Polar fluids in the liquid-liquid system

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Abstract— In this paper polar fluids and their behaviors in the liquid-liquid system were examined. The interactions between polar molecules was taking into account.The polarity parameters for the size shape and polar effects were considered. The polar fluids diffusivity was studing according to the absolute rate theory. Diffusion coefficients for solvents mixtures were examined taking into account activity coefficients and viscosity. Distribution coefficient between solvents is modified by polarity coefficient.

Keywords— Polar mixture, dimmerization, gyraton factor, diffusion coefficient.

1 Introduction

The interactions involved in polar systems are complex, and an empirical development can not be completely free from shortcoming. Yet, the well identified drawbacks of the previous formulations suggest definite possibilities for improvement. For polar molecules, the critical constants are certainly influenced by the dipole and quadrupole moments. Though it would be desirable to correct for these effects, undue complications are avoided. If true critical properties are used even for polar molecules. The next step is to obtain suitable parameters for the size-shape and polarity effects[1].

This polar compound extraction has the significant ability of separating temperature sensitive components such as those found in pharmaceutical, food processing and nuclear industries. The methanol removal from the alcoholic mixtures by azeotrope extraction was examined in the previously papers [2]-[4].

Liquid-liquid extraction for separation of components of a solution which depend upon the unequal distribution of the components is well known. The process may be carried out in a number ways. In most instances, the liquid solution to be treated is contacted intimately with a suitable incompletely miscible liquid which preferentially extracts one or more components. In this paper a polar component from the liquid solution was extracted by a suitable solvent[5]-[20].

This work polar fluids and their behaviors are considered in the liquid-liquid system.

2 Basic polarity parameters

Separate size-shape effects from polarity effects has been made commonly used third parameters. This renders it impossible to obtain a true measure of the size-shape effects for polar systems. Thompson attempted to overcome this problem by defining a size –shape parameter, the radius of gyration $\overline{R}$, strictly in terms of molecular structure [1]. The radius of gyration in terms of the product of the principal moments of inertia A, B and C, and molecular mass m can be defined: for three dimensional molecules:

$$\overline{R} = \sqrt{2\pi \frac{(ABC)^{1/3}}{m}} \tag{1}$$

For planar molecules

$$\overline{R} = \sqrt{\frac{(AB)^{1/2}}{m}} \tag{2}$$

$\overline{R}$

is expressed in units of Angstroms. Different classes of hydrocarbons exhibited a smooth behavior on a plot of the acentric factor versus a smooth behavior on a plot of the acentric factor versus the radius of gyration. Different homologues series of nonpolar fluids are all really quite close to each other. The monoatomic gases, the nonpolar diatomics, the normal paraffins, the branched paraffins, the olefins, the naphthenates, and aromatics all have similar behavior.

The Thompson radius of gyration $\overline{R}$ thus appears to be an appropriate parameter to account for size-shape effects.

Firstly, $\overline{R}$ is defined from considerations of molecular structure alone and is unaffected by polarity. Secondly, it is a fundamental parameter, whereas other common third parameters require direct experimental information and values of the critical constants for their definition, $\overline{R}$ can be calculated from a knowledge of bond angles and bond lengths. Finally, the moments of merits, in terms of which the radius of gyration is defined, have long been used in classical physics to characterize the distribution of mass about the center of gravity of a system.

3 Polar fluids behavior

Mixing of the fluids on molecular scale making possible the homogenous fluid mixture. Behind convection, diffusion occurs between polar components.

A pure fluid is considered in itself to be a mixture, containing monomers and dimmers. Here, a one component polar system contains two species, monomer and dimmer. A two component system, where both components are polar, contains five species two monomers and three dimmers. A two component system, where one component is polar and the other is not, contains three species two monomers and one dimmer.

Consider a pure fluid along the liquid-liquid saturation curve. The fluid consists of monomers(M) and dimmers (D).

$$2Monomers \Leftrightarrow Dimmer \qquad (3)$$

The equilibrium constant is given by

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (4)$$

where T is the absolute temperature, ΔS^0 is the entropy of dimmerization in the standard state, ΔH^0 is enthalpy of dimmerization in the standard state.

In this work a classic concept to take into account strong interactions between polar molecules was applied. It was assumed a that two strongly polar molecules have a tendency to form weakly stable dimmers and that this tendency can be quantitatively described through a suitably defined chemical equilibrium constant. This classic description of chemical interactions has been used by numerous workers to fit liquid-liquid and liquid-vapor equilibrium data.

4 Polar fluids diffusion

Diffusion is a phenomenon by which the particle group as a whole spreads according to the irregular motion of each particle. Rephrasing, when the microscopic irregular motion of each particle gives rise to a regularity of motion of the total particle group, macroscopic regularity, the phenomenon of diffusion arises.

The diffusion concept in polar fluid may be viewed as the tendency for a group of compounds monomers and dimmers initially concentrated near a point in space to spread out in time, gradually occupying an ever larger area around the initial point. Herein the term particles refers not only to any species molecules, but to any other identifiable units as well.

The Knudsen diffusion coefficient is expressed as [2]:

$$D = \frac{2r\overline{u}}{3} \qquad (5)$$

where $\overline{u}$ represents the average molecular velocity, and 2r is the molecular mean free path.

Einstein's definition of the diffusion coefficient has given by expression[3],[4]:

$$D = \frac{\overline{\lambda^2}}{2t} \qquad (6)$$

where $\overline{\lambda}^2$ 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.

$$2M_A \Leftrightarrow Dimmer_{2A} \qquad (7)$$

$$2M_B \Leftrightarrow Dimmer_{2B} \qquad (8)$$

$$M_A + M_B \Leftrightarrow ComplexAB \qquad (9)$$

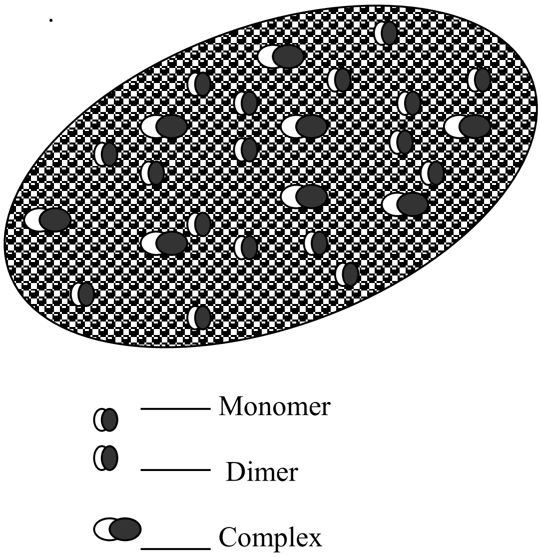

Fig. 1. Polar solvents diffusion

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).

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

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

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

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

The activation energy ΔG_{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,

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

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

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

where

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

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

$$\lim_{x_i \to 0} D_{ij} = (D_{ji}{}^{o}) \qquad x_i = 0$$

$$\lim_{x_j \to 0} D_{ji} = (D_{ij}{}^{o}) \qquad x_j = 0$$

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

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

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:

$$D_{ij}\eta_{ij} = (D_{ij}{}^{o}\eta_{ij})^{x_j} (D_{ji}{}^{o}\eta_{ji})^{x_i}$$

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

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

η 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 ternery 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 transfered from one liquid phase to another liquid phase at the equilibrium is :

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

Then, distribution constant is defined as:

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

where μ_i^o is the chemical potential in the standard state of an ideally dilute solution, x is specie composition, γ 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 Lusis-Ratcliff,1968.

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

where v is mole fraction and T is temperature.

Appendix B

Viscosity and density

Viscosity η 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 ρ for the binary mixtures at low pressure was calculated by the following equation:

$$\rho_L=\rho_{12}(=)\frac{M_{mix}}{\frac{x_1M_1}{\rho_1}+\frac{x_2M_2}{\rho_2}}\quad(2)$$

Notation
A-methanol
B-ethyl acetate
c - component concentration, mole/cm^3
D - diffusivity, cm^2 /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)
$\overline{R}$ -gyration factor
2r - the molecular mean free path
$R_{\dim mer.}$ -dimerization rate term
T - the absolute temperature
t -time
$\overline{u}$ -represents the average molecular velocity
z - height, cm
x -direction in a time t.

Greek letters
γ -activity coefficient
ΔS^0 -entropy of dimerization in the standard state
ΔH^0 -enthalpy of dimerization in the standard state
η -viscosity, Pas
$\overline{\lambda}^2$ -mean square distance of a molecule travels
λ -specie distance travel
ρ -density g/cm^3

Subscript
i, j, k …n - general subscripts for components
L – liquid
A-component methanol
B- component ethyl acetate

Reference

[1] J.Savković-Stevanović, Diffusion rate in polar liquid-liquid system,SS-Diffusion Systems*, 4th Inter. Conference on Fluid Mechanics and Heat and Mass Transfer-FLUIDSHEAT'* 13, ID 70 20 81 03, Dubrovnik, Croatia, June 25-27, 2013.
5.J.Savković-Stevanović, The substance transfer rate in the liquid –liquid system with azeotrope formation, *Comput. Ecol. Eng*. **7**(1)(2011)8-14, ISSN 1452-0729.
[2] J.Savković-Stevanović,The methanol extraction by azeotrope from the liquid mixture, *The 7th World Congress of Chemical Engineering, Proceedings*, Glasgow 10-14 July, 2005, pp.522.
[3] J.Savković-Stevanović, Mass transfer phenomena investigation of the azeotropic extraction, *The First South-East European Congress of Chemical Engineering* Book of

Abstracts,GCENP-27, 25-28 September 2005, pp.57.

[4] J.Savković-Stevanović, Solutions purification by azeotrope formation, *Comput. Ecol. Eng.* ,**1** (2) 111-123,2005.

[5] J. Savković-Stevanović, Fizičke i hemijske interakcije kod polarnih smeša, *Letnja* škola, Beograd, 20.septembar, 2013.

[6] J.Djurovic, An inverse control of the extraction column, *International Journal of Mathematical Models and Methods in Applied Science*, **5**(1) 67-76, 2011.

[7] M. Knudsen, Die Gesetze der Molecularstromung und der inneren Reibungsstromung der Gase durch Rohren, *Ann. Physik*. **28**, 75, 1909.

[8]A. Einstein, Zur Thearie der Brownschen Bewegung, *Ann. der Physik*. **19**, 371, 1906.

[9] F.Barr, B.David, F.Dodge, *J.Chem. Eng. Data*, **4**,107,1959.

[6] P.J.Dalager,*Chem.Eng. Data*, **14,** 298, 1969.

[10] J.Hong, M.R.Ladisch,G.T.,Tsao *J.Chem.Eng. Data*,**26**,305-307, 1981.

[11] Cullinan, *Ind. Eng.Chem. Fundamentals*, **5**,281,1966.

[12] J.Leffler J., H.T Cullinan,. Variation of liquid diffusion coefficients with composition- Binary systems, *Ind. Eng.Chem. Fundamentals*, **9**,83-88,1970.

[13] P.S.Murty, M.Van Winkle(1958) *Chem. Eng. Data,***3**,72,1958.

[14] H.T Cullinan, *Ind. Eng.Chem. Fundamentals*, **5**,281,1966.

[15] A.Vignes, *Ind. Eng. Chem. Fundamentals*, **5**,189,1966.

[16] R.J.Bearman,,*J.Phys.Chem*.,**68**,37- 90, 1964.

[13] M.A.Lusis, G.A.Ratcliff (1968) *Can. J. Chem. Eng,* **46**,385,1964.

[17] J.Leffler, H.T Cullinan, Variation of liquid diffusion coefficients with composition- Binary systems, *Ind. Eng.Chem. Fundamentals*, **9**,83-88,1970.

[18] J.Leffler, H.T.Cullinan, Variation of liquid diffusion coefficients with composition- Dilute ternary systems,*Ind. Eng.Chem. Fundamentals*, **9**,88-93,1970.

[19] H.A.Kooijman, R.Taylor' *Ind.Eng. Chem*. Res.1217-1222,1991.

[20] Wesselingh, J. A.Krishna R.,*Elements of mass Transfer*, Eilis Horwood, Chichester, U. K,1990.

[21] J.M.Prausnitz, C.A.Eckert ,R.V.Orye, J.P. O'Connel, *Computer Calculations for multicomponent vapour- liquid equilibrium*, Prentice Hall , New Jersey,1967.

[22] C.A.Wilson, *J.Amer. Chem. Soc*., **86**,12,1964.

[23] J.Savković-Stevanović, Substance transfer at the azeotrope formation and extraction, *Comput. Ecol. Eng.* 3(1)(2007)26-35.

[24] J. Savković-Stevanović J., M.M.Stevanović-Huffman, J.Djurović Polar solvents in enzymes extraction, Summer school, Belgrade, 20. Sept, 2013.