Intermolecular Interactions in Binary Liquid Mixtures Containing Alkanes, Aromatic Hydrocarbons and Higher Alkanols

ABSTRACT

Thesis Submitted for the Degree of

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

Submitted by

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August 2005

Liquid mixtures exhibit various phenomena that are absent in pure state. Aqueous solutions of organic solvents are particularly interesting due to their extensive use in many fields of solution chemistry. Investigations have been made to study the role of interactions through physico-chemical properties in binary liquid mixtures. A deeper knowledge of the solvent at a molecular level is essential for the understanding of many chemical and biological processes in solutions. The investigation on physico-chemical properties of non-aqueous binary liquid mixtures have been found to provide useful information about the physical nature and strength of intermolecular interactions in the binary liquid mixtures. Such investigations in the liquid state pose a fascinating and challenging problem to both theoreticians and experimentalists. For this reason, we studied the behaviour of intermolecular interactions in non-aqueous binary liquid mixtures experimentally as well as theoretically. The properties like density (ρ), viscosity (η), ultrasonic speed (u), refractive index (n), and derived parameters from these properties of liquids provided an insight into investigation of the intermolecular interactions in binary liquid mixtures. In the present study, the experimental density (ρ), viscosity (η), ultrasonic speed (u), refractive index (n_D) were determined using pycnometer, Ubbelohde viscometer, ultrasonic interferometer, and Abbe refractometer at desired temperatures and compositions. These experimental properties were used to deduce numerous derived parameters such as molar volume (V); isentropic compressibility (k_s); intermolecular free length (L_f); isothermal compressibility (k_T); thermal expansion coefficient (α); acoustic impedance (Z); free volume (V_f); internal pressure (π); apparent molar volume (V_ϕ); apparent molar compressibility (K_ϕ); molar refraction (R_m); molecular radii (r); etc., as given below:

$$V = \frac{x_1 M_1 + x_2 M_2}{\rho} \tag{1}$$

$$k_s = u^{-2} \cdot \rho^{-1} \tag{2}$$

$$L_f = K \cdot k_s^{1/2} \tag{3}$$

$$k_T = \frac{1.71 \times 10^{-3}}{T^{4/9} \cdot u^2 \cdot \rho^{4/3}} \tag{4}$$

$$\alpha = \left[\left(\frac{-1}{\rho}\right)\left(\frac{\partial \rho}{\partial T}\right)\right] \tag{5}$$

$$Z = u \cdot \rho \tag{6}$$

$$V_f = \left[\frac{\left(M_{eff} \cdot u\right)}{\left(K_a \cdot \eta\right)}\right]^{3/2} \tag{7}$$

$$\pi = bRT\left(\frac{K_a \cdot \eta}{u}\right)^{1/2} \cdot \frac{\rho^{2/3}}{M^{7/6}} \tag{8}$$

$$V_\phi = V^* + \frac{V^E}{x} \tag{9}$$

$$K_\phi = K_\phi^* + \frac{K_s^E}{x} \tag{10}$$

$$R_m = \left[\frac{M_{eff}}{\rho}\right]\left[\frac{\left(n_D^2 - 1\right)}{\left(n_D^2 + 2\right)}\right] \tag{11}$$

$$\mathrm{r} = \left[\left\{\left(\frac{3}{4}\right)\pi N\left(\frac{n_D^2 - 1}{n_D^2 + 2}\right)\right\} \cdot V\right]^{1/3} \tag{12}$$

The theoretical study of binary liquid mixtures has drawn the interest of Chemists, Physicists, Biotechnologists, and many other researchers towards the elucidation of intermolecular interactions. Here, we have used some liquid models/theories to study the intermolecular interactions between component molecules in binary solutions. The various theoretical models/theories used in the present studies are summarized below:

A. EXCESS MOLAR VOLUME

The excess molar volume is used as a quantitative guide to the study of intermolecular interactions and complex formation in binary mixtures. The experimental excess molar volumes were compared with the theoretically calculated volumes by using different statistical model/theories as given below:

***Flory theory*:**

$$V_F^E = \left[\sum_{i=1}^{2} x_i V_i^*\right]\left[\tilde{V}^{o7/3} / \left\{(4/3) - \left(\tilde{V}^o\right)^{1/3}\right\}\right]\left(\tilde{T} - \tilde{T}^o\right) \tag{13}$$

***Prigogine-Flory-Patterson theory*:**

$$\frac{V_{PFP}^E}{\left(x_1 V_1^* + x_2 V_2^*\right)} = V_{\text{int}}^E + V_{fv}^E + V_{ip}^E \tag{14}$$

where

$$V_{\text{int}}^E = \left\{\frac{\left(\tilde{V}^{1/3} - 1\right)\tilde{V}^{2/3}}{\left[(4/3)\tilde{V}^{-1/3} - 1\right]}\right\} \cdot \Psi_1 \theta_2 \cdot \left(\frac{\chi_{12}}{P_1^*}\right) \tag{15}$$

$$V_{fv}^E = \frac{-\left(\tilde{V}_1 - \tilde{V}_2\right)^2 \left\{(14/9)\tilde{V}^{-1/3} - 1\right\} \Psi_1 \Psi_2}{\left\{(4/3)\tilde{V}^{-1/3} - 1\right\}\tilde{V}} \tag{16}$$

$$V_{ip}^E = \frac{\left(\tilde{V}_1 - \tilde{V}_2\right) \cdot \left(P_1^* - P_2^*\right)}{\left(P_1^* \Psi_2 + P_2^* \Psi_1\right)} \tag{17}$$

B. THERMAL EXPANSION COEFFICIENT

Flory theory:

$$\alpha = \frac{3\left(\tilde{V}^{1/3} - 1\right)}{T\left[1 - \left\{3\left(\tilde{V}^{1/3} - 1\right)\right\}\right]} \tag{18}$$

***Thiele-Lebowitz Model*:**

$$\alpha = \left(\frac{1}{T}\right) \cdot \frac{\left(1 - y^3\right)}{\left(1 + 2y\right)^2} \tag{19}$$

Thiele Model:

$$\alpha = \left(\frac{1}{T}\right) \cdot \frac{\left(1+2y+3y^2\right) \cdot (1-y)}{\left(1+5y+9y^2-3y^3\right)} \tag{20}$$

Carnhan-Starling Model:

$$\alpha = \left(\frac{1}{T}\right) \cdot \frac{\left(1+y+y^2-3y^3\right) \cdot (1-y)}{\left(1+4y+4y^2-4y^3+y^4\right)} \tag{21}$$

Guggenheim Model:

$$\alpha = \left(\frac{1}{T}\right) \cdot \frac{(1-y)}{(1+3y)} \tag{22}$$

Scaled-Particle Model:

$$\alpha = \left(\frac{1}{T}\right) \cdot \frac{(1-y)}{(1+y)} \tag{23}$$

Henderson Model:

$$\alpha = \left(\frac{1}{T}\right) \cdot \frac{\left(8+y^2\right) \cdot (1-y)}{\left(8+8y+3y^2-y^3\right)} \tag{24}$$

Hoover-Ree Model:

$$\alpha = \left(\frac{1}{T}\right) \cdot \frac{\left(1+4y+10y^2+18.36y^3+28.2y^4+39.5y^5\right)}{\left(1+8y+30y^2+73.44y^3+141y^4+237y^5\right)} \tag{25}$$

C. INTERNAL PRESSURE

Internal pressure has been a subject of interest during recent past and attempts have been made to show the significance of internal pressure as a fundamental property of liquid state. Internal pressure can be predicted theoretically by using

Buehler-Wentorf-Hershfelder Model:

$$\pi = \frac{2^{1/6} \cdot R \cdot T}{\left(2^{1/6} \cdot V\right) - dN^{1/3} \cdot V^{2/3}} \tag{26}$$

Pandey Model:

$$\pi = \frac{\alpha \cdot T}{k_T} \quad (27)$$

Flory Model:

$$\pi = \frac{P^*}{\tilde{V}^2} \quad (28)$$

D. ULTRASONIC SPEED

The ultrasonic speed were evaluated theoretically by using various empirical and semi-empirical relations:

Free length theory:

$$u = \frac{K'}{\left(L_{f,mix} \cdot \rho^{1/2}\right)} \quad (29)$$

Collision factor theory:

$$u = u_\infty S r_f = u_\infty S\left(\frac{B}{V}\right) \quad (30)$$

Nomoto relation:

$$u = \left[\frac{\left(x_1 R_1 + x_2 R_2\right)}{\left(x_1 V_1 + x_2 V_2\right)}\right]^3 \quad (31)$$

Van Dael and Vangeel relation:

$$u = u_1 u_2 \left\{\frac{M_1 M_2}{\left(x_1 M_2 u_2^2 + x_2 M_1 u_1^2\right)\left(x_1 M_1 + x_2 M_2\right)}\right\}^{1/2} \quad (32)$$

Junjie relation:

$$u = \frac{\left\{\left(x_1 M_1 / \rho_1\right) + \left(x_2 M_2 / \rho_2\right)\right\}}{\left[\left(x_1 M_1 + x_2 M_2\right)^{1/2} \cdot \left\{\left(x_1 M_1 / u_1^2 \rho_1^2\right) + \left(x_2 M_2 / u_2^2 \rho_2^2\right)\right\}^{1/2}\right]} \quad (33)$$

E. MOLECULAR RADIUS

The molecular radius is one of the parameters of pure liquids and liquid mixtures, which reflects their structural features. The theoretical determination of molecular radii is as follows:

Schaaff's relation:

$$r = \sqrt[3]{\frac{M}{\rho N}} \cdot \sqrt[3]{\frac{3}{16\pi}\left[1-\frac{\gamma RT}{Mu^2}\left(\sqrt{1+\frac{Mu^2}{3\gamma RT}}-1\right)\right]} \tag{34}$$

Rao's relation:

$$r = \sqrt[3]{\frac{M}{\rho N}} \cdot \sqrt[3]{\frac{3}{16\pi}\left[1-\frac{\gamma RT}{Mu^2}\left(\sqrt{1+\frac{Mu^2}{\gamma RT}}-1\right)\right]} \tag{35}$$

Eyring relation:

$$r = \sqrt[3]{\frac{M}{\rho N}} \cdot \frac{1}{2}\sqrt[3]{\left\{1-\left(1-\frac{1}{u}\sqrt{\frac{\gamma RT}{M}}\right)^3\right\}} \cdot \sqrt{2} \tag{36}$$

Kittel's relation:

$$r = \sqrt[3]{\frac{M}{\rho N}} \quad \frac{1}{2}\sqrt[3]{\left(1-\frac{1}{u}\sqrt{\frac{3\gamma RT}{M}}\right)} \cdot \sqrt{2} \tag{37}$$

F. ISOTHERMAL COMPRESSIBILITY

Flory Model:

$$k_T = \frac{T\tilde{V}^2\alpha}{P^*} \tag{38}$$

Thiele-Lebowitz Model:

$$k_T = \left(\frac{V}{RT}\right) \cdot \frac{(1-y)^3}{(1+2y)^2} \tag{39}$$

Thiele Model:

$$k_T = \left(\frac{V}{RT}\right) \cdot \frac{(1-y)^3}{\left(1+5y+9y^2-3y^3\right)} \tag{40}$$

Guggenheim Model:

$$k_T = \left(\frac{V}{RT}\right)\cdot\frac{(1-y)^5}{(1+3y)} \quad (41)$$

Carnhan-Starling Model:

$$k_T = \left(\frac{V}{RT}\right)\cdot\frac{(1-y)^4}{\left(1+4y+4y^2-4y^3+y^4\right)} \quad (42)$$

Hoover-Ree Model:

$$k_T = \left(\frac{V}{RT}\right)\cdot\left(\frac{1}{1+8y+30y^2+73.44y^3+141y^4+273y^5}\right) \quad (43)$$

G. VISCOSITY

A number of semi-empirical relations have been proposed to predict the viscosity of the mixtures as summarized below:

Grunberg-Nissan relation:

$$\ln\eta = x_1\ln\eta_1 + x_2\ln\eta_2 + x_1x_2G_{12} \quad (44)$$

Hind-McLaughlin-Ubbelohde relation:

$$\eta = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2H_{12} \quad (45)$$

Katti-Chaudhari relation:

$$\ln(\eta V) = x_1\ln(\eta_1V_1) + x_2\ln(\eta_2V_2) + x_1x_2\frac{W_{vis}}{RT} \quad (46)$$

Heric-Brewer relation:

$$\ln\eta = x_1\ln\eta_1 + x_2\ln\eta_2 + x_1\ln M_1 + x_2\ln M_2 - \ln\left(x_1M_1 + x_2M_2\right) + x_1x_2\left[\alpha_{12} + \alpha_{21}(x_1 - x_2)\right] \quad (47)$$

McAllister relation:

$$\ln\eta = x_1^3\ln\eta_1 + x_2^3\ln\eta_2 + 3x_1^2x_2\ln\eta_{12} + 3x_1x_2^2\ln\eta_{21} - \ln\left(x_1 + x_2\frac{M_2}{M_1}\right) - 3x_1^2x_2\ln\left(\frac{2}{3} + \frac{M_2}{3M_1}\right) + 3x_1x_2^2\ln\left(\frac{1}{3} + \frac{2M_2}{3M_1}\right) + x_2^3\ln\left(\frac{M_2}{M_1}\right) \quad (48)$$

Auslander relation:

$$\eta = \frac{\eta_1 x_1 (x_1 + B_{12} x_2) + \eta_2 [A_{21} x_2 (B_{21} x_1 + x_2)]}{x_1 (x_1 + B_{12} x_2) + [A_{21} x_2 (B_{21} x_1 + x_2)]} \qquad (49)$$

Teja-Rice relation:

$$\ln(\eta\xi) = x_1 \ln(\eta_1 \xi_1) + x_2 \ln(\eta_2 \xi_2) \qquad (50)$$

where $$\xi = \frac{V_c^{2/3}}{(T_c M)^{1/2}}$$

H. REFRACTIVE INDEX

Lorentz-Lorenz relation:

$$\left[\frac{(n^2-1)}{(n^2+2)}\right] = \left[\frac{(n_1^2-1)}{(n_1^2+2)}\right]\phi_1 + \left[\frac{(n_2^2-1)}{(n_2^2+2)}\right]\phi_2 \qquad (51)$$

Gladstone-Dale relation:

$$(n-1) = \phi_1 (n_1 - 1) + \phi_2 (n_2 - 1) \qquad (52)$$

Wiener's relation:

$$\left[\frac{(n^2-n_1^2)}{(n^2+2n_2^2)}\right] = \phi_2 \left[\frac{(n_2^2-n_1^2)}{(n_2^2+2n_2^2)}\right] \qquad (53)$$

Heller's relation:

$$\frac{(n-n_1)}{n_1} = \frac{3}{2}\left[\frac{(m^2-1)}{(m^2+2)}\right]\phi_2 \qquad (54)$$

Eykman's relation:

$$\left[\frac{(n^2-1)}{(n+0.4)}\right]V = \left[\frac{(n_1^2-1)}{(n_1+0.4)}\right]x_1 V_1 + \left[\frac{(n_2^2-1)}{(n_2+0.4)}\right](1-x_1)V_2 \qquad (55)$$

Oster's relation:

$$\left[\frac{(n^2-1)(2n^2+2)}{n^2}\right]V = \left[\frac{(n_1^2-1)(2n_1^2+2)}{n^2}\right]V_1 + \left[\frac{(n_2^2-1)(2n_2^2+2)}{n^2}\right]V_2 \qquad (56)$$

Arago-Biot relation:

$$n = \phi_1 n_1 + \phi_2 n_2 \tag{57}$$

All the above-mentioned theoretical relations were successfully employed in the present study and satisfactory results were obtained.

01/02/06

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