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Measurement of Activity Coefficients at Infinite Dilution Using Gas−Liquid Chromatography. 10. Results for Various Solutes with the Stationary Phases Dimethyl Sulfoxide, Propylene Carbonate, and *N*-Ethylformamide

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Using gas−liquid chromatography (GLC), activity coefficients at infinite dilution have been measured for 37 solutes (alkanes, alkenes, cyclic hydrocarbons, aromatic hydrocarbons, alcohols, ketones, ethers, aldehydes, esters, and halocarbons) in the solvents dimethyl sulfoxide, propylene carbonate, and *N*-ethylformamide. The measurements were carried out in the temperature range between 303.15 and 333.15 K. The obtained γ^∞ values are compared with published data, and the observed temperature dependence of the limiting activity coefficients is confirmed using excess enthalpy data. Furthermore, the selectivities and capacities of the investigated solvents for the separation of aliphatics from aromatics are compared.

Introduction

Limiting activity coefficients have important practical applications for different industrial problems; for example, activity coefficients at infinite dilution can be directly used for the selection of selective solvents for extractive distillation or extraction. To be able to estimate the selectivity of an entrainer, it is often sufficient to know the separation factor at infinite dilution (Gmehling and Brehm, 1996). In the highly dilute range the ratio of the activity coefficients of the components to be separated is denoted as the selectivity S_{12}^∞:

$$S_{12}^\infty = \gamma_1^\infty/\gamma_2^\infty \tag{1}$$

To minimize the number of theoretical stages required, the selectivity should be far from 1. Assuming that 2 is the component to be extracted with the selective solvent, selectivities greater than 1 are desired. Apart from the selectivity, the capacity of the solvent has to be considered (Hradetzky et al., 1989). 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_2^∞ can be defined as:

$$k_2^\infty = 1/\gamma_2^\infty \tag{2}$$

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 the selectivity. Therefore, an economic and effective separation needs a solvent that combines a high selectivity with a sufficient capacity. Furthermore, there are many other aspects which have to be considered (high thermal stability, low viscosity, low corrosiveness, low vapor pressure, low price, etc.).

In this systematic study the limiting activity coefficients have been determined for 37 substances in three solvents in order to obtain quantitative information for entrainer selection. The GLC technique was chosen as the most preferable measuring technique for the planned investigations, because GLC shows several advantages in comparison to other methods, for example static methods or the dilutor technique (Gruber et al., 1998; Kojima et al., 1997). 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. At the same time the reliability of the γ^∞ data obtained by GLC has been confirmed by different authors (Gmehling et al., 1994).

Experimental Procedure

For all measurements Chromosorb P-AW-DMCS 60/80 mesh (acid-washed dimethyldichlorosilane-treated Chromosorb) was used as the solid support for the stationary phase. The coating of the predried carrier material with solvent was carried out with methanol (solubilizer) in a rotary evaporator. After the solubilizer was removed, the column (length 200 mm, inner diameter 4.1 mm) was carefully filled with the coated solid support. A scheme of the homemade gas chromatograph used for these investigations, the detailed description of the measurement procedure, and the most important equations for evaluation purposes together with the theoretical explanations are given by Knoop et al. (1989).

The solvents used, dimethyl sulfoxide, propylene carbonate, and *N*-ethylformamide, were applied with a purity greater than 99.8 mass % (GLC analysis of peak areas, CP-Wax 52 column, temperature 150 °C, FID detector) and a water content smaller than 150 ppm (Karl Fischer titration). γ^∞ values for 37 solutes (alkanes, alkenes, cyclic hydrocarbons, aromatic hydrocarbons, alcohols, ketones, ethers, aldehydes, acetates, and halocarbons) were mea-

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sured in the temperature range between 303.15 and 333.15 K. 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.

To check if solvent losses occurred during the measurements, the liquid loading was determined before and after the measurement gravimetrically. Under the stated conditions the pure uncoated Chromosorb suffers from a loss of mass due to the removal of strongly adsorbed water, which has been taken into account, too. With the use of presaturators the loss of solvent was kept to a minimum. This ranged typically between 2 and 6 mass % over a period of about 6 h and was taken into account assuming linear solvent loss during the isothermal measurements. Furthermore, the experimental conditions (gas flow, solvent loss, etc.) were checked by measuring the retention time of a reference substance (hexane) at regular intervals.

Equation 3 relates the activity coefficient of the solute at infinite dilution to the measured specific net retention volume V_g° at 0 °C:

$$\gamma_i^\infty = \frac{273.15R}{V_g^\circ P_i^s \varphi_i^s M_L} \tag{3}$$

where R is the gas constant, M_L is the molar mass of the solvent, and P_i^s is the saturation vapor pressure of the solute calculated using Antoine constants taken from the Dortmund Data Bank (DDB). The saturation fugacity coefficient of the solute φ_i^s is calculated with the help of the Soave–Redlich–Kwong equation of state following Gmehling and Kolbe (1992). The required critical data and acentric factors are also taken from the DDB. According to Conder and Young (1978), sometimes adsorption effects have to be taken into account; for example:

(i) Adsorption at the gas–liquid interface occurs with increasing polarity of the solvent.

(ii) Polar solutes on nonpolar stationary phases lead to adsorption at the gas–liquid interface, often accompanied by adsorption on the solid support.

To examine the presence of adsorption effects, the relative amount of stationary phase (liquid loading: 14–30%) and the sample volume of injected solutes (0.02–0.5 μL) were varied. Contrary to the observations in our previous investigations for *n*-octanol as stationary phase (Gruber et al., 1997) no adsorption effects were observed.

Results and Discussion

The values of the activity coefficients at infinite dilution are listed for the various temperatures in Tables 1–3. The main source of error in the calculation of the specific retention volume corrected to 0 °C (V_g°) is the measurement of the mass of the stationary phase in the column (±2%). In addition, there is a small error in the determination of the difference between the retention time and the death time (Knoop et al., 1989). The total error in the determination of the specific retention volume is about ±2.5%. Taking into account that the Antoine constants taken from the DDB used for the calculation of the saturation vapor pressure are also subject to error, the resulting error in γ^∞ is ±3.0%. Measurements with different masses of stationary phase or flow rates lead to results within this error.

Table 1. Experimental Activity Coefficients at Infinite Dilution γ^∞ for Various Solutes in the Solvent Propylene Carbonate

solute	γ^∞ 303.15K	313.15 K	323.15 K	333.15 K
hexane	40.6	37.6	34.6	32.0
heptane	59.4	52.4	48.1	42.7
octane	81.7	70.7	63.8	56.5
decane	164	135	118	99.6
1-hexene	21.1	19.7	18.3	17.0
1-octene	40.4	36.1	31.8	28.9
cyclohexane	23.8	21.5	19.2	17.4
methylcyclopentane	25.6	23.0	20.8	18.7
methylcyclohexane	32.3	29.1	25.8	23.3
cyclohexene	13.0	12.1	11.0	10.4
benzene	3.33	3.29	3.24	3.18
toluene	4.81	4.68	4.57	4.47
ethylbenzene	6.68	6.33	6.00	5.74
1,2-xylene	6.30	6.05	5.78	5.56
1,3-xylene	7.05	6.63	6.07	5.67
1,4-xylene	7.00	6.69	6.42	6.17
diethyl ether	5.17	5.07	4.93	4.84
diisopropyl ether	10.7	10.2	9.88	9.57
methyl *tert*-butyl ether	5.04	4.96	4.88	4.84
ethyl *tert*-butyl ether	10.0	9.73	9.34	9.09
methyl *tert*-amyl ether	7.43	7.25	7.07	6.95
isopropyl *tert*-butyl ether	13.7	13.0	12.4	11.9
2-butanone	1.58	1.56	1.54	1.53
2-pentanone	2.03	2.02	1.99	1.97
dichloromethane	1.39	1.37	1.35	1.32
chloroform	1.48	1.51	1.52	1.54
1,2-dichloroethane	1.76	1.70	1.65	1.58

Table 2. Experimental Activity Coefficients at Infinite Dilution γ^∞ for Various Solutes in the Solvent *N*-Ethylformamide

solute	γ^∞ 303.15 K	318.15 K	333.15 K
pentane	13.1	12.2	11.6
hexane	16.7	15.5	14.7
heptane	21.5	19.6	18.3
octane	27.7	24.9	22.9
1-pentene	8.10	7.87	7.63
1-hexene	10.3	9.91	9.55
1-octene	16.8	15.7	14.9
cyclohexane	10.7	10.0	9.60
cyclohexene	7.16	6.88	6.72
benzene	3.22	3.16	3.11
toluene	4.26	4.13	4.00
methanol	0.924	0.893	0.855
ethanol	1.04	1.02	0.993
2-propanol	1.15	1.10	1.07
diethyl ether	4.07	3.97	3.93
diisopropyl ether	6.81	6.65	6.58
methyl *tert*-butyl ether	4.23	4.16	4.11
ethyl *tert*-butyl ether	6.34	6.22	6.18
methyl *tert*-amyl ether	5.28	5.13	4.95
tetrahydrofuran	1.95	1.90	1.84
acetone	1.91	1.83	1.79
2-butanone	2.05	2.00	1.98
2-pentanone	2.46	2.39	2.33
vinyl acetate	2.82	2.78	2.74
dichloromethane	1.11	1.16	1.22
chloroform	0.755	0.842	0.957

One of the reasons for the investigation of the solvents dimethyl sulfoxide, propylene carbonate, and *N*-ethylformamide was to extend and verify the database for γ^∞ values in these solvents. Limiting activity coefficients were measured for several classes of compounds. Figure 1 shows that the experimental data for the solvents dimethyl sulfoxide and propylene carbonate are in good accordance with the published data. There are only relatively strong deviations at high temperatures for the propylene carbonate system. In the case of *N*-ethylformamide, published data are only available for some halocarbons (Kobilarov et al., 1976).

Figure 2 shows examples of the linear relationship between the natural logarithm of the limiting activity coefficient and the inverse absolute temperature for four

Table 3. Experimental Activity Coefficients at Infinite Dilution γ^∞ for Various Solutes in the Solvent Dimethyl Sulfoxide

solute	γ^∞ 303.15 K	318.15 K	333.15 K
hexane	67.2	53.7	42.9
heptane	94.5	73.9	58.1
octane	144	109	80.2
1-pentene	23.7	21.1	19.7
1-hexene	30.0	24.5	21.7
1-octene	69.1	57.1	51.0
benzene	3.30	3.17	3.00
methanol	0.388	0.411	0.435
ethanol	0.684	0.649	0.613
1-propanol	0.811	0.760	0.697
2-propanol	1.00	0.935	0.856
diethyl ether	9.78	9.02	8.53
diisopropyl ether	24.4	21.8	20.0
methyl *tert*-butyl ether	11.7	10.6	9.61
ethyl *tert*-butyl ether	21.3	18.7	17.2
methyl *tert*-amyl ether	16.4	14.3	12.9
isopropyl *tert*-butyl ether	31.5	27.8	24.8
tetrahydrofuran	3.32	3.14	2.99
acetone	1.96	1.93	1.89
2-butanone	2.55	2.47	2.40
2-pentanone	3.55	3.35	3.20
acetaldehyde	1.66	1.65	1.68
vinyl acetate	2.95	2.76	2.50
dichloromethane	0.602	0.661	0.750
chloroform	0.455	0.514	0.603

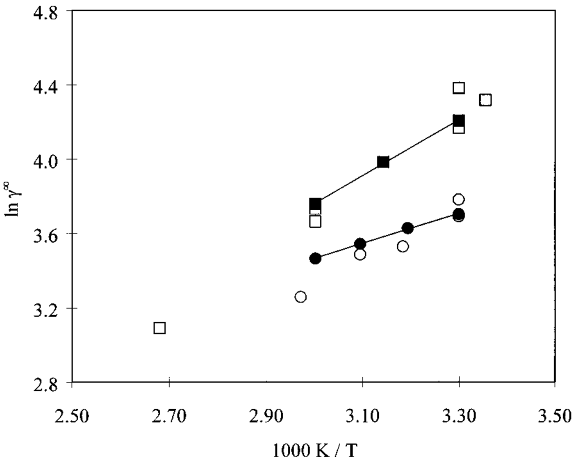

Figure 1. Activity coefficients at infinite dilution γ^∞ for the solute hexane in different solvents as a function of temperature. This work: (■) dimethyl sulfoxide; (●) propylene carbonate; (—) linear regression. Published values (Gaile et al., 1974; Deal and Derr, 1964; Rawat et al., 1976; Sarius et al., 1978): (□) dimethyl sulfoxide; (○) propylene carbonate.

different alkanes in *N*-ethylformamide. As expected, the limiting activity coefficient diminishes with decreasing chain length (octane > heptane > hexane > pentane). The obtained activity coefficients at infinite dilution in *N*-ethylformamide were used together with additional data for the introduction of the monoalkylamide group into the modified UNIFAC (Dortmund) model.

A graph of ln γ^∞ versus the inverse absolute temperature often shows a straight line in a limited range of temperature (see Figures 1−3). According to the Gibbs−Helmholtz equation, the value for the partial molar excess enthalpy at infinite dilution $H_i^{\mathrm{E},\infty}$ can directly be obtained from the slope of this straight line (Gmehling and Kolbe, 1992):

$$\left(\frac{\partial \ln \gamma_i^\infty}{\partial 1/T}\right)_{P,x} = \frac{H_i^{E,\infty}}{R} \tag{4}$$

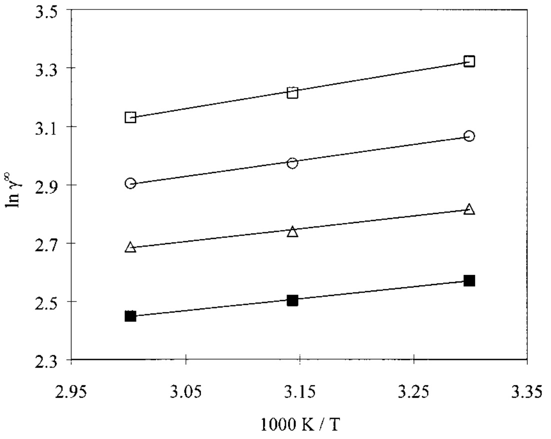

Figure 2. Experimental activity coefficients at infinite dilution γ^∞ for four solutes in the solvent *N*-ethylformamide as a function of temperature: (□) octane; (○) heptane; (△) hexane; (■) pentane; (—) linear regression.

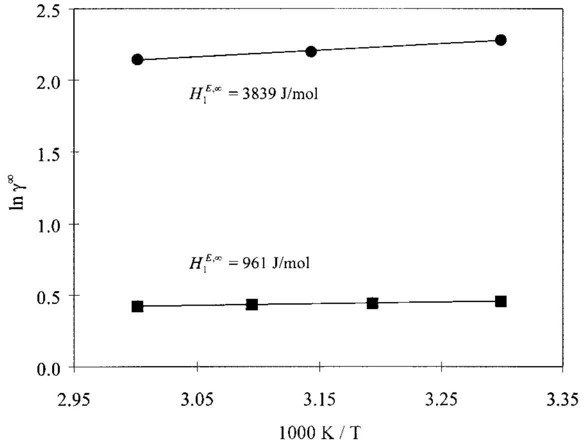

Figure 3. Temperature dependence of the limiting activity coefficient γ^∞ and the calculated partial molar excess enthalpies at infinite dilution $H_i^{\mathrm{E},\infty}$ for the systems (■) 2-butanone (1) in propylene carbonate and (●) diethyl ether (1) in dimethyl sulfoxide: (—) linear regression.

Experimental H^{E} data can be used to confirm the observed experimental temperature dependence. With the help of a polynomial (Redlich−Kister or SSF (sum of symmetrical functions)), the value of the partial molar excess enthalpy at infinite dilution $H_i^{\mathrm{E},\infty}$ can be calculated. Figure 3 illustrates the temperature dependence of the limiting activity coefficient for the solute diethyl ether in the solvent dimethyl sulfoxide and for the solute 2-butanone in the solvent propylene carbonate. For both systems the γ^∞ values decrease with increasing temperature and a positive value of the partial molar excess enthalpy at infinite dilution can be expected. A confirmation of the calculated $H_i^{\mathrm{E},\infty}$ values is shown in Figure 4, where experimental heat of mixing data (Kimura and Takagi, 1995; Comelli and Francesconi, 1995) for the same systems are shown. In both cases the $H_i^{\mathrm{E},\infty}$ values obtained by GLC agree reasonably well with the values derived from experimental H^{E} data. The correct reproduction of the temperature dependence of the limiting activity coefficients can be seen as a good criterion for the reliability of the γ^∞ data.

Another aim of the investigation was the selection of new potential entrainers, especially for the separation of aromatics from aliphatics. Therefore, the selectivity and the capacity of the commercially used entrainers dimethyl sulfoxide and propylene carbonate (Hradetzky et al., 1989;

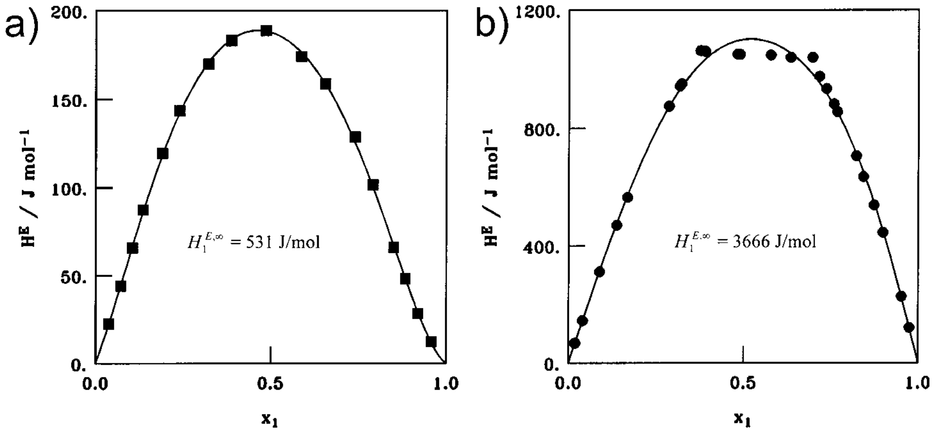

Figure 4. H^E data at 25 °C for the systems (a) (■) 2-butanone (1) in propylene carbonate (Comelli and Francesconi, 1995) and (b) (●) diethyl ether (1) in dimethyl sulfoxide (Kimura and Takagi, 1995): (—) polynomial interpolation.

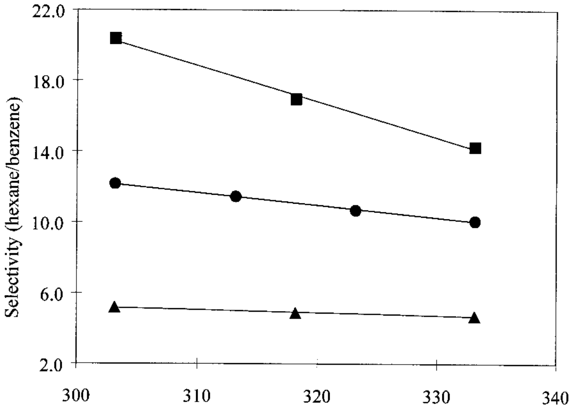

Figure 5. Selectivities at infinite dilution for three solvents at different temperatures regarding the separation of hexane from benzene: (■) in dimethyl sulfoxide; (●) in propylene carbonate; (▲) in *N*-ethylformamide; (—) linear regression.

Gaile and Semenov, 1993) were compared with those of *N*-ethylformamide.

Regarding the selectivity at infinite dilution S_{12}^∞ (eq 1) for the typical aliphatic/aromatic separation of hexane (1) from benzene (2), the solvent *N*-ethylformamide shows a lower selectivity than the other two solvents (see Figure 5).

With respect to the capacity at infinite dilution k_2^∞ (eq 2), which is a measure for the solubility of a substance in the extractive solvent, all investigated solvents show nearly the same value (see Figure 6). However, the observed temperature dependence of the solvent dimethyl sulfoxide is higher than the temperature dependence of the other solvents.

To decide what solvent is the most suitable one, the quantity Q_{12} is introduced (Hradetzky et al., 1989). Assuming that component 2 is the component to be extracted, the quantity at infinite dilution is defined as the product of selectivity and capacity:

$$Q_{12}^\infty = S_{12}^\infty k_2^\infty \qquad (5)$$

Regarding the typical aliphatic/aromatic separation problem hexane/benzene, the quantities at infinite dilution of *N*-ethylformamide are a factor of 2 or 3 lower in comparison to those of the commercially used solvents dimethyl sulfoxide and propylene carbonate (Figure 7). These data indicate that the solvent dimethyl sulfoxide shows advantages for the aliphatic/aromatic separation when compared with the solvents propylene carbonate and *N*-ethylformamide.

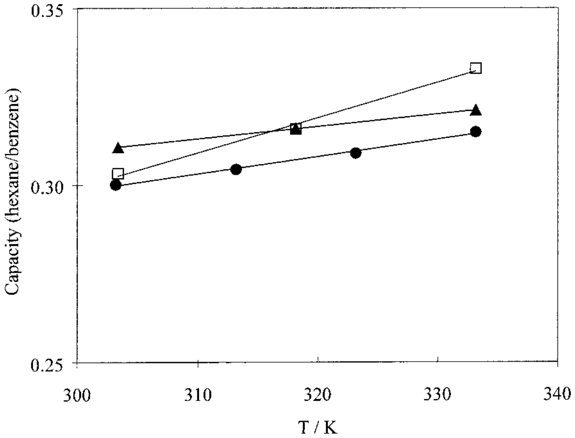

Figure 6. Capacities of benzene at infinite dilution for three solvents at different temperatures: (□) in dimethyl sulfoxide; (●) in propylene carbonate; (▲) in *N*-ethylformamide; (—) linear regression.

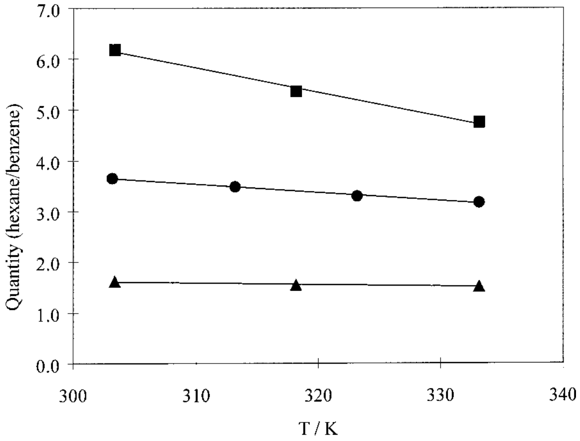

Figure 7. Quantities at infinite dilution for three solvents at different temperatures regarding the separation of hexane from benzene: (■) in dimethyl sulfoxide; (●) in propylene carbonate; (▲) in *N*-ethylformamide; (—) linear regression.

Conclusion

Activity coefficients at infinite dilution for 37 solutes in the solvents dimethyl sulfoxide, propylene carbonate, and *N*-ethylformamide have been measured at different temperatures with the help of GLC. The GLC technique was chosen due to the possibility of a fast and reliable determination of γ^∞ values. The reliability of the obtained data was confirmed by comparing these data with literature values. Furthermore, the temperature dependence of the limiting activity coefficients was verified using experimental H^E data. To check if the investigated solvents can be used as selective solvents for the aliphatic/aromatic separation, the data of selectivity and capacity and the product Q_{12} at infinite dilution were compared.

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