





where  $\bar{\lambda}^2$  is the mean square distance a molecule travels in the  $x$  direction in a time  $t$ .

### 5 Diffusion in the binary two polar components in the liquid-liquid system

The component diffusion in polar mixture of the methanol (A) with water (B) has shown in Fig. 1.

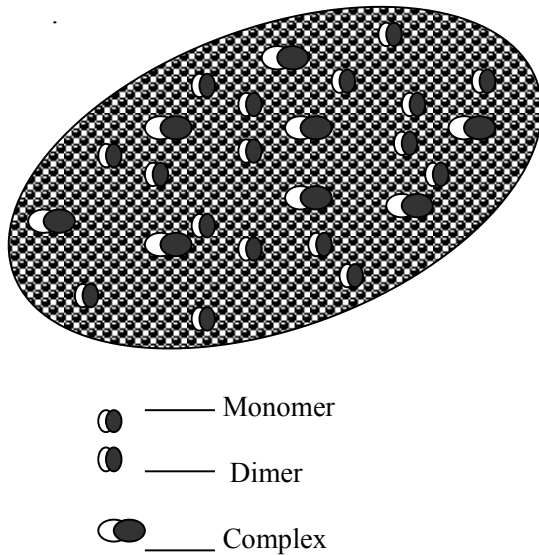
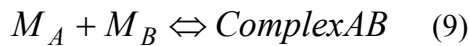
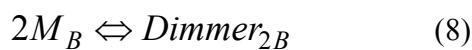
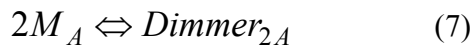


Fig. 1. Polar solvents diffusion

Mathematical description of molecules migration to the dimer formation, if mixing is neglected, derived as follow. The unsteady-state description will be given by equations (10).

$$\frac{\partial c_i}{\partial t} = D \left( \frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} + \frac{\partial^2 c_i}{\partial z^2} \right) + R_{dimer} \quad (10)$$

where  $D$  is molecular diffusivity,  $c$  is concentration of  $i^{th}$  specie, and  $R_{dimer}$  is dimerization rate term.

According to the theory of absolute rate the resistance term is given in term of a frictional activation energy  $\Delta G_{12}$  and a characteristic diffusion distance  $\lambda$  [10][11]. If the activation energy is taken to be linear in mole fraction and diffusion distance is constant it is follows:

$$D_L \eta_L = (D_{ij} \eta_{ij}) = (D_{ij}^0 \eta_{ij})^{x_2} (D_{ji}^0 \eta_{ji})^{x_1} \left( 1 + \frac{d \ln \gamma_i}{d \ln x_i} \right) \quad (11)$$

The activation energy  $\Delta G_{12}$  should actually be identified with a energy of formation of a diffusion activated complex, according to absolute rate theory, the equilibrium constant for which ought to depend only on temperature eq.(4). If this case, a geometric mean diffusion distance,

$$\lambda_D = (\lambda_1)^{x_1} (\lambda_2)^{x_2} \quad (12)$$

then leads equality to equation (11). Although the Vignes proposal [11] correlated existing binary data well for a large number of systems, use of equation (11) as a predicative device can lead to substantial error even though existing data could be fitted with a straight line with

$$\ln D_{ij} / \left( 1 + \frac{d \ln \gamma_i}{d \ln x_i} \right)$$

$x_i$  there exists sufficient deviation from the correlation in some case to cause significant error when limiting values are used in equation (11) to predict values of  $D_{ij}$  in a mixture.

Equation (11) although accounting for the solution in an appropriate way, does not explicitly incorporate the effect of solution viscosity. This implies that either diffusion and viscous flow are independent processes or viscosity has a composition variation of an analogous type[10]-[15]. The notation that diffusion and viscous flow are independent phenomena directly contradicts

hydrodynamic theories of diffusion. Relationships between diffusion coefficients and viscosity emerge from most usable statistical mechanical results [12]. Interpretations of absolute rate theory description also usually results in such relations.

The correct equation (11) for the effect of viscosity, the absolute rate theory interpretation can be adjusted accordingly.

This is the desired modification incorporating the effect of solution viscosity.

## 6 Diffusion coefficient for multicomponent mixture

Formulas for estimating diffusion coefficients in ternary liquid mixtures are described based on a geometrically consistent generalization of the Vignes equation for binary systems without including viscosity in the paper [16]. It has been suggested method of estimating binary diffusion coefficients (of which the Vignes equation is but one many examples) be used with the actual mole fractions replaced by their equivalent binary compositions.

$$D_{ij} = (D_{ij}^o)^{x_{ji}} (D_{ji}^o)^{x_{ij}} \quad (14)$$

where

$$x_{ij} = x_i / (x_i + x_j); \quad x_{ji} = (1 - x_{ij}); \quad (15)$$

It should be pointed out that eq.(10) has two different limits when both  $x_i$  and  $x_j$  vanish [17]. The two limits are given by

$$\lim_{x_i \rightarrow 0} D_{ij} = (D_{ji}^o) \quad x_i = 0$$

$$\lim_{x_j \rightarrow 0} D_{ji} = (D_{ij}^o) \quad x_j = 0$$

The generalization of the Vignes equation for multicomponent system are given by the following equation:

$$D_{ij} = (D_{ij}^o)^{x_j} (D_{ji}^o)^{x_i} \prod_{\substack{k \neq 1 \\ k \neq i, j}}^n (D_{jk, x_k \rightarrow 1})^{x_k} \quad (16)$$

Including geometric average of the  $i$ - $j$  and  $k$ - $j$  and  $i$ - $k$  and  $j$ - $k$  infinite dilution diffusivities ( $i \neq j \neq k$ ) and viscosity it obtaining:

$$D_{ij} \eta_{ij} = (D_{ij}^o \eta_{ij})^{x_j} (D_{ji}^o \eta_{ji})^{x_i} \prod_{\substack{k \neq 1 \\ k \neq i, j}}^n (D_{ik}^o \eta_{ik} D_{jk}^o \eta_{jk})^{x_k / 2} \quad (17)$$

$$\left(1 + \frac{\partial \ln \gamma_i}{\partial x_i}\right)$$

$\eta$  is the viscosity which is calculated according to Appendix A [13],[15]. The densities were calculated according to Appendix B. Interactive diffusion coefficients for the ternary and quaternary liquid mixture taking into account viscosity and activity coefficients have been calculated, too [8],[28].

## 7 Distribution coefficient

Chemical potential of the specie  $i^{th}$  where one substance ( $i$ ) is transferred from one liquid phase to another liquid phase at the equilibrium is :

$$\mu_i(P, T, x_i)^I = \mu_i(P, T, x_i)^{II} \quad (18)$$

Then, distribution constant is defined as:

$$K_i = \frac{x_i^I \gamma_i^I p_i^I}{x_i^{II} \gamma_i^{II} p_i^{II}} \quad (19)$$

where  $\mu_i^o$  is the chemical potential in the standard state of an ideally dilute solution,  $x$  is specie composition,  $\gamma$  is activity coefficient and  $p$  is polarity.

## 8 Conclusion

This work polar fluids behavior in the liquid-liquid system are considered. Basic polarity parameters were studied. Diffusion coefficients in the liquid-liquid phases were considered. Diffusion coefficients taking into account viscosity was defined.

Distribution coefficient in the liquid-liquid

system was defined.

## Appendix A

### Diffusion coefficient in infinite dilution

Diffusivities  $D_{12}^0$  and  $D_{21}^0$  were calculated by the equation of Lysis-Ratcliff, 1968.

$$\frac{D_{12}^0 \eta_2}{T} = [8.52 \cdot 10^8 v_2^{(-1/3)} (1.40 (\frac{v_2}{v_1})^{(1/3)} + \frac{v_1}{v_2})] \quad (1)$$

where  $v$  is mole fraction and  $T$  is temperature.

## Appendix B

### Viscosity and density

Viscosity  $\eta$  of the binary mixtures at low pressure was determined by the following equation:

$$\eta_L (=) \eta_{12} = x_1 \eta_1^{1/3} + x_2 \eta_2^{1/3} \quad (1)$$

Density  $\rho$  for the binary mixtures at low pressure was calculated by the following equation:

$$\rho_L = \rho_{12} (=) \frac{M_{mix}}{\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}} \quad (2)$$

### Notation

A-methanol

B-ethyl acetate

c - component concentration, mole/cm<sup>3</sup>

D - diffusivity, cm<sup>2</sup>/s

K - distribution coefficient

M - monomer

m-mass

p - component polarization coefficient (methanol=0.56; ethyl-acetate=0.95; water=0.20; ethanol=0.60)

$\bar{R}$  - gyration factor

2r - the molecular mean free path

$R_{dimer}$  -dimerization rate term

$T$  - the absolute temperature

$t$  -time

$\bar{u}$  -represents the average molecular velocity

$z$  - height, cm

$x$  -direction in a time t.

### Greek letters

$\gamma$  -activity coefficient

$\Delta S^0$  -entropy of dimerization in the standard state

$\Delta H^0$  -enthalpy of dimerization in the standard state

$\eta$  -viscosity, Pas

$\bar{\lambda}^2$  -mean square distance of a molecule travels

$\lambda$  -specie distance travel

$\rho$  -density g/cm<sup>3</sup>

### Subscript

$i, j, k \dots n$  - general subscripts for components

$L$  - liquid

$A$  -component methanol

$B$  - component ethyl acetate

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