures

Dielectric permittivity is a macroscopic property of the liquid linked with the structure of its molecules. Measurements of dielectric permittivity serve often as a source of information regarding intermolecular interactions in liquid systems [4, 5]. According to Onsager's theory, dielectric permittivity behaves as an additive property if its changes are plotted as a function of volume fractions:

$$(\varepsilon_{12})^{(v)}_{\text{ideal}} = (\varepsilon_{12})^{(v)}_{\text{add.}} = v_1 \cdot \varepsilon_1 + v_2 \cdot \varepsilon_2$$

In reference to binary mixtures of two different apolar or weakly polar and/or not associated components, the following approximated dependence given by Debye's theory may be applied for studies of their deviations from ideality:

$$\Delta(\varepsilon_{12})^{(v)}_{\text{ideal}} \cong \Delta(\varepsilon_{12})^{(v)}_{\text{add.}} = \varepsilon_{12} - (v_1 \cdot \varepsilon_1 + v_2 \cdot \varepsilon_2) \tag{1.12}$$

However, many authors [25–27] for studies of different binary liquid mixtures of polar and associated components also applied the given below equation expressing only the concentration of components as molar fractions:

$$\Delta(\varepsilon_{12})^{(x)}_{\text{ideal}} \cong \Delta(\varepsilon_{12})^{(x)}_{\text{add.}} = \varepsilon_{12} - (x_1 \cdot \varepsilon_1 + x_2 \cdot \varepsilon_2) \tag{1.13}$$

or less often as weight fractions:

$$\Delta(\varepsilon_{12})^{(w)}_{\text{ideal}} \cong \Delta(\varepsilon_{12})^{(w)}_{\text{add.}} = \varepsilon_{12} - (w_1 \cdot \varepsilon_1 + w_2 \cdot \varepsilon_2) \tag{1.14}$$

It seems also worth mentioning that up to now there is no theoretical foundation for the last two equations and they are strictly empirical. Equations (1.12)–(1.14) given above should be applied simultaneously and results obtained from them ought to be compared with other physicochemical parameters of these liquid mixtures.

Molar polarization $[P_{12}]$ is an example of another property related to dielectric permittivity which is often applied for the analysis of intermolecular interactions in liquid binary mixtures. As results from Debye's theory, molar polarization of binary mixtures behaves as a molar additive quantity only for dilute solutions [4, 5].

In binary systems composed of polar and associating components for which there is no theoretical basis to apply Eq. (1.13), also use of mole-additive properties cannot be theoretically justified. Nevertheless, many authors [28–30] in their physicochemical analyses of both apolar as well as strongly polar binary systems used the following empirical dependence:

$$\Delta[P_{12}]^{(x)}_{\text{ideal}} \cong \Delta[P_{12}]^{(x)}_{\text{add.}} = [P_{12}]_{\text{exp.}} - (x_1 \cdot [P_1] + x_2 \cdot [P_2]) \tag{1.15}$$

where:

$$[P_{12}]_{\text{exp.}} = [(\varepsilon_{12} - 1)/(\varepsilon_{12} + 2)] \cdot [(x_1 \cdot M_1 + x_2 \cdot M_2)/d_{12}]$$

Besides molar polarization, we also used to study changes of the so called polarization of solutions (P_{12}) applying equations derived on the basis of two different theories:

$$\Delta(P_{12})^{(x)}_{\text{ideal}} \cong \Delta(P_{12})^{(x)}_{\text{add.}} = P_{12} - (x_1 \cdot P_1 + x_2 \cdot P_2) \qquad (1.16)$$

(a) where P is the so called "polarization of the mixture" defined on the basis of Kirkwood's theory of dielectrics [30]

$$P \equiv (\varepsilon + 1) \cdot (2 \cdot \varepsilon + 1)/(9 \cdot \varepsilon)$$

(b) where P was defined by Barriol and Weibecker [31] in agreement with Onsager's theory of dielectrics.

$$P \equiv (\varepsilon - n^2) \cdot (2 \cdot \varepsilon + n^2)/[\varepsilon \cdot (n^2 + 2)^2] \qquad (1.17)$$

I.d. The Surface Tension of Binary Liquid Mixtures

The surface tension (σ_{12}) of binary liquid mixtures is also an additive property. However, it is necessary to mention that the composition of surface of studied solutions is not the same as in bulk, especially for aqueous solutions of nonelectrolytes [28]. For mixtures of liquid hydrocarbons, which approximately may be treated as ideal, Hadden suggested to apply a simple dependence of the following type:

$$\sigma_{12} \cong x_1 \cdot \sigma_1 + x_2 \cdot \sigma_2$$

Many authors in their analyses of intermolecular interactions in liquid binary mixtures used the following dependence:

$$\Delta(\sigma_{12})^{(x)}_{\text{ideal}} \cong \Delta(\sigma_{12})^{(x)}_{\text{add.}} = (\sigma_{12})_{\text{exp.}} - (x_1 \cdot \sigma_1 + x_2 \cdot \sigma_2) \qquad (1.18)$$

In one of our earlier works [32] we postulated, more satisfactorily according to us, an equation in which the ideal term is given in the form of the Arrhenius equation.

$$\Delta(\sigma_{12})^{(x)}_{\text{ideal}} = \sigma_{12} - [(\sigma_1)^{x_1} \cdot (\sigma_2)^{x_2}]$$

However, other authors [4, 5] recommended to apply for studies of liquid solutions given below equations including the parachor, $P \equiv \sigma_1^{1/4} \cdot V$, which may be treated with an a certain approximation as a molar-additive property for the ideal binary mixture.

$$\Delta[P_{12}]^{(x)}_{\text{ideal}} \cong \Delta[P_{12}]^{(x)}_{\text{add.}} = [P_{12}]_{\text{exp.}} - (x_1 \cdot [P_1] + x_2 \cdot [P_2]) \qquad (1.19)$$

Here the calculated parachor of the real binary liquid mixture is expressed by the following equation:

$$[P_{12}] = \sigma_{12}^{1/4} \cdot V_{12} \quad \text{and} \quad (V_{12})^{(x)}_{\text{add.}} = x_1 \cdot V_1 + x_2 \cdot V_2$$

Mierzecki [33] recommends another dependence (shown below) for studies of the internal structure of binary liquid mixtures.

$$\begin{aligned} \Delta(\sigma_{12})^{(x)}_{\text{ideal}} &\cong (\sigma_{12})_{\text{exp.}} - \left[\frac{x_1 \cdot [P_1] + x_2 \cdot [P_2]}{x_1 \cdot V_{M_1} + x_2 \cdot V_{M_2}}\right]^4 = \\ &= (\sigma_{12})_{\text{exp.}} - \left[\frac{x_1 \cdot (\sigma_1)^{1/4} \cdot \frac{M_1}{d_1} + x_2 \cdot (\sigma_2)^{1/4} \cdot \frac{M_2}{d_2}}{x_1 \cdot \frac{M_1}{d_1} + x_2 \cdot \frac{M_2}{d_2}}\right]^4 \end{aligned} \qquad (1.20)$$

After taking into account literature data, concerning possible application of the surface tension and derived from it quantities for analysis of the internal structure of binary liquid mixtures, it occurs that all the above mentioned methods should be treated as supplementary in that they should only used to confirm conclusions derived from other studies.

I.e. The Index of Refraction of Monochrome Light

The index of refraction (n usually n^D), due to the simplicity of its measurements, is one of the most often determined physicochemical properties of liquid mixtures. Isotherms of the index of refraction plotted as a function of the composition of binary mixtures seldom exhibit any maxima. It has been recommended for refractometric analysis of intermolecular interactions in liquid binary mixtures to study deviations from additivity of the coefficient n_{12} plotted as a function of the concentration expressed as a molar fraction according to the given below equation:

$$(n_{12})^{(v)}_{\mathrm{ideal}} \cong (n_{12})^{(v)}_{\mathrm{add.}} = (n_{12})_{\mathrm{exp.}} - (v_1 \cdot n_1 + v_2 \cdot n_2) \qquad (1.21)$$

The above equation has a certain theoretical foundation only for liquid systems composed from nonpolar or weakly polar and not associated components. Many authors [4, 5, 34, 35] recommended for systems prepared from polar and associated liquids a strictly empirical equation according to which the ideal state of the solution is approximated in the scale of molar fraction.

$$(n_{12})^{(x)}_{\mathrm{ideal}} \cong \Delta(n_{12})^{(x)}_{\mathrm{add.}} = (n_{12})_{\mathrm{exp.}} - (x_1 \cdot n_1 + x_2 \cdot n_2) \qquad (1.22)$$

The molar refraction $[R_{12}]$ has been also applied for studies of intermolecular interactions in liquid systems. For calculations of its deviations from ideality the approximate dependence given below has been recommended:

$$\Delta[R_{12}]^{(x)}_{\mathrm{ideal}} \cong \Delta[R_{12}]^{(x)}_{\mathrm{add.}} = \left[\frac{n_{12}^2 - 1}{n_{12}^2 + 2} \cdot \frac{x_1 M_1 + x_2 M_2}{d_{12}}\right] - \left[x_1 \cdot \frac{n_1^2 - 1}{n_1^2 + 2} \cdot \frac{M_1}{d_1} + x_2 \cdot \frac{n_2^2 - 1}{n_2^2 + 2} \cdot \frac{M_2}{d_2}\right] \qquad (1.23)$$

Serious limitations of this method result from the fact that deviations of $\Delta[R_{12}]^{(x)}_{\mathrm{add.}}$, calculated from the above equation, are usually very small. It makes difficult the precise designation of composition of possible complexes detected using this method. However, several authors [4, 20] seem to believe that refractometry should not applied for such studies. According to them this method is not enough sensitive and sometimes non-chemical interactions can be a cause of relatively strong deviations from additivity approaching even to $5 \cdot 10^{-3}$. However, among advantages of refractometry such aspects should be mentioned as the very short time of the measurement as well as the simplicity of this method. Due to this, refractometry can be helpful in preliminary studies aimed to confirm the presence of significant intermolecular interactions in the liquid binary mixture.

I.f. The Velocity of Sound Propagation in Liquid Binary Systems

Experimental data shows that for liquid binary systems in which nonchemical interactions are weak, the velocity of sound propagation (u_{12}) is a weight-additive property assuming that the square of its value is taken into consideration [36, 37]:

$$(u_{12}^2)_{\text{ideal}} \cong w_1 \cdot u_1^2 + w_2 \cdot u_2^2$$

Therefore, the deviation from ideality for nonideal binary liquid mixtures is given by the following approximate dependence:

$$\Delta(u_{12}^2)_{\text{ideal}}^{(w)} \cong \Delta(u_{12}^2)_{\text{add.}}^{(w)} \cong (u_{12}^2)_{\text{exp.}} - (w_1 \cdot u_1^2 + w_2 \cdot u_2^2) \qquad (1.24)$$

Natta and Baccaredda [38] recommended use of another equation for analysis of intermolecular interactions in binary liquid mixtures:

$$\left(\frac{1}{u_{12}}\right)_{\text{ideal}}^{(v)} \cong v_1 \cdot \left(\frac{1}{u_1}\right) + v_2 \cdot \left(\frac{1}{u_2}\right)$$

and

$$\Delta\left(\frac{1}{u_{12}}\right)_{\text{ideal}}^{(v)} \cong \Delta\left(\frac{1}{u_{12}}\right)_{\text{add.}}^{(v)} = \left(\frac{1}{u_{12}}\right)_{\text{exp.}} - \left[v_1 \cdot \left(\frac{1}{u_1}\right) + v_2 \cdot \left(\frac{1}{u_2}\right)\right] \qquad (1.25)$$

The above equation is based on a model of a solution treated as a hypothetical system composed from very thin parallel layers of both components. The thickness of these layers according to this model is proportional to volume fractions of components. Hence mutual interactions of components of the mixtures are neglected in Eq. (1.25) and it has not been given an adequate physical interpretation.

I.g. Temperature Coefficient of Intensive Properties Characterising Binary Liquid Mixtures

Studies of liquid systems carried at various temperatures prove in many cases to be more useful than isothermal analysis.

The comparison of a series of isotherms of a chosen intensive property for the studied mixture may be a source of the additional information regarding intermolecular interactions and possible shifts of the state of equilibrium. Usually, the graphs of absolute temperature coefficient (α_p) of the given property (p) of the mixture measured at various temperatures are used in the physicochemical analysis:

$$\alpha_p = \frac{p_{T_2} - p_{T_1}}{T_2 - T_1} = \frac{\Delta p}{\Delta T} \quad \text{or} \quad \alpha_p = \frac{dp}{dT} \tag{1.26}$$

or relative temperature coefficient (β_p):

$$\beta_p = \frac{\alpha_p}{p_{T_2}} \quad \text{or} \quad \beta_p = \frac{1}{p} \cdot \frac{dp}{dT} \tag{1.27}$$

Some authors introduced different modifications of dependences given above in reference to changes in given properties of the system (*e.g.*, introduced by Räetzsch [39] the temperature coefficient of dielectric permittivity which will be discussed later).

According to Fialkow and co-workers [4] the temperature coefficient of density of binary liquid mixtures is given by:

$$\alpha_d = \frac{d^{t_1}/d^{t_2} - 1}{t_2 - t_1} \quad (t_2 > t_1) \tag{1.28}$$

L. Skulski [12] calculated for several binary liquid systems temperature coefficients of density using values of density measured at various temperatures; however, the extremes at graphs α_d *vs.* x were found for compositions of solutions not corresponding to other characteristics discussed in this work. According to Skulski [12] the utility of the coefficient α_d for studies of internal structures of binary liquid systems is questionable. However, some authors believe that the position of the maximum of the relative temperature coefficient of viscosity is a good criterion of estimation of intermolecular interactions in nonideal binary mixtures. Values of such coefficient were calculated form the dependence given below:

$$\beta_\eta = \frac{\eta_{t_1} - \eta_{t_2}}{(t_2 - t_1) \cdot \eta_{t_2}} \quad (t_2 > t_1) \tag{1.29}$$

We have successfully applied the above equation for interpretation of our viscosimetric results.

Different temperature coefficients of dielectric permittivity are very often applied in studies of intermolecular interactions in liquid binary mixtures for which measurements of temperature dependences of dielectric permittivity have been carried out. The absolute values of ($\alpha_\varepsilon^{\text{abs.}}$) and relative values ($\beta_\varepsilon^{\text{relative}}$) can be calculated from experimental data of ε_{12} measured at various temperatures:

$$\alpha_\varepsilon^{\text{abs.}} = \frac{\Delta p}{\Delta T} \tag{1.30}$$

$$\beta_\varepsilon^{\text{relative}} = \frac{1}{\varepsilon} \cdot \frac{\Delta\varepsilon}{\Delta T} \tag{1.31}$$

It results from the dependences given above that the course of changes in the coefficient $\alpha_\varepsilon^{\text{abs.}}$ *vs.* molar fraction should resemble the course of changes in dielectric permittivity *vs.* x_1. Whereas, the course of changes in the relative coefficient $\beta_\varepsilon^{\text{relative}}$ as a function molar fraction exhibits very often an extremum or a distinct inflexion for systems where intermolecular interactions are exhibited within a composition range corresponding to the stoichiometry of the complex formed in such systems. The other type of the temperature coefficient of dielectric permittivity was proposed by Räetzsch and co-workers [39].

$$\alpha_\varepsilon = \frac{1}{\varepsilon} \cdot \frac{d\varepsilon}{d(1/T)} = \frac{E^*}{\mathrm{R}} \quad (\mathrm{R} - \text{the gas constant}) \tag{1.32}$$

They proved on the basis of thermodynamic considerations that this coefficient can be treated an an excess energy E^* for binary mixtures of polar solvent and that it may be used as a criterion of their internal order. The composition range of liquid binary mixtures, within which the coefficient α_{12} attains the highest value, should be interpreted as a most internally ordered region characterized by maximal intermolecular interactions between two different components of the given liquid mixture. However, the presence of the minimum at the discussed course of changes in the coefficient α_ε as a function of composition (expressed as molar fraction) should be interpreted as the most internally disordered region.

Frontasev [40] studied also the possibility of application of the temperature coefficient of molar refraction $[R_{12}]$ for the physicochemical analysis of some binary liquid systems from the point of view of occurrence therein of intermolecular interactions. All available data show that the position of the minimum at the course of changes in the temperature coefficient of molar refraction is in good accord with characteristic points at courses of changes in other physicochemical properties indicating the area of maximal intermolecular interactions between components of the binary liquid mixture.

The analysis of changes of the temperature coefficient of the surface tension (k), or more precisely its negative value:

$$k = -\left(\frac{d\sigma_{12}}{dT}\right) \tag{1.33}$$

within the whole composition range enables the assessment of intermolecular interactions between components of binary mixtures. Additionally, as has been shown by Landau [41] and Torianik [42], the fluctuations of the temperature coefficient of the surface tension should be interpreted as changes of entropies of aggregates forming the free surface of the mixture studied.

II. ^{1}H-NMR STUDIES OF BINARY LIQUID MIXTURES

There is a large number of important effects and hence of NMR applications. There are extensive tables of chemical shifts for protons in various chemical environments, and the NMR spectrum of a molecule not only serves to "fingerprint" it but usually allows quite detailed conclusions as to its isomeric structure, the influence of a solvent, formation of inter- and intramolecular hydrogen bonds [43, 44] and so on. Starting from the pioneering work of Swinehart and Taube [45], the ^{1}H-NMR spectroscopy began to be used for studies on mixed solvents and selective solvation. An elarly NMR study of a cation in a solvent mixture was concerned with Mg^{2+} in aqueous methanol [45]. Solvent ^{1}H resonances were observed for coordinated methanol and for coordinated water molecules as well as for "bulk" methanol and "bulk" water at low temperatures. A few years later, mixed solvates were identified in the case of aluminium (III) in acetonitrile–water mixtures [46]. Later, Akitt [47] reported that NMR spectra of dimethyl sulphoxide–acetonitrile containing Al^{3+} show separate signals for DMSO protons.

NMR spectroscopy provides the most direct evidence that mixed solvates exist for different cations at which solvent exchange is sufficiently slow relative to NMR frequencies. It is also useful in fast solvent exchange situations, though here supplying less direct and more limited information. They can be derived either from chemical shifts or from linewidths. Studies on the dependence of linewidths on solvent composition may also serve as a source of information on different cations primary solvation shells. Matwiyoff [48], in his early work on the variation of ^{1}H-NMR spectra with temperature for Mg^{2+} cation in magnesium perchlorate solution in aqueous acetone has shown the usefulness of the NMR spectroscopy for studies on kinetics and mechanisms of solvent exchange at several cations in binary liquid mixtures. We have carried out ^{1}H-NMR studies on binary liquid mixtures. Changes of chemical shifts are observed when molecules of a solvent and dissolved substance form a certain type of a "complex" which is determined by occurring in the mixture dipole–dipole, van der Waals and specific interactions and as the outcome a different influence of solvent at individual protons of molecules of dissolved compound is visible in the ^{1}H-NMR spectrum. Therefore, we expected to monitor analogous effects in binary liquid mixtures in purpose to gain a valuable information regarding the structure of formed associates. We have applied ^{1}H-NMR spectra of liquid binary mixtures, $A-B$, for determination of the chemical shift differences, [$\delta(A-B)$], between the centers of the ^{1}H-NMR signals corresponding to both components [49–70]. Values of $\delta(A-B)$ visualized as a function of the mixture compositions expressed as a molar fraction did not exhibit any extremes. Therefore, we have attempted to calculate deviations from ideality of $\delta(A-B)_{\mathrm{exp.}}$ in purpose to find values of the spectral parameter, $\Delta\delta(A-B)$ (in Hz). Extremes of the mentioned above parameter as a function of x_A were fairly concordant with extremes of some other physicochemical parameters (isotherms discussed in previous chapters). This was explained in terms of some assumed internal structures of the binary mixtures studied and made possible a proposal for the composition of postulated complexes. The extremes of the ^{1}H-NMR spectral parameter for all systems studied by us were in accord with extremes of the temperature coefficient of dielectric permittivity, α_{12} (see Eq. (2.31)) which (as shown in Räetzsch's thermodynamic consideration [39]) should be interpreted as a region characterized by maximal intermolecular interactions between two different components of the given liquid mixture. There was also observed good agreement of the ^{1}H-NMR spectral parameter with extremes obtained from the analysis of dynamic viscosity, η_{12}, and other physicochemical properties derived from it. Besides the spectral parameter discussed above we have also applied another spectral method for studies of internal structures of various dioxane–water mixtures [49].

^{1}H-NMR spectra of tetraethylammonium bromide dissolved in different aqueous solutions of dioxane were run over the wide salt concentration range [50].

By scrutinizing the shifts of the center of resonance signals of β-methyl protons in the salt under study (Δ_a) as a function of the salt concentration, the theoretical values corresponding to the shifts of resonance signals of β-methyl protons of free (*i.e.*, completely dissociated) tetraethylammonium cations were found graphically (Δ_i) and then the values of association constants for tetraethylammonium bromide were calculated. We found that the aforementioned Δ_i values, obtained from ^{1}H-NMR solution spectra for infinite dilutions of the electrolyte dissolved were fairly sensitive towards composition changes of the binary solvents applied. However, more conclusive evidence was supplied by their deviations from linearity, $\Delta\Delta_i$. We compared the newly-proposed ^{1}H-NMR spectral characteristics with the corresponding macroscopic physicochemical properties (*e.g.*, the temperature coefficient of dielectric permittivity) of the same dioxane–water mixtures. From the respective property–composition isotherms it was found that they displayed fairly concordant extremes for the some definite weight–composition (wt%). This was explained in terms of formation of some assumed internal structures of the studied binary mixture.

All considerations discussed in the present work on analysis of intermolecular interactions, from the point of view of ^{1}H-NMR and physicochemical studies on properties of binary liquid mixtures, were the subject of our earlier works [49–71].

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