

Computational Problems in Evaluation of Colligative Property Equilibrium Data

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Computational problems in evaluation of colligative property data are discussed. Especially, the problem of the determination of the calibration constants is analyzed. Calibration constants may be determined either using reference substances or simultaneously with the aggregation constants of the compounds studied. However, calibration constants should be considered as "danger" parameters and experimental determination is highly recommended.

The aggregation equilibria of bis(2-ethylhexyl)monothiophosphoric acid (DEHTPA) and trioctylmethylammonium chloride (TOMACl) dissolved in toluene were investigated by vapour pressure osmometry. The experimental data were treated numerically by the program CPLET and the average aggregation number \bar{n} of the extractants, as well as the aggregation constants were determined. It was found that DEHTPA exists in toluene as an equilibrium mixture monomer—dimer—dodecamer and TOMACl as monomer, trimer, and tetramer species, respectively.

Knowledge of aggregation equilibria of extraction reagents in the organic phase is of high importance in extraction chemistry. Aggregation of some extractant reagents like long-chain amines [1–4], dialkylphosphoric acids [5], dialkyl(thio)phosphoric acids, *etc.* in diluents can be studied with advantage by vapour pressure osmometry (VPO). The method can be applied to study aggregation equilibria of solutes A, B, C, and D



$$\beta_{pqrs} = \frac{[A_p B_q C_r D_s]}{[A]^p [B]^q [C]^r [D]^s} \quad (2)$$

Osmometry is similar to cryoscopy and ebullioscopy. Generally, these methods are used in equilibria studies based on a relationship

$$Y = K_x S \quad (3)$$

or more generally

$$Y = K_{x1} S + K_{x2} S^2 + K_{x3} S^3 \quad (4)$$

where Y is *e.g.* vapour pressure lowering, freezing point depression, or resistance difference ΔR in VPO, S is the sum of the concentrations of all solute species

and K_x is a proportionality factor which can be usually considered as a constant for a given solvent. In some cases the second and the third term can also be applied to correct the nonideal behaviour. Colligative property equilibrium data, particularly in VPO, can be evaluated with the CPLET program [6] using the general least-squares method while applying pitting, Simplex, Davidon—Fletcher—Powell and the steepest descendent minimizing routines. The program CPLET using optimization approach calculates the equilibrium, calibration constants, and the stoichiometric coefficients, which give U , the minimal sum of squares of residuals, defined as

$$U = \sum (\Delta R_{\text{calc}} - \Delta R_{\text{exp}})^2 \quad (5)$$

From the measurement of colligative property as a function of the reactant concentrations, the "best" set of complexes and corresponding equilibrium constants are found. Also the stoichiometry of the species can be directly searched for *via* simultaneous regression estimation of equilibrium constant and stoichiometric indices. The program is afforded with a complete statistical analysis of residuals.

Computational problems when evaluating this kind of data are observed if oligomerization constants are too high, if limited number of experimental data

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are available, and calibration constants of the apparatus are evaluated simultaneously with equilibrium constants.

These problems are studied in this work and bis(2-ethylhexyl)monothiophosphoric acid (DEHTPA) and trioctylmethylammonium chloride (TOMACl) oligomerization in toluene was investigated experimentally. The results of this work were briefly reported elsewhere [7].

EXPERIMENTAL

TOMACl (Fluka), tributyl phosphate (TBP) (Merck AR), toluene (Merck AR), anthracene (Merck), and DEHTPA (Bayer AG Leverkusen) were used without further purification. Benzil (Merck, AR) was twice recrystallized from dried methanol. Solutions of benzil, anthracene, TBP, TOMACl, and DEHTPA were prepared by weighing. The molality range used was up to $0.150 \text{ mol kg}^{-1}$.

The osmometric measurements were carried out at 303 K using a Knauer Vapour Pressure Osmometer, model No. A0280 and a universal probe. Benzil, anthracene, and TBP were used as the external standards because they are expected to be monomeric in toluene in the concentration range of interest.

The differences of resistance ΔR were measured as a function of the concentration for the standards, organothiophosphoric acid and TOMACl.

Table 1. Calibration Constants K_x Obtained for Different Reference Substances in Toluene at 303 K

Substance	K_x
Benzil	621 ± 19
Anthracene	676 ± 14
TBP	679 ± 11
Average	658 ± 33

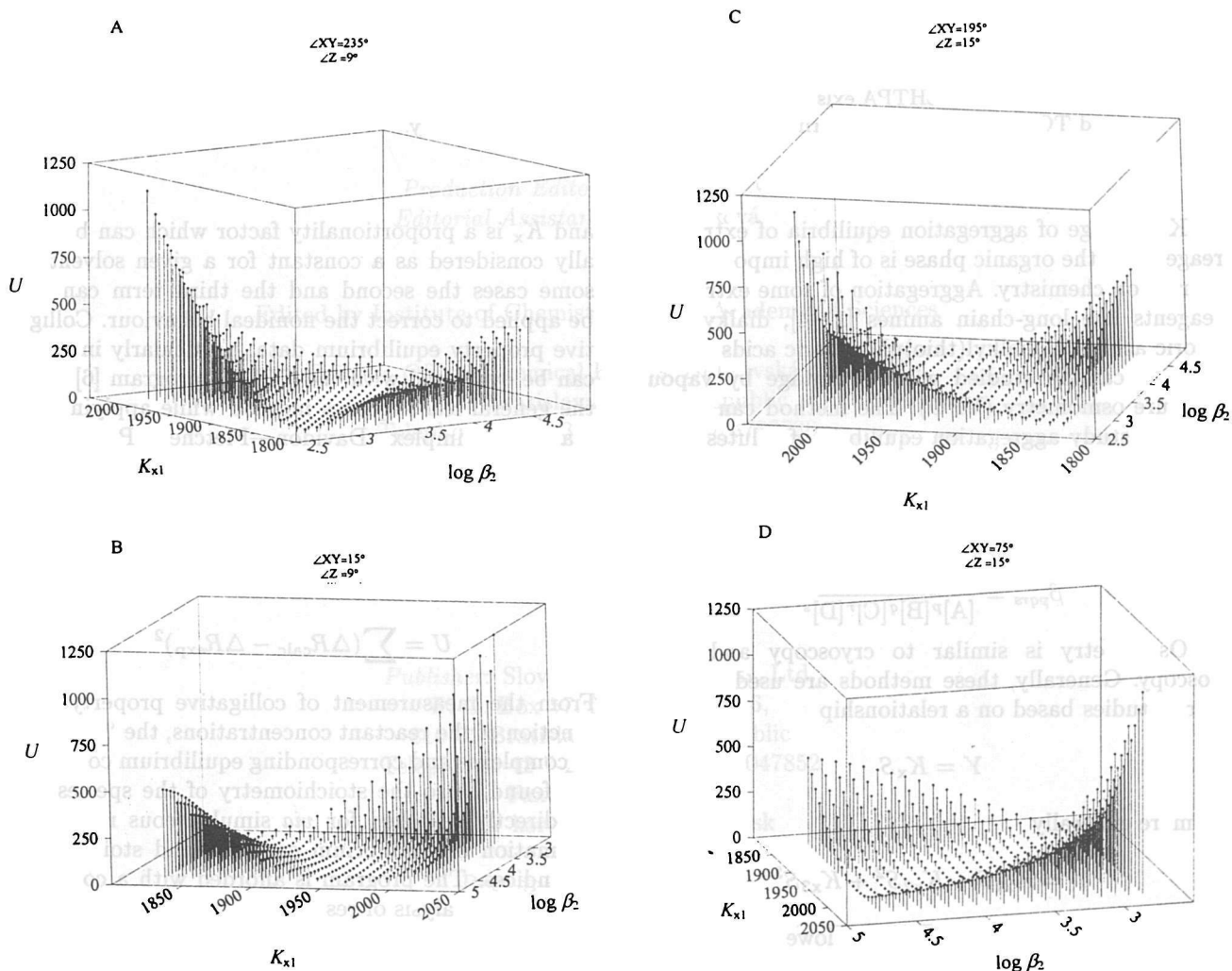


Fig. 1. Shape of the minimum of $U = \sum (\Delta R_{\text{calc}} - \Delta R_{\text{exp}})^2$ as a function of dimerization constant $\log \beta_2$ of bis(2-ethylhexyl)phosphoric acid (HDEHP) and calibration constant K_{x1} at various view angles $\angle XY$ and $\angle Z$. The values in minimum are $\log \beta_2$ and $K_{x1} = 1920$. Simulated data are taken from [6].

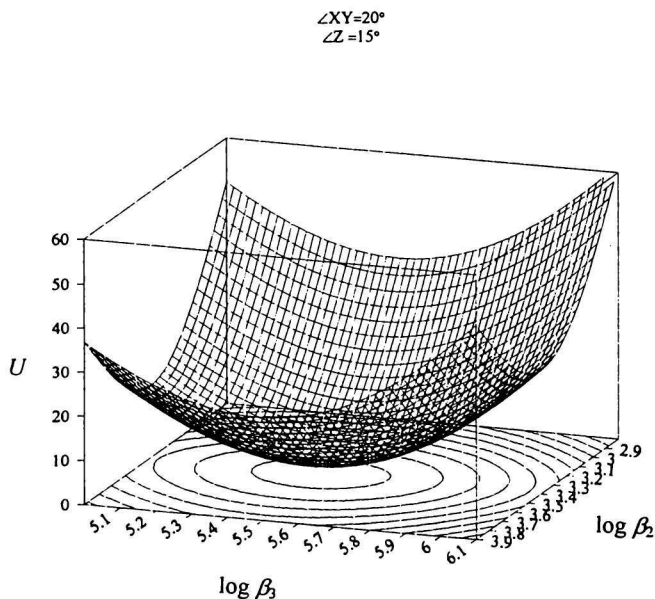


Fig. 2. Shape of the minimum of U as a function of $\log \beta_2$ and $\log \beta_3$ for aggregation of mono(2-ethylhexyl) ester of 2-ethylhexylphosphonic acid (DINA.HCl), cf. data in [6]. The values in minimum are $\log \beta_2 = 3.40$, $\log \beta_3 = 5.56$, and calibration constant $K_x = 405.2$ (fixed).

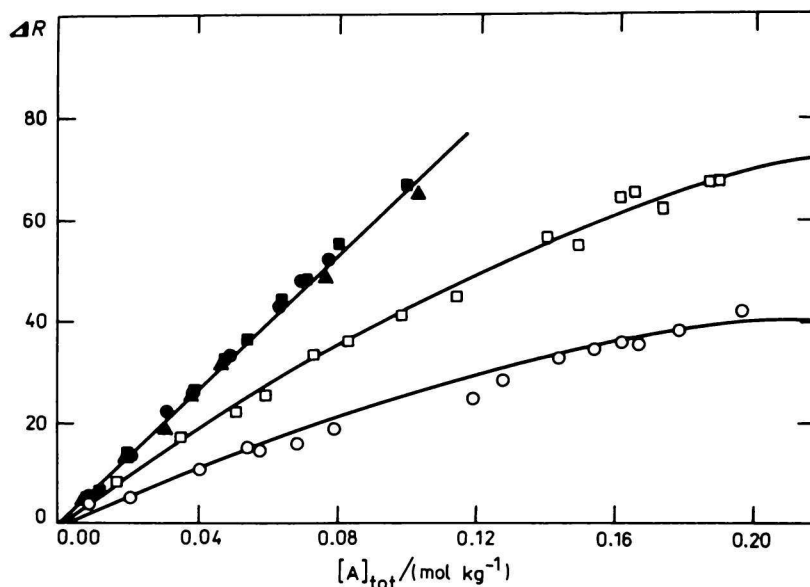


Fig. 3. ΔR plotted as a function of the total reagent molality in toluene. ● Anthracene, ■ tributyl phosphate, ▲ benzil, □ DEHTPA, ○ TOMACI.

The measured property ΔR may be expressed as a function of the sum of the concentrations of all species S

$$\Delta R = K_x S \quad (6)$$

where K_x is the calibration constant and may be obtained by measuring ΔR for different standard solutions, which are monomeric in toluene [3]. The values of the calibration constants are given in Table 1.

In order to obtain reliable ΔR values the drop size

was kept as constant as possible and equal in both thermistors, and the measurements were performed by reading ΔR five minutes after placing the drops on the thermistors. In this manner the precision of ΔR was maintained below 2 %.

RESULTS AND DISCUSSION

Using simulated data for dimerization of bis(2-ethylhexyl)phosphoric acid (HDEHP) ($\log \beta_2 = 3.67$)

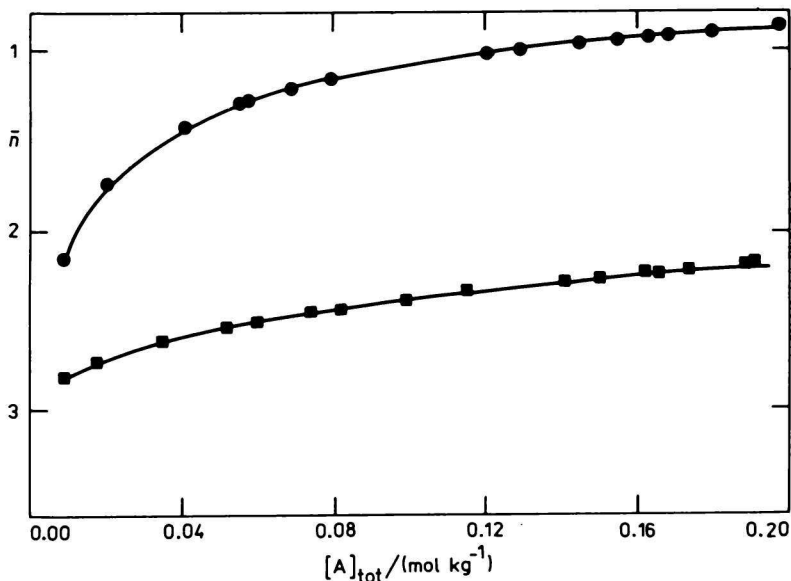


Fig. 4. Average aggregation number \bar{n} as a function of the total molality of DEHTPA (■) and TOMACI (●) in toluene.

at various levels of random noise while calibration constant was $K_{x1} = 1920$, it was shown that from sufficiently accurate data both, the dimerization constant β_2 and the calibration constant K_{x1} can be safely computed [6].

However, when looking at the minimum, visualized in 3-D diagrams, it is evident that U , the sum of squares of residuals as a function of $\log \beta$ and K_{x1} is highly dependent on $\log \beta$ but not on the calibration constant K_{x1} . The sum of squares of residuals as a function of parameters around the minimum shown from different view angles is given in Fig. 1A—D.

Thus, calibration constant(s) should be considered in colligative property equilibrium studies as “danger” parameters and even if they can be computed by the CPLET [1] program simultaneously with the aggregation equilibria, independent experimental determination is highly recommended.

On the other hand, it is demonstrated in Fig. 2 that quite expressive minimum is obtained when plotting U , the sum of squares of residuals, as a function of oligomerization constants. The system is that one published by Miralles [6], *i.e.* for the formation of dimer and trimer of mono(2-ethylhexyl) ester of 2-ethylhexylphosphonic acid.

At the study of the oligomerization the experimental data ΔR were plotted as a function of the total molality of DEHTPA and TOMACI in toluene and are given in Fig. 3. As may be observed, the experimental points for DEHTPA and TOMACI in toluene system deviate strongly from the monomeric behaviour of the standards in toluene. Thus, it can be assumed that deviations of the measured ΔR values from those of the standards solutions are due to the formation of the aggregates.

Treatment of Data

The aggregation of the bis(2-ethylhexyl)monothio-phosphoric acid and trioctylmethylammonium chloride can be described by an equation

$$nA = (A)_n \quad (7)$$

Assuming ideal behaviour of organophosphinic acid the stoichiometric constant β_n can be written as

$$\beta_n = \frac{[(A)_n]}{[A]^n} \quad (8)$$

Then, from the experimental data (ΔR , $[A]_{\text{tot}}$) for each temperature and system, and using eqn (1) with the calibration constants given in Table 1, the values of S may be calculated. The average aggregation number \bar{n} of the extractant reagents in toluene may be determined as

$$\bar{n} = \frac{[A]_{\text{tot}}}{S} \quad (9)$$

where $[A]_{\text{tot}}$ and S are defined as

$$[A]_{\text{tot}} = n\beta_n[A]^n \quad (10)$$

$$S = [A] + \beta_n[A]^n \quad (11)$$

and n varies from 1 to N .

In Fig. 4 the average aggregation number has been plotted as a function of the total concentration of the extractant reagents for the systems DEHTPA—toluene and TOMACI—toluene.

The experimental data (ΔR , $[A]_{\text{tot}}$) have been treated with the CPLET program [6]. As the calibration constants are “danger” parameters, they were

Table 2. Summary of CPLET Calculations for the Aggregation of DEHTPA in Toluene

Run	Parameter	Calculated*	Fitness test
1	$\log \beta_2$ K_x 658 n 2	2.06 ± 0.09	$\sigma = 2.55$ $U = 104$
2	$\log \beta_2$ K_x 658 n	2.02 ± 0.09 2.47 ± 0.21	$\sigma = 2.11$ $U = 71.2$
3	$\log \beta_2$ K_x n 2	0.89 ± 0.13 514 ± 15	$\sigma = 2.20$ $U = 77.8$
4	$\log \beta_2$ K_x n	1.52 ± 0.09 583 ± 30 2.42 ± 0.25	$\sigma = 2.04$ $U = 66.9$
5	$\log \beta_2$ $\log \beta_3$ K_x 658 n 2 n 3	1.30 ± 0.28 2.44 ± 0.07	$\sigma = 2.06$ $U = 68.0$
6	$\log \beta_2$ $\log \beta_3$ K_x n 2 n 3	1.11 ± 0.32 2.07 ± 0.13 615 ± 21	$\sigma = 2.03$ $U = 66.4$
7	$\log \beta_2$ $\log \beta_3$ K_x 658 n 2 n	1.40 ± 0.25 2.75 ± 0.47 3.23 ± 0.42	$\sigma = 2.04$ $U = 67.1$
8	$\log \beta_2$ $\log \beta_4$ K_x 658 n 2 n 4	1.48 ± 0.13 3.56 ± 0.02	$\sigma = 2.01$ $U = 64.7$
9	$\log \beta_2$ $\log \beta_4$ K_x n 2 n 4	1.19 ± 0.15 2.92 ± 0.08 600 ± 7	$\sigma = 1.98$ $U = 63.0$
10	$\log \beta_2$ $\log \beta_{12}$ K_x 658 n 2 n	1.76 ± 0.03 14.84 ± 0.12 12.01 ± 0.08	$\sigma = 1.93$ $U = 55.8$
11	$\log \beta_2$ $\log \beta_{12}$ K_x 658 n 2 n 12	1.76 ± 0.03 14.84 ± 0.12	$\sigma = 1.93$ $U = 55.8$
12	$\log \beta_2$ $\log \beta_{12}$ K_x n 2 n 12	1.76 ± 0.03 14.84 ± 0.12 658 ± 6	$\sigma = 1.93$ $U = 55.8$

* Parameters not calculated have been fixed at the given values.

determined experimentally for several substances. The

Table 3. Summary of CPLET Calculations for the Aggregation of TOMACl in Toluene

Run	Parameter	Calculated*	Fitness test
1	$\log \beta_3$ K_x 658 n 3	10.22 ± 2.37	$\sigma = 1.43$ $U = 33.1$
2	$\log \beta_4$ K_x 658 n 4	5.84 ± 0.10	$\sigma = 1.36$ $U = 27.7$
3	$\log \beta_3$ K_x n	8.52 ± 9.45 648 ± 55 3.0 ± 0.2	$\sigma = 1.42$ $U = 30.4$
4	$\log \beta_2$ $\log \beta_4$ K_x 658 n 2 n 4	3.42 ± 0.03 8.69 ± 0.05	$\sigma = 1.05$ $U = 15.6$
5	$\log \beta_2$ $\log \beta_4$ K_x n 2 n 4	3.22 ± 1.06 8.45 ± 1.76 672 ± 7	$\sigma = 1.05$ $U = 15.5$
6	$\log \beta_3$ $\log \beta_4$ K_x 658 n 3 n 4	4.69 ± 0.085 6.67 ± 0.07	$\sigma = 1.037$ $U = 15.0$
7	$\log \beta_3$ $\log \beta_4$ K_x n 3 n 4	3.40 ± 1.08 7.25 ± 0.12 758 ± 7	$\sigma = 1.03$ $U = 15.0$
8	$\log \beta_2$ $\log \beta_3$ 4.69 $\log \beta_4$ K_x 658 n 2 n 3 n 4	2.58 ± 0.05 7.44 ± 0.05	$\sigma = 1.05$ $U = 15.4$
9	$\log \beta_3$ 4.69 $\log \beta_4$ 6.67 K_x n n	682 ± 7 3.06 ± 0.03 3.91 ± 0.06	$\sigma = 1.03$ $U = 15.0$

* $\sigma(K_x)$ is the standard deviation obtained from five parallel determinations.

resulting values are given in Table 1.

The results of the calculations for the aggregation of DEHTPA and TOMACl in toluene are summarized in Table 2 and 3, respectively.

It follows from Table 2 that the assumption of dimer formation (Run 1) yields rather high standard deviation $\sigma(\Delta R)$ equal to 2.55 and that the calculation of stoichiometry gives the value $n = 2.47$ in Run 2 which is far from integer. In addition, in Run 3 simultaneous calculation of K_x yields the value of K_x equal to 5.14, which is far from the experimental value

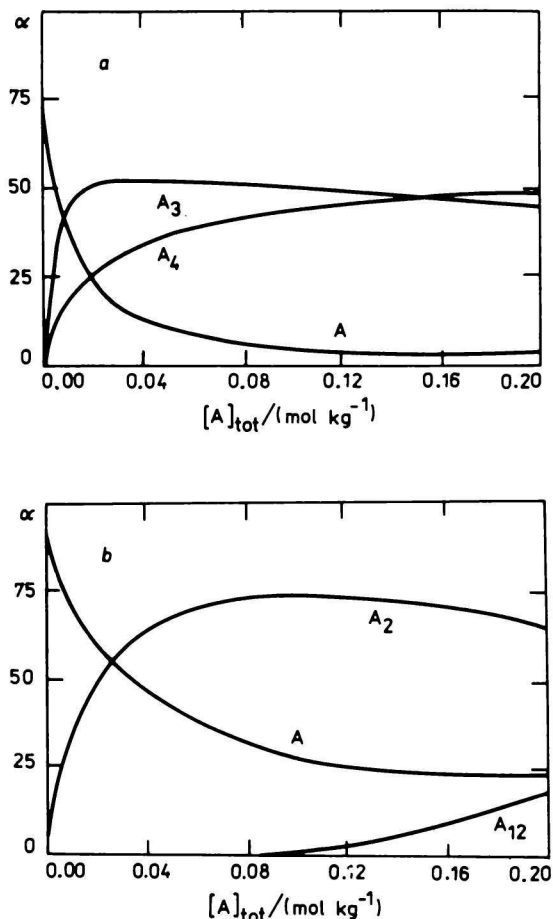


Fig. 5. Distribution diagrams as a function of the total molality of TOMACl (a) and DEHTPA (b) in toluene.

$$\alpha = \frac{n[A]_n}{[A]_{\text{tot}}} \cdot 100$$

$K_x = 658$. Simultaneous calculation of $\log \beta_2$, K_x , and n (Run 4) is giving slight improvement only. Assumption of dimer and trimer (Runs 5–7) was not improving fitness test too much. Only slight improvement was also observed in Runs 8 and 9 for dimer and tetramer. After complicated search for a better model formation it was found that dodecamer is accepted instead of a tetramer (Run 10). If n is rounded to integer, *i.e.* to 12 in Run 11 “the best” values for $\log \beta_2$ and $\log \beta_{12}$ were obtained. Correctness of the model was proved (Run 12) at the calculation of K_x . In this case the value near to the experimental one was found.

Similarly, from Table 3 it is clear that only trimer (Runs 1, 3) or tetramer (Run 2) cannot explain data sufficiently. Dimer and tetramer (Runs 4, 5) are improving slightly the fit. Still better fit was obtained assuming trimer and tetramer (Runs 6, 7). An attempt with dimer, trimer, and tetramer (Run 8) was not successful. “The best” seems to be the formation of trimer and tetramer (Run 6). An attempt to calculate simultaneously with $\log \beta_3$ and $\log \beta_4$ calibration constant K_x yields, however, the value of K_x far from

the experimental one (758) (Run 7). Thus, as “the best” model, $\log \beta$ values obtained in Run 6 are recommended. Correctness of the model was proved in Run 9, where it is shown that the calculated values of stoichiometric indices are near to 3 and 4. Distribution diagrams for the best models are given in Fig. 5.

CONCLUSION

The results reported in this work for the aggregation of DEHTPA and TOMACl in toluene indicate that these compounds at the experimental conditions used exist in toluene in equilibrium of the monomer with dimer and dodecamer (the former), and as monomer, trimer, and tetramer (the latter), respectively.

As seen from Fig. 4 the average aggregation number \bar{n} increases with the total molality of DEHTPA and TOMACl in toluene. In Fig. 5 the distribution diagrams are plotted as a function of the total concentration of DEHTPA and TOMACl in toluene calculated from the constants given in Run 12 of Table 2 and Run 6 of Table 3, respectively.

For the DEHTPA–toluene system, the monomer is the predominant species at molality lower than $0.030 \text{ mol kg}^{-1}$ while dimeric species is predominant at the higher molalities, while the amount of dodecamer accounts for less than 15%. Concentration of monomer species is lower than 25% in the range of molalities studied.

For the TOMACl–toluene system, trimer species is dominant up to molality equal to 0.16 mol kg^{-1} while tetramer is the dominant species at higher molalities. Mass fractions of monomeric species are lower than 10% in the molality range used.

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REFERENCES

- Scibona, G., Basol, S., Danesi, P. R., and Orlandini, F., *J. Inorg. Nucl. Chem.* 28, 1441 (1966).
- Madariaga, J. M., Aurrekoetxea, M., and Katime, I., *Chemica Scripta* 22, 90 (1983).
- Paatero, J., *Acta Academiae Aboensis* 34, 1 (1974).
- Markovits, G. and Kertes, A. S., in *Solvent Extraction Chemistry*. (Dyrssen, D., Liljenzin, J. O., and Rydberg, J., Editors.) P. 391. North-Holland, Amsterdam, 1967.
- Miralles, N., Sastre, A., Martinez, M., and Aguilar, M., *Analytical Sciences* 8, 773 (1992).
- Havel, J., Miralles, N., Sastre, A., and Aguilar, M., *Comput. Chem.* 16, 319 (1992).
- Lubalová, M., Havel, J., Miralles, N., Sastre, A., and Martinez, M., *Proc. Conf. CHEMOMETRICS '95*, p. 69. Pardubice, 1995.

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