

## Note

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### Evaluation of solvent properties

#### A comparison of esters of 2-ethylhexanol\*

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The selection of the most suitable solvent to be used in industrial separations (*e.g.*, liquid-liquid extraction or extractive distillation) is of paramount importance to the chemical engineer. The best separating agent for a mixture of close-boiling compounds can be established on the basis of the relative volatilities and selectivities. As selectivity can be defined as the ratio of the activity coefficients at infinite dilution of two components separately dissolved in the solvent, and relative volatility can be defined as the product of this selectivity and the ratio of the vapour pressures of the two components, it is necessary to make a preliminary calculation, *e.g.*, by gas-liquid chromatography (GLC), of the limiting activity coefficients in the solvent examined for both components of the mixture to be separated.

#### EXPERIMENTAL

Four esters of 2-ethylhexanol were investigated with a view to their possible use as separating agents: di-2-ethylhexyl adipate (DOA), di-2-ethylhexyl sebacate (DOS), di-2-ethylhexyl phthalate (D2EEP) and tri-2-ethylhexyl phosphate (TOP). The activity coefficients at infinite dilution of some organic compounds in D2EEP and TOP were already available<sup>1-3</sup>. The activity coefficients in DOA and DOS were calculated by using homologous series of organic compounds (alkanes, alkenes, cycloalkanes, aromatic hydrocarbons, alcohols and acetates) as GLC solutes. To this end a thermal conductivity chromatograph (Carlo Erba Fractovap, Model B) was employed as the GLC apparatus; stationary phases were supported on pre-treated Chromosorb W (60-80 mesh) and pure hydrogen was used as the carrier gas. The GLC investigation was carried out over a wide range of temperature (25-125°).

#### RESULTS AND DISCUSSION

The activity coefficients at infinite dilution,  $\gamma_i^\infty$ , were evaluated<sup>3,4</sup> at five temperatures. The data obtained for DOA and DOS are reported in Tables I and II. The following effects were observed:

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TABLE I

NATURAL LOGARITHMS OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION IN DOA

Compound	$\ln \gamma_i^\infty$				
	25°	50°	75°	100°	125°
<i>n</i> -Pentane	0.03	-0.06	-0.10	-0.14	-0.14
<i>n</i> -Hexane	0.10	0.01	-0.03	-0.06	-0.06
<i>n</i> -Heptane	0.15	0.05	0.02	-0.01	0.00
<i>n</i> -Octane	0.19	0.09	0.06	0.03	0.02
1-Pentene	-0.20	-0.26	-0.27	-0.29	-0.27
1-Hexene	-0.13	-0.20	-0.20	-0.20	-0.18
1-Heptene	-0.09	-0.16	-0.15	-0.15	-0.10
1-Octene	-0.07	-0.13	-0.11	-0.10	-0.04
Cyclohexane	-0.21	-0.29	-0.30	-0.32	-0.30
Benzene	-0.72	-0.75	-0.72	-0.70	-0.65
Toluene	-0.67	-0.70	-0.65	-0.63	-0.57
Ethylbenzene	-0.58	-0.61	-0.55	-0.52	-0.45
Methanol	0.90	0.58	0.36	0.17	0.04
Ethanol	0.97	0.62	0.37	0.14	-0.02
<i>n</i> -Propanol	0.82	0.46	0.22	0.04	-0.07
<i>n</i> -Butanol	0.84	0.42	0.20	0.02	-0.07
Methyl acetate	-0.01	-0.17	-0.23	-0.29	-0.31
Ethyl acetate	-0.08	-0.20	-0.24	-0.28	-0.28
<i>n</i> -Propyl acetate	-0.03	-0.17	-0.22	-0.26	-0.26
<i>n</i> -Butyl acetate	0.07	-0.09	-0.15	-0.21	-0.21

TABLE II

NATURAL LOGARITHMS OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION IN DOS

Compound	$\ln \gamma_i^\infty$				
	25°	50°	75°	100°	125°
<i>n</i> -Pentane	-0.09	-0.19	-0.22	-0.25	-0.25
<i>n</i> -Hexane	0.02	-0.10	-0.15	-0.20	-0.21
<i>n</i> -Heptane	0.09	-0.04	-0.09	-0.14	-0.14
<i>n</i> -Octane	0.19	0.02	-0.04	-0.11	-0.12
1-Pentene	-0.24	-0.34	-0.38	-0.41	-0.42
1-Hexene	-0.16	-0.26	-0.30	-0.33	-0.33
1-Heptene	-0.11	-0.22	-0.25	-0.28	-0.26
1-Octene	-0.08	-0.19	-0.21	-0.23	-0.21
Cyclohexane	-0.29	-0.40	-0.44	-0.48	-0.48
Benzene	-0.75	-0.82	-0.82	-0.83	-0.80
Toluene	-0.69	-0.76	-0.75	-0.75	-0.71
Ethylbenzene	-0.57	-0.65	-0.65	-0.65	-0.61
Methanol	1.17	0.73	0.40	0.11	-0.11
Ethanol	1.14	0.67	0.36	0.08	-0.12
<i>n</i> -Propanol	0.93	0.50	0.22	-0.02	-0.17
<i>n</i> -Butanol	0.94	0.46	0.18	-0.05	-0.17
Methyl acetate	0.01	-0.17	-0.28	-0.37	-0.41
Ethyl acetate	-0.06	-0.21	-0.28	-0.34	-0.36
<i>n</i> -Propyl acetate	-0.16	-0.29	-0.34	-0.38	-0.36
<i>n</i> -Butyl acetate	-0.20	-0.32	-0.35	-0.37	-0.34

(a) only slight differences occur with increasing chain length of the esterifying acid;

(b) the limiting activity coefficients generally decrease in the order alcohols > alkanes > alkenes > cycloalkanes > aromatics; the  $\gamma_i^\infty$  values of acetates are close to those of alkenes; in all instances they are generally less than unity, with the exception of the alcohols;

(c) the  $\gamma_i^\infty$  values of hydrocarbons generally increase with increasing number of carbon atoms within each homologous series considered;

(d) a non-linear behaviour of  $\ln \gamma_i^\infty$  versus  $1/T$  is observed, although good correlations were found between the logarithms of specific retention volumes and  $1/T$  and, within each homologous series, between the logarithms of specific retention volumes and the number of carbon atoms. In addition, for some solutes minima are found in the  $\ln \gamma_i^\infty$  versus  $1/T$  curve: the most appreciable effects occur for alkenes, cycloalkanes and aromatics in DOA, and for alkenes, aromatics and acetates in DOS.

Table III gives, in logarithmic form, the relative volatilities ( $\alpha$ ) and the selectivities ( $\beta$ ) calculated at 25° by means of the equations

$$\alpha = \frac{P_1^0 \gamma_1^\infty}{P_2^0 \gamma_2^\infty}$$

and

$$\beta = \frac{\gamma_1^\infty}{\gamma_2^\infty}$$

where  $P^0$  and  $\gamma^\infty$  are, respectively, the vapour pressure and the activity coefficient at infinite dilution of a pair of solutes individually dissolved in the solvent being exam-

TABLE III

VOLATILITIES AND SELECTIVITIES RELATIVE TO *n*-HEXANE AT 25°

Compound	$\ln \alpha_{12}$	DOA		DOS		D2EEP		TOP	
		$\ln \alpha$	$\ln \beta$	$\ln \alpha$	$\ln \beta$	$\ln \alpha$	$\ln \beta$	$\ln \alpha$	$\ln \beta$
<i>n</i> -Pentane	1.22	1.15	-0.07	1.11	-0.11	1.12	-0.10	1.13	-0.09
<i>n</i> -Hexane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>n</i> -Heptane	-1.20	-1.15	0.05	-1.13	0.07	-1.11	0.09	-1.12	0.08
<i>n</i> -Octane	-2.38	-2.29	0.09	-2.21	0.17	-2.20	0.18	-2.27	0.11
1-Pentene	1.44	1.14	-0.30	1.18	-0.26	1.03	-0.41	1.17	-0.27
1-Hexene	0.21	-0.02	-0.23	0.03	-0.18	-0.05	-0.26	-0.02	-0.23
1-Heptene	-0.99	-1.18	-0.19	-1.12	-0.13	-1.10	-0.11	-1.02	-0.03
1-Octene	-2.16	-2.33	-0.17	-2.26	-0.10	-2.16	0.00	-2.09	0.07
Cyclohexane	-0.44	-0.75	-0.31	-0.75	-0.31	-0.80	-0.36	-0.60	-0.16
Benzene	-0.46	-1.28	-0.82	-1.23	-0.77	-1.30	-0.34	-1.06	-0.60
Toluene	-1.67	-2.44	-0.77	-2.38	-0.71	-2.41	-0.74	-2.15	-0.48
Ethylbenzene	-2.77	-3.45	-0.68	-3.36	-0.59	-3.47	-0.70	-3.19	-0.42
Methanol	-0.19	0.61	0.80	0.96	1.15	0.25	0.44	-0.57	-0.38
Ethanol	-0.93	-0.06	0.87	0.19	1.12	-0.15	0.78	-1.35	-0.42
<i>n</i> -Propanol	-1.98	-1.26	0.72	-1.07	0.91	-1.18	0.80	-2.53	-0.55
<i>n</i> -Butanol	-3.20	-2.46	0.74	-2.28	0.92	-2.26	0.94	-3.73	-0.53
Methyl acetate	0.36	0.25	-0.11	0.35	-0.01	-0.04	-0.40	0.50	0.15
Ethyl acetate	-0.47	-0.65	-0.18	-0.55	-0.08	-0.79	-0.32	-0.34	0.13

ined. The values in Table III are given relative to *n*-hexane; for a more complete discussion of the results, the ideal relative volatilities ( $\alpha_{id}$ ) are also given, where  $\alpha_{id}$  is defined as the ratio of the vapour pressures of the two components.

It can be seen that with the solvents examined the selectivities are low for all pairs of solutes tested; in addition, because (as noted earlier in this paper and elsewhere<sup>1-3</sup>) the  $\gamma_i^\infty$  values are generally less or, in some instances, slightly more than unity, it can be concluded that these esters are not suitable for use as solvents for liquid-liquid extraction.

So far as the relative volatilities are concerned, no significant differences were observed between  $\alpha_{id}$  and  $\alpha$  for alkene-alkane pairs. A moderate improvement in  $\alpha_{id}$  occurred for alkane-cycloalkane pairs and a marked one for alkane-aromatic pairs for all the esters examined, but particularly for D2EEP, whose values of  $\alpha$  for alkane-cycloalkane and alkane-aromatic pairs are as high as 2 and 3.5, respectively, while the  $\alpha_{id}$  values are about 1.5 in both instances. Moreover, as can be seen from Table IV, the values of  $\alpha$  vary only slightly as the temperature increases. All of the solvents behave similarly towards the cycloalkane-aromatic pairs, giving good values of relative volatility. As regards the acetate-alcohol pairs, only TOP improves the ideal relative volatility; moreover, no variations in  $\alpha$  are observed on increasing the number of carbon atoms of the pairs considered; for these pairs TOP shows  $\alpha$  values of about 3. Therefore, the four esters tested can be considered to be satisfactory for use as solvents in extractive distillation, particularly in the separation of alkane-aromatic mixtures.

TABLE IV

VOLATILITIES RELATIVE TO *n*-HEXANE FOR D2EEP AT 25°, 75° AND 125°

Compound	$\ln \alpha$		
	25°	75°	125°
<i>n</i> -Heptane	-1.11	-0.87	-0.70
<i>n</i> -Octane	-2.20	-1.72	-1.38
Cyclohexane	-0.80	-0.67	-0.62
Benzene	-1.30	-1.09	-1.00
Toluene	-2.41	-2.02	-1.77
Ethylbenzene	-3.47	-2.85	-2.44

The values of the excess partial molar Gibbs free energy of a methylene group,  $\Delta G^E(\text{CH}_2)$ , are reported in Table V.  $\Delta G^E(\text{CH}_2)$  is defined<sup>5,6</sup> by the following relationship:

$$\Delta G^E(\text{CH}_2) = -RT \cdot \frac{d \ln (V_g^0 P^0)}{dn}$$

where  $R$  is the gas constant,  $T$  the absolute temperature,  $V_g^0$  the specific retention volume,  $P^0$  the vapour pressure and  $n$  the number of methylene groups.  $\Delta G^E(\text{CH}_2)$  was calculated at five temperatures by utilizing the retention parameters of the *n*-alkanes; in Table V the mean values of  $\Delta G^E(\text{CH}_2)$  are reported. On the basis of the results obtained, the four esters studied can be arranged according to the following order

TABLE V

## EXCESS PARTIAL MOLAR GIBBS FREE ENERGIES OF A METHYLENE GROUP

<i>Ester</i>	$\Delta G^E(\text{CH}_2)$	<i>Ester</i>	$\Delta G^E(\text{CH}_2)$
DOA	59.7	D2EEP	68.9
DOS	58.6	TOP	64.2

of increasing polarity:  $\text{DOS} < \text{DOA} < \text{TOP} < \text{D2EEP}$ . It should be pointed out that the differences in polarity among the compounds tested are only slight and, in particular, the difference in polarity between DOA and DOS is insignificant in spite of the different length of the esterifying acid.

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