Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

An Attempt to Theoretically Predict Third-Phase Formation in the Dimethyldibutyltetradecylmalonamide (DMDBTDMA)/Dodecane/Water/Nitric Acid Extraction System

Lydie Lefrancois[a]; Frédéric Belnet[b]; Didier Noel[b]; Christian Tondre[c]
[a] LABORATOIRE DE CHIMIE PHYSIQUE ORGANIQUE ET COLLOÏDALE, UNIVERSITÉ HENRI POINCARÉ-NANCY I, NANCY-VANDOEUVRE, FRANCE [b] EDF, CENTRE DE RECHERCHE DES RENARDIÈRES SECTION CHIMIE ET CORROSION, MORET-SUR-LOING, FRANCE [c] LABORATOIRE DE CHIMIE PHYSIQUE ORGANIQUE ET COLLOÍDALE, UNIVERSITE HENRI POINCARE-NANCY I, NANCY-VANDOEUVRE, FRANCE

To cite this Article Lefrancois, Lydie , Belnet, Frédéric , Noel, Didier and Tondre, Christian(1999) 'An Attempt to Theoretically Predict Third-Phase Formation in the Dimethyldibutyltetradecylmalonamide (DMDBTDMA)/Dodecane/Water/Nitric Acid Extraction System', Separation Science and Technology, 34: 5, 755 — 770
To link to this Article: DOI: 10.1080/01496399908951143
URL: http://dx.doi.org/10.1080/01496399908951143

SEPARATION SCIENCE AND TECHNOLOGY, **34**(5), pp. 755–770, 1999

An Attempt to Theoretically Predict Third-Phase Formation in the Dimethyldibutyltetradecylmalonamide (DMDBTDMA)/Dodecane/Water/Nitric Acid Extraction System

LYDIE LEFRANCOIS
LABORATOIRE DE CHIMIE PHYSIQUE ORGANIQUE ET COLLOÏDALE
UNIVERSITÉ HENRI POINCARÉ-NANCY I
UNITÉ MIXTE DE RECHERCHE CNRS-UHP (UMR 7565)
BP 239, 54506 NANCY-VANDOEUVRE, FRANCE

FRÉDÉRIC BELNET and DIDIER NOEL
EDF, CENTRE DE RECHERCHE DES RENARDIÈRES
SECTION CHIMIE ET CORROSION
B.P. 1, ECUELLES, 77250 MORET-SUR-LOING, FRANCE

CHRISTIAN TONDRE*
LABORATOIRE DE CHIMIE PHYSIQUE ORGANIQUE ET COLLOÏDALE
UNIVERSITÉ HENRI POINCARÉ-NANCY I
UNITÉ MIXTE DE RECHERCHE CNRS-UHP (UMR 7565)
BP 239, 54506 NANCY-VANDOEUVRE, FRANCE

ABSTRACT

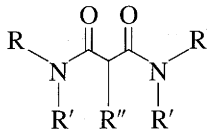
The formation of a third phase in solvent extraction (due to splitting of the organic phase into two layers) often occurs when the aqueous phase is highly concentrated in acids. This has been reported with the extraction system dimethyldibutyltetradecylmalonamide (DMDBTDMA)/*n*-dodecane/water/nitric acid, both in the presence and absence of metal ions. Whereas many experimental efforts have been made to investigate the effects of different parameters on third-phase formation, very few attempts have been made to predict this phenomenon on theoretical grounds. Because the part played by aggregation of the extractant molecules is recognized, we propose a new

*To whom correspondence should be addressed.

predictive approach based on the use of the Flory–Huggins theory of polymer solutions, which had been successfully applied for the prediction of phase separation phenomena in nonionic surfactant solutions. We show that this model can provide an excellent prediction of the demixing curve (in the absence of metal ions) when establishing the relation between the interaction parameter χ_{12} calculated from this theory and the nitric acid content of the aqueous phase. Apparent values of the solubility parameter δ_2 of the diamide extractant at different acid loadings have been calculated, from which the effect of the nature of the diluent can also be very nicely predicted.

INTRODUCTION

The separation of radioelements, and especially actinides, from nuclear wastes is a big challenge which concerns the reprocessing of spent nuclear fuel. Specific processes, like PUREX or DIAMEX, are currently under investigation (1). A great deal of work has been done in the past few years to improve these technologies through finding new extracting agents which have some required properties (1–4). For instance, a number of investigations have concerned malonamide derivatives of the following general formula (1, 3–5):



Among this series of new reagents, *N,N′*-dimethyl *N,N′*-dibutyltetradecylmalonamide (DMDBTDMA, in which R = CH_3, R′ = C_4H_9 and R″ = $C_{14}H_{29}$) has proved to be a well-suited compound to extract trivalent actinides from nitric acid solutions into aliphatic diluents like TPH (hydrogenated tetrapropylene). Besides its good extracting properties, it is completely incinerable and has very low water solubility. On the other side, some of its negative characteristics are its ability to coextract lanthanides with actinides and its tendency to form a third liquid phase under certain extracting conditions (1).

The phase behavior of DMDBTDMA/*n*-dodecane/water/HNO_3 quaternary systems has been recently investigated (6) with *n*-dodecane being a good model for TPH. A phase analysis has been performed with HNO_3 concentrations up to about 10 M. The demixing leading to third-phase formation has been shown from small-angle x-ray scattering (SAXS) and surface tension measurements to be very likely associated with the interactions of primary aggregates of DMDBTDMA molecules in the organic phase. The analysis of the x-ray scattering curves has demonstrated that the primary aggregates are probably pentameric and look like small reverse micelles with a very low water content (6). This is a confirmation of previously reported NMR data (7) sug-

gesting a self-assembling of DMDBTDMA molecules in the form of small aggregates (aggregation numbers of 4 in TPH and 6 in benzene were found to be consistent with the data).

Third-phase formation is a general problem often encountered in extraction processes taking place in highly acidic media and has strong implications for industrial developments. The splitting of the organic phase has been well documented in the case of the extractant TBP (tributylphosphate) and the main results have been reviewed by Osseo-Asare (8) and by Vasudeva Rao and Kolarik (9). Parameters influencing third-phase formation in systems including alkylmalonamides have recently been examined by Smith et al. (10). Nevertheless, most information in this domain is essentially of an empirical character, and very little has been done so far to predict third-phase formation on theoretical grounds. A first approach toward predicting phase splitting was suggested by Erlinger et al. (6) who considered short-range interactions between the colloidal aggregates within the framework of the model proposed by Baxter (11) for the hard sphere sticky potential.

It should be emphasized that third-phase formation occurs both in the presence or absence of metal ions: only the maximum attainable concentration of nitric acid before demixing is more or less affected by the presence of metallic species (1). For this reason we will not consider the addition of metal ions in the present work, but we will simply attempt to predict phase separation in the quaternary system consisting of DMDBTDMA/*n*-dodecane/water/nitric acid. Our approach has been adopted after considering that there was some analogy between the present situation, in which interaggregate interactions seem to be responsible for the phase separation, and the clouding phenomenon that occurs in aqueous solutions of nonionic surfactant (12–14) (note, however, that the interaggregate interactions are taking place in a water continuum in the latter case and in an organic continuum in the former one). The clouding point phenomenon is related to the decrease of the solubility in water of the hydrophilic polar heads of the surfactant molecules when the temperature is increased. When the cloud point temperatures are plotted as a function of the surfactant concentration, a demixing line is obtained showing a lower consolute temperature. Similar to what is observed in our case, the phase diagrams (phase compositions versus temperature for nonionic surfactants or phase compositions versus nitric acid concentration for DMDBTDMA) are highly unsymmetrical with separation in one surfactant (extractant)-rich phase and one surfactant (extractant)-poor phase. In the case of nonionic surfactants the demixing line during increasing temperature can be successfully predicted using the Flory–Huggins theory of polymer solutions (12–14). We have attempted to use the same approach here to calculate the interaction parameters between DMDBTDMA and the diluent (*n*-dodecane) when the nitric acid concentration is varied. The evolution of an apparent solubility parameter of the

extractant molecule was consequently determined, from which the phase behavior in other diluents could in principle be predicted.

THEORETICAL BACKGROUND AND HYPOTHESIS

The theory of Flory–Huggins (15) strictly describes only solutions of linear polymers. It is based on calculation of the mixing entropy, ΔS_M, from a statistical description of the total number of configurations of the polymer chain when the monomeric units are placed, one after the other, in a quasi-lattice. In the simplest case each cell of the quasi-lattice is occupied by a solvent molecule whose molar volume is approximately equivalent to that of a monomeric unit. The enthalpy of mixing, ΔH_M, is calculated using the concepts of regular solution theory, introducing the so-called interaction parameter, χ_{12}, between the solvent and the macromolecule. The free energy of mixing, ΔG_M, is then readily calculated from the expressions of ΔS_M and ΔH_M.

Knowing the expression of ΔG_M, the thermodynamics of phase separation allows the calculation of the composition of the coexisting phases. At equilibrium the chemical potentials of the solvent and of the solute are indeed equal in each phase. This can be described by the following equations:

$$\ln v_1' + \left(1 - \frac{1}{x}\right) v_2' + \chi_{12} v_2'^2 = \ln v_1'' + \left(1 - \frac{1}{x}\right) v_2'' + \chi_{12} v_2''^2 \quad (1)$$

and

$$\frac{1}{x} \ln v_2' - \left(1 - \frac{1}{x}\right) v_1' + \chi_{12} v_1'^2 = \frac{1}{x} \ln v_2'' - \left(1 - \frac{1}{x}\right) v_1'' + \chi_{12} v_1''^2 \quad (2)$$

where v_1' and v_2' are the volume fractions of the solvent and solute in one phase (the less concentrated one), respectively; v_1'' and v_2'' are their volume fractions in the second phase ($v_1' = 1 - v_2'$ and $v_1'' = 1 - v_2''$); and x is the molar volume ratio between solute and solvent (in the simplest case mentioned above, it is proportional to the degree of polymerization). A method of resolution of these equations has been proposed by Flory, from which the demixing curve can be predicted (16).

The χ_{12} parameter of the Flory–Huggins theory can be shown, from the concepts of the regular solution theory, to be of the form (17):

$$\chi_{12} = \frac{V_1}{RT} (\delta_1 - \delta_2)^2 \quad (3)$$

where V_1 is the molar volume of the solvent and δ_i are the solubility parameters of the solvent ($i = 1$) and solute ($i = 2$), respectively.

Although the distribution of the segments of a polymer chain in a lattice model does not have much to do with the possible arrangements of micelles of surfactants in a similar lattice, the Flory–Huggins theory was previously used in micellar systems (12–14). In fact, even if it is not rigorously adapted, it can provide a useful tool for understanding some of the properties of micellar systems, and this is the way we have approached the problem in the present paper. We are perfectly aware of the limitations of the Flory–Huggins theory when treating the case of micellar aggregates. These limitations have recently been pointed out by Blankschtein et al. (18), who emphasized that it is normally necessary to take into account the unique characteristics of micellar aggregates and their size distribution, which distinguish them from classical mixtures.

However, in the case of DMDBTDMA, we are supposed to be dealing with small aggregates (4 to 6 monomers, as said above), and one can imagine the atoms of the long tetradecyl chains (R″) followed by the amido groups and by the butyl substituents (R′) to be distributed in a quasi-lattice in the same way as a polymer chain. The interactions between DMDBTDMA molecules inside the aggregates are nevertheless expected to be responsible for a decrease of the configurational chain entropy compared to what it would be for a simple polymer chain. Following previous works in the same direction (13, 14), and remembering that x is the molar volume ratio between solute and solvent, we have adopted the following definition:

$$x = \frac{nV_2}{V_1} \tag{4}$$

where n is the aggregation number and V_2 is the molar volume of a monomeric unit in the aggregates.

The following hypothesis or approximations have been made in order to apply this model to the problem of third-phase formation.

1. We have only considered the splitting of the organic phase, ignoring the presence of the aqueous phase [the volume of the latter changes only slightly with increasing acidity, and its concentration in DMDBTDMA can be neglected according to a previous work (6)].
2. We have assumed that the entities which self-associate close to the phase separation limit in the aggregates are constituted of complexes of DMDBTDMA and HNO_3 in a 1:1 ratio [this is consistent with the fact that the third phase has been shown (6) to occur in a region where the ratio between the extracted acid concentration and the initial concentration of DMDBTDMA is around 0.8, i.e., not very far from 1]. Since the molar volume of this complex is not known, the V_2/V_1 ratio was approximated by M_2/M_1, where M_2 and M_1 are the molecular weights of the complex DMDBDTMA:HNO_3 and dodecane, respectively.

3. The use of the regular solution theory normally implies that the enthalpy of mixing is small, which is the condition for the mixing entropy to be expressed as that of an ideal solution. This requirement is not strictly satisfied here (see above).

In the present approach the diamide aggregates will be treated similarly to the polymer of the Flory–Huggins theory. The idea is to quantify the change of solubility of DMDBTDMA in dodecane while varying the nitric acid concentration in the aqueous phase by associating a value of the interaction parameter χ_{12} with a nitric acid content. We will then obtain an apparent solubility parameter, δ_2, for the diamide extractant or, more exactly, for its aggregates. The change in solubility obviously has a close relationship with the protonation state of the extractant. We made a very rough approximation by considering that we are always dealing with the same form of the extractant, but this is justified by the fact that the addition of one proton to the molecule only changes by one unit a molecular weight as large as 501.7 for the DMDBTDMA:HNO_3 complex, whereas it may drastically change the interactions with the solvent (dodecane).

EXPERIMENTAL

Chemicals

The dimethyldibutyltetradecylmalonamide (DMDBTDMA), 99% pure, was obtained from Panchim (France) and used as received. *N*-Dodecane (purum) and nitric acid (65%) were from Fluka. Deionized doubly distilled water was used throughout the study. The multiphase systems were prepared as reported in a previous publication (6).

Techniques

The determination of DMDBTDMA concentrations in the organic phases were carried out using HPLC. The apparatus (Kontron Instrument) was equipped with a UV-visible detector (220 mm). Details concerning the column (C_{18}-grafted silica) and the eluent (methanol/water mixture) can be found in Ref. 6.

The density measurements for obtaining the apparent molal volumes were performed with a digital densimeter (Anton Paar, Austria). The apparatus measures the resonant frequency of a mechanical oscillator (U-glass tubing) filled with the solution, and it gives, after adequate calibration with air and water, the density value to four significant digits.

The theoretical calculations to obtain the curves predicted from the Flory–Huggins treatment were performed with Excel software (Microsoft).

RESULTS AND DISCUSSION

A diagram showing the demixing line between the single organic phase and the biphasic system issued from its split into a middle phase and an upper one was presented in a previous publication (6). The initial concentration of DMDBTDMA in the organic phase was 0.46 M. Further experiments demonstrated that the concentrations of diamide measured in the separated phases for each particular equilibrium concentration of HNO_3 in the aqueous phase are independent of the initial DMDBTDMA concentration. The results appear to be consistent with the so-called lever rule (19). The experimental curve obtained in this manner is represented in Fig. 1, where the equilibrium composition of the organic phases has been plotted as a function of the nitric acid content of the aqueous phase. In order to apply treatment of the Flory–Huggins theory to these data, it was necessary to convert the extractant concentrations measured in both phases into volume fractions. This was done by calculating

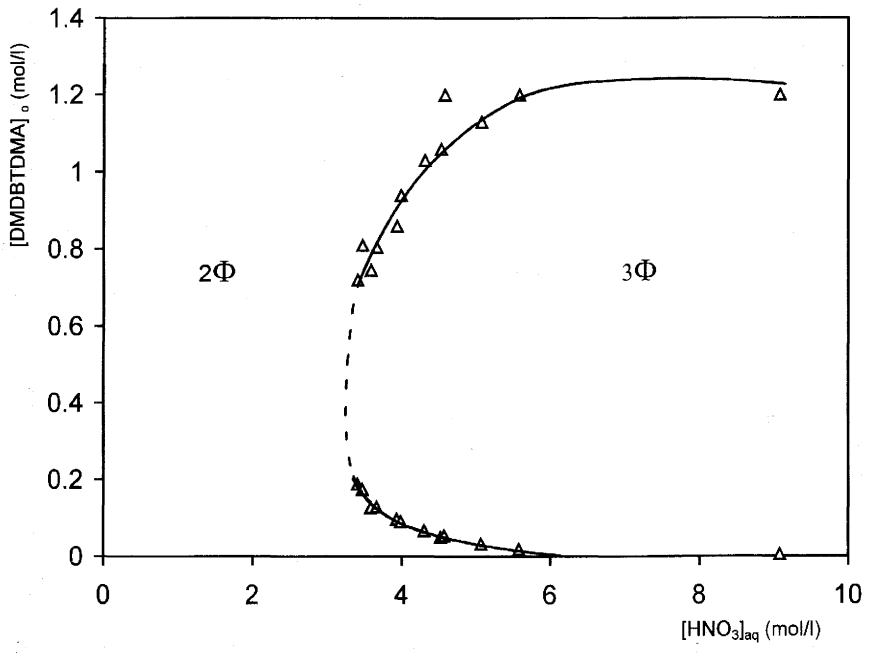


FIG. 1 Demixing line separating the 2-phase and the 3-phase systems: diagram showing the DMDBTDMA concentrations as a function of the aqueous equilibrium concentration of nitric acid (upper part of the curve: concentrations in the middle phase; lower part of the curve: con centrations in the upper phase).

the apparent molal volumes φ_2' and φ_2'' of the assumed DMDBTDMA:HNO_3 complex (of molecular weight M_2) from the densities d of each phase according to (20):

$$\varphi_2 = \frac{M_2}{d_0} - 10^3 \frac{d - d_0}{d_0 C} \tag{5}$$

where d_0 is the density of dodecane (0.7460) and C is the concentration of DMDBTDMA. The values of φ_2' and φ_2'' are necessarily roughly approximated since the nitric acid content was a simple estimate and the presence of a small amount of water in the organic phase was neglected. It was then assumed that

$$v_2 = C\varphi_2/1000 \tag{6}$$

where the concentration C is in $mol \cdot dm^{-3}$ and φ_2 is in $cm^3 \cdot mol^{-1}$.

We have used the procedure described by Flory (16) to solve Eqs. (1)–(2). After series expansion of the logarithmic terms, introduction of new variables, and rearrangements we obtain

$$(\gamma - 1)^3 v_2'^2 + 12 v_2' (\gamma + 1)[(\gamma + 1)(\ln \gamma)/2 - (\gamma - 1)]/x - 12 \times [(\gamma + 1)(\ln \gamma)/2 - (\gamma - 1)]/x = 0 \tag{7}$$

where

$$\gamma = v_2''/v_2' \tag{8}$$

By fixing the value of x, this quadratic equation is easily solved for different values of γ to obtain v_2', from which v_2'' is immediately calculated. The values of the interaction parameter are then deduced from Eq. (2) which can be rearranged to give

$$\chi_{12} = \frac{\alpha + (v_2'' - v_2') - \beta v_2'}{(v_2'' - v_2')[2 - (v_2'' + v_2')]} \tag{9}$$

with

$$\alpha = (\ln \gamma)/x \tag{10}$$

$$\beta = (\gamma - 1)/x \tag{11}$$

The approximation made in establishing Eq. (6) is normally strictly valid when v_2' and v_2'' are small. However, the percentage error introduced by the approximation [3.6% at a volume fraction of 0.6 (17)] can be considered small enough even at the large volume fractions considered in the present work.

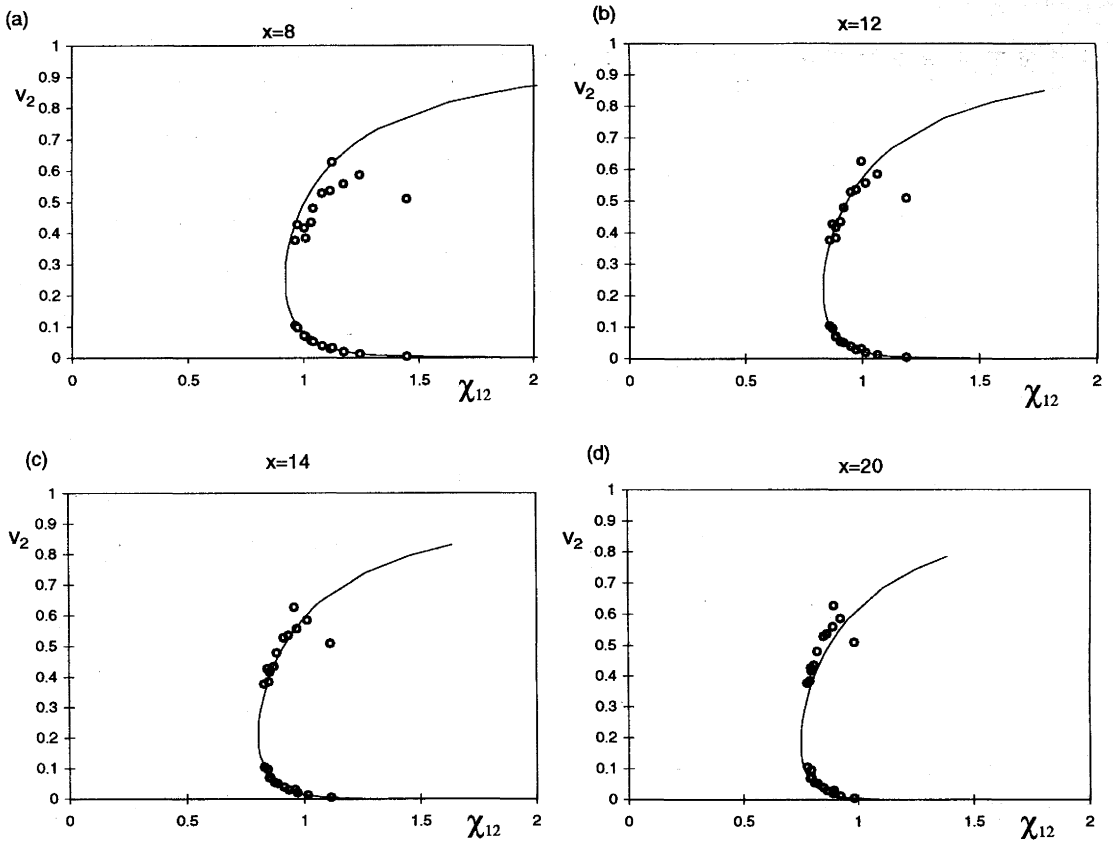


FIG. 2 Phase compositions as a function of the interaction parameter χ_{12} for different values of x. Prediction of the Flory–Huggins theory compared with the experimental determinations of the volume fractions of the DMDBTDMA extractant (see text). Solvent: dodecane.

For a given value of the parameter x, we can calculate the interaction parameter χ_{12} for each pair of experimental values (v'_2, v''_2) corresponding to a well-defined equilibrium concentration of nitric acid in the aqueous phase. The results of the simulations obtained for different values of x are represented in Figs. 2(a–d), and we recall that, according to Eq. (4), each value of x is associated with a value of the aggregation number n. The agreement between the experimental points and the theoretical prediction has been tested in the range of x between 8 ($n = 2.7$) and 20 ($n = 6.8$). Outside this range the quality of the fitting of the experimental data becomes very poor. The sum of squared deviations have been plotted as a function of the assumed value of x in Fig. 3. We have either considered all the data points available or omitted the two of them corresponding to the highest χ_{12} value. This is justified by the fact that the approximations made become less and less acceptable when the HNO_3 concentration is increased, making questionable the calculation of the apparent molal volume. When the two data points obtained for the largest acidity are omitted, the minimum deviation is obtained for $x = 14$, which corresponds to an aggregation number $n = 4.75$ (note that these values are only slightly different when the calculations involve all the data). This result is extremely in-

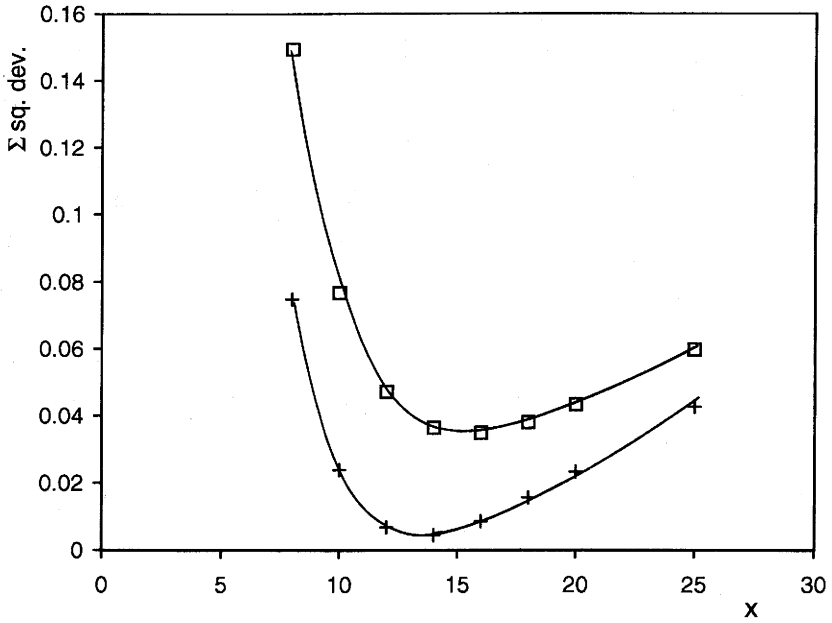


FIG. 3 Sum of squared deviations (between the predicted curves and the experimental values) as a function of x. □: considering all available data points. +: omitting the two data points obtained for the largest acidity.

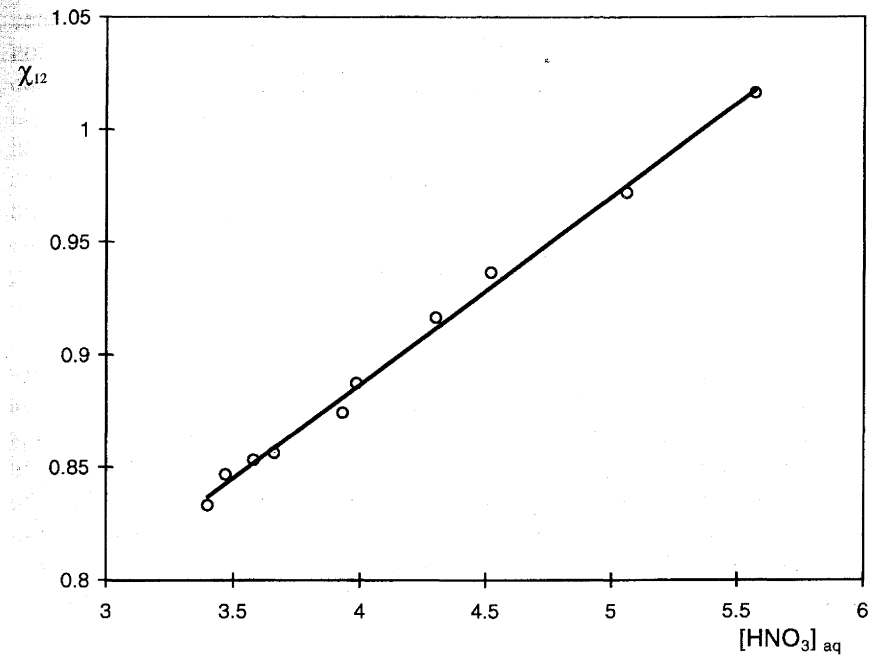


FIG. 4 Relation between the interaction parameter χ_{12} and the concentration of nitric acid in the aqueous phase for the best x-value ($x = 14$). Solvent: dodecane. The equation of the straight line best fitting the data is $\chi_{12} = 0.0833[HNO_3] + 0.5539$.

teresting because it is in very close agreement with the previous determinations [$n = 4$ in TPH (7) and $n = 5$ in dodecane (6)]. It thus strongly reinforces our confidence in the present approach to the problem of third-phase formation.

The relation between the aqueous phase acidity and the interaction parameter χ_{12} is shown in Fig. 4. The linear behavior observed makes very easy to change the scale from χ_{12} to $[HNO_3]$, and the results presented in Figs. 2(a–d) could just as well have been plotted as a function of the nitric acid concentration in the abscissa. It should be emphasized here that the curve giving the pair of values (v_2', v_2'') as a function of χ_{12} is universal for a fixed value of x. Only the relation between χ_{12} and $[HNO_3]$ will change. When $v_2' = v_2''$, the critical value of χ_{12} obtained in dodecane for $x = 14$ ($\chi_{12} = 0.80$) is thus expected to control the stability of the organic phase, whatever the nature of the diluent.

The model is indeed able to predict in a very satisfying way the influence of the nature of the diluent on the maximum loading of nitric acid in the aqueous phase before the formation of a third phase. Referring to the experimental

TABLE 1
Molecular Parameters Characterizing the Different Solvents Used in This Work (from Ref. 22).

Solvent	δ_1	V_1 (cm^3/mol)
n-Hexane	7.3	131.6
n-Dodecane	7.8	228.6
n-Hexadecane	8	294.1
Toluene	8.9	106.8

data obtained in *n*-hexane, *n*-hexadecane, and toluene which have been reported by Erlinger et al. (21), we have calculated the phase separation curves for these three solvents. Using Eq. (3), we can calculate for each value of χ_{12} (associated with a nitric acid concentration through the linear dependence shown in Fig. 4: $\chi_{12} = 0.0833\ [HNO_3] + 0.5539$), an apparent value of δ_2, the solubility parameter characterizing the behavior of the diamide extractant at each specific acidity. For that we only need the values of V_1 and δ_1 for dodecane (see Table 1). Knowing the variations of δ_2 with the equilibrium con-

TABLE 2
Apparent Values of the Solubility Parameter δ_2 in Dodecane for the Assumed 1:1 Extractant/HNO_3 Complex at Different Acidities and Corresponding Calculated Values of the Interaction Parameter χ_{12} in Hexane, Hexadecane, and Toluene

		χ_{12}			
$[HNO_3]_{aq}$ (mol/L)	δ_2	*n*-Hexane	*n*-Dodecane	*n*-Hexadecane	Toluene
0	10.327	0.49	0.59	0.64	0.09
1	10.47	0.53	0.66	0.72	0.11
2	10.613	0.58	0.73	0.81	0.13
3	10.756	0.63	0.81	0.9	0.15
4	10.899	0.69	0.89	1	0.17
5	11.041	0.74	0.97	1.1	0.2
6	11.184	0.8	1.06	1.2	0.22
7	11.327	0.86	1.15	1.31	0.25
8	11.47	0.92	1.24	1.43	0.28
9	11.613	0.99	1.34	1.55	0.32
10	11.756	1.05	1.44	1.67	0.35
11	11.899	1.12	1.55	1.8	0.39
12	12.042	1.19	1.66	1.94	0.42
13	12.185	1.27	1.77	2.08	0.46
14	12.328	1.34	1.89	2.22	0.51

centration of nitric acid in the aqueous phase and assuming that the values are not affected (or very weakly affected) by the nature of the diluent, we can calculate the χ_{12} values associated with the three solvents mentioned above, using the parameters given in Table 1, which have been taken from Ref. 22. We have collected in Table 2 the corresponding values of χ_{12} when the nitric acid concentration is varied. It can be easily checked that, as for dodecane (Fig. 4), the variation of χ_{12} with the aqueous concentration of HNO_3 is practically linear or very close to linear (a slight upward curvature could better fit the experimental points).

Figure 5 shows the simulated curves for three of the solvents considered in this work. For toluene there is no possible demixing (χ_{12} always remains smaller than the critical value of 0.80): the calculated values are outside the accessible range of nitric acid concentration, in perfect agreement with the observations of Erlinger et al. (21). For the three linear hydrocarbons, the demixing values drawn from Fig. 5 are almost exactly as expected from the above-mentioned results. The experimental (theoretical) values for the lower nitric acid concentrations leading to phase separation are the following: *n*-hexade-

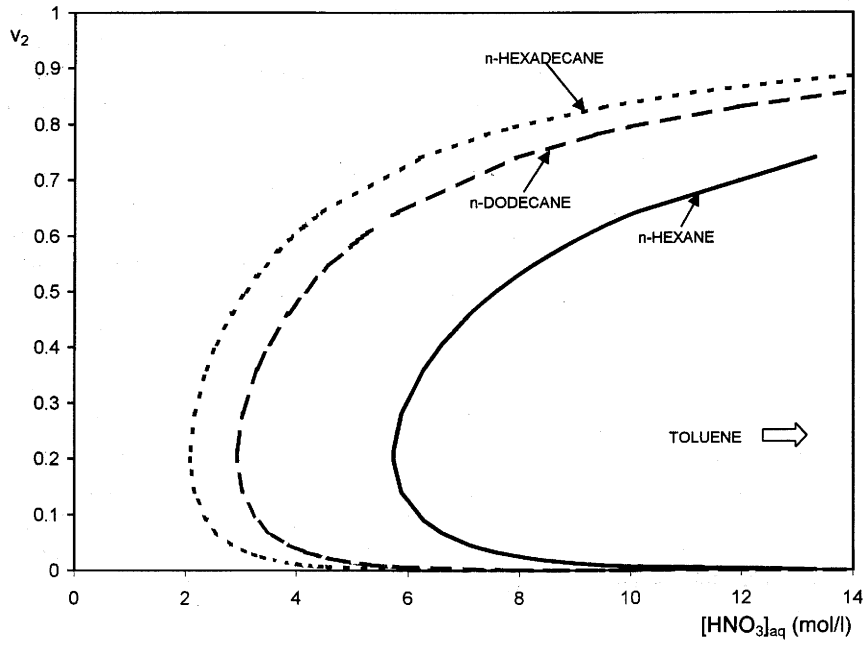


FIG. 5 Predictions of the demixing lines separating the 2-phase and the 3-phase systems for the solvents *n*-hexadecane, *n*-dodecane, and *n*-hexane. The prediction for toluene is outside the indicated range of nitric acid concentration.

cane, 2.2 ± 0.1 (2.1); *n*-dodecane, 3.5 ± 0.1 (3.0); and *n*-hexane, 5.4 ± 0.1 (5.7). A complete comparison of the experimental results with the predicted demixing lines would require new experiments to convert the DMDBTDMA concentrations reported in Ref. 21 in volume fractions. Nevertheless, the theoretical prediction from the Flory–Huggins theory and from the solubility parameters can already be considered as excellent.

This work should only be considered as a first attempt to predict third-phase formation using the same concepts as in the Flory–Huggins theory, which applies to the thermodynamics of polymer solutions. The striking point is that, in spite of the approximations involved, the regular solution theory appears to be well suited for this purpose, as indicated by the excellent agreement between the experimental results and the theoretical prediction in any particular solvent. A posteriori, this strongly suggests that the phase splitting is essentially governed by the solubility gap between the diluent (characterized by a solubility parameter δ_1) and the diamide/HNO_3 aggregates (characterized by a parameter δ_2, which is a function of the acidity but is almost independent of the nature of the diluent). The physical phenomenon behind the variation of δ_2 with the acidity can be attributed to the modification of the polarity in the core of the aggregates. The fact that this simple modification is able to drastically change the solvent/aggregates interactions argues in favor of an open aggregate structure (open meaning accessible to the solvent; see Fig. 14 in Ref. 6) rather than in favor of a classical reverse micellar structure (note that from this point of view, the term "reverse micelle" is probably improper to qualify such aggregates, although it has often been used).

We have made the hypothesis that the dependence of χ_{12} *with the nitric acid concentration* is entirely supported by δ_2 and not by δ_1. This can be further justified by the fact that very little nitric acid can be extracted by the organic solvent itself (distribution coefficient $<< 1$). Consequently δ_1 can be considered as an intrinsic solubility parameter of the solvent, contrary to δ_2 which is only an apparent parameter. At the present stage of this work the good predictions of the solvent effect were obtained taking the same value of x as for dodecane ($x = 14$) and ignoring the implied change of the aggregation number of the diamide molecules.

Coming back to the value of the diamide aggregation number n, which was estimated from the best fit of the experimental data obtained in dodecane with the curve predicted from the Flory–Huggins theory, the following comments have to be made. According to the definition used for x (Eq. 4), it should be emphasized that the obtained value of n depends on the value adopted for the V_2/V_1 ratio (or for the M_2/M_1 ratio used as a first approximation). For reasons already discussed in the preceding parts, we felt it justified to assume in the treatment a DMDBTDMA:HNO_3 complex in a 1:1 stoichiometry, and this has led us to an aggregation number $n = 4.75$ (in dodecane), in remarkable agree-

ment with other values from the literature. Any change in the adopted value for the M_2/M_1 ratio would lead to different values of n. So, for instance, if the simple diamide molecule was considered in place of the diamide:HNO_3 complex, we would end up with an aggregation number close to 9 instead of being close to 5. This would not drastically change the conclusions of the present work except that the interacting aggregates would be slightly larger than previously reported.

CONCLUSIONS

In this paper we have proposed a new approach to predict the phenomenon of third-phase formation. This approach, based on the analogy of the demixing curve with that obtained for the clouding point phenomenon of nonionic surfactants, makes use of the Flory–Huggins theory of polymer solutions. The theory allows the calculation of the interaction parameter χ_{12} between the extractant aggregates and the diluent. χ_{12}, which has been shown to be correlated with the nitric acid content of the system, provides a way of measuring the solubility of the extractant aggregates. The prediction of the demixing curves was shown to take into account the effect of the nature of the diluent by simply introducing in the model the relevant molecular parameters (molar volume and solubility parameter). This preliminary work needs to be extended in order to examine the effect of factors known to reduce third-phase formation; for instance, the use of branched solvents or the addition of phase modifiers (9, 10).

The next step will be to see how to explain the fact that the presence of metal ions in one particular solvent can change the acid content inducing third-phase formation. The general observation is that the presence of metal ions decreases the concentration of nitric acid necessary for demixing (1). The metal complexation thus decreases the solubility parameter δ_2 associated with the extractant. One can consequently assume that the interactions between the metal ions and DMDBTDMA play a role analogous to the interactions of the extractant with the protons and can, in some manner, replace them.

ACKNOWLEDGMENTS

This joint project was initiated within the framework of GDR (Groupement de Recherche) P.R.A.C.T.I.S. The authors thank Drs. C. Madic and M. C. Charbonnel (CEA, Marcoule) for providing them with the DMDBTDMA extractant and for fruitful discussions. They also acknowledge the valuable help of E. Dumortier (L.C.P.O.C., Nancy) for computer work.

REFERENCES

1. L. Nigond, N. Condamines, P. Y. Cordier, J. Livet, C. Madic, C. Cuillerdier, C. Musikas, and M. J. Hudson, *Sep. Sci. Technol., 30*, 2075 (1995).
2. G. M. Gasparini and G. Grossi, *Ibid., 15*, 825 (1980).
3. L. Nigond, C. Musikas, and C. Cuillerdier, *Solv. Extr. Ion Exch., 12*, 261 (1994).
4. L. Nigond, C. Musikas, and C. Cuillerdier, *Ibid., 12*, 297 (1994).
5. M. C. Charbonnel, Thèse de Doctorat de l'Université Blaise Pascal, 1988. Published as CEA-R-5469.
6. C. Erlinger, D. Gazeau, T. Zemb, C. Madic, L. Lefrancois, M. Hebrant, and C. Tondre, *Solv. Extr. Ion Exch., 16*, 707 (1998).
7. L. Nigond, Thèse de Doctorat de l'Université Blaise Pascal, 1992. Published as CEA-R-5610.
8. K. Osseo-Asare, *Adv. Colloid Interface Sci., 37*, 123 (1991).
9. P. R. Vasudeva Rao and Z. Kolarik, *Solv. Extr. Ion Exch., 14*, 955 (1996).
10. B. F. Smith, K. V. Wilson, R. R. Gibson, M. M. Jones, and G. D. Jarvinen, *Sep. Sci. Technol., 32*, 149 (1997).
11. R. J. Baxter, *J. Chem. Phys., 49*, 2770 (1968).
12. J. Goldfarb and L. Sepulveda, *J. Colloid Interface Sci., 31*, 454 (1969).
13. R. Kjellander, *J. Chem. Soc., Faraday Trans. 2, 78*, 2025 (1982).
14. K. Weckström and M. Zulauf, *J. Chem. Soc., Faraday Trans. 1, 81*, 2947 (1985).
15. G. Champetier (Ed.), *Chimie Macromoléculaire, Vol. II*, Hermann, Paris, 1972, p. 13.
16. P. J. Flory, *J. Chem. Phys., 12*, 425 (1944).
17. J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott (Eds.), *Regular and Related Solutions*, Van Nostrand Reinhold, New York, NY, 1970, p. 189.
18. D. Blankschtein, G. M. Thurston, M. R. Fish, and G. B. Benedek, in *Micellar Solutions and Microemulsions* (S.-H. Chen and R. Rajagopalan, Eds.), Springer-Verlag, New York, NY, 1990, Chap. 10, p. 185.
19. D. F. Evans and H. Wennerström (Eds.), *The Colloid Domain*, VCH Publishers, New York, NY, 1994, p. 419.
20. F. J. Millero, in *Water and Aqueous Solutions* (R. A. Horne, Ed.), Wiley-Interscience, New York, NY, 1972, p. 159.
21. C. Erlinger, C. Madic, and T. Zemb, Communication at Journées P.R.A.C.T.I.S. 1997, Villeneuve-les-Avignon, January 15, 1998.
22. A. Beerbower and M. W. Hill, *McCutcheon's Detergents and Emulsifiers Manual*, Allured Publishing Co., Ridgewood, NJ, 1971, p. 223.

Received by editor May 12, 1998
Revision received September 1998