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The role of natural convection in the dissolution of benzoic acid in wafer,
carbon tetrachloride and benzene-carbon tetrachloride mixtures

ΕΚΠΑ

By TH. YANNAKOPOULOS and M. PIPINIS

The role of natural convection in the dissolution of benzoic acid in water, carbon tetrachloride and benzene - carbon tetrachloride mixtures

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The distribution of the rate of dissolution of rods of benzoic acid, vertically immersed in water is found to be inversely proportional to the fourth root of the distance from the origin of the density current. The dependence of the dissolution rate on the deviation from the vertical position is also investigated. In the case of mixture of carbon tetrachloride - benzene the results show a nearly independent rate of dissolution from the composition of the solvent up to a composition of 60% in benzene. Beyond this composition the rate of dissolution increases steadily. The results are discussed and explained in terms of the density current existing at the interface.

The limiting current density distribution at a height x on a vertical plate electrode under natural convection conditions is given by several authors (1, and references therein). The final expressions of the limiting current density distribution are of the form:

$$i_x = k'x^{-1/4} \quad (1)$$

Where: i_x the limiting current density at a height x from the leading edge, and k' includes quantities such as bulk concentration, density, kinematic viscosity, acceleration of gravity, diffusion coefficient and the Faraday constant. Such a distribution of the limiting current

identical to that of vertical electrodes and thus an expression similar to Eq. (1) must be valid.

Thus one can write for the dissolution rate s_x at a height x from the leading edge (from the

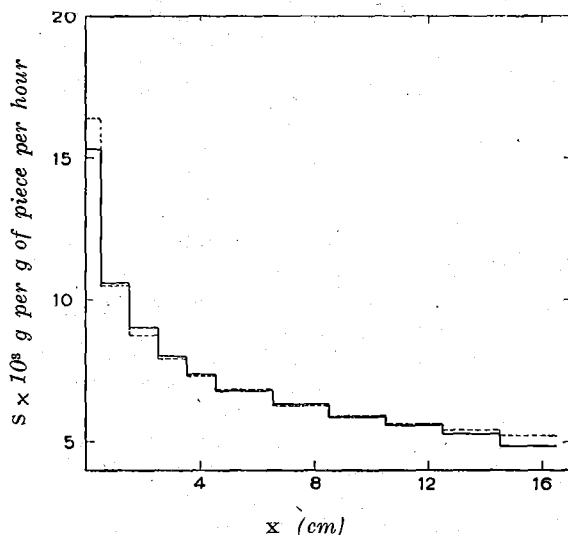


Fig. 1. Observed distribution in water. The dashed line corresponds to the values of last column of table I.

density has been confirmed experimentally by several authors (2, 3, 4).

The problem of the distribution of dissolution rate of nonelectrolytes should be mathematically

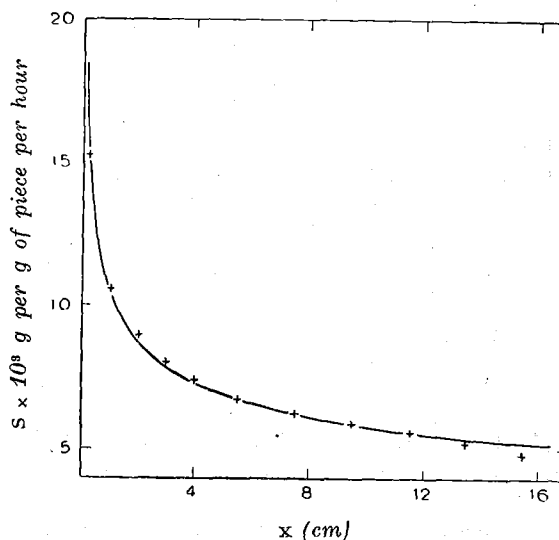


Fig. 2. Distribution rate. The observed mean values were taken as true values at the middle of each piece.

origin of the density current) of a rod immersed vertically in a suitable bath

$$s_x = \frac{k}{x^{1/4}} \quad (2)$$

Where: k contains the same quantities as the analogous expression (1) except the Faraday constant. In a previous paper the authors (5) have attempted to verify Eq. (2) in the case of dissolution of rods of marble in aqueous hydrochloric acid solution. The results showed a shift of the dissolution distribution from an inverse fourth root dependence on x to a uniform shape with

increasing concentration of hydrochloric acid.* Only at very low concentrations of hydrochloric acid an inverse fourth root dependence on x is to be expected. The deviations observed at finite concentrations were attributed to the disruptive effect of carbon dioxide bubbles on the diffusion layer, especially at higher concentrations of the acid.

This paper is concerned with the dissolution rate distribution of benzoic acid rods vertically immersed in solvents such as water, carbon tetrachloride and mixtures of benzene-carbon tetrachloride without any mechanical stirring.

Solvent water

The experimental technique was essentially the same as the one we used in the case of marble (5). Benzoic acid powder was pressed to form

This is nearly true in this case, as it will be shown shortly, except for the first two pieces located at the origin of the current density.

In Fig. 3 a logarithmic plot of the distribution is shown. From this plot the exponent $n = 0.26$ and the value of $k = 105.8 \times 10^{-4}$ was calculated. Averaging the expression (2) in its general form one obtains:

$$(s)_{\text{avg}} = \frac{1}{x_2 - x_1} \int_{x_1}^{x_2} (s)_x dx = \frac{k}{(1+n)(x_2 - x_1)} \left(x_2^{1-n} - x_1^{1-n} \right) \quad (3)$$

on the other hand

$$s_x = \frac{k}{x^n} \quad (4)$$

Equating these two expressions

Table I. Experimental results for the dissolution of vertical benzoic acid rods.

Piece No.	Covered distance x cm	R u n N o.							Mean of 7 Runs	Calculated Eq. 3
		1	2	3	4	5	6	7		
Avg. loss of weight in g per g of piece per hour $\times 10^3$										
1	0 to 0.5	16.74	14.58	15.14	15.56	14.56	15.26	15.18	15.29	16.40
2	0.5 to 1.5	11.35	10.31	10.86	10.81	9.77	10.16	10.80	10.58	10.49
3	1.5 to 2.5	9.47	8.39	8.75	9.58	8.24	9.05	9.57	9.01	8.74
4	2.5 to 3.5	8.21	7.51	8.01	8.81	7.73	8.05	7.85	8.02	7.88
5	3.5 to 4.5	7.72	6.95	6.80	8.06	7.86	7.40	7.30	7.44	7.30
6	4.5 to 6.5	6.58	6.33	6.22	8.13	6.85	6.56	6.66	6.76	6.78
7	6.5 to 8.5	6.18	5.74	5.98	7.38	6.47	6.11	6.12	6.28	6.25
8	8.5 to 10.5	5.83	5.31	5.93	6.55	5.93	5.83	5.77	5.88	5.90
9	10.5 to 12.5	5.41	5.07	5.92	6.39	5.50	5.40	5.52	5.60	5.62
10	12.5 to 14.5	5.41	5.02	5.22	6.12	5.36	4.83	4.73	5.24	5.40
11	14.5 to 16.5	4.94	4.73	4.95	6.22	5.13	3.95	3.85	4.80	5.22

cylindrical rods in a way similar to that of Wildermann (6). The pressure applied was estimated at 1500 kg/cm^2 . The rods had a diameter of 1.2 cm. For each run, eleven rods of three different heights were used as follows: six of 2 cm, four of 1 cm and one of 0.5 cm height. These pieces were placed on top of one another to form a rod of a total height of 16.5 cm.

The rod, tightly clamped by means of a plastic frame, was immersed in a 10 lit. water bath for a period of 15 hours.

The temperature of the bath was controlled at 21°C .

The loss of weight of each piece of benzoic acid during the immersion was determined.

In Table I the results of seven runs are summarized.

In Fig. 1 the mean values of Table I are plotted against the distance x . In Fig. 2 the same dissolution rate distribution is shown with the assumption that the observed average values represent the true values at the middle of each piece.

$$x^n = \frac{(1-n)(x_2 - x_1)}{1 - \frac{x_2^{1-n}}{x_1^{1-n}}} \quad (5)$$

By using $n = 0.26$ in Eq (4) one obtains for the first three pieces (0 to 0.5, 0.5 to 1.5, 1.5 to 2.5 cm) the values of x : 0.157, 0.953, 1.972 cm which differ from the distance of the middle of each piece by 37%, 5% and 1.5% respectively. In Fig. 3 the dashed line corresponds to the values corrected as just described.

The slope of this line is -0.25 and the value of k obtained from this is 103.5×10^{-4} .

The values of the last column in Table I are obtained by using the above value of k .

Experiments were also made to show the possible effects of deviations of the rod from the vertical position. A comparison among the three main positions e.g. vertical, horizontal and at an angle of 45 degrees, showed that the rate

* Note that column n in Table II, ref. 5 should be inverted (see erratum p. 64 this issue).

of dissolution was the same in the two last positions and more than 50% higher than in the vertical one.

rod was immersed only for a period of ten minutes. A typical curve obtained from those ex-

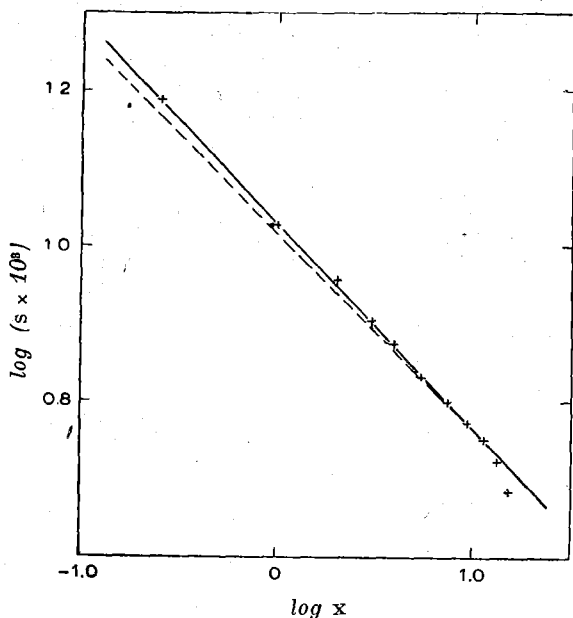


Fig. 3 Distribution rate in a logarithmic scale. The dashed line corresponds to the corrected values.

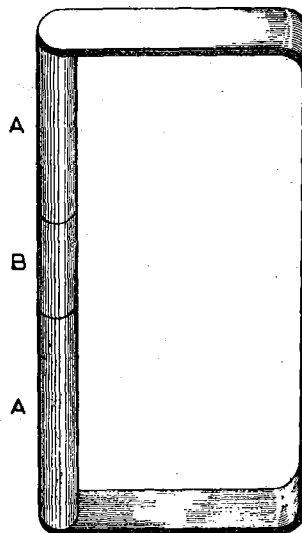


Fig. 5. Holder for the benzoic acid rod.
B: benzoic acid. A: glass rods

Solvent carbon tetrachloride and benzene-carbon tetrachloride mixtures.

Experiments were also made in order to

periments is shown in Fig. 4. However the results are of qualitative character, because at the end of the experiment the rods had become very porous. It is clear from Fig. 4 that the den-

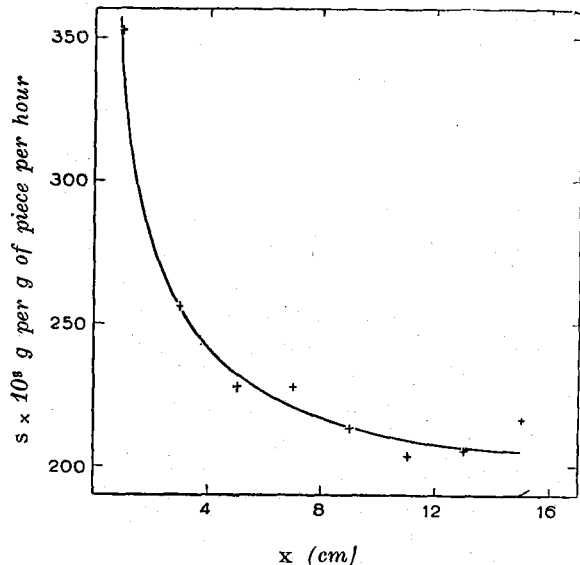


Fig. 4. Distribution rate of benzoic acid rods in carbon tetrachloride.

establish the dissolution rate distribution in carbon tetrachloride. Owing to greater solubility of benzoic acid in this solvent, the composite

sity current is directed upwards showing that the density of the saturated solution is lower than that of the pure solvent. On the contrary in ben-

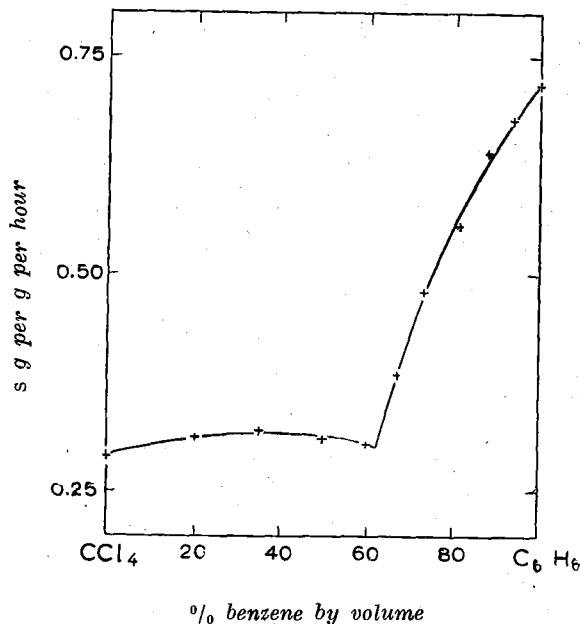


Fig. 6. Dissolution rate of benzoic acid rods, in mixtures of carbon tetrachloride - benzene.

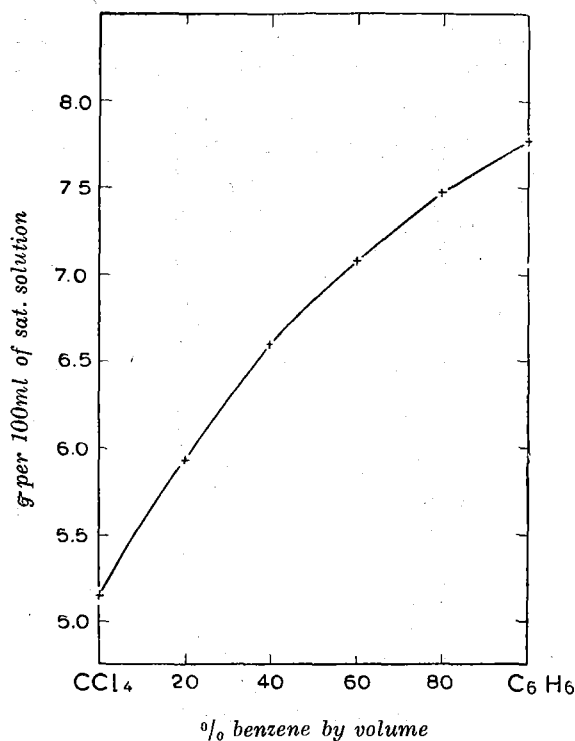


Fig. 7. Solubility of benzoic acid in carbon tetrachloride-benzene mixtures.

zene the density current is reverse. Consequently it would be of some interest to study the rate of

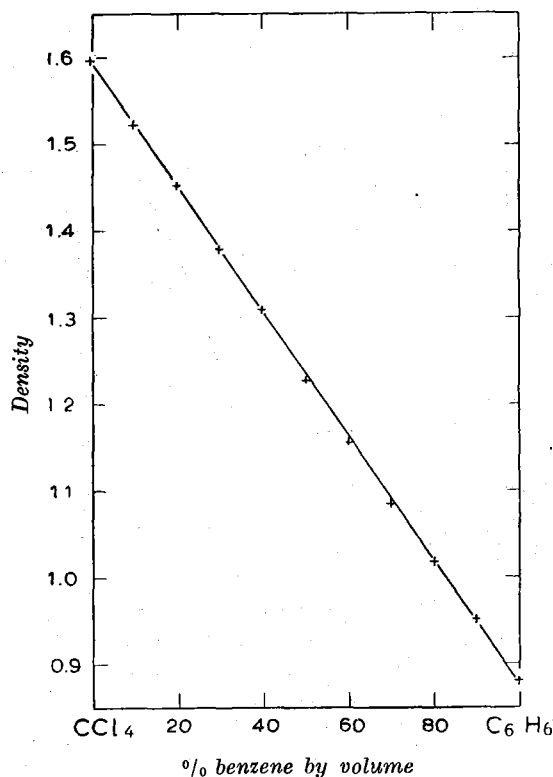


Fig. 8. Density of carbon tetrachloride-benzene mixtures

dissolution of benzoic acid, in form of rods, in mixtures of the above solvents ranging from pure benzene to pure carbon tetrachloride.

For this purpose a rod of benzoic acid of 2 cm height was clamped as it is shown in Fig. 5 and was immersed in the solvent, for ten minutes. The loss of weight was determined. The experiments were made at 21°C. The results are shown in Fig. 6.

For a qualitative explanation of the curve shown in Fig. 6 we measured a) the solubilities of benzoic acid in benzene-carbon tetrachloride mixtures b) the densities of these mixtures and c) the densities of saturated solutions of benzoic acid in mixtures of the same solvents. The re-

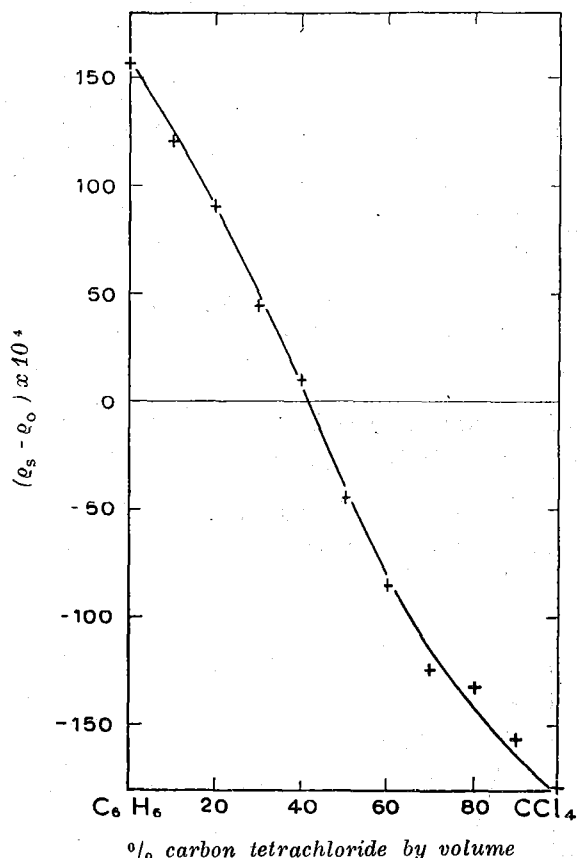


Fig. 9. Density difference as a function of composition. ρ_0 , density of the pure mixture. ρ_s , density of the same mixture saturated with benzoic acid.

sults are shown in Fig. 7, 8, 9. It is clear that the dependence of the rate of dissolution on the composition of the solvent can not be explained in terms of the solubility behaviour of benzoic acid as shown in Fig. 7 only. In Fig. 9 the difference of the density of the pure solvent ρ_0 from the density ρ_s of the saturated solution of benzoic acid in the same solvent is plotted against the composition of the solvent. The difference $\rho_s - \rho_0$ is equal to the difference of the densities

at the interface and in bulk solution during the dissolution process. It is positive in mixtures rich in benzene and decreases continuously with increasing carbon tetrachloride percentage up to a composition of 60% in benzene where it becomes zero, to attain subsequently negative values. Fig. 9 allows for an adequate interpretation of the dependence of the dissolution rate on the composition of the solvent (Fig. 6). Thus along the first branch of the diagram the rate of dissolution should increase by addition of benzene, because in benzene the solubility of benzoic acid is higher. Addition of benzene however reduces at the same time the density difference and consequently the density current too. Thus there appear two counter acting factors which result almost in an independence of the dissolution rate from the composition up to 60% in benzene. Beyond this composition there is a simultaneous increase in both the solubility and the density difference (the latter increasing in absolute value, which merely means an inversion of the density current). Thus the subsequent steady increase of the dissolution rate is understood.

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(National University, Lab. of Physical Chemistry Athens, Greece).

Π Ε Ρ Ι Λ Η Ψ Ι Σ

Ἡ ἐπίδρασις τῆς φυσικῆς ἀναταράξεως ἐπὶ τῆς ταχύτητος διαλύσεως τοῦ βενζοϊκοῦ ὀξέος εἰς ὕδωρ, τετραχλωράνθρακα καὶ μίγματα βενζολίου-τετραχλωράνθρακος

ΥΠΟ Θ. ΓΙΑΝΝΑΚΟΠΟΥΛΟΥ καὶ Μ. ΠΙΠΙΝΗ

Εἰς προγενεστέραν ἐργασίαν (5) εἶχεν δειχθῆ ὅτι ἡ κατανομή τῆς ταχύτητος διαλύσεως ράβδων μαρμάρου, κατακορύφως βυθιζομένων εἰς ἀραιὰ ὕδατικά διαλύματα ὑδροχλωρικοῦ ὀξέος εἶναι συνάρτησις τῆς συγκεντρώσεως τοῦ ὀξέος.

Ἡ ἐξάρτησις τῆς ταχύτητος διαλύσεως ἀπὸ τὴν ἀπόστασιν ἐκ τῆς ἀφετηρίας τοῦ ρεύματος πυκνότητος εἶναι μόνον εἰς τὴν ὀρικὴν περίπτωσιν ($c = 0$) ὁμοία πρὸς τὴν προβλεπομένην διὰ τὸ μαθηματικῶς ἀνάλογον πρόβλημα τῆς ὀρικῆς πυκνότητος ρεύματος κατὰ μήκος καθόδου, ὑπὸ συνθήκας φυσικῆς ἀναταράξεως. Αὐξανομένης τῆς συγκεντρώσεως ὁ ἐκθέτης n (ἐξισ. 4) συνεχῶς μειοῦται τείνων πρὸς τὸ μηδέν. Τοῦτο ἀπεδόθη εἰς τὴν ἀνατάραξιν τῆς στιβάδος διαχύσεως ὑπὸ τῶν φυσαλλίδων τοῦ ἐκλυομένου, διοξειδίου τοῦ ἀνθρακος.

Εἰς τὴν παροῦσαν ἐργασίαν ἐρευνᾶται ἡ κατα-

νομή τῆς ταχύτητος διαλύσεως ράβδων βενζοϊκοῦ ὀξέος εἰς ὕδωρ, τετραχλωράνθρακα καὶ μίγματα βενζολίου-τετραχλωράνθρακος. Τὰ ἀκόλουθα ἀποτελέσματα προέκυψαν :

α) Εἰς τὴν περίπτωσιν τοῦ ὕδατος διεπιστώθη ὅτι ἡ κατανομή τῆς ταχύτητος διαλύσεως εἶναι ἀντιστρόφως ἀνάλογος τῆς τετάρτης ρίζης τῆς ἀποστάσεως ἀπὸ τὴν ἀφετηρίαν τοῦ ρεύματος πυκνότητος. Ἐπίσης ἠρευνήθη ἡ ἐπίδρασις τῆς ἀποκλίσεως τῆς ράβδου ἀπὸ τὴν κατακόρυφον. Συγκεκριμένως ἐγένετο σύγκρισις τῆς διαλυτότητος 1) μὲ τὴν ράβδον κατακορύφως βυθιζομένην εἰς τὸ λουτρόν, 2) ὑπὸ γωνίαν 45° καὶ 3) ὀριζοντίως τοποθετημένην. Εἰς τὰς δύο τελευταίας περιπτώσεις ἡ ταχύτης διαλύσεως ἦτο περίπου ἡ αὐτή, ὑπερδιπλασία ὁμῶς τῆς παρατηρηθείσης μὲ τὴν ράβδον κατακορύφως τοποθετημένην.

β) Εἰς τὴν περίπτωσιν τετραχλωράνθρακος τὰ ἀποτελέσματα ἔχουν μᾶλλον ποιοτικὸν χαρακτήρα λόγω κυρίως τῆς μεγαλύτερας ταχύτητος διαλύσεως, ἡ ὁποία καθιστᾷ τὴν ἐπιφάνειαν τῆς ράβδου πορώδη καὶ γενικῶς ἀνώμαλον. Πάντως, ὡς ἐμφαίνεται ἐκ τοῦ Σχ. 4, τὸ ρεῦμα πυκνότητος εἶναι εἰς τὴν περίπτωσιν ταύτην ἀντίστροφον λόγω τοῦ γεγοῦστος, ὅτι ἡ πυκνότης κεκορεσμένου διαλύματος βενζοϊκοῦ ὀξέος εἶναι μικρότερα τῆς τοῦ καθαροῦ τετραχλωράνθρακος.

γ) Ἐνδιαφέρον παρουσιάζουν τὰ ἀποτελέσματα ταχύτητος διαλύσεως εἰς μίγματα βενζολίου-τετραχλωράνθρακος (Σχ. 6). Ὡς ἐμφαίνεται ἐκ τοῦ διαγράμματος τούτου ἡ ταχύτης διαλύσεως εἶναι σχεδὸν σταθερὰ ἀπὸ τοῦ καθαροῦ τετραχλωράνθρακος μέχρις συνθέσεως περίπου 60% εἰς βενζόλιον. Ἀπὸ τῆς συνθέσεως ταύτης αὐξάνεται ἡ ταχύτης διαλύσεως σταθερῶς. Ἀντιθέτως ἡ διαλυτότης τοῦ βενζοϊκοῦ ὀξέος εἰς μίγματα τῶν ὡς ἄνω διαλυτῶν μεταβάλλεται ὁμαλῶς μὲ τὴν σύνθεσιν (Σχ. 7). Εἰς τὸ Σχ. 9 δίδεται ἡ διαφορὰ τῆς πυκνότητος τοῦ διαλύτου ἀπὸ τὴν πυκνότητα κεκορεσμένου διαλύματος τούτου εἰς βενζοϊκὸν ὀξύ, ὡς ἐξάρτησις τῆς συνθέσεως τοῦ διαλύτου. Αὕτη εἶναι θετικὴ πρὸς τὴν πλευρὰν τοῦ βενζολίου μειουμένη συνεχῶς μέχρι συνθέσεως 60%, ὅπου καὶ μηδενίζεται, λαμβάνουσα ἀκολουθεῖ ἀρνητικὰς τιμὰς. Τὸ ὡς ἄνω διάγραμμα ἐπιτρέπει ἐπαρκῆ ἐρμηγίαν τῆς ταχύτητος διαλύσεως συναρτήσῃ τῆς συνθέσεως τοῦ διαλύτου (Σχ. 6). Οὕτω, εἰς τὸν πρῶτον κλάδον τοῦ διαγράμματος ἡ προσθήκη βενζολίου, εἰς τὸ ὁποῖον ἡ διαλυτότης τοῦ βενζοϊκοῦ εἶναι μεγαλύτερα, ἔπρεπε νὰ αὐξήσῃ τὴν ταχύτητα διαλύσεως. Ἐν τούτοις ἡ προσθήκη τοῦ βενζολίου ἔχει συγχρόνως ὡς ἀποτέλεσμα τὴν μείωσιν τῆς διαφορᾶς πυκνότητος καὶ ἐπομένως τῆς ταχύτητος τοῦ ρεύματος πυκνότητος. Ἡ ἀλληλεπίδρασις τῶν ὡς ἄνω δύο παραγόντων ἔχει ὡς ἀποτέλεσμα τὴν ἀνεξαρτησίαν τῆς ταχύτητος διαλύσεως ἀπὸ τὴν σύνθεσιν, μέχρι συνθέσεως 60% εἰς βενζόλιον. Ἀπὸ τῆς συνθέσεως ταύτης ἀκολουθεῖ αὐξήσις καὶ τῆς διαλυτότητος καὶ τῆς διαφορᾶς πυκνότητος (κατ' ἀπόλυτον τιμὴν, συνεπαγομένη μόνον ἀναστροφήν τοῦ ρεύματος πυκνότητος). Οὕτω

δικαιολογείται ή ακόλουθοῦσα σταθερά αύξησης τῆς ταχύτητος διαλύσεως.

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ΕΚΠΑ - Βιβλιοθήκη Γεωλογίας



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