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EXCESS GIBBS ENERGY OF MIXING AND REFRACTIVE INDEX OF BINARY SOLUTIONS OF ACETONITRILE AND OF DIMETHYLSULFOXIDE WITH SEVERAL AROMATIC HYDROCARBONS *

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ABSTRACT

Total intensity Rayleigh scattering and depolarization were measured from the six binary solutions of acetonitrile and of dimethylsulfoxide with benzene, 1,4-dimethylbenzene and 1,3,5-trimethylbenzene at 546 nm and 303 K. Values of the refractive index gradient $\Delta n/\Delta x$ were also determined. The scattering and gradient results were used to calculate activity coefficients, excess Gibbs energies of mixing and refractive indices of the solutions.

INTRODUCTION

Total intensity Rayleigh scattering is recognized as a useful tool in the determination of activity coefficients and of excess Gibbs energy of mixing of binary solutions. It has been applied to mixtures of simple non-electrolytes, to polymer and to polyelectrolyte solutions. There are some severe limitations on the method, however, and it is not as accurate as the classical vapor pressure method. For the Rayleigh scattering method to work well, the excess Gibbs energy should be positive and the refractive index gradient should be large with a difference of about 0.1 in the refractive indices of the pure components. Many solutions of polar molecules in aromatic hydrocarbons, including the acetonitrile + hydrocarbon solutions, meet both requirements. The dimethylsulfoxide + aromatic hydrocarbon solutions meet only the first requirement.

THEORY

The theory was developed by Coumou and Mackor [1] who put it into a useful form for experimental testing. This method has been applied to a

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* Dedicated to Professor E.F. Westrum, Jr., in honor of his contribution to calorimetry and thermal analysis.

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number of systems in our laboratory with varying success [2–5]. Recently there has been a revival of interest in the method for acetonitrile-containing solutions [6,7] and for other solutions [8,9].

The total Rayleigh scattering R_{90} consists of an anisotropic R_{an} and an isotropic R_{is} contribution.

$$R_{90} = R_{is} + R_{an} \tag{1}$$

The isotropic scattering term is separated from the Rayleigh scattering by the Cabannes relation, a function of the solution and pure liquid depolarizations.

For a pure liquid, the isotropic part is due to density fluctuations R_d. For a solution, the isotropic part of the scattering comes from three contributions:

$$R_{is} = R_d + R_c + R^{\#} = R_d + (R_{id} + R_{nid}) + R^{\#} \tag{2}$$

where R_d is the density fluctuation, R_c the concentration fluctuation and $R^{\#}$ the density–concentration fluctuation. The concentration fluctuation scattering is the sum of an ideal R_{id} and non-ideal R_{nid} contribution. All terms are evaluated from either experiment or theoretical calculation except the non-ideal contribution which is obtained by difference. The activity coefficients and excess Gibbs energy are evaluated to match the non-ideal scattering contribution consistent with the Gibbs–Duhem relation. A complete description of the calculation is in our earlier papers [2–5].

EXPERIMENTAL

The source, purification and physical properties of the solution components are described elsewhere [10]. The purification of the acetonitrile deserves further comment. The method of O'Donny [11] was used because the acetonitrile from this procedure gave a reliable and stable depolarization value of 0.302. Other purification procedures gave a solvent with a smaller, less stable depolarization value.

Solutions were prepared by weight in a special weighing bottle which allowed their compositions to be corrected for vapor losses. Solutions were filtered through an ultra-fine fritted glass disk in an all-glass device designed to exclude atmospheric dust from the light-scattering cell used for depolarization and Rayleigh scattering measurements.

Depolarization and Rayleigh scattering measurements were made with a Brice–Phoenix series 2000 universal light-scattering photometer. Values of the refractive index gradient in both $\Delta n/\Delta c_2$ and $\Delta n/\Delta x_2$ were determined with a Brice–Phoenix model BP-200-V differential refractometer.

RESULTS AND DISCUSSION

The experimental values of the refractive index gradient are displayed in Fig. 1, and the calculated refractive index values are in Table 1. The starting point for the refractive index calculation was the hydrocarbon refractive index values reported by Forziati [12]. For the hydrocarbon + dimethylsulfoxide solutions, values of $\Delta n/\Delta x_2$ range from -0.01 to -0.04, while for the hydrocarbon + acetonitrile solutions values range from -0.08 to -0.40. The larger values allow for more certain calculations of the R_d, R_{id} and $R^{\#}$ terms needed to obtain the non-ideal contribution.

The activity coefficients and excess Gibbs energies calculated from the Rayleigh scattering and depolarization values with the aid of the refractive index measurements are given in Table 2. All of the Gibbs energy values are positive and all activity coefficients are greater than one.

There are two reports of activity coefficients and excess Gibbs energies of mixing for the benzene + acetonitrile system by vapor pressure measurements. Brown and Fock [13] reported values at 318 K and Smith and co-workers [14,15] reported values at 298.16, 348 and 397.86 K. The light-scattering values calculated with a pure acetonitrile depolarization of 0.30 agree well with the literature values by the vapor pressure method. Other literature values of the depolarization are not satisfactory.

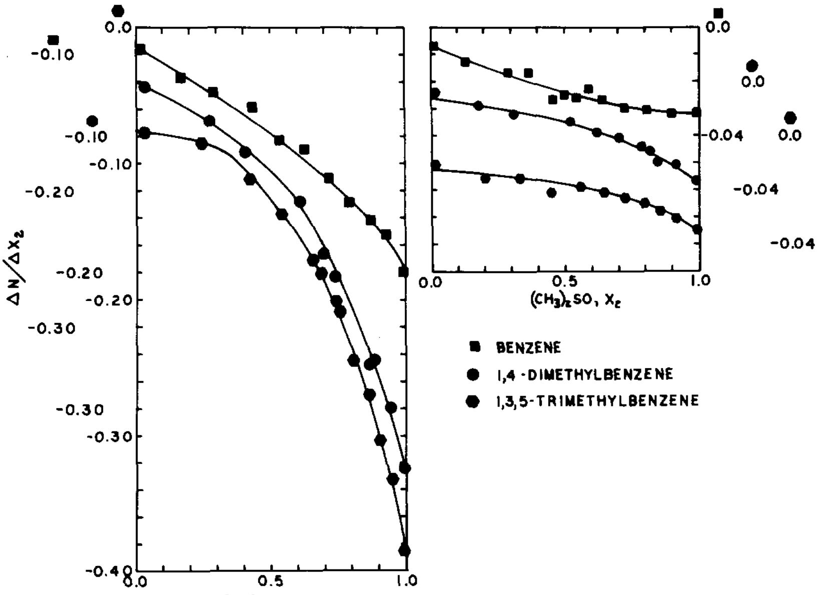

Fig. 1. Experimental values of the refractive index gradient $\Delta n/\Delta x_2$ vs. mole fraction, measured at 546 cm and 303 K.

TABLE 1

Values of the refractive index as a function of mole fraction at 546 nm and 303 K calculated from $\Delta n/\Delta x_2$ values

Mole fraction x_2	Benzene(1) + acetonitrile(2)	1,4-Dimethyl benzene(1) + acetonitrile(2)	1,3,5-Trimethyl benzene(1) + acetonitrile(2)
0	1.49881	1.49434	1.49810
0.1	1.4890	1.4876	1.4903
0.2	1.4783	1.4799	1.4822
0.3	1.4667	1.4709	1.4736
0.4	1.4539	1.4604	1.4638
0.5	1.4398	1.4483	1.4522
0.6	1.4241	1.4344	1.4385
0.7	1.4066	1.4182	1.4220
0.8	1.3872	1.3988	1.4018
0.9	1.3659	1.3747	1.3760
1.0	1.3425	1.3437	1.3428

Mole fraction x_2	Benzene(1) + dimethyl sulfoxide(2)	1,4-Dimethyl benzene(1) + dimethyl sulfoxide(2)	1,3,5-Trimethyl benzene(1) + dimethyl sulfoxide(2)
0	1.49881	1.49434	1.49810
0.1	1.4980	1.4937	1.4968
0.2	1.4968	1.4930	1.4955
0.3	1.4953	1.4921	1.4940
0.4	1.4935	1.4911	1.4924
0.5	1.4913	1.4898	1.4907
0.6	1.4889	1.4883	1.4888
0.7	1.4862	1.4864	1.4867
0.8	1.4834	1.4841	1.4843
0.9	1.4804	1.4813	1.4816
1.0	1.4773	1.4780	1.4784

Enthalpy of mixing of the benzene + acetonitrile system measured at 298 K [10] when combined with our Gibbs energy values at 303 K implies an entropy of mixing of the same sign and magnitude as the values reported by Brown and Fock [13]. These consistencies with the literature values give us confidence that the values of the 1,4-dimethyl- and 1,3,5-trimethylbenzene solutions with acetonitrile are reliable. Other alkylbenzene + acetonitrile values were recently reported [16].

The excess Gibbs energy values of benzene + dimethylsulfoxide reported by Kenttamaa et al. [17] by vapor pressure measurements agree satisfactorily with the light-scattering values reported here. In spite of this agreement, the hydrocarbon + dimethylsulfoxide activity coefficients and excess Gibbs energies are suspected to be less reliable than the acetonitrile solution values even though the experiments were carried out with equal care. The problem

TABLE 2

Activity coefficients and excess Gibbs energy (kJ mol^{-1}) of mixing at 303 K

Mole fraction, x_2	Benzene(1) + acetonitrile(2)			1,4-Dimethylbenzene(1) + acetonitrile(2)			1,3,5-Trimethylbenzene(1) + acetonitrile(2)		
	f_1	f_2	ΔG^E	f_1	f_2	ΔG^E	f_1	f_2	ΔG^E
0	1.00	(4.14)	0	1.00	(6.81)	0	1.00	(5.70)	0
0.1	1.03	2.44	0.27	1.03	3.57	0.40	1.02	3.65	0.375
0.2	1.07	1.86	0.46	1.10	2.47	0.65	1.08	2.64	0.65
0.3	1.14	1.58	0.563	1.19	1.96	0.815	1.16	2.10	0.835
0.4	1.21	1.39	0.63	1.29	1.67	0.90	1.29	1.75	0.94
0.5	1.32	1.26	0.63	1.45	1.46	0.94	1.46	1.51	0.985
0.6	1.46	1.16	0.605	1.67	1.29	0.90	1.72	1.31	0.96
0.7	1.63	1.08	0.50	2.03	1.17	0.795	2.12	1.17	0.86
0.8	1.86	1.04	0.40	2.59	1.08	0.63	2.78	1.07	0.65
0.9	2.19	1.01	0.23	3.50	1.02	0.355	3.75	1.02	0.375
1.0	(2.98)	1.00	0	(5.09)	1.00	0	(5.11)	1.00	0

Mole fraction, x_2	Benzene(1) + dimethylsulfoxide(2)			1,4-Dimethylbenzene(1) + dimethylsulfoxide(2)			1,3,5-Trimethylbenzene(1) + dimethylsulfoxide(2)		
	f_1	f_2	ΔG^E	f_1	f_2	ΔG^E	f_1	f_2	ΔG^E
0	1.00	–	0	1.0	–	0	1.00	(7.0)	0
0.1	1.07	4.9	0.56	1.1	–	0.8	1.01	5.7	0.45
0.2	1.19	2.7	0.84	–	–	–	1.07	4.1	0.85
0.3	1.3	2.1	1.00	1.4	4.2	1.7	1.20	3.0	1.15
0.4	1.4	1.8	1.08	–	–	–	1.4	2.2	1.30
0.5	1.6	1.6	1.11	2.2	2.2	2.0	1.7	1.8	1.40
0.6	1.8	1.4	1.08	–	–	–	2.1	1.5	1.35
0.7	2.1	1.3	0.98	3.2	1.7	1.8	2.7	1.3	1.25
0.8	2.8	1.16	0.81	–	–	–	4.0	1.16	1.00
0.9	4.7	1.06	0.52	–	1.2	1.1	7.1	1.05	0.60
1.0	–	1.00	0	–	0	0	(17)	1.00	0

is in the smaller magnitude $\Delta n/\Delta x_2$ values used in the calculation of R_d, R_{is} and $R^{\#}$ values. This is a method based on small differences, and small errors in R_d, R_{id} and $R^{\#}$ can make substantial errors in the excess Gibbs energy. Although we cannot pinpoint the exact reason, we believe that the 1,4-dimethylbenzene + dimethylsulfoxide values are less reliable than our other values.

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