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Gas Chromatographic Investigation of Solvents with Partial Miscibility*

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The solubility parameter theory has been used for the correlation of infinite dilution activity coefficients of hydrocarbons in mixed solvents (diethylene glycol and diethylphthalate) having partial miscibility in the liquid phase. The calculated values were in good agreement with those determined experimentally by GLC.

INTRODUCTION

Mixed solvents have been studied extensively with regard to the use of mixed liquid phases for analytical purposes[1,2], as well as to the comparison between the gas-liquid chromatographic (GLC) performances of mixed stationary phases and those of special couplings of GLC columns filled with pure stationary phases[3,4].

In this work we have investigated a pair of polar solvents (diethylene glycol and diethylphthalate) partially miscible in the liquid state with the aim to find a correlation between the activity coefficients of solutes in mixed solvents and those in pure solvents. The literature reports some investigations made by Maffiolo[5], Renon[6] and Wakzmundzki[7,8] on this subject, but only mixtures with complete miscibility were taken into consideration by these authors.

The study of solvents with partial miscibility is of considerable interest from both a theoretical and a practical point of view, because it can throw some light on the behaviour of the solvents in liquid-liquid chromatography[9].

EXPERIMENTAL

The activity coefficients of hydrocarbons in the stationary phases were determined according to the procedure of Desty and Swariton[10]. The various quantities appearing in the equation which gives the activity coefficients were evaluated as described before[11,12]. The GLC apparatus was a thermal conductivity chromatograph (Erba, Fractovap mod. B). The solvents and solutes used were reagent grade products (Erba, Fluka, BDH). To prepare the saturated stationary phases the two solvents were equilibrated at 25 °C.

RESULTS AND DISCUSSION

Table I reports the experimental activity coefficients of some hydrocarbons at 25 °C, 50 °C, 75 °C in the following stationary phases: diethylene glycol

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TABLE I.

Natural logarithms of the experimental infinite dilution activity coefficients at 25 °C, 50 °C and 75 °C of hydrocarbons in the pure stationary phases and in the mixed stationary phases (saturated at 25 °C): diethylene glycol (DEG), *diethylene glycol with diethylphthalate* ($x_{DEP} = 0.0353$) (DEG-DEP), *diethylene glycol saturated with diethylphthalate* (DEG_{sat}), *diethylphthalate saturated with diethylene glycol* (DEP_{sat}) *and diethylphthalate* (DEP).

Temperature/°C	DEG			DEG-DEP			DEG_{sat}			DEP_{sat}			DEP		
	25	50	75	25	50	75	25	50	75	25	50	75	25	50	75
Compound															
n-pentane	4.49	4.16	3.90	4.10	3.83	3.62	3.89	3.63	3.43	1.69	1.37	1.21	1.64	1.37	1.16
n-hexane	4.91	4.52	4.22	4.60	4.23	3.92	4.34	3.99	3.71	1.88	1.51	1.33	1.82	1.50	1.29
n-heptane	5.37	4.92	4.56	5.05	4.60	4.25	4.76	4.36	4.04	2.04	1.66	1.46	1.97	1.65	1.40
n-octane	5.81	5.34	4.94	5.57	5.02	4.57	5.20	4.76	4.38	2.20	1.81	1.60	2.14	1.79	1.53
n-nonane	6.22	5.71	5.30	6.02	5.46	4.90	5.63	5.12	4.70	2.36	1.95	1.72	2.33	1.92	1.65
n-decane	6.64	6.10	5.66	6.50	5.80	5.22	6.07	5.51	5.04	2.52	2.10	1.86	2.48	2.07	1.76
1-pentene	3.66	3.42	3.24	3.50	3.23	3.03	3.35	3.12	2.95	1.10	0.95	0.89	1.07	0.93	0.84
1-hexene	4.17	3.90	3.66	3.91	3.62	3.37	3.76	3.48	3.26	1.31	1.10	1.00	1.25	1.09	0.98
1-heptene	4.71	4.34	4.04	4.40	4.03	3.73	4.17	3.84	3.57	1.51	1.25	1.12	1.45	1.23	1.08
1-octene	5.22	4.77	4.43	4.92	4.45	4.07	4.64	4.20	3.84	1.68	1.40	1.26	1.67	1.38	1.18
cyclohexane	4.02	3.72	3.47	3.73	3.45	3.20	3.65	3.35	3.10	1.46	1.13	0.95	1.39	1.12	0.95
methylcyclohexane	4.53	4.19	3.90	4.29	3.96	3.65	4.07	3.72	3.43	1.60	1.29	1.13	1.56	1.27	1.07
ethylcyclohexane	5.00	4.57	4.26	4.83	4.32	3.95	4.44	4.03	3.70	1.75	1.44	1.26	1.74	1.42	1.22
benzene	2.06	1.94	1.83	1.95	1.80	1.67	1.75	1.62	1.53	0.10	0.04	0.10	0.04	0.05	0.11
toluene	2.60	2.41	2.25	2.45	2.23	2.06	2.21	2.02	1.89	0.27	0.14	0.07	0.20	0.09	0.02
ethylbenzene	3.09	2.88	2.70	2.94	2.65	2.44	2.68	2.51	2.36	0.44	0.32	0.22	0.36	0.22	0.15

(DEG), diethylene glycol with diethylphthalate (DEG-DEP; $x_{DEP} = 0.0353$ expressed as mole fraction), diethylene glycol saturated with diethylphthalate (DEG_{sat}), diethylphthalate saturated with diethylene glycol (DEP_{sat}) and diethylphthalate (DEP).

To give an example, the variation of the activity coefficients of some solutes at 25 °C as a function of the concentration (expressed as mole fraction) of the mixed stationary phase is presented in Fig. 1. It can be observed that no linear relation exists; this is a consequence of the excess free energy of the binary mixture of the two solvents and depends on the nature of the solute.

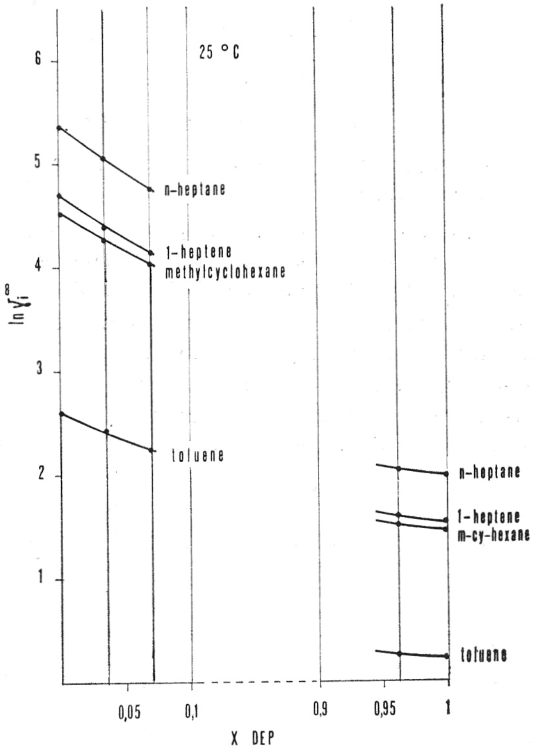


Fig. 1. Variation of activity coefficients of hydrocarbons at 25 °C as a function of stationary phase concentration (expressed as molar fraction).

In order to correlate the data obtained in mixed solvents with those obtained in pure solvents we have used the extension of the solubility parameter theory of Hildebrand and Scott[13-15], according to which the activity coefficient can be expressed as follows:

$$\ln \gamma_2^{\infty} = \frac{v_2}{RT} (C_{11} + C_{22} - 2\,C_{12}) + \ln \frac{v_2}{v_1} + \left(1 - \frac{v_2}{v_1}\right) \tag{1}$$

where

$$C_{ii} = \frac{\Delta U_i}{v_i} \quad C_{12} = (C_{11} \cdot C_{22})^{1/2} \tag{1a}$$

or

$$\ln \gamma_2^{\infty} = \frac{v_2}{RT}[(\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 - 2\,\psi_{12}] + \ln\frac{v_2}{v_1} + (1 - \frac{v_2}{v_1}) \tag{2}$$

where

$$C_{ii} = \lambda_i^2 + \tau_i^2$$

$$C_{12} = (\lambda_1 \cdot \lambda_2)^{1/2} \tag{2a}$$

The superscripts 1 and 2 refer to the pure stationary phase and to the solute, respectively. When mixed stationary phases are used, the solubility parameters λ_1 and τ_1 and the molar volume v_1 are replaced by $\bar{\lambda}$, $\bar{\tau}$ and $\bar{v}$:

$$\bar{\lambda} = \varphi_1 \lambda_1 + \varphi_3 \lambda_3$$

$$\bar{\tau} = \varphi_1 \tau_1 + \varphi_3 \tau_3 \tag{3}$$

$$\bar{v} = \varphi_1 v_1 + \varphi_3 v_3$$

where λ_1, λ_3, τ_1, τ_3 are the solubility parameters of the pure solvents (1 and 3) and φ_1 and φ_3 are volume fractions.

In Eq. (2) the cohesive energy of the solvents (C_{11}) and the solutes (C_{22}) is divided into a dispersional (λ) and a polar (τ) contribution, and an empirical parameter (ψ_{12})[15] (a function of the nature of the solute) is introduced, so that the deviations of the C_{12} term from the geometrical mean $\sqrt{C_{11} \cdot C_{22}}$ can be taken into account satisfactorily (Eqs. 1a and 2a).

We have assigned the solubility parameters to the various solutes and to diethylene glycol as described before[16]; the solubility parameters of diethylene glycol, of diethylphthalate and of the mixed solvents are reported in Table II;

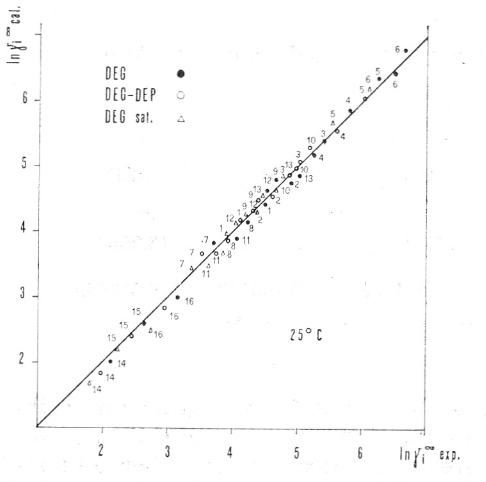
TABLE II.

Solubility parameters at 25 °C of the pure and mixed solvents.

	v	λ	τ
DEG	96.3	8.22	10.26
DEG-DEP	103.67	8.25	9.94
DEG_{sat}	110.48	8.28	9.65
DEP_{sat}	196.06	8.67	5.88
DEP	200.0	8.68	5.80

Temperature = 25 °C

the solubility parameters of the mixed solvents have been determined as the volume mean of those of the pure solvents. Using these solubility parameters in Eq. 2, we have calculated the activity coefficients of the solutes: the values obtained were in good agreement with the experimental activity coefficients (Figs. 2 and 3). The deviations are, on the average, less than 6%, and do not exceed 20%; this value, according to Maffiolo *et al.*[5] is still reasonable for the prediction of activity coefficients. The error is not enough to mask the effect due to the presence of the mixed solvent.



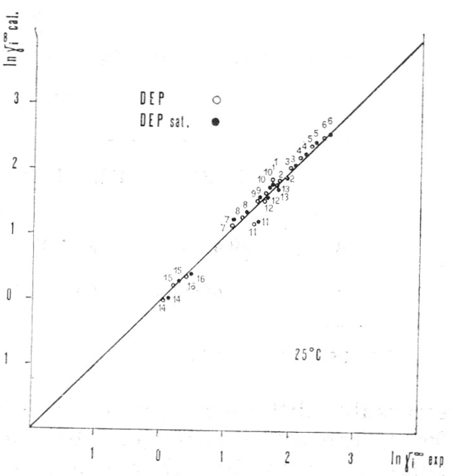


Fig. 2. Comparison between experimental activity coefficients and those calculated in according to ref. 15, and to eq. 2 in DEG, DEG—DEP, DEG_{sat} at 25 °C.

Fig. 3. Comparison between experimental activity coefficients and those calculated in according to ref. 15, and to eq. 2 in DEP, DEP_{sat} at 25 °C.

In order to overcome the difficulties involved (as various authors[15] still admit) in the choice of the suitable homomorph for dividing a solubility parameter into a polar and a non-polar contribution, we have adopted the treatment proposed by Maffiolo[5]. Accordingly, for the interpretation of the data relative to a series of solutes in a same solvent, the C_{12} term of eq. 1 can be expressed as follows:

$$C_{12} = A\,\lambda_2^{a} \tag{4}$$

where λ_2 is the solubility parameter of the solute, A and a are constants.

On the basis of the experimental activity coefficients of n-pentane and n-octane we have calculated the A and a values for the various stationary phases (Table 3). For the mixed stationary phases we have observed that the A value can be calculated according to the equation:

$$A_{\text{mixed phase}} = A_{\text{DEG}} \cdot x_{\text{DEG}} + A_{\text{DEP}} \cdot x_{\text{DEP}}$$

(x is the mole fraction), and that A and a are related by the following expression:

$$a = 0.00110847\ A^2 - 0.0630301\ A + 1.51716$$

This relation is valid for each mixed phase within its field of miscibility.

On the basis of these A and a values (Table III) we have estimated the activity coefficients for paraffins and cycloparaffins in the mixed phases considered (Fig. 4). The agreement between calculated and experimental values is very good (the discrepancies are on the average $< 4\%$); only n-hexane and cyclohexane show anomalous discrepancies ($> 10\%$) in the mixed stationary phases. The method proposed by Maffiolo has the advantage of being more sensitive to small errors in the evaluation of the cohesive energy of the solvent and enables the use of the concept of homomorph to be avoided. It has, however, the limitation of not being applicable in the given form[5] to the prediction of activity coefficients of olefins and aromatics. In fact, we have found

TABLE III.

A and a values of the eq. 4 for the pure and mixed stationary phases.

$$C_{12} = A \cdot \lambda_2^a$$

	DEG	DEG-DEP	DEG_{sat}	DEP_{sat}	DEP
A	29.4177	28.9176	28.4219	15.7951	15.2542
a	0.625008	0.621414	0.621152	0.798140	0.813699

Temperature = 25 °C

remarkable differences for olefins (about 40%) and for aromatics (more than 100%). The differences could be due to the existence in these solutes of a »polarity« (even through partial), as already pointed out by other authors[14].

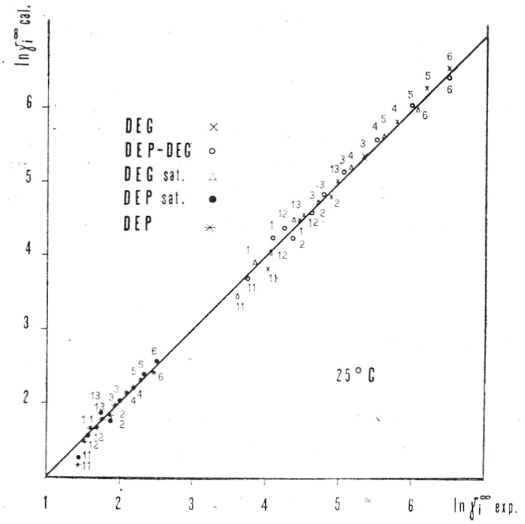


Fig. 4. Comparison between experimental activity coefficients of paraffins and cycloparaffins and those calculated with the eqs. 1 and 4 in DEG, DEG—DEP, DEG_{sat}, DEP_{sat}, DEP at 25 °C.

Evidently, in the case of olefins and aromatics the correlation with undivided solubility parameter of the solute is less significant, whereas the method based on the dividing of the solubility parameter gives better results, and the discrepancies between calculated and experimental activity coefficients are generally about or below 10%.

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SAŽETAK

Ispitivanje otapala s ograničenim mešanjem gasnom kromatografijom

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Upotrebili smo teoriju parametara topivosti za korelaciju koeficijenata aktiviteta beskonačno razređenih ugljikovih hidrata u mešanim razređivačima (dietilenglikol, dietilftalat) sa ograničenom stopom mešanja u tekućem stanju. Eksperimentalne vrednosti postignute sa gas-kromatografijom dobro se slažu sa teoretskim računima.

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