AL – OSTATH

Excess Molar Volume, Excess Viscosity and Excess Activation Energy for Binary and Ternary Systems of n-hexane, Propan-2-ol, and Butan-1-ol at Different Temperatures

*Mawaheb M. Derdar, (M.Derdar@.uot.edu.ly) **Ali R. Mira, **Mohamed M. Amer

Abstract

This study aims to predict the excess thermodynamic properties for new desirable mixtures. Densities, viscosities, excess volume, excess viscosity and excess activation energies of viscous flow were reported for binary and ternary mixtures of n-hexane, propan-2-ol, and butan-1-ol at temperatures 298.15, 308.15, 318.15, 328.15, and 338.15 K and over the whole mole fraction range to understand the effect of polar and nonpolar and temperature increase in the systems. Many works carried out to predict the excess thermodynamic properties, but the mixtures of this work have not been studied so far at such conditions. It is hoped that the present work will help in the availability of experimental data for some unknown mixtures to understand their behavior in the chemical processes, petrochemical industries and design processes.

Keywords: Excess properties, Density, Viscosity, n-hexane and Alcohols, Binary and Ternary mixtures.

Introduction

Extensive studies have been conducted on the thermodynamic properties of binary and ternary mixture systems to comprehend their thermodynamic behavior. The excess thermodynamic property (M^E) is defined as the disparity between the actual properties (M) and the properties in the ideal case (M^{id}) of a solution at identical temperature, pressure, and composition (Robert, 1987).

*Staff member at faculty of engineering University of Tripoli Libya

** Staff member at faculty of engineering University of Tripoli Libya

*** Staff member at faculty of engineering University of Tripoli Libya

In previous papers [Derdar, 2015, and Amer 2017], Densities, kinematic viscosities, excess volume, excess viscosities and excess activation energies of viscous flow were reported for binary and ternary mixtures of toluene + n-hexane + n-decane + n-dodecane + hexadecane at temperatures 293.15, 308.15, 323.15 K and over the whole mole fraction range to understand the effect of carbon atom number and temperature increasing in the systems. In this paper, we extend our studies to the binary and ternary mixtures of n-alkane (n-hexane) and alcohols (propan-2-ol and butan-1-ol) at 298.15, 308.15, 318.15, 328.15, and 338.15 K. This study aims to provide additional insights into the development of mixed species and their impact on the excess properties of the mixtures. Furthermore, this study will serve as a validation test for various empirical equations designed to correlate property data of binary mixtures comprising both polar and nonpolar components.

Experimental section

1. Materials

The anhydrous grade n-hexane, propan-2-ol, and butan-1-ol were obtained from Sigma-Aldrich. The claimed mole fraction purity for these chemicals was greater than 99%. The purity of all samples was ascertained by comparing the values of their measured densities and viscosities with their literature values at 298.15 K. The determined densities and viscosities of pure components agree well with literature values and given in Table (1), (Peng, 2007, Yingmin et al, 2020, Deepika, 2023).

2. Apparatus and Procedure

Calibration of measuring density and kinematic viscosity by using reference compounds. The pure components were degassed ultrasonically and dried over molecular sieves type 4A $1/_{16}$ in. Precautions were taken such as using samples recently prepared and reducing to a minimum the vapor space in the vessels to avoid preferential evaporation during manipulation errors and the subsequent composition errors. The possible error in the mole fraction is less than $\pm 2 \times 10^{-4}$.

AL – OSTATH

Table (1) Densities	and viscosities of the pure component	nts at $308.15~{ m K}$ in the literatures (Per	٦g,
2007, Yingmin et a	al, 2020, Deepika, 2023), and this wo	rk.	
	$\rho (g/cm^3)$	ν (cSt)]

	$ ho (g/cm^3)$		ν (cSt)	
Component	Literature	This work	Literature	This work
n-hexane	0.6906	0.6872	0.4495	0.4428
Propan-2-ol	0.7185	0.7185	1.0305	1.0306
Butan-1-ol	0.7080	0.7082	1.7215	1.7212

Results and Discussion

The study was done to get the excess thermodynamic properties data experimentally for n-hexane + propan-2-ol, n-hexane + butan-1-ol, and propan-2-ol + butan-1-ol in the binary system. In addition, n-hexane + propan-2-ol + butan-1-ol in ternary system. However, the study was undertaken at five different temperatures 298.15 K, 308.15 K, 318.15 K, 328.15 K, and 338.15 K for each mixture.

The excess molar volume (V^E), viscosity deviations($\Delta \mu$), and the excess activation energy (G^{*E}) of viscous flow were calculated from the following equations respectively:

$$V_{m}^{E} = \frac{\sum_{i=1}^{n} x_{i} M w t}{\rho_{m}} - \sum_{i=1}^{n} \frac{x_{i} M w t}{\rho_{i}}$$
(1)

$$\Delta \mu = ln\mu_m - \sum_{i=1}^n x_i \mu_i \tag{2}$$

$$G^{*E} = RT(ln\mu_m V_m - \sum_{i=1}^n x_i ln(\mu_i V_i))$$
(3)

The excess molar volume for the binary mixtures n-hexane + propanol, and n-hexane + butanol has been noticed that negative and increases with increasing temperature as shown in Figures (1, 2). In contrast, the excess molar volume for alcohols (propanol and butanol) has been shown in Figure (3) which is positive and slightly increases with increasing temperature. It can be seen from this study that excess volumes, excess viscosities and excess activation energies change wherever degrees of temperature change as shown in the results which has been collected. For example, in Figure (1) the excess volume for mixture (n-hexane + propanol)

system is a negative signal at 65° C and it increases by the increasing of the quantity of the alcohol also in increasing the temperature the change becomes obvious in the excess volume as it is quite clear at 25° C. it can be seen here the hydroxide group (-OH) has a clear effect on n–alkane when dissolved with alcohols. It was observed that at low concentrations of alcohol, the excess volume is negative, but as the alcohol content in the mixture increases, it transitions to a positive value. This underscores the positive diffraction characteristics of the alcohol mixture as shown in Figures (1, 2, and 3). Furthermore, the excess volume is negative in a ternary system as shown in Figure (4).

The predicted viscosity and kinematic viscosity for the binary systems of n-hexane + alcohol at different temperatures mild smoothly without distinct extremes from the values of pure alcohols to that of n-hexane as shown in Figures (5–7). In some cases, it has been noticed that un smooth curves lead to the instability of the system which means the mass transfer still occurred between the molecules in Figure (8). The excess activation energy for binary system mixtures fluctuated gradually as illustrated in Figures (9, 10, and 11)

From these findings, it is evident that the shift from negative to positive values in excess volume, excess viscosity, and excess activation energy is a result of the interaction and divergence of molecules, as illustrated in the Figures. This transformation occurs as molecules draw closer and exhibit attraction, decreasing the original volume and viscosity before the dissolution of the two compounds. Conversely, a positive sign signifies that molecules move apart and become discordant, leading to an increase in volume. (Dikko et al. 2014, Sameti et al 2011, Vadamalar et al. 2009, and Visak et al 2000).



Figure (1) Excess Molar Volume (cm³/gmol) for n-Hexane and Propan-2-ol at different Temperatures



Figure (2) Excess Molar Volume (cm³/gmol) for n–Hexane and Butan–1–ol at different Temperatures.





Figure (3) Excess Molar Volume (cm³/gmol) for Propan-2-ol and Butan-1-ol at different Temperatures.



Figure (4) Excess Molar Volume (cm³/gmol) for n–Hexane, Butan–1–ol, and Propan– 2–ol at different Temperatures





Figure (5) Excess Viscosity (CP) for n-Hexane and Propan-2-ol at different Temperatures.



Figure (6) Excess Viscosity (CP) for n–Hexane and Butan–1–ol at different Temperatures.



Figure (7) Excess Viscosity (CP) for Propan-2-ol and Butan-1-ol at different Temperatures



Figure (8) Excess Viscosity (CP) for n-Hexane, Butan-1-ol, and Propan-2-ol at different Temperatures.



Figure (9) Excess Activation Energy (J/gmol) for n-Hexane and Propan-2-ol at different Temperatures.



Figure (10) Excess Activation Energy (J/gmol) for n-Hexane and Butan-1-ol at different Temperatures.



Figure (11) Excess Activation Energy (J/gmol) for Propan-2-ol and Butan-1-ol at different Temperatures.



Figure (12) Excess Activation Energy (J/gmol) for n-Hexane, Butan-1-ol, and Propan-2-ol at different Temperatures

Conclusion

It can be concluded that the change which occurs in excess volume from negative to positive is due to the integration of molecules and divergence within them. The thermodynamic properties of the solutions for systems were different when the temperature changed and nonpolar and polar compounds mixed.

Nomenclature

M ^E	= Molar excess property
Μ	= Molar property
V	= Molar volume
G	= Molar Gibbs free energy
V ^E	= Molar excess volume
μ ^E	= Excess viscosity
G^{*E}	= Molar excess activation energy
x _i	= Mole fraction of pure compound i
R	= Universal gas constant
μ _m & μ _i	= Viscosity of mixture and pure component i respectively
ρ_m & ρ_i	= Density of mixture and pure component i respectively
Vi	= the volume of pure component i
Mwt	= Molecular weight of the pure compound

References

- Alonsu M. C., J. L P. Vilches, R. G. Sanchez-Pajares and J. N. Delgado, (1983), "J. Chem. Thermodynamics", 15(10), pp: 913–917.
- 2. Amer M. M, M. M. Derdar, A. A. Arajehi, and K. M. Mezughi, (2016), University Bulletin Issue No. 18 Vol. (1), pp: 18–37.
- Arenosa R. L., C. Henduina, G. Taradajos and M. Dias Pena, (1972), "J. Chem.Thermodynamics", 11(1), pp: 825–832.
- 4. Barbe M., and D. Patterson, (1980), "J. Solution Chem", 9(10), pp: 753-769.
- 5. Delmas G., P. Purves, and P. De Saint-Romain, (1975), "J. Phy. Chem.", 79(18),

pp: 1970-1974.

- 6. Deepika and S. Pandey, (2023), "Liquids", 3, pp:48-56
- 7. Derdar M. M., and M. M. Amer, (2015), Al-Ostath Issue 8.
- Dikko A. B. and A. Alkasim (2012), "International J of Recent Research in Physics and Chemical Sciences", 1(2), pp: 8–12.
- Dikko A. B., A. D.Ahmed, T. Pascal, and A. Alkasim (2014) "International J of Recent Research in Physics and Chemical Sciences", 3(9), pp: 306–308.
- 10. Dominguez M., J. L. Pardo, I. Gascon, F. Roya, and J.Urieta (2000), "Fluid phase Equilibria", 169(2), pp: 277–292.
- 11. Finkers H. J.m J. C. Bosma, and A.A. Broekhuis, (2011) "Chemical Emgineering Science" 66, pp: 2889–2897.
- 12. Kumar A., O. Prakash, and S. Prakash, (1981), "J. Chem. Eng. Data", 26(1), pp: 64–67.
- 13. Jayalakshmi T., and K. S. Reddy, (1985), "J. Chem. Eng. Data", 30(1), pp: 51-53.
- 14. Morrison R. T., and N. Boyd, (1973), "Organic Chemistey" Allyn and Bacon, INC. 3rd edition, New York University.
- 15. Patil P.P., S. R. Patil, A. U. Borse, and D. G. Hundiwale, (2011), "Rasayan J. Chem.", 4(3), pp:599-604.
- 16. Pang F., C. Seng, T. Teng, and M.H. Ibrahim, (2007), "Journal of Molecular Liquids", 136, pp: 71–78.
- 17. Robert A. Alberty, (1987), "physical Chemistry" 7th edition.
- 18. Reddy D. R., and M. V. Prabhakara Rao, (1985), "J. Chem. Eng. Data", 30(1), pp: 38-42.
- 19. Sameti M. R., and M. Rakhshi, (2011), "African Journal of pure and Applied Chemistry", 5(7), pp: 158–167.
- 20. Smith J., H. C. Van Ness, and M. M. Abbott (2005), "Introduction to Chemical Engineering Thermodynamics" 7th edition, Mc Graw Hill.
- 21. Vadamalar R., P. Mani, R. Balakrishnan, and V. Arumugam, (2009), "E–Journal of Chemistry", 6(1), pp: 261–269.

- 22. Visak Z. P., A. G. Ferreira, and I. M Fonseca, (2000), "J. Chem. Data", 45, pp: 926–931.
- 23. Wu J., A. Nhaesi, A. Fattah, and A. Asfour (1999), "Fluid phase Equilibria" 164(2), pp: 285–293.