Thermodynamics of Mixtures Containing Organic Carbonates. Part XV. Application of the Kirkwood-Buff Theory to the Study of Interactions in Liquid Mixtures Containing Dialkyl Carbonates and Alkanes, Benzene, CCl₄ or 1-Alkanols

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Received: 20 September 2005/Accepted: 2 March 2006 / Published online: 29 June 2006
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Abstract Binary liquid mixtures containing a dialkyl carbonate (dimethyl or diethyl carbonate) and organic solvents such as alkanes, benzene, CCl₄, or 1-alkanols were studied within the framework of the Kirkwood-Buff formalism. The Kirkwood-Buff integrals, linear coefficients of preferential solvation and local mole fractions were calculated. Results were interpreted assuming that the mixtures with alkanes or 1-alkanols are not random mixtures, which can be ascribed to the existence of strong dipolar interactions between like molecules. Systems containing benzene or CCl₄ are both random and more ordered because of the charge transfer or dipole/induced dipole interactions between the polar group of the solute (O–CO–O) and the polarizable solvent molecules. The effect of increasing temperature was also examined.

Keywords Kirkwood-Buff Theory · Organic carbonates · Solvents · Interactions

1. Introduction

Organic carbonates, both linear or cyclic, are widely employed in industry. They are used in the synthesis of organic compounds [1], e.g., pharmaceuticals and agricultural chemicals, and as solvents for many synthetic and natural resins [2]. They are also very important in lithium battery technology [3, 4]. Dimethyl carbonate (DMC) is used as a replacement for some hazardous chemicals [5, 6], as a fuel additive, and in the design of new refrigerants [7, 8].

From the theoretical point of view, understanding the simpler linear organic carbonates is desirable before analyzing the more complex cyclic carbonates and the ethylene and...
propylene carbonates. It is well known that the position of a functional group in a ring or on an open chain may considerably change the molecular properties and hence change the interaction parameters when mixtures of these compounds are treated theoretically. On the other hand, propylene carbonate is an aprotic solvent of high dipole moment that is interesting to study in view of its local structure [9, 10].

During the last few years we have been conducting detailed studies of mixtures containing linear organic carbonates. As a matter of fact, we have published experimental data on vapor-liquid [11–14], liquid-liquid and solid-liquid equilibria [15–18], excess molar volumes [19, 20] and excess molar enthalpies [21, 22] for such systems. On the other hand, we have studied these mixtures [18, 23, 34] in terms of the so-called dispersive-quasichemical (DISQUAC) model [25], a purely physical model based on the rigid-lattice theory developed by Guggenheim [26]. Some 1-alkanol + linear organic carbonate systems have also been analyzed by us [18] in terms of the extended real associated solution (ERAS) model [27]. The present work is concerned with an analysis, using the Kirkwood-Buff theory [28], of systems formed by mixing dialkyl carbonates (dimethyl carbonate, DMC, or diethyl carbonate, DEC) and solvents such as alkanes, aromatic compounds, CCl₄, or 1-alkanols.

2. Theory

The Kirkwood-Buff theory [29, 30] describes the thermodynamic properties of solutions in an exact manner over the whole concentration range, using the quantities:

\[
G_{ij} = \int_0^\infty (g_{ij} - 1)4\pi r^2 dr
\] (1)

that are called the Kirkwood-Buff integrals. The radial distribution function, \(g_{ij}\), denotes the probability of finding a molecule of species \(i\) in a volume element at a distance \(r\) from the center of a molecule of species \(j\). Thus, this function provides information about the solution structure at the microscopic level. The product \(\rho_j G_{ij}\) (\(\rho_j\) is the number density of molecules of species \(j\)) represents the average excess (or deficiency) of the number of molecules \(j\) in the whole space surrounding a molecule \(i\) relative to their corresponding bulk average concentration. Thus, the \(G_{ij}\) values can be obtained from \(\rho_j G_{ij}\) by a process of normalization with respect to concentration and can be interpreted as follows: \(G_{ij} > 0\) represents the excess number of molecules of type \(i\) in the space around a given molecule of species \(j\). Under this condition, attractive interactions occur between molecules of \(i\) and \(j\). Also, \(G_{ij} < 0\) means that interactions of \(i-j\) and \(j-i\) are preferred to mutual interactions [29, 31]. The Kirkwood–Buff integrals can be derived from experimental thermodynamic data such as chemical potentials, partial molar volumes and isothermal compressibility. The resulting equations are: [29, 32]

\[
G_{11} = RT\kappa_T + \frac{x_2 V_2^2}{x_1 V D} - \frac{V}{x_1} \tag{2}
\]

\[
G_{22} = RT\kappa_T + \frac{x_1 V_1^2}{x_2 V D} - \frac{V}{x_2} \tag{3}
\]