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Response Surface Models on the Determination of Partial Molar Volume, Partial Molar Refraction, Electronic Polarizability and Molecular Radii from Dilute Multi-Component Data Alone

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Keywords: inverse problems, experimental design, multi-component solutions, parameter identification, solutions, thermodynamic process

Prepared for Presentation at the 2005 Annual Meeting AICHE

Abstract

A quaternary system consisting of three solutes, e.g. ethanol, diethylene glycol (DEG), and trietyhlene glycol (TEG) in benzene at 298.15 K and 1.0125 x 10^5 Pa was studied. On-line simultaneous measurements using a densitometer and a refractometer were utilized to determine bulk solution density and refractive index, respectively. Response surface models were employed in total molar volume and total molar refraction to determine partial molar volume and partial molar refraction, electronic polarizability and molecular radii of each solute from dilute multi-component data alone. An experimental design in the range of concentration $0.006 < x_{\text{solute-}i} < 0.022$ was explored, optimizing the metric distance among the solutes to avoid clustering. The results determined from multi-component system were very consistent with literature values (obtained from binary systems) as well as those obtained from our separate binary experiments.

1.0. Introduction

There have been extensive studies employing in-situ spectroscopy (e.g. FT-IR, UV/VIS, RAMAN, NMR, etc) showing that many observable organic and organometallic reactive intermediates are present as non-isolatable transient intermediates in highly complex multi-component reactive systems.[1] Such advanced signal processing techniques like Band-Target Entropy Minimization (BTEM) have been successfully utilized in deconvoluting, then identifying as well as quantifying the non-isolatable reacting species.[2] However, the corresponding determination of the associated physico-chemical solution properties of the individual solutes (non-isolatable as well as isolatable) in multi-component systems has not advanced to the same degree, due to combined numerical, analytical and methodological difficulties.

In this present contribution, a simultaneous straightforward thermodynamic measurement of density and refractive index measurements were carried out in a quaternary system consisting of three polar solutes, namely ethanol, diethylene glycol (DEG), and trietyhlene glycol (TEG) in benzene at 298.15 K and 1.0125 x 10^5 Pa to obtain total molar volume and total molar refraction and these lead to the determination of partial molar volumes, partial molar refractions, mean electronic polarizabilities and molecular radii based on multi-component data alone.

2.0. Experimental Equipment

The experimental system for density and refractive index measurements consisted of a glass reactor (Aceglass) equipped with a magnetic stirrer, a Teflon membrane pump (Cole-Parmer), an Anton-Paar DMA 5000 (accuracy of ± 5 x 10^{-6} g cm^{-3}, resolution of ± 10^{-6} g cm^{-3}) vibration tube densitometer thermostatically controlled to within ± 0.001 K and an Abbemat-HP (accuracy of ± 2 x 10^{-5} n_D, resolution of ± 10^{-6} n_D) automatic refractometer measured at the wavelength of the sodium D-line, 589.3 nm and thermostatically controlled to within ± 0.01 K. The fluid was pumped under isobaric (Argon, 1.0125 x 10^5 Pa) and isothermal conditions from the reactor through the pump (Temp control Polyscience 9105, with temperature stability ± 0.05 K) to the densitometer then refractometer with recycle back to the reactor. Connections for vacuum and argon were provided. A 2.000 piezo-transducer (PAA-27W, Keller AG, Switzerland) was used throughout for pressure measurements.

3.0. Results and Discussion

It has been shown that experimental design is crucial for utilizing response surface models for direct determination of partial molar volumes of each individual species from a multi-component system.[3] A similar approach is thus taken in the present contribution with further application to other properties, namely partial molar refraction, mean electronic polarizability and molecular radii. Three sets of semi-batch experiments consisting of 12 different compositions each were pre-designed prior to experimental work. All experiments were started with pure benzene as a major component (solvent)

under argon, and subsequently adding one solute at a time to change the solution composition.

A response surface model for total molar volume $V_m^T(T, P, \mathbf{x})$ consisting of 3 sets of terms, namely linear, bilinear and higher interaction terms[3] was applied to describe total molar volume as a response of compositional variation of this multi-component solution. Subsequently, the partial molar volumes for all solutes and the limiting values at infinite dilution at the same temperature and pressure can be derived as a function of compositional space. The corresponding partial molar volumes at infinite dilution are then readily obtained. The calculated the partial molar volume at infinite dilution in benzene are 60.6, 95.6, and 135.9 cm^{-3} $mole^{-1}$ for ethanol, DEG, and TEG, respectively. These partial molar volumes at infinite dilution for all solutes obtained from multi-component system are in very good agreement with those obtained from independent binary systems. The average error for all solutes with respect to independent binary system is circa 0.6% and considered very small.

Two truncated surface models for total molar refraction are also proposed. First model is a strictly additive model. Second model is a model with linear and bilinear terms. The corresponding partial molar refractions at infinite dilution $\overline{R}_i^{\infty}$ obtained from first and second models are 12.91 and 12.97 cm^{-3} $mole^{-1}$ for ethanol, 25.10 and 25.29 cm^{-3} $mole^{-1}$ for DEG, 36.04 and 36.15 cm^{-3} $mole^{-1}$ for TEG. The average errors in comparison with those obtained from independent binary system are circa 0.57% and 0.27%, respectively. The results showed that both models performed very well. It also suggests that additive model is sufficient to be used in this dilute solution even for highly interacting solutes system.

The resulting partial molar refractions at infinite dilution $\overline{R}_i^{\infty}$ can be subsequently used to determine mean electronic polarizability and molecular radii.[4] Mean electronic polarizability α_i^e and molecular radii a_i of solute-*i* determined from partial molar refraction at infinite dilution obtained from binary system and from multi-component solution by using the additive model are summarized in Table 1.

Table 1. Mean Electronic Polarizability α_i^e, and Molecular Radii a_i of Solute-*i* at 298.15 K and 1.0125 x 10^5 Pa Calculated from Molar Refraction of Binary, and Multi-Component Solution by Using the Additive Model

Component	$\alpha_i^e .10^{23}$/ (cm^3 $molecule^{-1}$)		a_i / (Å)	
	Binary[a]	Multicomponent[a]	Binary[a]	Multicomponent[a]
ethanol	0.52	0.51	1.73	1.71
DEG	1.00	1.00	2.16	2.15
TEG	1.42	1.43	2.43	2.43

[a)] Note: the partial molar refraction at infinite dilution of solute-*i* can be assumed to be approximately equal to its pure molar refraction.

The results suggest that subsequent determination of individual mean electronic polarizability and molecular radii of each solute from its respective molar refraction obtained from multi-component solution by using the additive model is reasonably accurate.

4.0. Conclusion

The determination of physico-chemical properties of solutes, namely partial molar volume, partial molar refraction, mean electronic polarizability and molecular radii from multi-component solution appears solved. The results obtained were very consistent with those obtained from independent binary experiments. The simple but reliable methodology proposed in this study, combined with on-line monitoring spectroscopy suggests a sufficient tool for the determination of partial molar volume, partial molar refraction, mean electronic polarizability as well as molecular radii of reactive species in the multi-component reactive system.

References

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