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Activity Coefficients at Infinite Dilution for Hydrocarbons in Fatty Alcohols Determined by Gas−Liquid Chromatography

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ABSTRACT: The selection of the most suitable selective solvent for separation processes such as extraction or extractive distillation plays an important role in the economical design. Since the largest deviation from ideality is observed at infinite dilution, limiting activity coefficients (γ^∞) provide a useful tool for the optimal choice of the selective solvent. Therefore, activity coefficients at infinite dilution have been measured for 22 solutes (paraffins, olefins, chloroparaffins, aromatics, ketones, ethers, alcohols, and acetates) in fatty alcohols: octadecanol and eicosanol as a solvent. The measurements were carried out with the help of gas−liquid chromatography (GLC) at five and four temperatures, respectively. Furthermore, the observed temperature dependence of limiting activity coefficients is confirmed using excess enthalpy data. To determine the different interactions between the solutes and the solvents, the linear solvation energy relationship (LSER) or "Abraham method" is applied. To verify the application as an entrainer, the selectivity and capacity of the investigated solvents are calculated from experimental activity coefficient data.

INTRODUCTION

Infinite dilution activity coefficients characterize the behavior of a single solute molecule completely surrounded by solvent; thus, it generally indicates a maximum nonideality and provides incisive information regarding solute−solvent interactions in the absence of solute−solute interactions,[1] and it is actually an excess property. Also, it is much simpler to describe or model by using statistical mechanical theories or computer simulation methods,[2] and thus, activity coefficients provide helpful information for testing the possible applicability of a theoretical model or a simulation method.[3]

From the industrial viewpoint, infinite dilution activity coefficient theory offers a wider applicability than any measurement at finite concentration, and it can be used to predict the phase behavior of a mixture over the entire concentration range.[4]

A reliable knowledge of the activity coefficients at infinite dilution ($\gamma^\infty{}_i$) is of particular importance for the synthesis, design, and optimization of separation processes, since the largest separation effort is required to remove the last traces of impurities. Furthermore, $\gamma^\infty{}_i$ values are required to select selective solvents (entrainers) for separation processes such as extractive distillation and extraction or to check for separation problems (azeotropic points, miscibility gaps). Additionally, more reliable g^E model or group interaction parameters are obtained by fitting the required parameters simultaneously to vapor−liquid equilibria (VLE), excess enthalpies (H^E), and limiting activity coefficients ($\gamma^\infty{}_i$).

Activity coefficients at infinite dilution can be determined by various methods: ebulliometry, static methods, the dilutor technique, and gas−liquid chromatography (GLC).[5] The GLC technique was chosen as the most preferable measurement technique for the planned investigation because GLC shows several advantages in comparison to other methods: static methods, dilutor technique, and so forth.[6] After the careful preparation of the column, the GLC method allows the measurement of a great number of γ^∞ values in a rather short time. The reliability of the γ^∞ data obtained by GLC has been confirmed by different authors[7] and in earlier parts of this measurement series.[8−14]

Fatty alcohols, such as octadecanol ($C_{18}H_{38}O$) and eicosanol ($C_{20}H_{42}O$), derived from natural fats and oils (Figure 1), are high molecular straight chain primary alcohols. There are synthetic fatty alcohols equivalent physically and chemically to natural alcohols obtained from oleochemical sources such as coconut and palm kernel oil. Fatty alcohols are emulsifiers and emollients to make skin smoother and prevent moisture loss. As chemical intermediates, the primary use of fatty alcohols is as raw material for the production of fatty sulfate salts and alcohol ethoxylates for foaming and cleaning purposes in the field of detergent industry. Chemical reactions of primary alcohols include esterifications, ethoxylation, sulfation, oxidation, and many other reactions. Their derivatives and end user applications include: nonionic surfactants (ethoxylates and propoxylates), anionic surfactants (alkyl sulfates and alkyl ethoxy sulfates), chemical intermediates and polymerization modifiers, quaternary ammonium compounds for detergent sanitizers, softener for textiles, phase transfer catalyst and biocides, flavor and fragrance, and water treatment.

Large amounts of fatty alcohols are used as special solvents, fillers in plasticizer, and insulating materials for the building industry. Fatty alcohols are used as ingredients in the industries of agriculture, foodstuff, metal processing, cosmetics, lube

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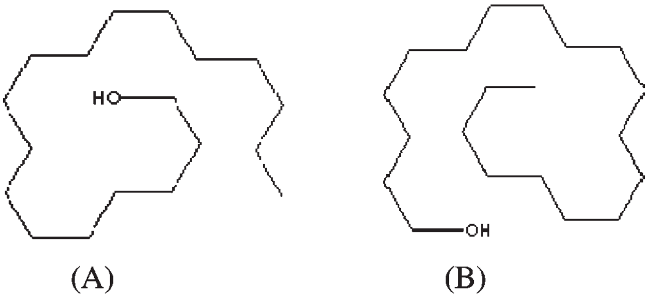
additive, pharmaceutical, rubber, textile, perfume, and flavoring as well as synthetic detergent.

Octadecanol and eicosanol have a potential of being good solvents for separating alkanes, alkenes, primary alcohols, and so forth. In this work, the activity coefficients at infinite dilution were determined using a GLC method, for 22 substances; interactions of solutes—solvents and excess molar enthalpy are also calculated. From the experimental results of activity coefficients at infinite dilution, the selectivity and capacity of an entrainer are estimated to check if the investigated solvents can be used as selective solvents for the aliphatic or aromatic separation.

■ EXPERIMENTAL SECTION

Chemicals. The octadecanol and the eicosanol were applied with a purity greater than 97.0 %; they were supplied by Fluka. The solutes used were pentane, hexane, octane, pentene, heptene, methanol, ethanol, propanol, butanol, chloroform, dichloromethane, chloropropan, chlorobutan, methane tetrachloride, acetone, acetonitrile, ethyl acetate, butyl acetate, cyclohexane, toluene, tetrahydrofuran (THF), and diethyl ether. They were all supplied by Fluka, and they have purities greater than 97 %. Since GLC is itself a separation technique, the results are not influenced by small solute impurities, and therefore the solutes were used without further purification.



(A) (B)

Figure 1. Molecular structure of (A) octadecanol and (B) eicoanol.

Apparatus and Procedure. For all measurements Chromosob WAW (Carlo Erba) 80−100 mesh was used as the solid support for the stationary phase. The coating of predried carrier material with the solvent was carried out with diethylether (solubilizer) in a rotary evaporator. After the solubilizer was removed, the coated material is filled in clean and dry stainless steel columns of 4 mm diameter and about 150 mm length. The weight of dry empty columns is determined prior to the filling. The columns filled with the stationary phases coated on the support material (quantitative ratio of support to stationary phase = 3/1 by weight) are turned into a spiral shape and fitted into the thermostatted oven of GC PYE UNICAM PU 304 instruments gas chromatograph. The column temperature was measured using an electronic thermometer to within ± 273.25 K. Each column is conditioned by passing nitrogen gas. The conditioning is done for 8 h. The weight of the columns is then determined, from which the weights of the stationary phases can be evaluated. It is ensured that the weights of the stationary phase remain constant throughout the experiment, by weighing at the beginning and at the end of the experiment, after evaporating all of the solvent present.

The carrier gas used for these experiments is nitrogen.

The inlet pressure was measured to within ± 1 mm Hg by means of a mercury manometer, while the outlet pressure is equal to the atmospheric pressure. The flow rate of the carrier gas was

Table 1. Experimental Activity Coefficient at Infinite Dilution, γ^∞, for Various Solutes in the Solvent Octadecanol

	γ^∞				
solute	T/K = 333.15	T/K = 338.15	T/K = 343.15	T/K = 348.15	T/K = 353.15
pentane	0.0292	0.0272	0.0259	0.0243	0.0231
hexane	0.0551	0.0468	0.0411	0.0359	0.0315
octane	0.0513	0.0497	0.0485	0.0473	0.0461
methanol	0.0423	0.0386	0.0357	0.0330	0.0306
ethanol	0.0433	0.0396	0.0369	0.0343	0.0320
propanol	0.0722	0.0625	0.0597	0.0550	0.0510
butanol	0.1537	0.1360	0.1209	0.1101	0.0992
dichloromethane	0.0262	0.0233	0.0212	0.0194	0.0178
chloropropane	0.0331	0.0294	0.0269	0.0245	0.0225
chlorobutane	0.0389	0.0360	0.0338	0.0321	0.0300
chloroform	0.0227	0.0220	0.0214	0.0208	0.0202
tetrachloride	0.0288	0.0285	0.0283	0.0280	0.0278
acetone	0.0185	0.0179	0.0174	0.0170	0.0166
THF	0.0204	0.0188	0.0177	0.0166	0.0156
ethyl acetate	0.0445	0.0408	0.0384	0.0360	0.0335
butyl acetate	0.0526	0.0468	0.0428	0.0391	0.0358
acetonitrile	0.1076	0.0969	0.0901	0.0832	0.0766
pentene	0.0261	0.0245	0.0234	0.0222	0.0213
heptene	0.0431	0.0417	0.0407	0.0397	0.0388
cyclohexane	0.0365	0.0337	0.0315	0.0294	0.0274
toluene	0.0372	0.0355	0.0343	0.0331	0.0318
diethyl ether	0.0257	0.0235	0.0219	0.0204	0.0190

Table 2. Experimental Activity Coefficient at Infinite Dilution, γ^{∞}, for Various Solutes in the Solvent Eicosanol

	γ^{∞}			
solute	T/K = 338.15	T/K = 343.15	T/K = 348.15	T/K = 353.15
pentane	0.0954	0.0801	0.0668	0.0564
hexane	0.1288	0.1239	0.1193	0.1148
octane	0.1870	0.1606	0.1381	0.1204
methanol	0.1219	0.0967	0.0737	0.0574
ethanol	0.1244	0.1174	0.1056	0.0950
propanol	0.2131	0.1930	0.1751	0.1586
butanol	0.431	0.3868	0.3521	0.3162
dichloromethane	0.0790	0.0642	0.0532	0.0435
chloropropane	0.0779	0.0778	0.0778	0.0777
chlorobutane	0.0991	0.0954	0.0919	0.0886
chloroform	0.0632	0.0622	0.0612	0.0604
tetrachloride	0.0862	0.0810	0.0760	0.0714
acetone	0.0557	0.0572	0.0587	0.0602
THF	0.0581	0.0543	0.0506	0.0471
ethyl acetate	0.1233	0.1104	0.0990	0.0888
butyl acetate	0.1400	0.1312	0.1229	0.1152
acetonitrile	0.3093	0.2647	0.2288	0.1972
pentene	0.0813	0.0742	0.0664	0.0600
heptene	0.1237	0.1181	0.1126	0.1076
cyclohexane	0.1080	0.1022	0.0969	0.0918
toluene	0.5437	0.4793	0.4207	0.3731
diethyl ether	0.0652	0.0624	0.0598	0.0572

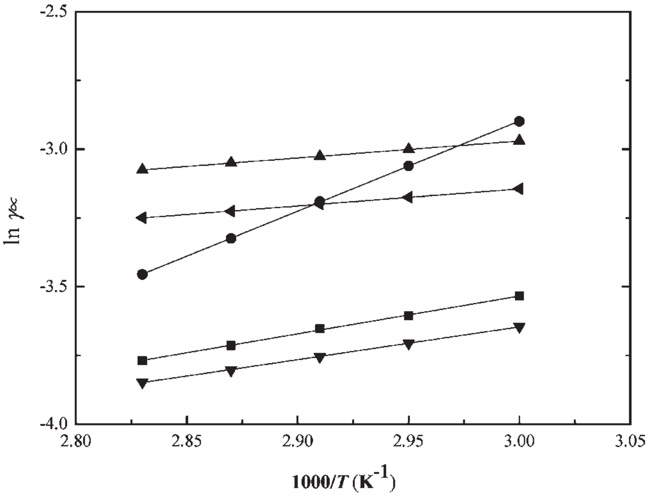


Figure 2. Experimental activity coefficients at infinite dilution for the alkanes and olefins in the solvent octadecanol as a function of temperature; ■, pentane; ●, hexane; ▲, octane; ▼, pentene; solid left-pointing triangle, heptene; —, linear regression.

maintained as constant as possible for each set of measurements on each column. This rate was measured using a calibrated soap bubble meter. The internal pressure gradient varies between (517.151 and 646.438) mm Hg. After the attainment of steady state conditions, 0.2 μL of the solute is injected and its retention time (t_r) noted.

The uncertainty in the values of γ^{∞}, taking into account the uncertainties in specific retention volume, flow rate of the carrier gas, vapor pressure of solute estimated, and second virial coefficient estimated, is better than 3 %.

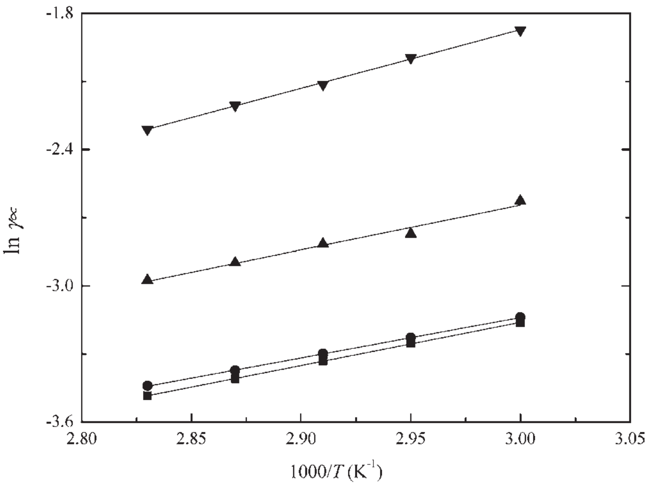


Figure 3. Experimental activity coefficients at infinite dilution for the alcohols in the solvent octadecanol as a function of temperature; ■, methanol; ●, ethanol; ▲, propanol; ▼, butanol; —, linear regression.

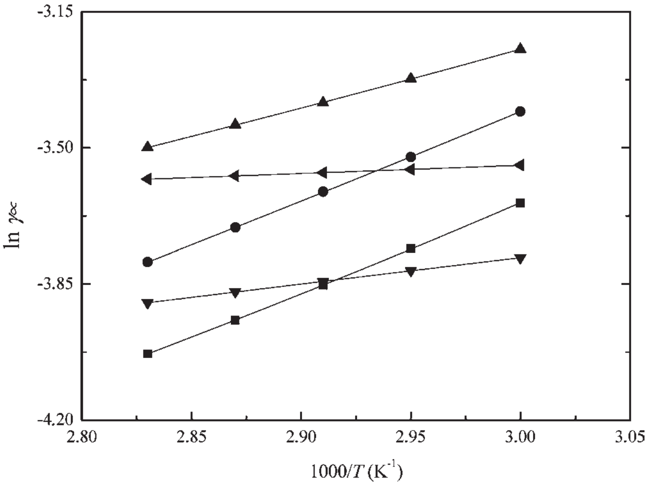


Figure 4. Experimental activity coefficients at infinite dilution for the chloroalkanes in the solvent octadecanol as a function of temperature; ■, dichloromethane; ●, chloropropane; ▲, chlorobutane; ▼, chloroform; solid left-pointing triangle, tetrachloromethane; —, linear regression.

Calculation of Limiting Activity Coefficients. Equation 1, proposed by Desty and Swanson[15] and discussed in detail by Laub and Pecsok,[16] is used for the calculation of the specific retention volume $V_g^{\,0}$

$$V_g^{\,0} = \left(\frac{JF_m}{W}\right)\left[\frac{(P_0 - P_{H_2O})}{P_0}\right]\left(\frac{273}{T_m}\right)(t_r - t_0) \qquad (1)$$

where F_m is the flow rate of the carrier gas ($m^3 \cdot s^{-1}$) at the ambient temperature T_m/K, W/kg is the mass of the stationary phase, P_{H_2O}/Pa is the vapor pressure of water at T_m, t_r/s is the retention time of the solute, and t_0/s is the retention time of the unretained solute. J is the James-Martin pressure-correction factor, given by

$$J = \left(\frac{3}{2}\right)\frac{[(P_i/P_0)^2 - 1]}{[(P_i/P_0)^3 - 1]} \qquad (2)$$

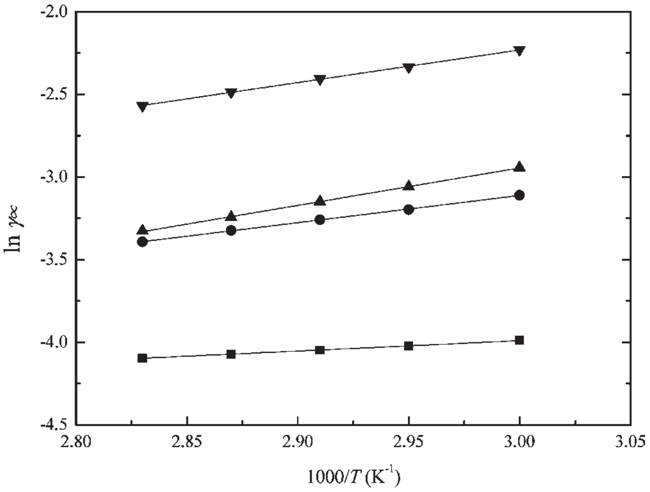


Figure 5. Experimental activity coefficients at infinite dilution for the ketone and acetates in the solvent octadecanol as a function of temperature; ■, propanone; ●, ethyl acetate; ▲, butyl acetate; ▼, acetonitrile; —, linear regression.

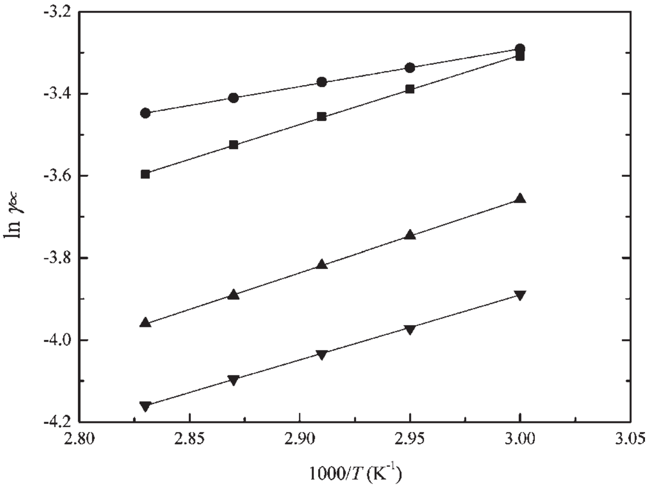


Figure 6. Experimental activity coefficients at infinite dilution for the cycloalkane, aromatic, and ethers in the solvent octadecanol as a function of temperature; ■, cyclohexane; ●, toluene; ▲, diethyl ether; ▼, THF; —, linear regression.

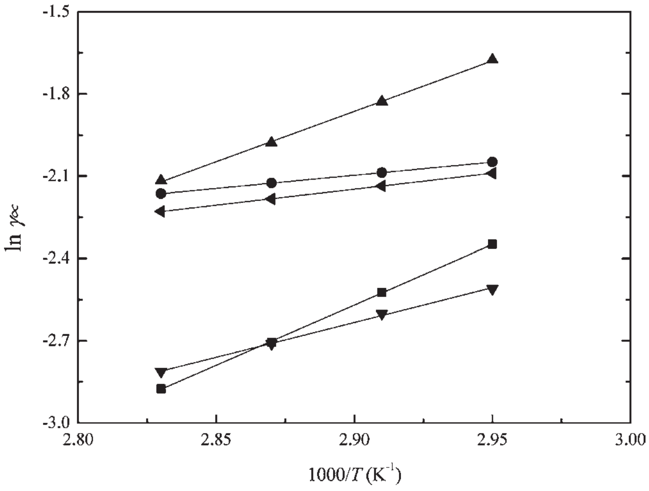


Figure 7. Experimental activity coefficients at infinite dilution for the alkanes and olefins in the solvent eicosanol as a function of temperature; ■, pentane; ●, hexane; ▲, octane; ▼, pentene; solid left-pointing triangle, heptene; —, linear regression.

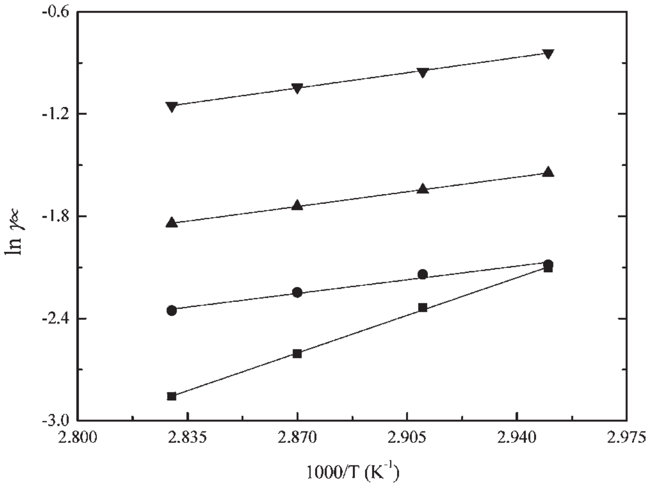


Figure 8. Experimental activity coefficients at infinite dilution for the alcohols in the solvent eicosanol as a function of temperature; ■, methanol; ●, ethanol; ▲, propanol; ▼, butanol; —, linear regression.

where P_i/Pa and P_0/Pa are the pressures at the inlet and outlet of the column, respectively. The activity coefficient of the solute at infinite dilution γ_i^∞ is given by

$$\ln \gamma_i^\infty = \ln\left[\frac{273R}{P_2{}^0 M_1 V_g{}^0}\right] - \left[\frac{(B_{22} - V_2{}^0)P_2{}^0}{RT_{\text{expt}}}\right] \quad (3)$$

where R is the gas constant ($8.3147\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), $P_2{}^0$/Pa is the vapor pressure of the solute at the experimental temperature T_{expt}/K, M_1/kg·mol is the molar mass of the stationary phase, B_{22}/m^3·mol is the second virial coefficient of the solute at T_{expt}, and $V_2{}^0$/m^3·mol is the molar volume of the solute at T_{expt}. The correction for gas phase nonideality, given by the second term on the right-hand side of eq 3, is included, as indicated by Morton and Young[17] in his review on the use gas chromatography for the determination of thermodynamic properties, to enable us to determine accurately the values of limiting activity coefficients. The vapor pressure values $P_2{}^0$ were calculated using the Antoine equation from constants obtained from the literature.[18] The method proposed by Hayden and O'Connell[19] is used for the calculation of second virial coefficient B_{22}. The necessary critical properties and molar volumes are either collected from, or estimated, according to the methods recommended by Reid et al.[20]

Abraham Correlation. The specific retention volumes $V_g{}^0$ experimentally obtained could be used to determine the different interactions between the solutes and the stationary phases. These interactions could be characterized using the Abraham method[21] or LSER (linear solvation energy relationship), which is given by:

$$\log V_g{}^0 = c + rR_2 + s\pi_2{}^H + a\alpha_2{}^H + b\beta_2{}^H + l \log L^{16} \quad (4)$$

Each term in this equation is assigned to solute−solvent interactions. In this equation five parameters characterize the solute properties:[22−24] R_2, the polarizability parameter which

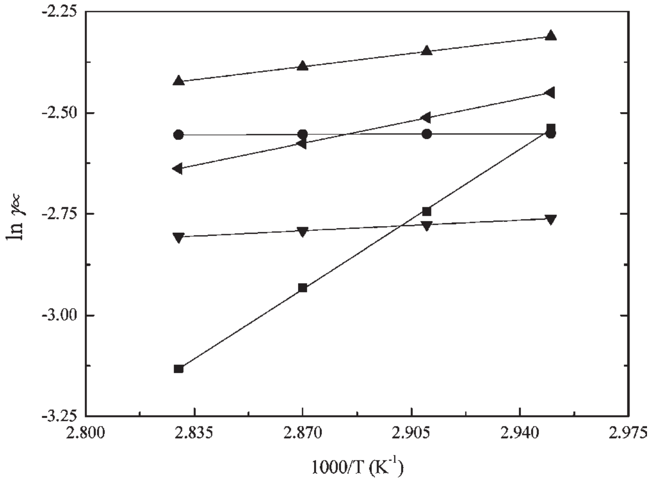


Figure 9. Experimental activity coefficients at infinite dilution for the chloroalkanes in the solvent eicosanol as a function of temperature; ■, dichloromethane; ●, chloropropane; ▲, chlorobutane; ▼, chloroform; solid left-pointing triangle, tetrachloromethane; —, linear regression.

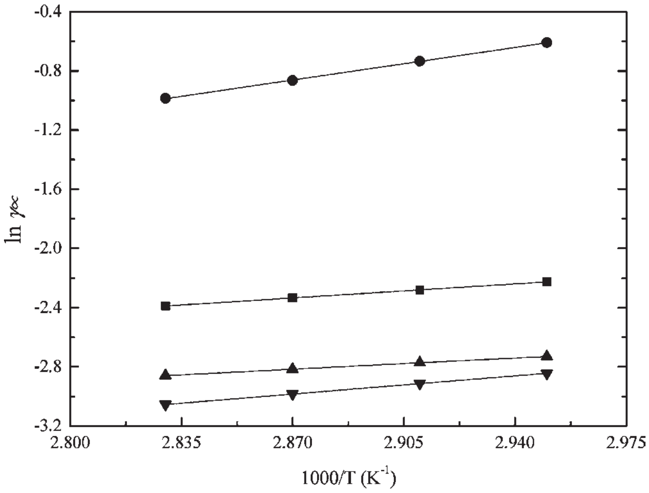


Figure 11. Experimental activity coefficients at infinite dilution for the cycloalkane, aromatic and ethers in the solvent eicosanol as a function of temperature; ■, cyclohexane; ●, toluene; ▲, diethyl ether; ▼, THF; —, linear regression.

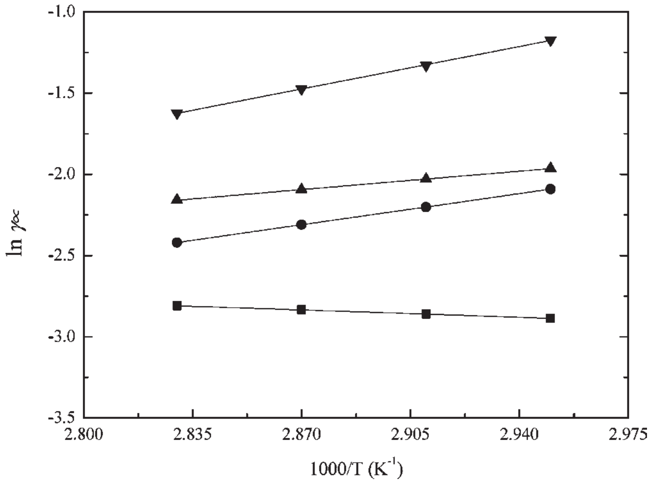


Figure 10. Experimental activity coefficients at infinite dilution for the ketone and acetates in the solvent eicosanol as a function of temperature; ■, propanone; ●, ethyl acetate; ▲, butyl acetate; ▼, acetonitrile; —, linear regression.

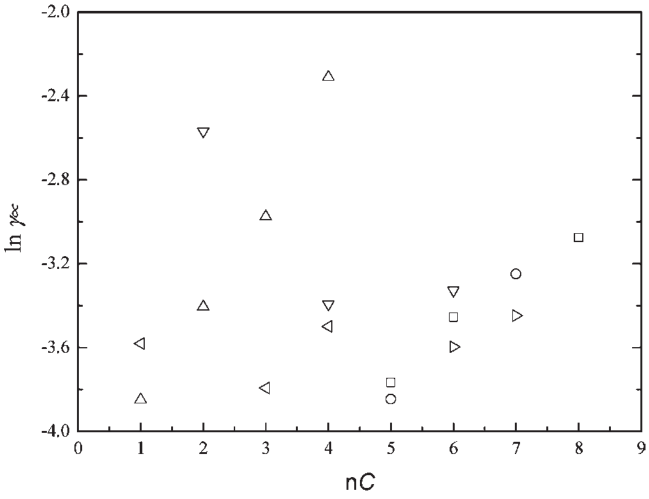


Figure 12. Variation of experimental activity coefficients for the solutes in the solvent octadecanol according to the carbon's atom numbers at T = 353.15 K. □, alkanes; ○, olefins; △, alcohols; ▽, acetate; open left-pointing triangle, chloroalkanes; open right-pointing triangle, aromatics and cycloalkane.

expresses the interaction capacity of the solute through the pair of π electrons; π_2^H, the dipolarity parameter of the solute; α_2^H, the acidity due to the solute's hydrogen bond; β_2^H, the basicity due to the solute's hydrogen bond; L,[16] the Oswald solubility coefficient of the solute in hexadecane at 298 K.

The constants c, r, s, a, b, and l calculated by meaning of the eq 4 using log V_g^0 values are experimentally determined. These constants characterize the solute−solvent interactions and describe the stationary phase behavior: c, the correlation constant; r, the interaction parameter of the solute−solvent through the pair of π and n electrons; s, the polarizability of the stationary phase; a, the interactions of acidic solutes through hydrogen bonding, measuring the basicity of the stationary phase; b, the interactions of basic solutes through hydrogen bonding, measuring the acidity of the stationary phase; l, assigned to the dispersive forces of the solute−solvent and to the effect of formation of the cavities within the stationary phase (association of the effect of cave formation and dispersive interactions).

Calculation of the Selectivity, Capacity, and Quantity at Infinite Dilution. To be able to estimate the selectivity of an entrainer, it is often sufficient to know the separation factor at infinite dilution.[25] In the high dilute range, the ratio of the activity coefficients at infinite dilution of the components to be separated is denoted as the selectivity S_{12}^{∞}.[26]

$$S_{12}^{\infty} = \gamma_1^{\infty}/\gamma_2^{\infty} \qquad (5)$$

Supposing that 2 is the component to be extracted with the selective solvent, apart from the selectivity, the capacity of the solvent has to be considered.[27] The capacity describes the solubility of the component to be extracted in the solvent; that is, small values for the activity coefficient indicate a high solubility. In the case of infinite dilution the capacity k_1^{∞} can be defined as:[26]

$$k_1^{\infty} = 1/\gamma_1^{\infty} \tag{6}$$

A typical application of extractive distillation or liquid−liquid extraction is the separation of aromatics from aliphatics. In most cases capacity and selectivity counteract; that is, high values for the capacity are accompanied by low values for selectivity. To decide what solvent is most suitable, the quantity Q_{12}^{∞} is introduced.[27] The quantity at infinite dilution is defined as the product of selectivity and capacity.

$$Q_{12}^{\infty} = S_{12}^{\infty} k_1^{\infty} \tag{7}$$

■ RESULTS AND DISCUSSION

Activity coefficients at infinite dilution of various types of solutes were determined for octadecanol at five temperatures T/K = (333.15 to 353.15) and for eicosanol at four temperatures T/K = (338.15 to 353.15). The results are presented in Tables 1 and 2.

Figures 2 to 6 and Figures 7 to 11 show the linear relationship between the natural logarithm of the activity coefficients for the solutes in octadecanol and eicosanol, respectively.

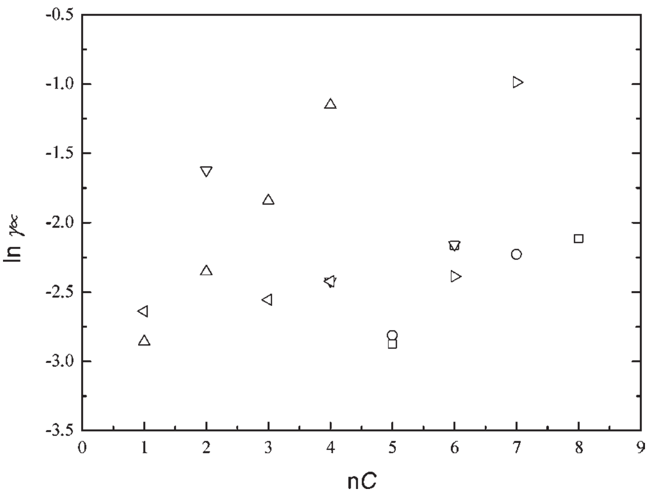


Figure 13. Variation of experimental activity coefficients for the solutes in the solvent eicosanol according to the carbon's atom numbers at T = 353.15 K. □, alkanes; ○, olefins; △, alcohols; ▽, acetate; open left-pointing triangle, chloroalkanes; open right-pointing triangle, aromatics and cycloalkane.

The γ^{∞} values are relatively slight (< 1) in the two solvents; they are greater in eicosanol than in octadecanol. The higher experimental values of γ^{∞} for the alcohols in the two solvents are probably due to the difference of the chemical nature, especially the polarity, between the solutes and the fatty alcohols; which explain their slight solubility. Conversely, the smallest experimental values of γ^{∞} are observed for the ethers in the two solvents. More the activity coefficient is lower than unity ($\gamma^{\infty} < 1$), better is the solvent's absorption capacity.[28]

Table 4. Abraham Parameters for Solvents Studied at Different Temperatures[a]

solvent	T/K	c	r	s	a	b	l	R^2
octadecanol	333.15	4.9462	0.5117	−0.0976	1.6699	1.5840	1.1443	0.7951
	338.15	5.0167	0.4933	−0.1114	1.4514	1.5655	1.0799	0.8159
	343.15	5.0768	0.5438	−0.1523	1.2691	1.5425	1.0176	0.8330
	348.15	5.1372	0.4958	−0.1497	1.1723	1.4443	0.9650	0.8438
	353.15	5.1042	0.3341	−0.0728	1.1352	1.3880	0.9420	0.8419
eicosanol	338.15	3.6986	0.6884	−0.0705	1.2808	1.5905	1.0872	0.8337
	343.15	3.8650	0.4544	0.0253	1.3093	1.3346	1.0281	0.8331
	348.15	3.9465	0.3618	0.0432	1.2453	1.1760	0.9715	0.8331
	353.15	4.0458	0.2443	0.1165	1.2174	0.9793	0.9136	0.8115

[a] R^2 is the correlation coefficient.

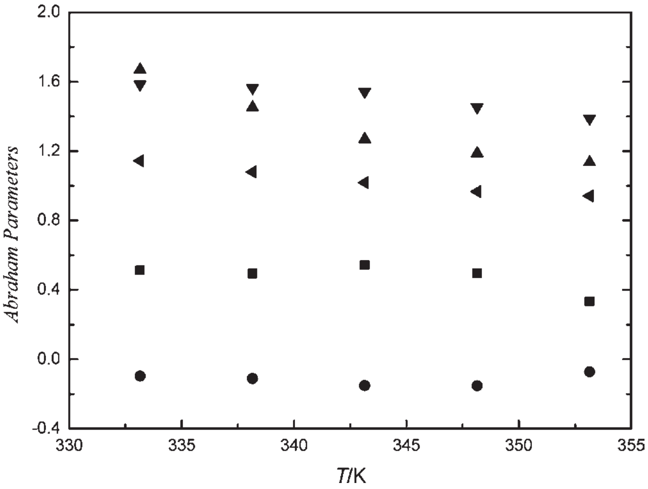


Figure 14. Evolution of Abraham parameters with temperature for octadecanol. ■, r; ●, s; ▲, a; ▼, b; solid left-pointing triangle, l.

Table 3. Values of $\Delta H^{E,\infty}$, ΔH^{dis}, and ΔH^{vap} as Determined from Equations 8 to 10 in the Two Solvents

	octadecanol			eicosanol			literature
	$\Delta H^{E,\infty}$	ΔH^{dis}	ΔH^{vap}	$\Delta H^{E,\infty}$	ΔH^{dis}	ΔH^{vap}	ΔH_{vap}
solute	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
hexane	27.252	−3.176	30.428	7.983	−20.313	28.296	28.84[a]
ethanol	14.829	−25.328	40.157	21.849	−20.469	42.318	39.33[b]
tetrachloride	1.759	−30.755	32.514	13.063	−19.705	32.768	33.47[b]
butyl acetate	18.854	−24.906	43.76	13.495	−30.370	43.865	43.89[c]
toluene	7.660	−31.913	39.573	26.193	−11.121	37.314	33.43[a]
diethyl ether	14.808	−10.730	25.538	9.010	−17.998	27.008	27.37[c]

[a] From ref 20. [b] From ref 32. [c] From ref 33.

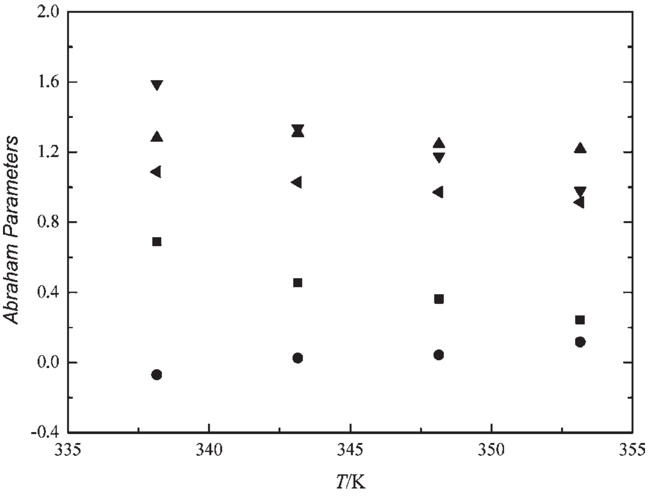


Figure 15. Evolution of Abraham parameters with temperature for eicosanol. ■, *r*; ●, *s*; ▲, *a*; ▼, *b*; solid left-pointing triangle, *l*.

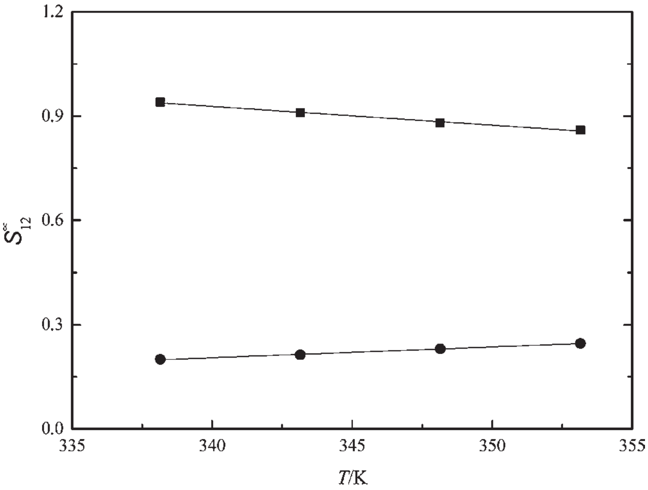


Figure 16. Selectivity at infinite dilution for two solvents at different temperatures regarding the separation of cyclohexane from toluene: ■, in octadecanol; ●, in eicosanol; —, linear regression.

The limiting activity coefficient increase with increasing carbon's atom numbers (Figures 12 and 13), which can be explained by the increase of the hydrophobic character of the solutes with increasing chain length. This behavior was observed in other stationary phases.[5−17]

A comparison of the alkanes (Figure 2 and 7) in the two solvents indicates that the activity coefficient is influenced by the molecular structure.

A graph of ln γ^∞ versus the inverse absolute temperature often shows a straight line in a limited temperature interval (Figures 2 to 11). According to the Gibbs−Helmholtz equation, the value for the partial molar excess enthalpy at infinite dilution $\Delta H_i^{E,\infty}$ can directly be obtained from the slope of this straight line.[29,30]

$$\left(\frac{\partial \ln \gamma_i^\infty}{\partial(1/T)}\right)_{p,x} = \frac{\Delta H_i^{E,\infty}}{R} \tag{8}$$

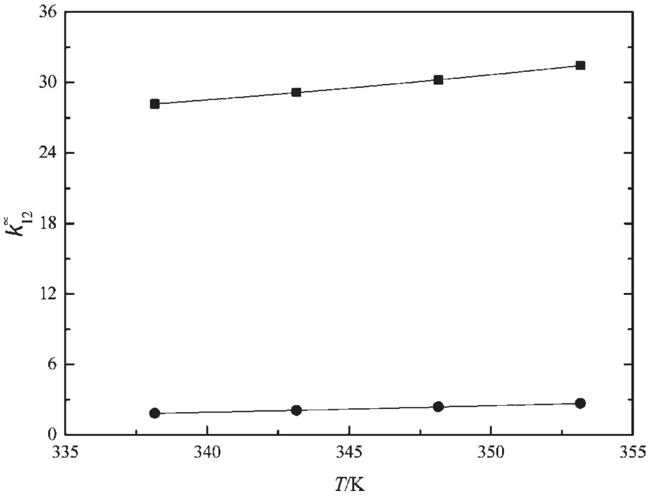


Figure 17. Capacity at infinite dilution for two solvents at different temperatures regarding the separation of cyclohexane from toluene: ■, in octadecanol; ●, in eicosanol; —, linear regression.

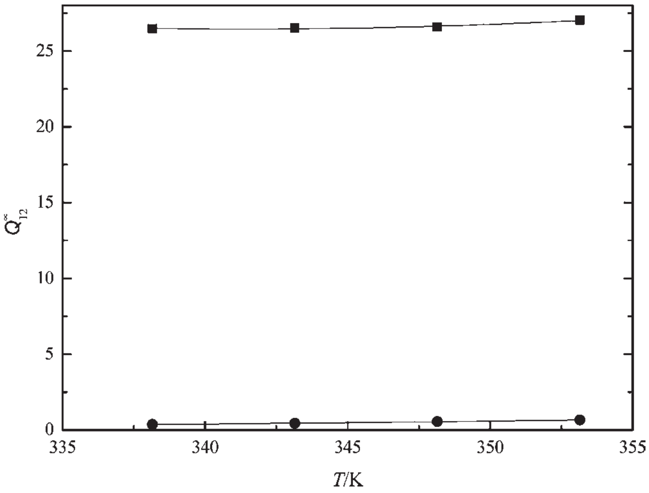


Figure 18. Quantity at infinite dilution for two solvents at different temperatures regarding the separation of cyclohexane from toluene: ■, in octadecanol; ●, in eicosanol; —, linear regression.

From the V_g^0 obtained data, we could determine the values of molar enthalpy of

$$\left(\frac{\partial \ln V_g^0}{\partial(1/T)}\right)_{p,x} = -\frac{\Delta H_i^{dis}}{R} \tag{9}$$

The molar enthalpy of vaporization is given by the relation:

$$\Delta H_i^{vap} = \Delta H_i^{E,\infty} - \Delta H_i^{dis} \tag{10}$$

The regression of experimental points by a straight line permits the determination of partial molar excess enthalpy at infinite dilution of different solutes. In this work, the activity coefficients decrease with increasing temperature for the two solvents: octadecanol and eicosanol. The smaller values of γ^∞ reflect the competition between the attractive association of the dissimilar compounds and the dissociation of each of the polar or polarizable pure compounds. The dissociation effect is dominant, and the activity coefficients are relatively slight.[31] This dissociation effects are also reflected in the large $\Delta H_i^{E,\infty}$ values. The enthalpies of vaporization of the solutes available in literature[20,32,33] are globally close to the values experimentally found (Table 3).

Another aim of the investigation was the calculation of different interactions between the solutes and the solvents using the Abraham method. The results are presented in Table 4, which give for each stationary phase the Abraham parameters corresponding to eq 4, with the correlation coefficients.

The weak values of b, comparatively to the values of a, show the acid character of fatty alcohols. The term $s\pi_2^H$ is important; it reflects the polarizability of the stationary phase. The values of s show their weak polarity. The values of r indicate the small interaction capacity through the pairs of π and n electrons.

For the two solvents, the evolution of Abraham parameters with the temperature is linear (Figure 14 and 15). This result is interesting, since it permit to broaden the temperature interval for the prediction of γ^∞.

This work involves also the study of the selection of new potential entrainer, especially for separation of aromatics from aliphatics. Regarding the selectivity at infinite dilution S_{12}^∞ for typical separation of cyclohexane (1) from toluene (2), the solvent octadecanol shows a better selectivity than eicosanol (Figure 16). With respect to the capacity at infinite dilution k_1^∞, which is a measure for the solubility of a substance in the extractive solvent, octadecanol show great advantages in comparison to eicosanol (Figure 17).

Comparing the Q_{12}^∞ values of octadecanol with eicosanol (Figure 18), the Q_{12}^∞ values of octadecanol are almost twenty times higher. The solvent octadecanol should be the best entrainer than eicosanol.

CONCLUSION

Activity coefficients at infinite dilution for paraffins, olefins, chloroparaffins, aromatics, alcohols, acetates, and ethers in the solvents octadecanol and eicosanol have been measured in the temperature range (333.15 to 353.15) K by GLC. The GLC technique was chosen owing to the possibility of a fast and reliable determination of γ^∞ values.[26] The results show the great solubility of the fatty alcohols in the ethers.

Thermodynamic data relative to these mixtures are not easily available. Using these data, the behavior of compounds can be evaluated under different conditions.[28] Furthermore, the temperature dependence of the limiting activity coefficients was verified using experimental H^E data.

The different interactions between the solutes and the solvents were calculated using the Abraham method. This method, which is called LSER, seems to be the most efficient method of interaction's calculation.

To check if the solvents can be used as selective solvents for the aliphatic or aromatic solvent separation, the data of selectivity, capacity, and the product Q_{12}^∞ at infinite dilution were investigated. The solvent octadecanol can be the selective solvent.

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